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**FURTHER STUDIES OF
GROUP 14 - COBALT CARBONYL
CHEMISTRY.**



**A THESIS SUBMITTED TO THE
UNIVERSITY OF WAIKATO
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
BY
MIRANDA SERVICE
DECEMBER, 1988**

ABSTRACT

This thesis describes investigations into several areas of group 14-cobalt carbonyl chemistry including substitution of a bridging carbonyl ligand by an R_2GeH_2 species to form a $GeCo_2$ triangle, reactions of germanium-cobalt carbonyl clusters with transition metal carbonyl anions and the reactions of Et_4NSnCl_3 with group 14-cobalt carbonyl compounds of the form $R_3M'Co(CO)_4$ ($R_3 = Me, ^nBu, Ph, Cl, Br$; $M' = Sn, Ge, Si$).

Further studies of the reaction between $MeGeH_3$ and $Co_2(CO)_8$ have led to a new proposal for the reaction scheme. That is:



Together with the results obtained from a study of the reaction of $H_3GeCo(CO)_4$ with $Co_2(CO)_8$, this has allowed the proposal that "In the absence of marked steric effects, where an even number of hydrogen atoms is attached to a germanium hydride species this will react with $Co_2(CO)_8$ to replace a bridging carbonyl group to form a $GeCo_2$ triangle with evolution of H_2 and CO ; where there is an odd number of attached hydrogen atoms this will react with $Co_2(CO)_8$ to also give cleavage of the $Co-Co$ bond to yield a $GeCo(CO)_4$ species and $HCo(CO)_4$ ".

It has been found that substitution of both bridging carbonyl groups of $GeCo_4(CO)_{14}$ by Me_2GeH_2 or $MeGeH_3$ is possible and the new compounds $[Me_2Ge]_2GeCo_4(CO)_{12}$ and $[MeGeH]_2GeCo_4(CO)_{12}$ have been spectroscopically characterised. An X-ray crystal structure determination has been carried out for $(Me_2Ge)_2GeCo_4(CO)_{12}$ which shows it to comprise of four $GeCo_2$ triangles connected by $Co-Co$ edges and Ge apices. An analysis of the carbonyl vibrations of $[MeGeR]_2GeCo_4(CO)_{12}$ ($R = Me, H$) and $GeCo_4(CO)_{14}$ has been carried out.

Good spectroscopic evidence has been obtained for the formation of $(MeGe)_2Co_4(CO)_{10}[Ge(R)Me]$ ($R = Me, H$) from the reaction of $(MeGe)_2Co_4(CO)_{11}$ with $Me(R)GeH_2$. Similarly, further evidence for the production of $[MeGeR]_2Ge_2Co_6(CO)_{18}$ from the reaction of $Ge_2Co_6(CO)_{20}$ with $Me(R)GeH_2$ has been obtained.

The two trigonal pyramidal clusters, $[(CO)_4Co]GeCo_3(CO)_9$ and $MeGeCo_3(CO)_9$, reacted with $Me(R)GeH_2$ to provide the open-skeleton derivatives $[MeGeR]Co_2(CO)_6[GeCo_2(CO)_7]$ and $[MeGeR]Co_2(CO)_6[Ge(Me)Co(CO)_4]$ respectively. These have been spectroscopically characterised.

The thermally initiated ligand substitution reactions of the *closo* hexanuclear clusters, $(RGe)_2Co_4(CO)_{11}$ ($R = Me, Co(CO)_4$), with PPh_3 or $P(OEt)_3$ resulted in breakdown of the cluster to afford mainly $[(R_3P)Co(CO)_3]_2$. However, the electron transfer catalysed reaction of $(MeGe)_2Co_4(CO)_{11}$ with $P(OEt)_3$ in a 1:1 ratio provided the monosubstituted derivative, $(MeGe)_2Co_4(CO)_{10}(POEt)_3$, in moderate yields which has been spectroscopically characterised. Similarly, the reaction of $(MeGe)_2Co_4(CO)_{11}$ with $tBuNC$ at room temperature appeared to yield the monosubstituted derivative $(MeGe)_2Co_4(CO)_{10}CN^tBu$.

Reaction of $[(CO)_4CoGe]_2Co_4(CO)_{11}$ with $Et_4N[Co(CO)_4]$ produced the known anionic cluster $Et_4N[Ge_2Co_7(CO)_{21}]$ in comparatively good yields. The same product was obtained from reaction of $Ge_2Co_6(CO)_{20}$ with $Et_4N[Co(CO)_4]$, however condensation to $[(CO)_4CoGe]_2Co_4(CO)_{11}$ was required before reaction with the anion takes place.

The reactions of Et_4NSnCl_3 with $R_3M'Co(CO)_4$ ($R = Me, nBu, Ph, M' = Sn; R = Ph, M' = Ge; R = Cl, M' = Si$) all yielded the known tin-cobalt carbonyl anion, $Et_4N[Cl_2[Co(CO)_4]Sn]_2Co(CO)_3$. Reaction of Et_4NSnCl_3 with $Br_3SnCo(CO)_4$, however, produced a mixture of anions of the form $Et_4N[(Br_xCl_{3-x}Sn)Co(CO)_3(SnCl_yBr_{3-y})]$ ($x, y = 0-3$). This mixture has been characterised by infrared, ^{119}Sn NMR and FAB mass spectroscopy and an X-ray crystal structure determination has been carried out for $Et_4N[(Br_2ClSn)_2Co(CO)_3]$.

Preliminary studies have been carried out for several other related systems.

ACKNOWLEDGEMENTS

I would like to take this opportunity to thank the following people:

Professor Kenneth M. Mackay for his invaluable advice and encouragement throughout this work, and particularly for his help in the analysis of vibrational spectra. I would also like to express my gratitude to him and his wife, Ann, for their kindness to me on my arrival in this country;

Dr Brian K. Nicholson for his help, particularly in solving crystal structures, and for his understanding of my loathing of computers;

Ralph Thomson for his patient instruction on the recording of ^1H NMR spectra, and to him, and Dr Jan Coddington of Auckland University, for recording ^{119}Sn NMR spectra;

Alan Brennan for recording mass spectra, and Mike Liddell of the University of Adelaide for running the FAB mass spectra;

Dr Tony Cartner, Brett Loper and Jacky Carroll for the Raman spectra;

Steven Stokes for performing the electron probe analysis;

Dr Ward T. Robinson for collection of X-ray data;

Kim Hewlett for typing this thesis and not complaining about the rush towards the end;

Skelte Anema and Dr Siew Kim Lee for their help in the laboratory, particularly when I first arrived and needed instruction in all the techniques used in this work. Also to Siew Kim for proof-reading;

Les Arnold, Glen Barris and Martin Van Tiel for proof-reading;

Wayne Takitimu for helping with diagrams and, more importantly, for enabling me to forget chemistry when I needed to.

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LIST OF ABBREVIATIONS

acac	acetylacetonato
Me	methyl
Et	ethyl
Pr	n-propyl
^t Bu	t-butyl
ⁿ Bu	n-butyl
Ph	phenyl
Xy	xylyl
Cp	cyclopentadienyl anion
pz	pyrazolyl, C ₃ H ₃ N ₂
THF	tetrahydrofuran
bpk	benzophenone ketyl
M'	group 14 element
M	transition metal
E	heteroatom
X	halide
R	substituent - commonly alkyl or aryl group
L	neutral ligand
m.p.	melting point
NMR	nuclear magnetic resonance
TLC	Thin layer chromatography
EHMO	extended huckel molecular orbital
int	internal
ext	external
eq	equatorial
ax	axial
vw	very weak intensity
w	weak intensity
m	medium intensity
s	strong intensity
vs	very strong intensity
br	broad
sh	shoulder
Lit.	literature
bppd	bis (1,3-diphenylpropane-1,3-dionate)
pd	pentane-2,4-dionate

CHAPTER 1: Introduction to Group 14 - Cobalt Carbonyl Chemistry

1.1 General

The first reports of compounds incorporating a bond between a transition metal, M, and a group 14 metal or metalloid, M', (M' = Si, Ge, Sn, Pb) stemmed from the early 1940's. Development of the class was slow until the strong surge of interest in the 1960's which focussed mainly on the formation of these M-M' bonds, and analogies were drawn with organic derivatives. In more recent years work has increased the number of known species, but has also concentrated more closely on their reactions and interconversions, their spectroscopic and bonding properties, potential catalytic properties and their, often, novel structures.

Commonly studied compounds contain manganese, iron, cobalt, platinum, ruthenium, osmium or rhodium. These range from simple monosubstituted derivatives to more complicated polynuclear di-, tri- and tetrasubstituted species. A number of comprehensive reviews have been published which document numerous examples within this group [1-15].

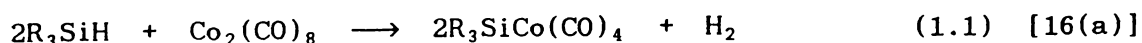
1.2 Preparations

At least 20 different routes to the M'-M bond have been reported. Only those most relevant to this work will be reviewed here.

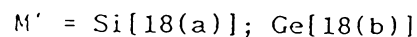
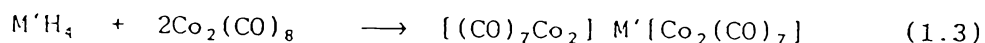
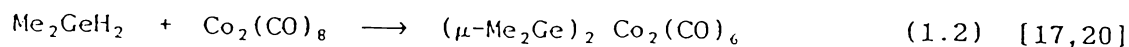
1.2.1 Preparations Involving Oxidation by Group 14 Hydrides.

The M'-H bond is intermediate in reactivity between M'-C and M'-X (X = halogen) species, and can often be functional under relatively mild conditions. The hydrides may oxidise low valent M complexes, yielding M'-M species. The main reactions are oxidative addition, directly or with accompanying elimination reactions, and addition to M-M bonds. The latter is of most importance here.

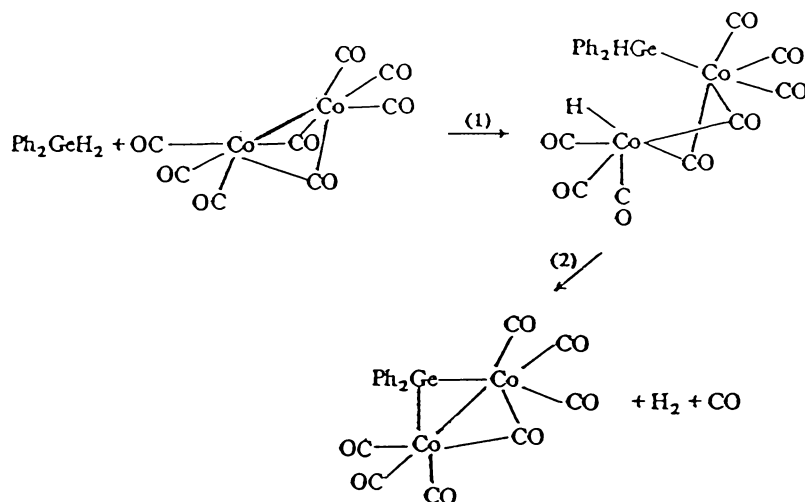
The group 14 hydride reaction with an M-M bonded species is rationalised as resulting from initial addition of M'-H across M-M, often followed by further reaction of the hydrido complex, probably via oxidative addition [12]. An example of this is shown in equation 1.1 [16(a)]



When the starting material contains a number of M'-H bonds, polynuclear species are formed (equations 1.2, 1.3)



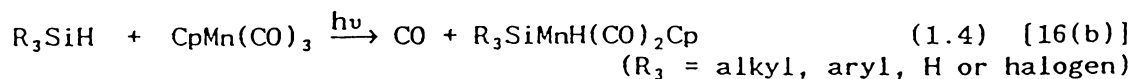
The pathway involved in these hydride reactions is not known definitely as yet. One possible route for the reaction between Ph_2GeH_2 and $\text{Co}_2(\text{CO})_8$ has been suggested [1] and is shown in scheme 1.1

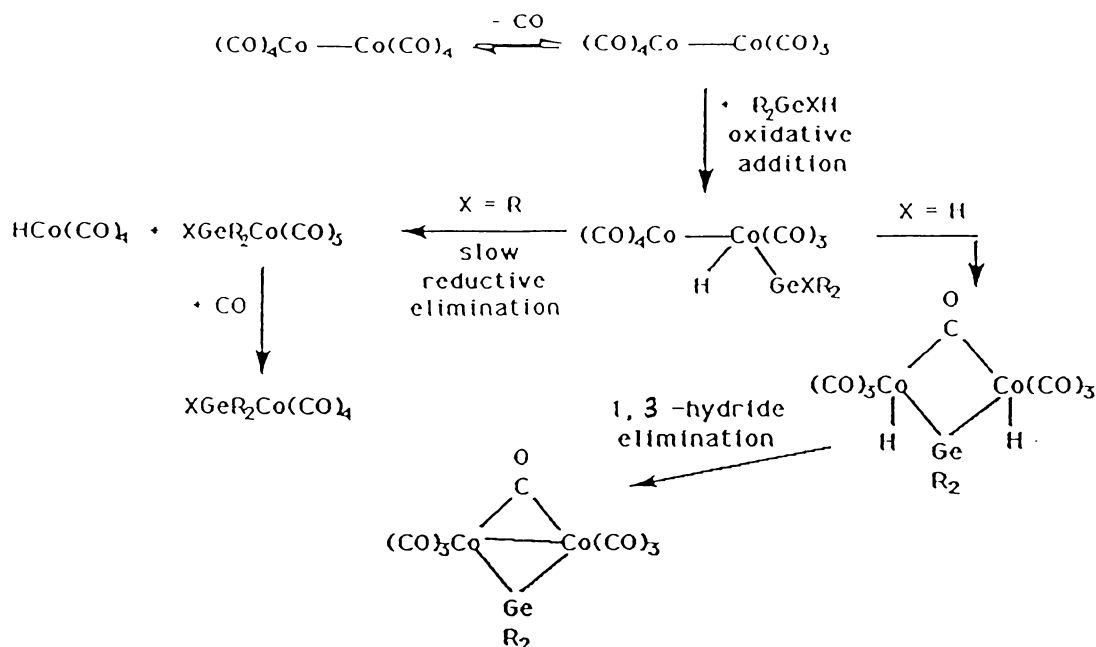


Scheme 1.1 [1]

Preliminary formation of $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$ and subsequent loss of CO can be discounted as this compound is known and loss of CO is not a favourable process [1].

Other pathways may be envisaged. For example, by analogy with the reaction of $\text{CpMn}(\text{CO})_3$ with HSiR_3 [16(b)] shown as equation 1.4., the route depicted as scheme 1.2 may be postulated.

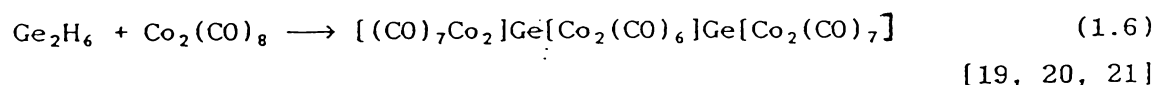
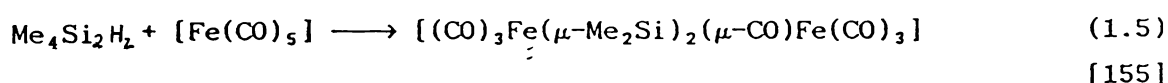




Scheme 1.2

This second scheme, although only suggested tentatively at this stage, has the advantage that it accounts for the two possible pathways that are observed to occur in these reactions. That is, metal-metal bond cleavage, as occurs in the reaction of trisubstituted silanes with dicobalt octacarbonyl [16(a)] (equation 1.1) or replacement of a bridging carbonyl group by an R_2Ge species with evolution of CO and molecular H_2 .

With an $\text{M}'\text{-M}'$ bonded starting material, parallel reactions to those of the mononuclear species are observed, also involving $\text{M}'\text{-M}'$ cleavage. For example, equations 1.5. and 1.6.

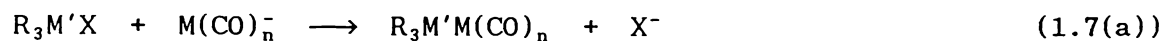


In the latter reaction, it has been reported [19] that carbon monoxide release predominates in the early stages while complete loss of hydrogen takes 2-3 times longer. Similar results have been noted for the reaction of GeH_4 and $\text{Co}_2(\text{CO})_8$ [19] (equation 1.3). These observations do not help in distinguishing between the two pathways proposed for these reactions, however, it does suggest that the first step is the loss of a carbonyl group. A subsequent, slower loss of H_2 intra- or intermolecularly would then give the observed GeCo_2 triangle.

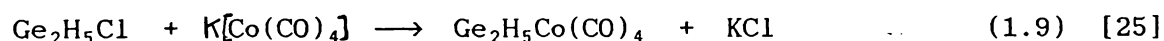
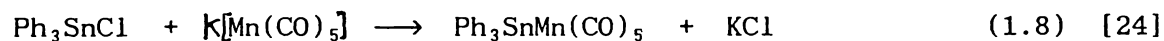
The formation of the longer chain clusters, such as $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (equation 1.6) and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (from the reaction of Ge_3H_8 with $\text{Co}_2(\text{CO})_8$ [20-23]) must occur via some intermediate in which the germanium atoms are held fairly closely together while CO and H_2 elimination take place. Cleavage of the Ge-Ge bonds is likely to occur in the final stages of the reaction. If this were not the case then the smaller cluster, $\text{GeCo}_4(\text{CO})_{14}$, would be expected to dominate the products.

1.2.2 Salt Elimination Reactions

Salt elimination is a commonly used route to M-M' bonded compounds. Two complementary pathways are available as depicted in equations 1.7(a) and (b)

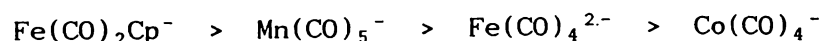


Route (a) is the most relevant to the work of this thesis. Transition metal carbonyl anions, such as $[\text{Co}(\text{CO})_4]^-$ and $[\text{Mn}(\text{CO})_5]^-$ are readily prepared from the neutral metal carbonyls using alkali metal amalgams [12]. Examples pertinent to this work are shown in equations 1.8 and 1.9.



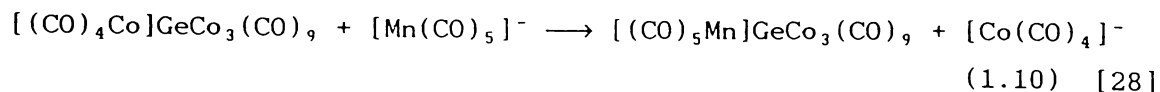
1.2.3. Substitution or Addition Reactions of Transition Metal Carbonyl Anions with Existing Group 14 - Cobalt Carbonyl Clusters

The work of Gerlach [26] and several Russian authors [27] on the reactions of transition metal carbonyl anions with M-M' bonded species has suggested the following displacement series:

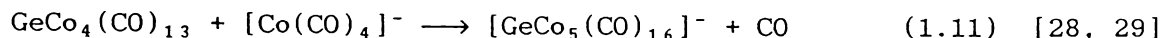


This also corresponds to the order of relative nucleophilicities of these anions. Thus, where a terminal $\text{Co}(\text{CO})_4$ unit exists in a molecule reaction with any of $\text{Fe}(\text{CO})_2\text{Cp}^-$, $\text{Mn}(\text{CO})_5^-$ or $\text{Fe}(\text{CO})_4^{2-}$ should result in its displacement to yield a compound containing the new terminal group.

This process has been employed recently to provide new analogues of the cluster $[(\text{CO})_4\text{Co}]\text{GeCo}_3(\text{CO})_9$. For example, equation 1.10. [28].



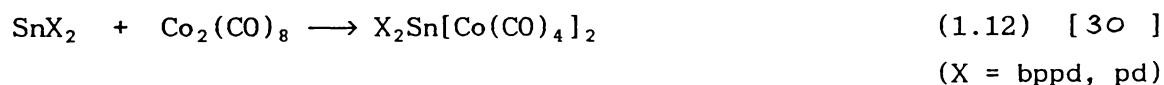
Reactions of group 14 - cobalt carbonyl clusters with either $[\text{Co}(\text{CO})_4]^-$ or $[\text{Fe}_2(\text{CO})_8]^{2-}$ have been observed to result in an addition process, giving rise to higher nuclearity species. For example, equation 1.11 [28, 29]



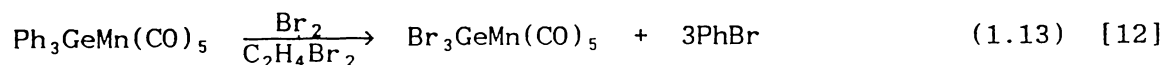
Thus interesting products may be provided by the reaction of transition metal carbonyl anions with existing clusters, although the products of the addition reactions are specific to the reactants and conditions used.

1.2.4. Other Routes to M-M' Bonded Species.

Numerous other routes are available to M-M' bonded species such as: elimination of small molecules, (hydrogen halides, oxygen species and nitrogen species); the use of lower valency M' compounds - for instance, insertion of an M'X₂ species into an M-M bond (eg. equation 1.12 [30]);



and interconversions of existing M-M' species - these may be ligand exchange reactions or condensations; equations 1.13 and 1.14 show examples of these two processes.



These other pathways are not directly relevant as synthetic routes in this work and are thus not discussed in detail here. Various reviews are available which cover these processes more thoroughly [1, 2, 9, 12].

1.3 Group 14 derivatives of cobalt carbonyl

Although group 14 - cobalt carbonyl compounds vary considerably in structural complexity, they may be categorised into three general types:

- (i) Compounds containing only terminal $-\text{Co}(\text{CO})_4$ units;
- (ii) Open chain clusters in which a group 14 atom bridges a Co-Co bond;
- (iii) Closed clusters in which a group 14 atom bridges a plane of cobalt atoms.

For convenience the structures of the simpler species are discussed separately from those containing a large number of group 14 atom - cobalt bonds.

1.3.1. Compounds Containing One to Four Cobalt Atoms.

Of the large number of known group 14 - cobalt carbonyl compounds, a significant proportion contains between one and four cobalt atoms. Table 1.1 gives the general picture of the series of compounds, where classification is made according to the general structural type and the number of cobalt atoms.

A great many of the known species contain only one or two cobalt atoms and these are not surveyed in detail here. For further information on these compounds see [12, 20, 32]. Compounds containing three and four cobalt atoms are well established and, as can be seen from table 1.1, several structural types are known.

Relatively few compounds containing lead have been reported, mainly reflecting the lack of work in this area [12]. Abundant examples of the simpler forms are known containing tin, however it is rarely found bonded to three or four cobalt atoms, and $\mu\text{-SnR}_2$ species are very uncommon, and generally unstable. Germanium forms all three structural types, ie. with $\text{M}'\text{Co}(\text{CO})_4$ units, $\text{M}'\text{Co}_2(\text{CO})_7$ units and *closo* structures. Finally, silicon tends to prefer the more closed types and will form these where possible. Clearly these structural features reflect the size of M' . In particular, for the tetrahedral clusters $\text{RM}'\text{Co}_3(\text{CO})_9$, Schmid [8] has proposed that the limiting covalent radius for M' to form this unit is about 130 pm (Ge = 122 pm; Sn = 141 pm). Until recently this statement had been applicable to all main group elements forming the $\text{ECO}_3(\text{CO})_9$ unit, but the formation of $\text{BiCo}_3(\text{CO})_9$ [33] has contradicted this. However, Schmid's proposal still

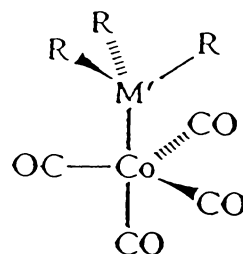
seems an appropriate explanation for the distribution of the $M'Co_3(CO)_4$ unit within the series of group 14 - cobalt carbonyl clusters.

Table 1.1 Structures of group 14 - cobalt carbonyl compounds containing up to four cobalt atoms.

(i) Compounds containing all terminal $Co(CO)_4$ units:

(a) $R_3M'Co(CO)_4$

$M' = Si$; $R = H, D, \text{alkyl}, Ph,$
 F, Cl, Br, I, OR, C_6F_5
 + combinations of the above [12]



$M' = Ge$; $R = H, D, \text{alkyl}, Ph,$
 $F, Cl, Br, I, Me_2(\text{vinyl})$
 + combinations of the above [12]

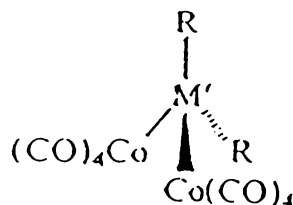
$M' = Sn$; $R = \text{alkyl}, Ph, Cl, Br, I$
 + combinations of the above [12]

$M' = Pb$; $R = \text{alkyl}, Ph, C_6H_{11}.$ [12]

Note: For Si, Ge and Sn, structures of the type $(R_3M')_2Co(CO)Cp$ are also known [12].

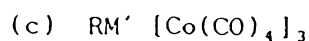
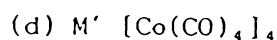
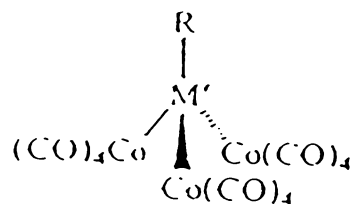
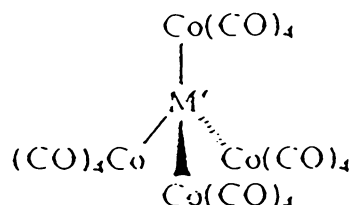
(b) $R_2M'[Co(CO)_4]_2$

$M' = Si$; $R = H$
 $M' = Ge$; $R = H, Me, Ph, Cl, I$
 $M' = Sn$; $R = \text{alkyl}, Ph, Cl, Br,$
 $I, CH_2=CH, MeCO_2, acac,$
 $M' = Pb$; $R = Ph$ [12]



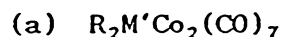
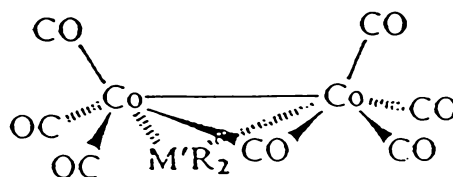
Note: For Ge and Sn most species will also occur with mixed ligands [12]

Table 1.1 continued

 $\text{M}' = \text{Ge}$ $\text{R} = \text{Cl}, \text{Br}$. [34] $\text{M}' = \text{Sn}$ $\text{R} = \text{H}, \text{alkyl}, \text{Ph}, \text{halogen}$. [12]. $\text{M}' = \text{Ge}, \text{Sn}, \text{Pb}$. [12]

Note: In each of (a), (b), (c) and (d), carbonyl groups on the $\text{Co}(\text{CO})_4$ units may be replaced by ligands such as PPh_3 . [12]

(ii) Compounds containing a group 14 atom bridging a Co-Co bond

 $\text{M}' = \text{Si}$; $\text{R} = \text{Ph}, \text{Cl}$. $\text{M}' = \text{Ge}$; $\text{R} = \text{Me}, \text{Ph}$. $\text{M}' = \text{Sn}$; $\text{R} = \text{Acac} + \text{other diketones}, \text{Me}^*$. [12]

* $\text{R} = \text{Me}$ is known but is unstable at 0°C . [12]

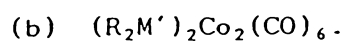
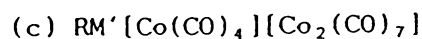
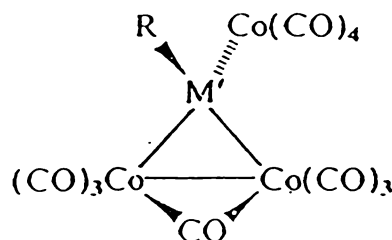
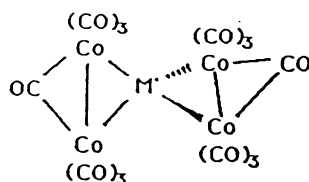
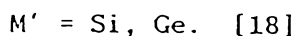
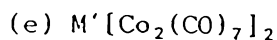
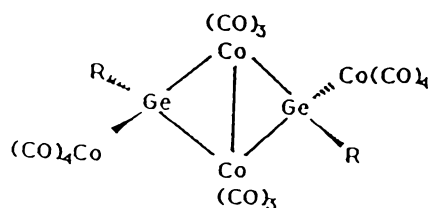
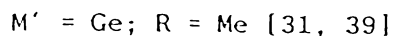
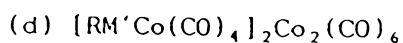
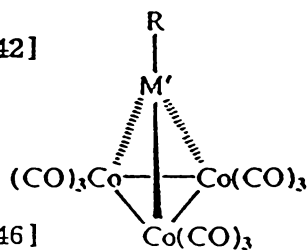
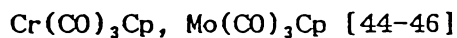
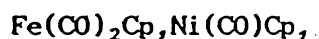
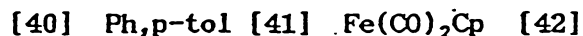
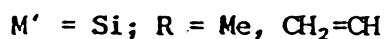
 $\text{M}' = \text{Ge}, \text{Sn}$; $\text{R} = \text{Me}$. [12] $\text{M}' = \text{Ge}$; $\text{R} = \text{Me}$, [35, 36] Ph , [37] Br [38]

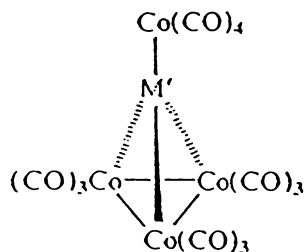
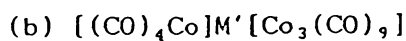
Table 1.1: continued



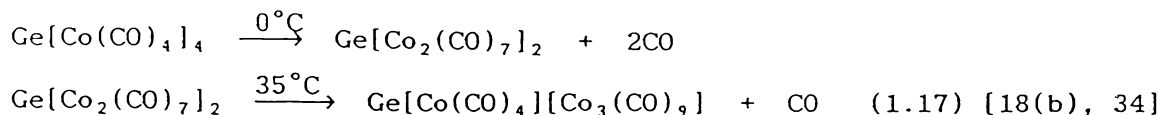
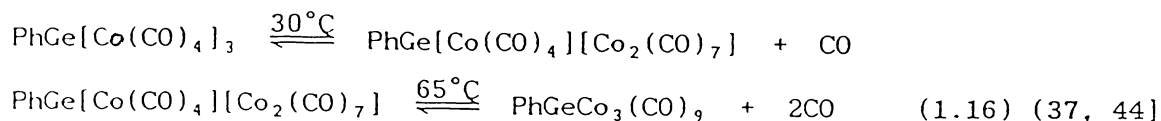
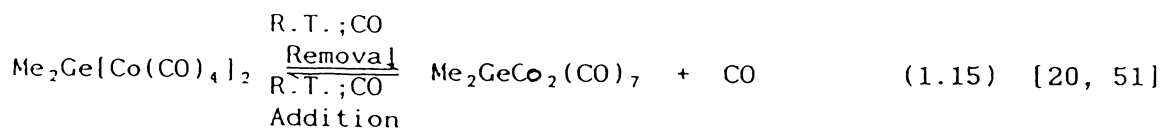
(iii) Compounds where a group 14 atom bridges a plane of cobalt atoms.



Related species: $\text{RM}'\text{Ir}_3(\text{CO})_9$, $\text{M}' = \text{Si}, \text{Ge}; \text{R} = \text{Me}$



For a given number of cobalt atoms, the germanium structures are interconvertible by CO loss, and in some cases by CO addition (equations 1.15 - 1.17)



For the process of equation 1.17, it is interesting that no evidence for a species such as $[(\text{CO})_7\text{Co}_2]\text{Ge}[\text{Co}(\text{CO})_4]_2$ has been obtained.

On the whole, the bridged species are formed in reactions involving a germanium hydride and $\text{Co}_2(\text{CO})_8$, while the non-bridged compounds are more commonly produced, at least initially, in halide coupling reactions.

The $\text{RM}'[\text{Co}(\text{CO})_4][\text{Co}_2(\text{CO})_6 \mu\text{-X}]$ clusters ($\text{X}=\text{CO}$, $\text{M}'\text{RCo}(\text{CO})_4$) are an extension of the $\text{R}_2\text{M}'[\text{Co}_2(\text{CO})_6 \mu\text{-X}]$ species ($\text{X}=\text{CO}$, $\text{M}'\text{R}_2$) where an R substituent has been replaced by a $\text{Co}(\text{CO})_4$ unit. $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ (figure 1.1) was recently prepared by the reaction of $\text{Fe}(\text{CO})_4(\text{GeMeH}_2)_2$ with $\text{Co}_2(\text{CO})_8$ [31].

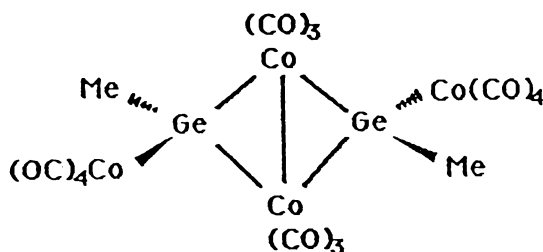


Figure 1.1

Analogous to $\text{M}'[\text{Co}_2(\text{CO})_7]_2$ ($\text{M}' = \text{Si}, \text{Ge}$) is $\text{M}'[\text{Fe}(\text{CO})_4]_4$ ($\text{M}' = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) (figure 1.2) [12]. The fact that the larger group 14 atoms are incorporated into this type of structure with iron, but not with cobalt, presumably reflects the lack of bridging carbonyl groups across the Fe-Fe bond, allowing a less compact structure.

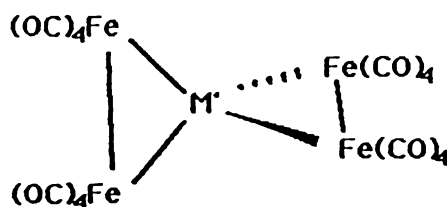


Figure 1.2

The compounds containing a group 14 atom bridging a cobalt triangle are directly analogous to the well established methylidyne clusters (figure 1.3).

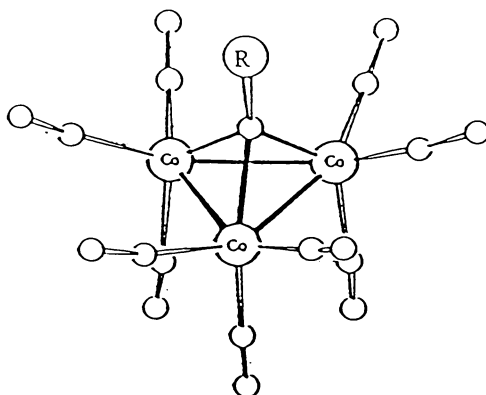
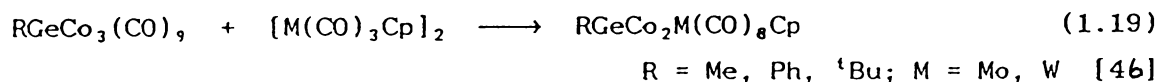
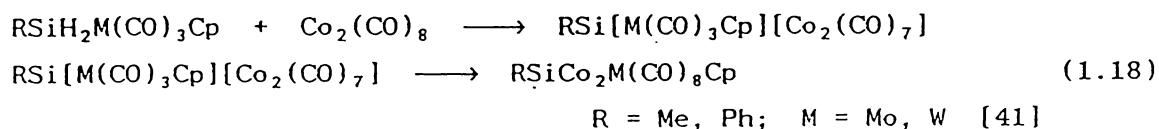


Figure 1.3

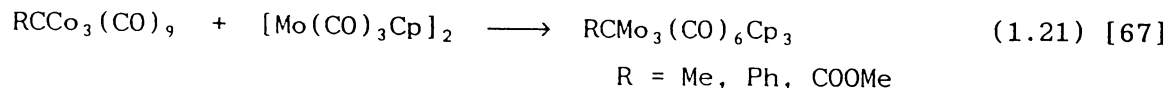
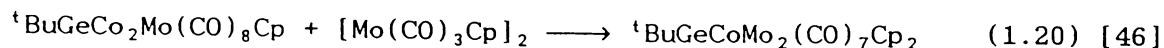
The carbon clusters are known for a wide range of substituents, R, and are generally extremely stable towards thermal decomposition [52].

The group 14 derivatives may be considered as a subset of the class of $L_nEM_3(CO)_x$ clusters which are formed by a variety of main group and transition metals [8]. Recent examples of these clusters include those where $M = Co$ [53], Fe [54, 55], Ru [56, 57], Os [58] and various mixed transition metal clusters, often containing cobalt [41, 44-46, 59-78].

Important preparative routes to MCo_2 heterometallic clusters are by reaction of $R_nM'ML_n$ with $Co_2(CO)_8$ [41] (equation 1.18) and direct metal exchange of the organometallic fragment, ML_n , with a $Co(CO)_3$ moiety of $RM'Co_3(CO)_9$ [46] (equation 1.19).

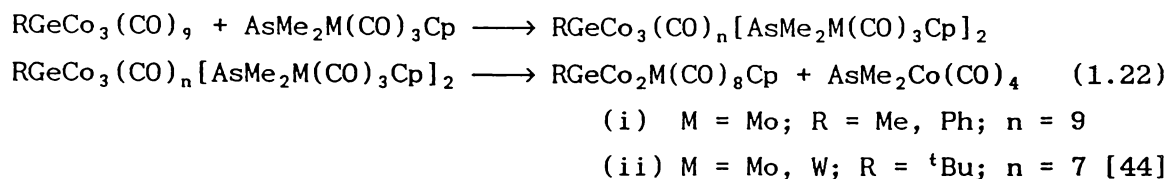


Multiple metal exchanges produce the mixed M_2Co cluster [46] (equation 1.20) and, in some cases, the homonuclear M_3 cluster [67] (equation 1.21).



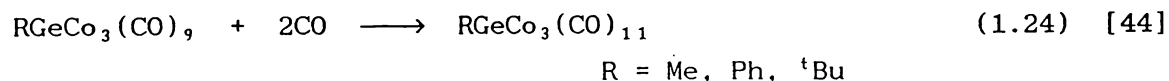
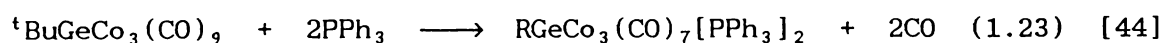
The Co(CO)_3 and ML_n groups are isoelectronic and isolobal, both providing three frontier orbitals and three electrons to the skeletal framework of the cluster.

Metal exchange of $\text{RGeCo}_3(\text{CO})_9$ has been achieved indirectly using $\text{AsMe}_2\text{M(CO)}_2\text{Cp}$ [44] (equation 1.22), by addition (R = Me, Ph) or by ligand substitution (R = ${}^t\text{Bu}$) with subsequent elimination of a Co-As fragment.

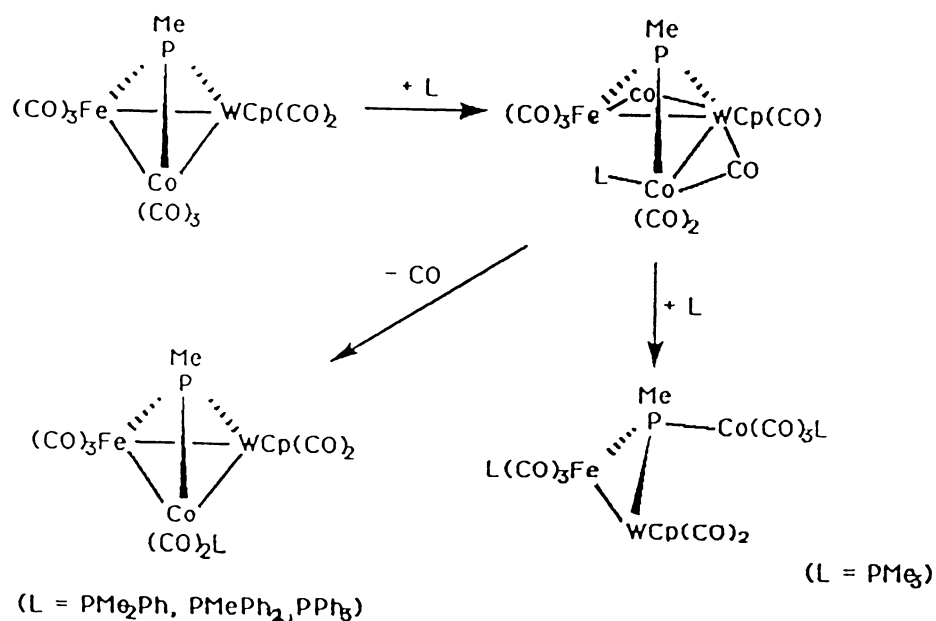


In case (ii), where R = ${}^t\text{Bu}$, a straightforward ligand substitution onto the closed cluster occurred, while in (i), where R = Me, Ph, the cluster opened out to $\text{RGe[Co(CO)}_4\text{][Co}_2(\text{CO})_7\text{]}$ before metal exchange was observed.

In addition to these metal exchange reactions [46, 60, 67, 68, 73], EM_3 clusters will undergo ligand substitution [44, 62, 72, 78] (equation 1.23) and cluster opening via ligand addition [44, 59, 77] (equation 1.24)

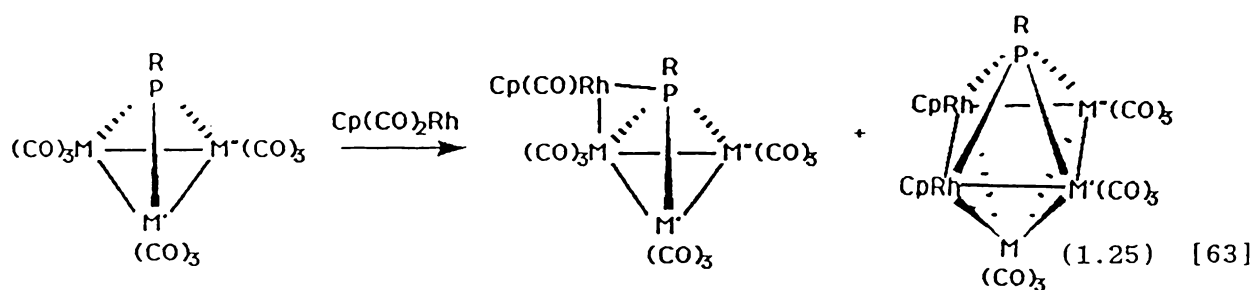


It has been suggested that a cluster opening/closing sequence may be a general pathway for ligand substitution of these clusters [77]; for example, scheme 1.3.



Scheme 1.3 [77]

The reaction of PM_3 with $\text{M}(\text{CO})_2\text{Cp}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) [63, 73] results in cluster expansion producing tetranuclear RPM_4 and pentanuclear RPM_5 clusters (equation 1.25). At low temperatures, and after short reaction times, the tetranuclear clusters have been isolated as intermediates, undergoing further reaction to the pentanuclear clusters.



1.3.2. Compounds Containing More Than Four Cobalt Atoms.

Other than carbido complexes, there are only a limited number of higher nuclearity group 14-cobalt carbonyl clusters, which may be subdivided into four structural classes as in table 1.2.

Table 1.2 Group 14- cobalt carbonyl compounds containing more than four cobalt atoms.

(i) Extended chain clusters of linked triangles.	reference
$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	20, 79
$(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$	20
$\{[(\text{CO})_4\text{CoHg}]\text{GeCo}_4(\text{CO})_{13}\}^-$	28, 80
$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$	19, 20, 21
$\text{Ge}_2\text{Fe}_2\text{Co}_4(\text{CO})_{21}$	22, 31
$\text{Si}_2\text{Co}_6(\text{CO})_{20}$	81
$(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$	20
$(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Fe}_2\text{Co}_4(\text{CO})_{19}$	82
$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$	20-23
(ii) Compounds incorporating the $\text{M}'\text{Co}_3$ tetrahedron.	
$\{[(\text{CO})_9\text{Co}_3]\text{Ge}[\text{Co}_2(\text{CO})_7]\}^-$	28, 29
$\{[(\text{CO})_9\text{Co}_3]\text{Ge}[\text{Co}_4(\text{CO})_{11}]\}^-$	83, 84
$\{[(\text{CO})_9\text{Co}_3\text{Ge}]_2\text{Co}(\text{CO})_3\}^-$	28, 83
$\{[(\text{CO})_9\text{Co}_3\text{Ge}][(\text{CO})_{10}\text{Fe}_2\text{CoGe}]\text{Co}(\text{CO})_3\}^-$	85
(iii) <i>Closo</i> -hexanuclear clusters $(\text{RM}')_2[\text{Co}_4(\text{CO})_{11}]$.	
$(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$	82
$[(\text{CO})_4\text{CoSi}]_2\text{Co}_4(\text{CO})_{11}$	81, 86
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	20, 87
$(\text{PhGe})_2\text{Co}_4(\text{CO})_{11}$	45, 88
$(^t\text{BuGe})_2\text{Co}_4(\text{CO})_{11}$	45, 88
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$	19, 20, 39
$(\text{RGe})[(\text{CO})_4\text{CoGe}]\text{Co}_4(\text{CO})_{11}$	39
(R = Me, Et, $\text{Mn}(\text{CO})_5$)	
(iv) Compounds with interstitial M' .	
$[\mu_8 - \text{SiCo}_9(\text{CO})_{21}]^{2-}$	89, 90

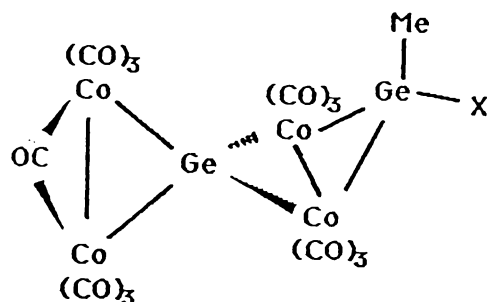
These compounds are divided into the above structural classes for discussion in the following sections.

1.3.2.1. Extended chain clusters.

These extended chain clusters are built up from successive $\text{M}'\text{Co}_2$ triangles and are the higher homologues of $\text{R}_2\text{M}'[\text{Co}_2(\text{CO})_6\mu\text{-X}]$ ($\text{X}=\text{CO}$, $\text{Me}_2\text{M}'$) and $\text{M}'[\text{Co}_2(\text{CO})_7]_2$ (table 1.1) They are generally prepared by the reaction

of a group 14 polyhydride with $\text{Co}_2(\text{CO})_8$ or by the reaction of a substituted group 14 hydride with an existing open chain cluster.

The reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ produced $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ where a GeMe_2 group had replaced one bridging carbonyl group of the starting cluster [20,79]. This resulted in a chain of three GeCo_2 triangles as depicted in figure 1.4.



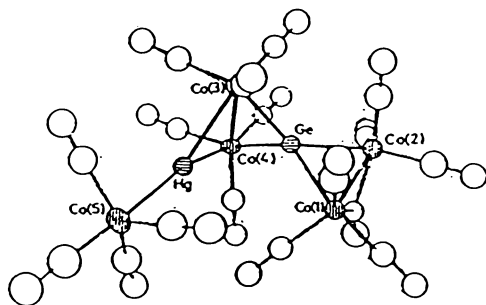
Proposed structure of
 $(\text{MeXGe})\text{GeCo}_4(\text{CO})_{13}$
 $\text{X} = \text{Me}, \text{H}$ [20]

Figure 1.4

$(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ (figure 1.4) was produced in the similar reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ [20].

The reactions of Me_2GeH_2 and Me_2SiH_2 with $\text{SiCo}_4(\text{CO})_{14}$ produced mainly $\text{Si}[\text{Co}(\text{CO})_4][\text{Co}_3(\text{CO})_9]$, although there was limited spectroscopic evidence for the formation of $(\text{Me}_2\text{Ge})\text{SiCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Si})\text{SiCo}_4(\text{CO})_{13}$ respectively [89].

A somewhat different member of this class is $\{[(\text{CO})_4\text{CoHg}]\text{GeCo}_4(\text{CO})_{13}\}^-$ (figure 1.5). This anion was found as a product in the reaction of GeI_4 with a solution of $\text{NaCo}(\text{CO})_4$ in which traces of finely suspended mercury amalgam were present [28, 80]. This is still the only example of a mercury bridged Co-Co bond

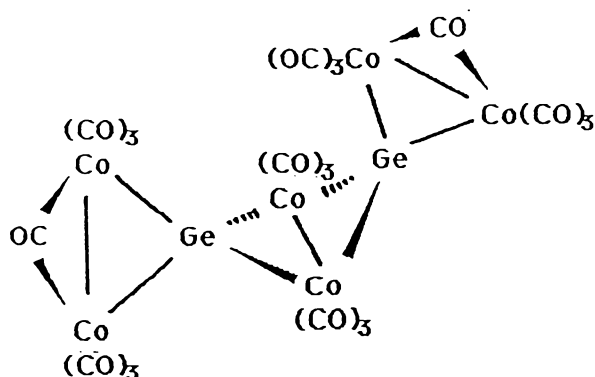


Structure of
 $\{[(\text{CO})_4\text{CoHg}]\text{GeCo}_4(\text{CO})_{13}\}^-$
[80]

Figure 1.5

$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was reported as the major product of the reaction of Ge_2H_6 with $\text{Co}_2(\text{CO})_8$ [19, 20, 21]. It was also produced in virtually quantitative yield by the reaction of $\text{Me}_2\text{Si}(\text{GeH}_3)_2$ with $\text{Co}_2(\text{CO})_8$ [19, 20] and in very low yields in the reaction of GeH_4 with $\text{GeCo}_4(\text{CO})_{14}$ [19, 20, 21]. Most

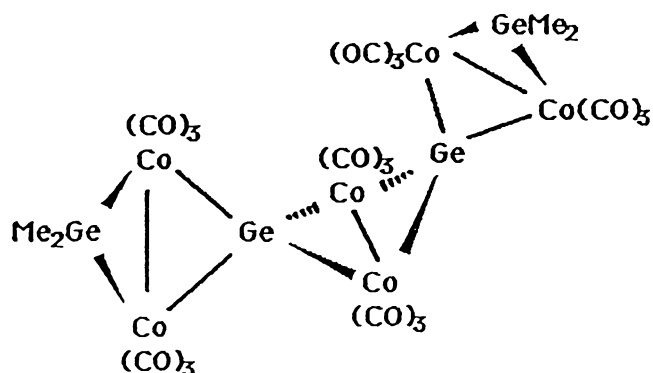
recently it was observed as a product in the reaction of $\text{Ge}_2\text{H}_5\text{Co}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$ [39]. It was proposed that the structure is that of four GeCo_2 triangles (figure 1.6), based on the similarities of its spectroscopic properties with those of the crystallographically characterised $\text{GeCo}_4(\text{CO})_{14}$ [18(b)] and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ [22, 23].



Proposed structure
of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ [19,20]

Figure 1.6

$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ underwent decarbonylation at 50°C to quantitatively produce $\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ [19, 20, 21] which will be discussed in section 1.3.2.3. A brief study of the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with Me_2GeH_2 suggested the major product to be $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (figure 1.7) where the two bridging carbonyl groups of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ had been replaced by Me_2Ge units, resulting in a chain of six GeCo_2 triangles [20].

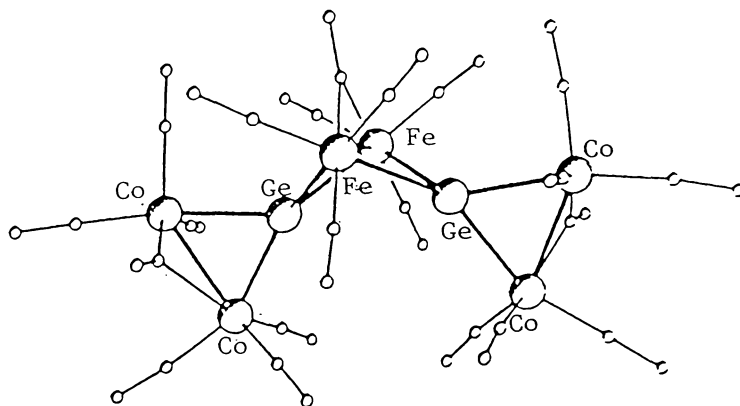


Proposed structure
of $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$
[20]

Figure 1.7

Closely related to $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ is $\text{Ge}_2\text{Fe}_2\text{Co}_4(\text{CO})_{21}$, produced in the reaction of $[\text{Fe}(\text{CO})_4\text{GeH}_2]_2$ with $\text{Co}_2(\text{CO})_8$ [22, 31]. Its structure has been determined crystallographically and contains a $\text{Fe}_2(\text{CO})_6$ moiety bridged by two $\text{Ge}[\text{Co}_2(\text{CO})_7]$ units and one carbonyl group (figure 1.8). It is the analogue of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ where the central $\text{Co}_2(\text{CO})_6$ unit has been replaced by a $\text{Fe}_2(\text{CO})_7$ group. The GeFe_2 and GeCo_2 units are asymmetric, as are the

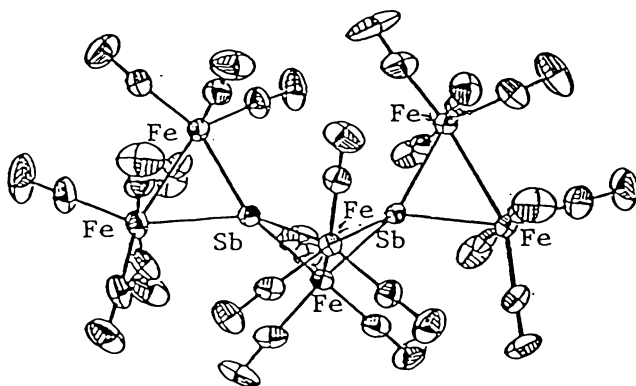
carbonyl groups that bridge the Co-Co bonds. The $\text{Fe}_2(\mu\text{-CO})$ arrangement is more nearly symmetrical [31].



Structure of
 $\text{Ge}_2\text{Fe}_2\text{Co}_4(\text{CO})_{21}$
[22, 31]

Figure 1.8

Closely related to both $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and $\text{Ge}_2\text{Fe}_2\text{Co}_4(\text{CO})_{21}$ is $\text{Sb}_2\text{Fe}_6(\text{CO})_{22}$. This has been prepared by two alternative routes, each giving crystal structures with the same molecular structure of four SbFe_2 triangles [75, 91] (figure 1.9) despite being determined in different space groups.



Structure of
 $\text{Sb}_2\text{Fe}_6(\text{CO})_{22}$
[75, 91]

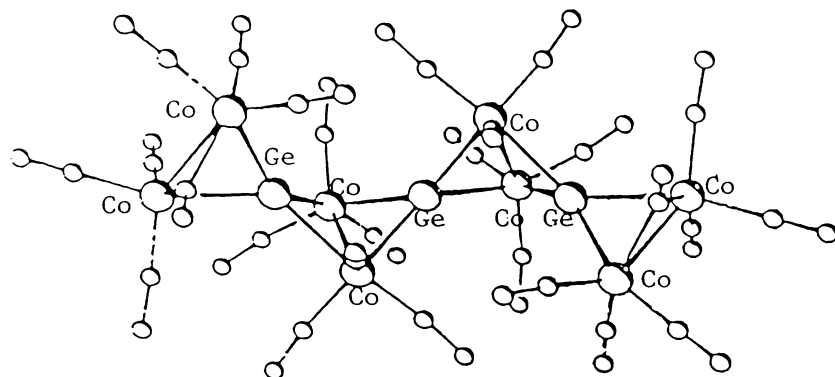
Figure 1.9

More recently two further isoelectronic species, $\text{Ge}_2\text{Fe}_6(\text{CO})_{23}$ and $\text{Sn}_2\text{Fe}_6(\text{CO})_{23}$, were prepared by the reaction of GeH_4 or SnH_4 respectively with $\text{Fe}_2(\text{CO})_9$ at 68°C [82]. The crystal structure of each of these species has been determined and these, again, comprise four $\text{M}'\text{Fe}_2$ triangles, linked by M' apices and Fe_2 edges [82].

$\text{Si}_2\text{Co}_6(\text{CO})_{20}$ is probably first formed in the reaction of Si_2H_6 with $\text{Co}_2(\text{CO})_8$, but readily decarbonylates to $\text{Si}_2\text{Co}_6(\text{CO})_{19}$ (section 1.3.2.3.) and a pure sample has not yet been obtained [81].

$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ was found as the major product of the reactions of Ge_3H_8 or $\text{MeSi}(\text{GeH}_3)_3$ with $\text{Co}_2(\text{CO})_8$ [20-23]. It was also observed as a minor

product in the reaction of GeH_4 or Ge_2H_6 with $\text{Co}_2(\text{CO})_8$ [20, 21, 23] and in the reaction of Ge_2H_6 with $\text{GeCo}_4(\text{CO})_{14}$ [23].



Structure of
 $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$
[22, 23]

Figure 1.10

This cluster, shown in figure 1.10., possesses a catenated structure in which $\text{GeCo}_2(\text{CO})_7$ units bridge either end of a central $\text{GeCo}_4(\text{CO})_{12}$ unit [22, 23]. Within the crystal, the central germanium is on a two fold axis so that half of the molecule is unique. The six GeCo_2 triangles are asymmetric, as are the bridging carbonyls which are displaced towards the cobalt atom with the longest Ge-Co bond [22, 23]. The bond lengths of the inner GeCo_4 unit are listed in table 1.3, together with the related bonds of some other molecules comprising GeCo_2 triangles.

Table 1.3 Inner GeCo_4 unit bond lengths of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ [22, 23], $\text{GeCo}_4(\text{CO})_{14}$ [18(b)] and $\{[(\text{CO})_4\text{CoHg}]\text{GeCo}_4(\text{CO})_{13}\}^-$ [80].

	$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (Ge_1 on 2-fold axis)	$\text{GeCo}_4(\text{CO})_{14}$	$\{[(\text{CO})_4\text{CoHg}]\text{GeCo}_4(\text{CO})_{13}\}^-$
$\text{Co}_1\text{-Co}_2$	2.664	2.565	2.536
$\text{Co}_3\text{-Co}_4$		2.565	2.751 (bridged by $\text{HgCo}(\text{CO})_4$ unit)
Ge-Co_1	2.361	2.38	2.432
Ge-Co_2	2.393	2.34	2.397
Ge-Co_3		2.34	2.317
Ge-Co_4		2.39	2.325

From table 1.3 it is clear that the introduction of a larger bridging group across the Co-Co bonds of the $\text{GeCo}_4(\text{CO})_{12}$ central unit of this series of molecules, results in the enlargement of all bonds of the GeCo_2 triangles.

On heating to 60°C , $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ broke up and the compounds $\text{GeCo}_4(\text{CO})_{13}$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ were obtained in approximately 25% and 5% yields

respectively, together with an insoluble residue [21]. Similarly, reaction of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ with Me_2GeH_2 was suggested to result in the breakdown of the cluster into Ge and Ge_2 units providing $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ among the products [23].

The only other extensive series of neutral clusters comprising chains of linked triangles are the loosely related polynuclear metal complexes described by Stone *et al.* [92]. In these compounds Pt-W, Pt-Mo or Ni-W bonds are held together by bridging alkylidyne groups and up to seven metal atoms may be found in a chain. The general form of these species is depicted in figure 1.11.

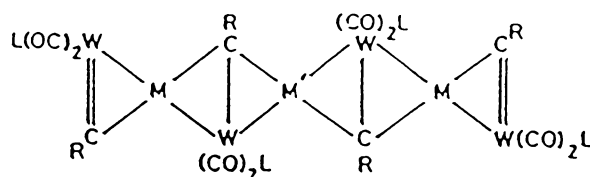
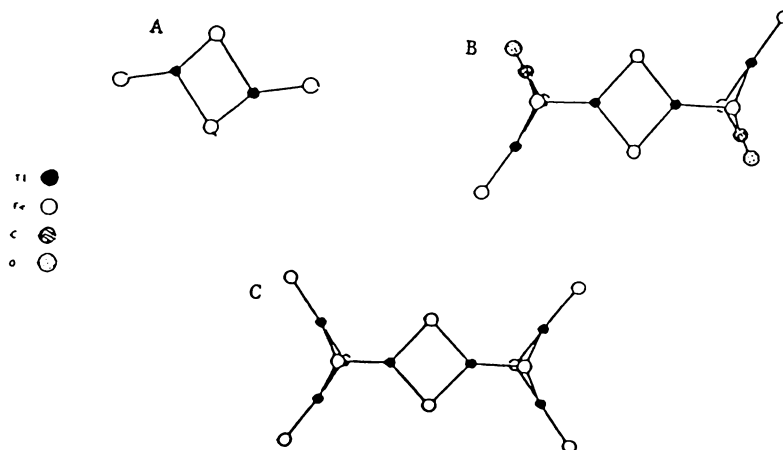


Figure 1.11 [92(b)]

These differ from the group 14-cobalt carbonyl chains of linked triangles since the metal atoms of the spine are co-planar rather than having a spiro arrangement.

Finally, a recent publication [157] has reported the preparation of three anionic thallium-iron carbonyl clusters, $[\text{Et}_4\text{N}]_2[\text{Tl}_2\text{Fe}_4(\text{CO})_{16}]$, $[\text{Et}_4\text{N}]_4[\text{Tl}_4\text{Fe}_8(\text{CO})_{30}]$ and $[\text{Et}_4\text{N}]_6[\text{Tl}_6\text{Fe}_{10}(\text{CO})_{36}]$. These all contain a central planar Tl_2Fe_2 parallelogram with the thallium atoms also bonded to either terminal $\text{Fe}(\text{CO})_4$ units or bridging $(\text{CO})_5\text{Fe}_2\text{TlFe}(\text{CO})_4$ or $(\text{CO})_4\text{Fe}_2\text{Tl}_2[\text{Fe}(\text{CO})_4]_2$ units. The metal core of the three anions are shown in figure 1.12.



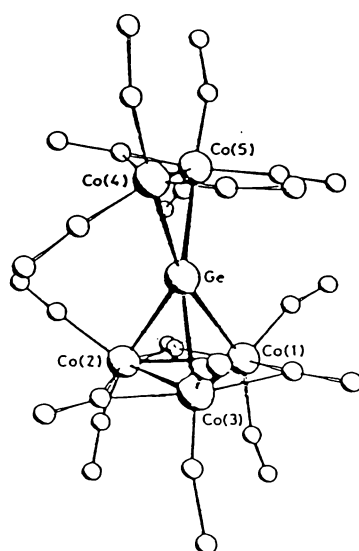
Metal frameworks of (a) $[\text{Tl}_2\text{Fe}_4(\text{CO})_{16}]^{2-}$; (b) $[\text{Tl}_4\text{Fe}_8(\text{CO})_{30}]^{4-}$ and (c) $[\text{Tl}_6\text{Fe}_{10}(\text{CO})_{36}]^{6-}$. Carbonyl ligands omitted for clarity [157].

Figure 1.12

1.3.2.2. Compounds incorporating the $M'Co_3$ tetrahedron.

These compounds, where the $M'Co_3$ trigonal pyramid is contained within the structure, are all anionic species and have been produced either by the reaction of a transition metal carbonyl anion with an existing group 14 cobalt carbonyl cluster, or by the reaction of an anionic cluster with $Co_2(CO)_8$.

$[GeCo_5(CO)_{16}]^-$ is produced in the reaction of $Et_4N[Co(CO)_4]^-$ with $GeCo_4(CO)_{16}$, $GeCo_4(CO)_{14}$ or $GeCo_4(CO)_{13}$ [28, 29]. The structure of this anion is shown in figure 1.13 and consists of a central germanium atom bridging both a $Co_2(CO)_7$ unit and a $Co_3(CO)_9$ triangle. This is still a unique structure for a five-coordinate germanium.

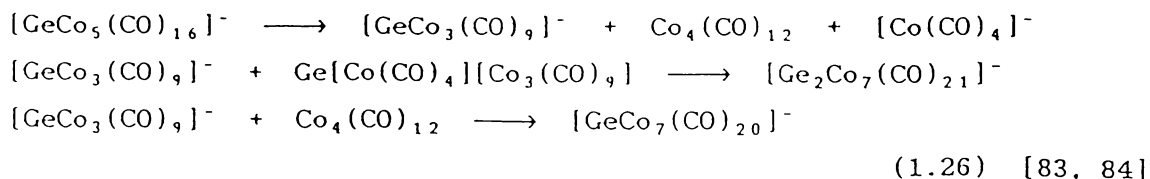


Structure of
 $[GeCo_5(CO)_{16}]^-$
[28, 29]

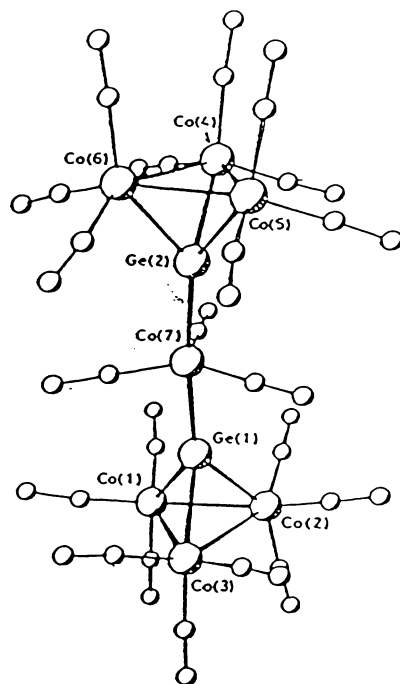
Figure 1.13

The reaction of $[Co(CO)_4]^-$ with $GeCo_4(CO)_{16}$ or $GeCo_4(CO)_{14}$ required heating to proceed, and it was indicated that initial formation of $GeCo_4(CO)_{13}$ (by decarbonylation of $GeCo_4(CO)_{16}$ or $GeCo_4(CO)_{14}$) was necessary before reaction with $[Co(CO)_4]^-$ would take place.

$[GeCo_5(CO)_{16}]^-$ reacted with $Co_2(CO)_8$ to produce $[Ge_2Co_7(CO)_{21}]^-$ [83, 84] while $[GeCo_7(CO)_{20}]^-$ was formed by recrystallisation of a sample of $[GeCo_5(CO)_{16}]^-$ which had been stored at $-30^\circ C$ for several months [84]. A scheme has been proposed to account for their formation [83, 84] (equation 1.26).



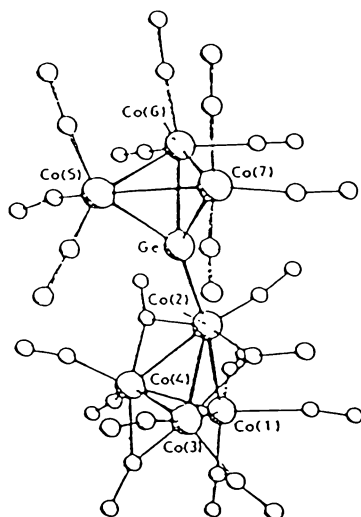
The structure of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ is shown in figure 1.14. It consists of two equivalent $\text{GeCo}_3(\text{CO})_9$ groups bonded through the Ge atoms to a planar $\text{Co}(\text{CO})_3$ moiety in a mutually trans configuration. The GeCo_3 groups are staggered with respect to each other and the carbonyl groups of the central $\text{Co}(\text{CO})_3$ moiety lie above the Co atoms of one cluster unit but point between the Co atoms of the other [83, 84].



Structure of
 $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$
 [83, 84]

Figure 1.14

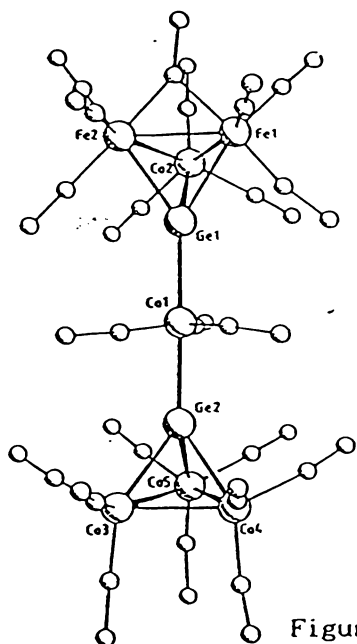
The structure of $[\text{GeCo}_7(\text{CO})_{20}]^-$ [83] is shown in figure 1.15. This may be regarded as a derivative of the C_{3v} form of $\text{Co}_4(\text{CO})_{12}$ with one terminal carbonyl group displaced by the $[\text{GeCo}_3(\text{CO})_9]^-$ unit. The metal core consists, therefore, of two individual tetrahedra, GeCo_3 and Co_4 , connected by a Ge-Co bond. A similar core has been reported for $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ [12] and a neutral arsenic analogue is also known [93].



Structure of
 $[\text{GeCo}_7(\text{CO})_{20}]^-$
 [83]

Figure 1.15

The final cluster of this group is $[\text{Ge}_2\text{Fe}_2\text{Co}_5(\text{CO})_{22}]^-$ which was produced in the reaction of $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{CO})_8]$ with $\text{GeCo}_4(\text{CO})_{14}$ [85]. This is analogous to $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ where a $\text{Co}_2(\text{CO})_6$ group of one GeCo_3 tetrahedron has been replaced by a $\text{Fe}_2(\text{CO})_7$ moiety. This, again, has been studied crystallographically, and the structure is shown in figure 1.16 [85].



Structure of
 $[\text{Ge}_2\text{Fe}_2\text{Co}_5(\text{CO})_{22}]^-$
 [85]

Figure 1.16

Also appropriate to this category is the recently prepared group of tin-cobalt carbonyl anions which are of the form $\{[\text{R}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ [94, 95]. In particular the compound $\{[(\text{CO})_4\text{Co}]_3\text{Sn}_2\text{Co}(\text{CO})_3\}^-$ (figure 1.17) is the open analogue of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ where the large tin atoms prevent closure to the $\text{M}'\text{Co}_3$ tetrahedra.

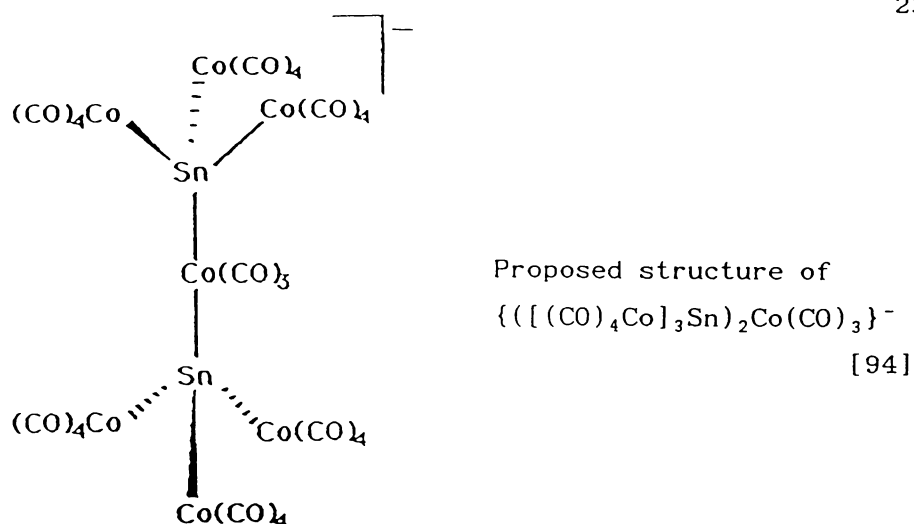
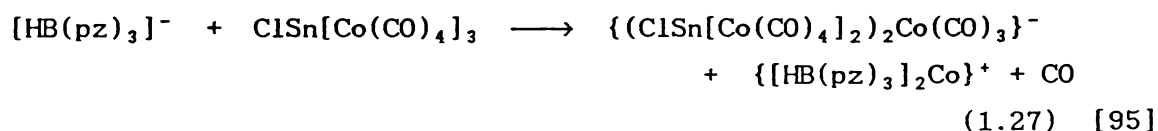
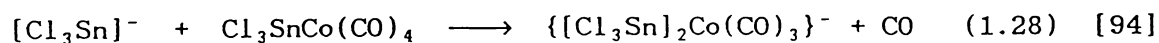


Figure 1.17

The other members of this series comprise $\{(\text{ClSn}[\text{Co}(\text{CO})_4]_2)_2\text{Co}(\text{CO})_3\}^-$, $\{[\text{Cl}_2\text{SnCo}(\text{CO})_4]_2\text{Co}(\text{CO})_3\}^-$ and $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ which have all been structurally characterised [94]. They were first prepared by the reactions of bis or tris(pyrazolyl-1)borate $[\text{H}_2\text{B}(\text{pz})_2]^-$ and $[\text{HB}(\text{pz})_3]^-$ respectively where pz = pyrazolyl, $\text{C}_3\text{H}_3\text{N}_2$) with the appropriate tin-cobalt carbonyl species [94, 95], for example equation 1.27.



It has recently been found that these anions may be more easily produced by reaction of $[\text{Cl}_3\text{Sn}]^-$ with an appropriate tin-cobalt carbonyl starting material [94]. For example, equation 1.28.



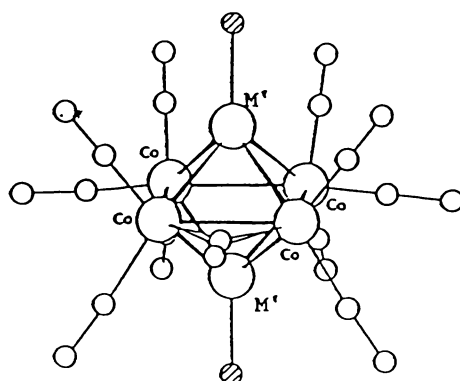
1.3.2.3. *Closo*-hexanuclear clusters.

The *closo*-hexanuclear clusters, $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$, consist of a quadrilateral plane of four cobalt atoms capped on each side by a quadruply bridging M'R group. This results in an irregular square bipyramidal core. Each of the core cobalts carries two terminal carbonyl ligands, while the remaining three carbonyl groups are bridging, each in a different manner.

These clusters are often prepared by the reaction of a group 14 polyhydride with $\text{Co}_2(\text{CO})_8$, or by decarbonylation and rearrangement of an existing open chain cluster. Preparations involving the reaction of RGeCl_3 species with $\text{KCo}(\text{CO})_4$ have also been reported [45, 88] although in these cases the clusters are produced in very low yield.

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was produced by decarbonylation of $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ [82] and was found in the reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ [20]. The latter system provided the cluster in low yield and its formation from this system was very difficult to rationalise. This is considered in some detail in Chapter 3. Other alkyl clusters, $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ ($\text{R} = \text{Ph}$, $t\text{Bu}$) have been prepared in low yields by the reaction of RGeX_3 with $\text{KCo}(\text{CO})_4$ [45, 88].

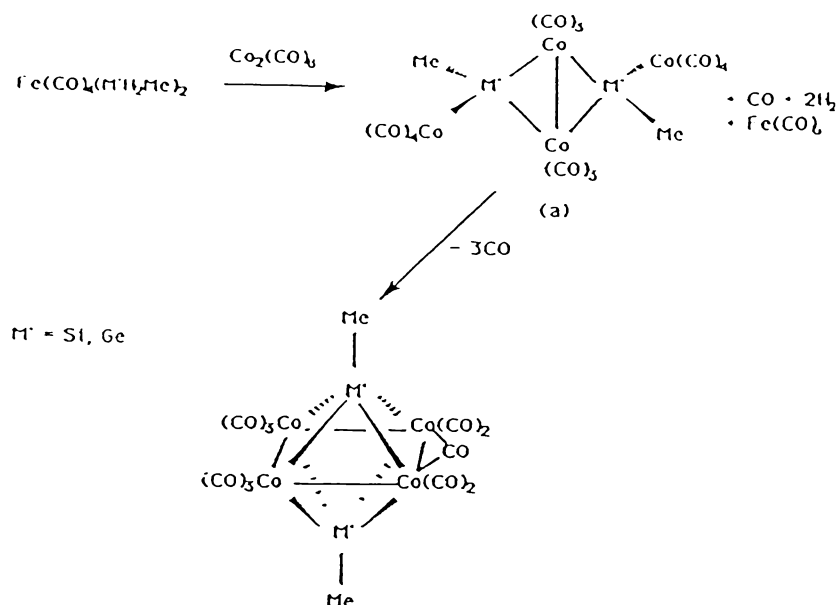
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ has the structure shown in figure 1.18 [20, 87]. The molecule possesses a crystallographic plane of symmetry which passes through the two germanium atoms, the methyl carbons and the bridging carbonyl.



Structure of
 $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$
 $\text{M}' = \text{Ge}$ [20, 87]
 Si [82]

Figure 1.18

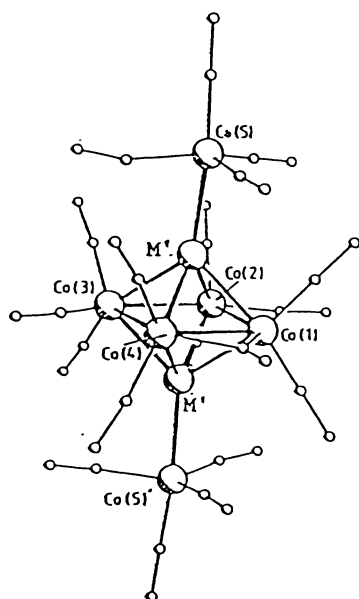
$\text{Fe}(\text{CO})_4(\text{GeH}_2\text{Me})_2$ was found to react with $\text{Co}_2(\text{CO})_8$ to form $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ [31] which subsequently decarbonylated to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [82]. $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ was produced by the corresponding reaction of $\text{Fe}(\text{CO})_4(\text{SiH}_2\text{Me})_2$ with $\text{Co}_2(\text{CO})_8$ [82]. These processes are depicted in scheme 1.4.



(a) Not observed for M = Si, but assumed to be an intermediate since the reaction process otherwise parallels the analogous germanium system.

Scheme 1.4 [31, 82]

$\text{Ge}_2\text{Co}_6(\text{CO})_{11}$, was produced by the decarbonylation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ [19, 20]. Its structure (figure 1.19) comprises a terminal $\text{Co}(\text{CO})_4$ unit attached to each germanium atom, which also bridges a central plane of four cobalt atoms lying on a crystallographic plane of symmetry.

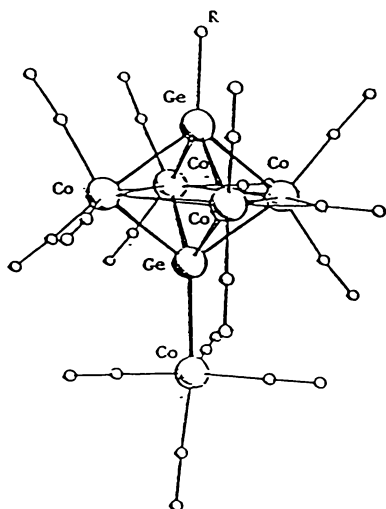


Structure of
 $\{[(\text{CO})_4\text{Co}]M'\}_2\text{Co}_4(\text{CO})_{11}$
 $M'=\text{Si}$ [81, 86]
 Ge [19, 20]

Figure 1.19

$\text{Si}_2\text{Co}_6(\text{CO})_{14}$ (figure 1.19) is closely related to the germanium analogue although the smaller silicon atom produces a more compact cluster [81, 86] (see table 1.4). This was obtained from the reaction of Si_2H_6 with $\text{Co}_2(\text{CO})_8$, however it differs from the equivalent Ge_2H_6 reaction since the open chain precursor, $\text{Si}_2\text{Co}_6(\text{CO})_{20}$, has never been isolated [81]. This is the first known compound incorporating five Si-M bonds.

Several *closa*-hexanuclear clusters of the form $(\text{RGe})(\text{R}'\text{Ge})\text{Co}_4(\text{CO})_{11}$ ($\text{R}=\text{Co}(\text{CO})_4$; $\text{R}'=\text{Me, Et, Mn}(\text{CO})_5, \text{Co}(\text{CO})_4$) have recently been prepared by the reaction of $\text{R}'\text{Ge}_2\text{H}_5$ with $\text{Co}_2(\text{CO})_8$ [39]. In general, the open chain precursor was also observed among the reaction products, but this readily decarbonylated to the *closa*-hexanuclear form. The structure shown in figure 1.20 is based on that obtained for $(\text{MeGe})[(\text{CO})_4\text{CoGe}]\text{Co}_4(\text{CO})_{11}$ [32]. Molecular structures have not been determined for the other clusters, but spectroscopic evidence suggests they are of the same form.

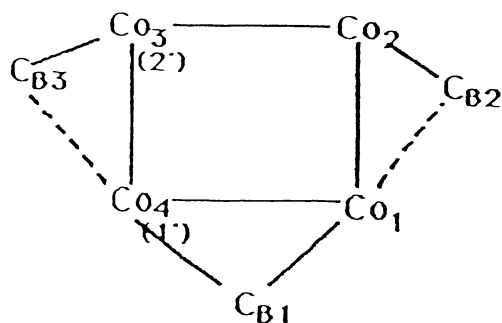


Structure of
 $(\text{R}'\text{Ge})[(\text{CO})_4\text{CoGe}]\text{Co}_4(\text{CO})_{11}$
 [32]

Figure 1.20

Also recently prepared, by a similar route, was the cluster $[(\text{CO})_4\text{CoSi}][\text{Cp}(\text{CO})_2\text{FeSi}]\text{Co}_4(\text{CO})_{11}$ [156].

Table 1.4 shows selected bond lengths of the $\text{M}'_2\text{Co}_4$ core of some of the above clusters, including those to the bridging carbonyl groups which are designated as shown in figure 1.21.



Designation of Co-C bonds
as applicable to table 1.4.

Figure 1.21

Table 1.4 Selected bond lengths of the M'_2Co_4 core of some $(R_2M')_2Co_4(CO)_{11}$ clusters.

$[(CO)_4CoSi]_2Co_4(CO)_{11}$ [81, 86]		$[(CO)_4CoGe]_2Co_4(CO)_{11}$ [19,20]		$[MeGe]_2Co_4(CO)_{11}$ [20,87]	
(mirror plane through Co ₄ atoms)		(mirror plane through Co ₄ atoms)		(mirror plane through two Ge's, methyl C's and bridging CO)	
Si-Co ₁	2.330 (2)	Ge-Co ₁	2.406 (4)	Ge ₁ -Co ₁	2.393 (2)
Si-Co ₂	2.351 (2)	Ge-Co ₂	2.423 (4)	Ge ₁ -Co ₂	2.381 (2)
Si-Co ₃	2.360 (2)	Ge-Co ₃	2.434 (5)	Ge ₂ -Co ₁	2.399 (2)
Si-Co ₄	2.308 (2)	Ge-Co ₄	2.390 (5)	Ge ₂ -Co ₂	2.385 (2)
Co ₁ -Co ₂	2.623 (2)	Co ₁ -Co ₂	2.671 (7)	Co ₁ -Co ₂	2.693 (2)
Co ₂ -Co ₃	2.653 (2)	Co ₂ -Co ₃	2.693 (8)	Co ₂ -Co ₂ '	2.721 (2)
Co ₃ -Co ₄	2.696 (2)	Co ₃ -Co ₄	2.735 (8)	Co ₁ -Co ₁ '	2.580 (2)
Co ₄ -Co ₁	2.569 (2)	Co ₄ -Co ₁	2.604 (7)		
Co ₁ -C _{B1}	1.97 (1)	Co ₁ -C _{B1}	1.95 (4)	Co ₂ -C _{B1}	1.92 (1)
Co ₄ -C _{B1}	1.86 (1)	Co ₄ -C _{B1}	1.94 (4)		
Co ₁ -C _{B2}	2.29 (1)	Co ₁ -C _{B2}	2.39 (4)	Co ₁ -C _{B2}	1.77 (1)
Co ₂ -C _{B2}	1.78 (1)	Co ₂ -C _{B2}	1.70 (4)	Co ₂ -C _{B2}	2.53 (1)
Co ₃ -C _{B3}	1.77 (1)	Co ₃ -C _{B3}	1.66 (5)		
Co ₄ -C _{B3}	2.63 (1)	Co ₄ -C _{B3}	2.61 (4)		
Average		Average		Average	
Co-C _{Terminal}	1.81	Co-C _{Terminal}	1.73	Co-C _{Terminal}	1.81

These data show that in each case there is one formal bridging carbonyl ligand across Co₁-Co₄, and two semi bridging carbonyl groups on the adjacent Co-Co bonds. The M'-Co bond lengths are reasonably close in each molecule. Since the thermal parameters are fairly high for these atoms, particularly in the silicon case, it is expected that the molecules undergo quite

extensive vibration and these slight bond differences are not, in fact, significant.

There are numerous clusters containing this square bipyramidal E_2M_4 core (M = transition metal, E = SiR, GeR, PR, AsR, S, Te) (see table 1.5) which indicates this as a very favourable structure. The electronic structure of this type of cluster has been analysed by Halet *et al.* [96]. It is shown that while the expected number of skeletal electron pairs (SEP) for an octahedral cluster is seven, for this type either seven or eight SEP will provide similar stability. An alternative opinion suggests that those clusters containing 7 SEP are unsaturated species. For example, the clusters $(RP)_2Fe_4(CO)_{11}$ [98] are two electrons short according to the eighteen electron rule. It is thus proposed that these are unsaturated, and since no formal double bond is observed (no significant difference was found in the Fe-Fe bond lengths) it is suggested that a delocalised 2π situation exists in the planar tetrairon ring [98]. In any event, this situation allows facile redox changes and reversible binding of CO, both of which are observed for several of these clusters. For example, $(PhP)_2RhFe_3(CO)_8(C_5Me_5)$ reversibly binds CO to form $(PhP)_2RhFe_3(CO)_9(C_5Me_5)$ [97]. $(PhP)_2RhFe_3(CO)_8(C_5Me_5)$ undergoes a pair of one-electron reversible reductions producing successively an anion and a dianion, while $(PhP)_2RhFe_3(CO)_9(C_5Me_5)$ undergoes a pair of one electron reversible oxidations producing successively a cation and a dication. The dication is isoelectronic with $(PhP)_2RhFe_3(CO)_8(C_5Me_5)$ while the dianion is isoelectronic with $(PhP)_2RhFe_3(CO)_9(C_5Me_5)$.

Table 1.5 Compounds possessing an E_2M_4 core.

			Reference
E = Si	M = Co $(RSi)_2Co_4(CO)_{11}$	R = Me	82
		Co(CO) ₄	81, 86
E = Ge	M = Co $(RGe)_2Co_4(CO)_{11}$	R = Me, Co(CO) ₄	19, 20, 87
		Ph, ^t Bu	45, 88
	mixed terminal $[(CO)_4CoGe](RGe)Co_4(CO)_{11}$	R = Me, Et, Mn(CO) ₅	39
	mixed metal $(^tBuGe)_2Co_3(CO)_8.ML_n$ $(^tBuGe)_2Co_2(CO)_5[NiCp]_2$	$ML_n = MoCp(CO)_2, NiCp$	45, 88 45, 88

Table 1.5 continued

E = P	M = Co	(RP) ₂ Co ₄ (CO) ₁₀	R = Ph	99-102
			BuO, EtN	99
			C ₆ H ₄ /SiO ₂	103
		(PhP) ₂ Co ₄ (CO) _{10-n} L _n	n = 1-4 L = P(OMe) ₃	104, 105
			n = 1,2 L = PPh ₃	101, 105
	(PhP) ₂ Co ₄ (CO) ₈ L		n = 1 L = H ⁻ , NCMe,	
			PEt ₃	102, 105
			L = Ph ₂ PCH ₂ PPh ₂	106
			Ph ₂ P(CH ₂) ₂ PPh ₂	105, 106
			Ph ₂ PCH=CHPPh ₂	106
			F ₂ PNMePF ₂	107
	M = Fe	(RP) ₂ Fe ₄ (CO) ₁₂	R = Me, Ph, ^t Bu, p-Tol	98, 108, 109
		(RP) ₂ Fe ₄ (CO) _{12-n} L _n	R = Ph, ^t Bu, p-Tol,	
			n 1,2 L = CO, P(OMe) ₃ ,	
			^t BuNC	109, 110
		(RP) ₂ Fe ₄ (CO) ₁₁	R = Me, Ph, ^t Bu, p-Tol	98, 108, 109, 111
	(RP) ₂ Fe ₄ (CO) _{11-n} L _n		R = Ph, ^t Bu, p-Tol	
			n = 1,4 L = CO, P(OMe) ₃ ,	
			^t BuNC	109, 110
	M = Rh	(PhP) ₂ Rh ₄ (COD) ₄		112
	M = Ru	(PhP) ₂ Ru ₄ (CO) ₁₁		113
	Mixed metal	(RP) ₂ Fe ₂ Co ₂ (CO) ₁₁	R = Me, Ph	109, 114
		(PhP) ₂ Fe ₂ Co ₂ (CO) ₁₀ L	L = H ⁻ , CHO ⁻ , CH ₃ CHO ⁻	115
		(MeP) ₂ Fe ₂ CoNiCp(CO) ₈		116
		(PhP) ₂ Rh(C ₅ Me ₅)Fe ₃ (CO) _n	n = 8,9	97
E = As	M = Co	(PhAs) ₂ Co ₄ (CO) ₁₀		102
E = P,S	M = Co	(RP)(S)Co ₄ (CO) ₁₀		117
E = S	M = Co	S ₂ Co ₄ (CO) ₁₀		118, 119
	M = Ru	S ₂ Ru ₄ (CO) ₁₀		120
		S ₂ Ru ₄ (CO) _{11-n} L _n	n = 0-2 L = PMe ₂ Ph	120
		(PhMe ₂ PS)(S)Ru ₄ (CO) ₉ (PMe ₂ Ph) ₂		121
	Mixed metal	S ₂ Fe ₂ Co ₂ (CO) ₁₁		114
E = Te	M = Co	Te ₂ Co ₄ (CO) ₁₀		100
E = Bi	M = Ru	Bi ₂ Ru ₄ (CO) ₁₂		122

Note: Also known are PM₅ species (M = Ru, Os) which may be considered as a halfway point between these E₂M₄ clusters and octahedral M₆ species [123].

Important reactions of these E_2M_4 clusters are ligand substitution [104-106, 110, 120, 124] and cluster opening by ligand addition [107, 124]. Little work has been carried out on the chemistry of the group 14-cobalt carbonyl clusters of this type as yet, however this is likely to be similar to the other E_2M_4 species, particularly the relatively straightforward ligand substitutions.

Carbonyl substitution on these clusters by ligands such as phosphines, phosphites and isocyanides may be achieved by thermal or ultraviolet means or by electronic pathways such as electron transfer catalysis. Multiple substitutions of monofunctional ligands occur sequentially on separate metal centres. For example, equation 1.29.

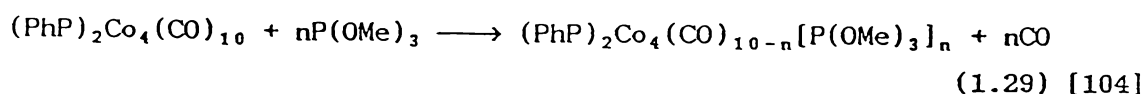


Figure 1.22 shows the tetrakis product $(\text{PhP})_2\text{Co}_4(\text{CO})_6[\text{P}(\text{OMe})_3]_4$ [104].

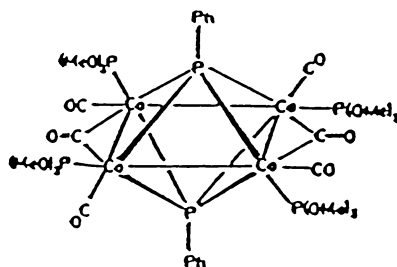
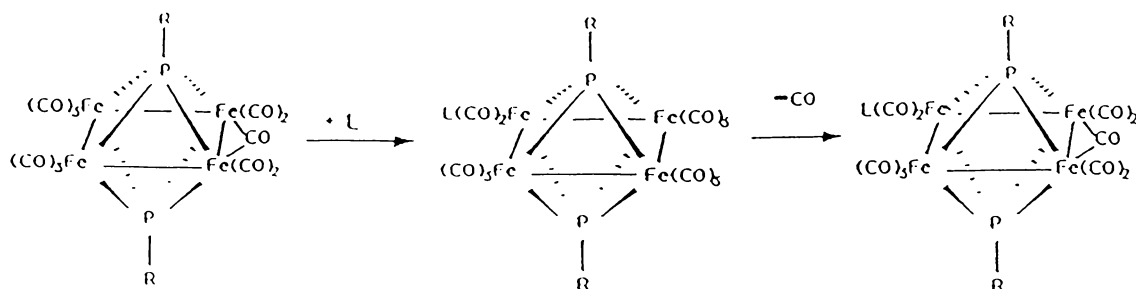


Figure 1.22 [104]

Here the syn/syn/anti/anti stereochemistry of the phosphite ligands is clear.

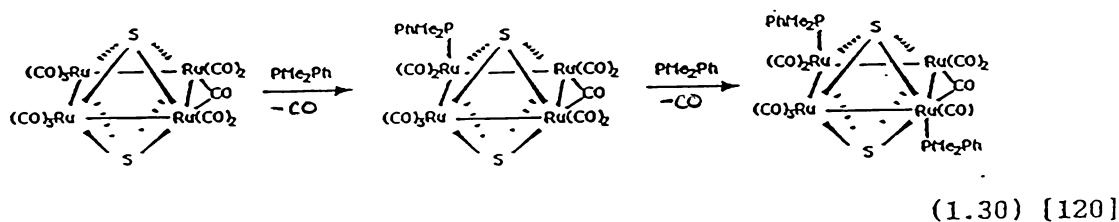
As stated earlier the clusters $(\text{RP})_2\text{Fe}_4(\text{CO})_{11}$ ($\text{R} = \text{t-Bu, Ph, p-Tol}$) are considered as unsaturated species. Support for this proposal was obtained by the facile addition of one ligand L , to these clusters ($\text{L} = \text{CO, P}(\text{OMe})_3, \text{t-BuNC}$) forming $(\text{RP})_2\text{Fe}_4(\text{CO})_{11}\text{L}$ [109, 110]. The new cluster then readily underwent carbonyl substitution, and reversion to the unsaturated form could then be achieved by CO elimination under vacuum [109, 110]. This process is depicted in scheme 1.5.



Scheme 1.5. [109, 110]

Bis substitution of these clusters generally led to only the unsaturated products which was most easily explained by the relatively strain free arrangement of the ligands in this form [110].

Related to these iron clusters are the **sulfidoruthenium** species prepared from $\text{S}_2\text{Ru}_4(\text{CO})_{11}$. These underwent facile thermal ligand substitution on reaction with PMe_2Ph and both the mono- and disubstituted derivatives were obtained [120] (equation 1.30). Although these clusters are also formally electron deficient no ligand adducts were observed as intermediates during these processes [120].



$(\text{PhP})_2\text{Ru}_4(\text{CO})_{11}$ was found to readily and reversibly add carbon monoxide. However, in contrast to the analogous iron cluster, the product of CO addition involved a rearrangement of the cluster framework to afford the tridecacarbonyl derivative $\text{Ru}_4(\mu_3\text{-PPh})_2(\text{CO})_{13}$ (figure 1.23) [125])

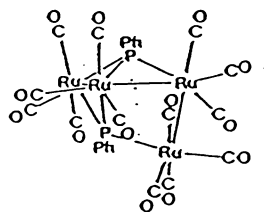
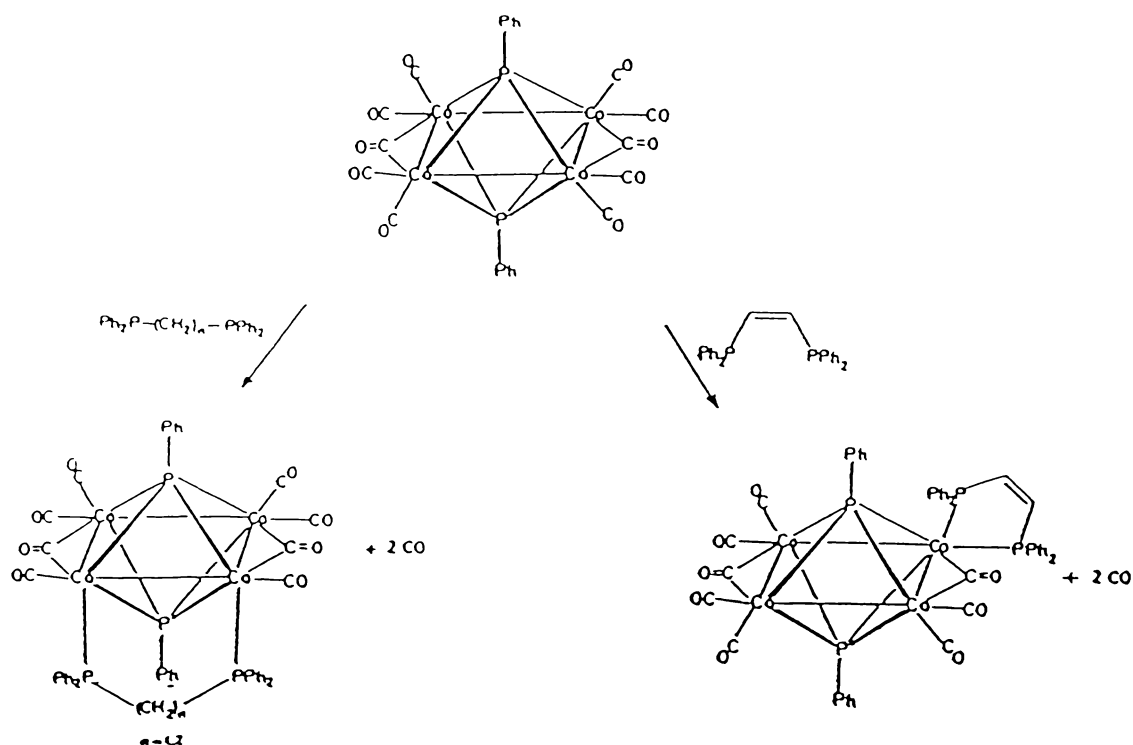


Figure 1.23 [125]

Where a difunctional ligand was employed, such as $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, this was observed to either bridge a pair of adjacent cobalt atoms or chelate a single cobalt atom depending on the length of the carbon backbone [106]. Examples of this are shown in scheme 1.6.



Scheme 1.6 [106]

$(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ was found to react readily with the difunctional fluorophosphine $(\text{F}_2\text{P})_2\text{NMe}$ to produce the tetrakis product shown in figure 1.24 [107]. This was the only product observed even where less than one molar equivalent of the ligand was used. However the monosubstituted species, $(\text{PhP})_2\text{Co}_4(\text{CO})_8[(\text{F}_2\text{P})_2\text{NMe}]$, was obtained from substitution of the electrogenerated anion $[(\text{PhP})_2\text{Co}_4(\text{CO})_{10}]^-$ [107] which formed during an electron transfer catalysed reaction.

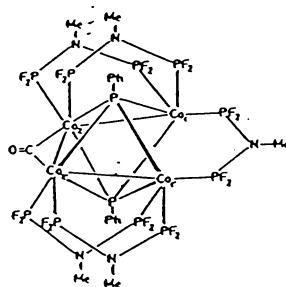


Figure 1.24 [107]

From figure 1.24 it is clear that the substitution of $(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ by four $(\text{F}_2\text{P})_2\text{NMe}$ ligands resulted in scission of one $\text{Co}-\text{Co}$ bond. This was attributed to the number of ancillary two electron donor ligands being eleven, one more than in the parent cluster. The coordination of the extra donor ligand provided the extra skeletal electron pair necessary for the observed polyhedral expansion [107].

Reaction of $(\text{PhP})_2\text{Ru}_4(\text{CO})_{11}$ with acetylene under ambient conditions led to the insertion of the acetylene into the skeletal framework resulting in the formation of $\text{Ru}_4(\mu_4\text{-PPh})(\mu_4\text{-}\eta^3) - \text{P(Ph)CHCH}](\text{CO})_{11}$ [126] (figure 1.25).

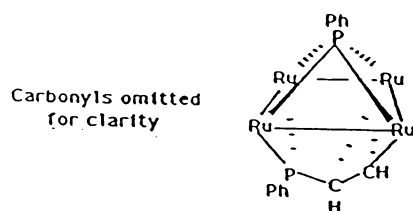
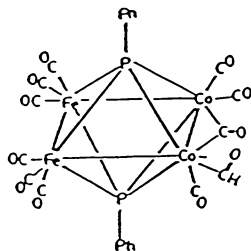
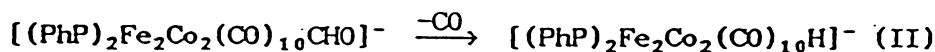
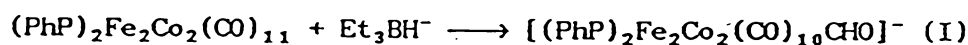
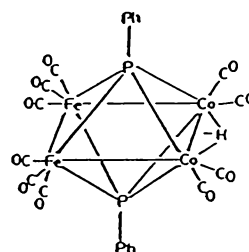


Figure 1.25 [126]

$(\text{PhP})_2\text{Fe}_2\text{Co}_2(\text{CO})_{11}$ was observed to undergo nucleophilic addition of Me-Li^+ and Et_3BH^- . This resulted in the clusters $[(\text{PhP})_2\text{Fe}_2\text{Co}_2(\text{CO})_{10}(\text{CO})\text{CH}_3]^-$ and $[(\text{PhP})_2\text{Fe}_2\text{Co}_2(\text{CO})_{10}\text{CHO}]^-$ respectively [115]. As shown in figure 1.26, the latter will readily lose CO to form the μ_2 -hydride $[(\text{PhP})_2\text{Fe}_2\text{Co}_2(\text{CO})_{10}\text{H}]^-$ [115].



(I)



(II)

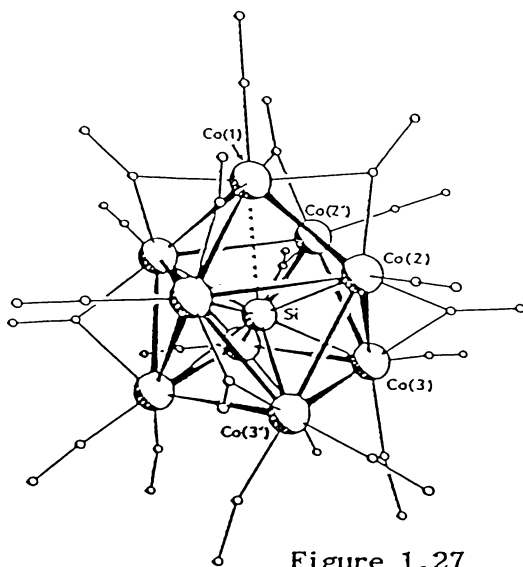
Figure 1.26 [115]

Although studies of the chemistry of $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$ clusters ($\text{M}' = \text{Si}, \text{Ge}$) have been minimal so far, the above observations indicate the fascinating range of products which may be anticipated.

1.3.2.4. Compounds with interstitial M'

Although carbido clusters are well established, until recently the only known compound incorporating an interstitial M' into its structure was the paramagnetic anion $[\mu_8\text{-SiCo}_4(\text{CO})_{21}]^{2-}$ (figure 1.27). This compound was formed in the reaction of $\text{SiCo}_4(\text{CO})_{14}$ with $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ [89, 90]. This

product is entirely different from that obtained in the analogous reaction of $\text{GeCo}_4(\text{CO})_{14}$ with $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$, which produced $[\text{GeCo}_5(\text{CO})_{16}]^-$ [28, 29] (figure 1.13). This, again, reflects how the products obtained are dependent on the size of the group 14 atom involved (see section 1.3.1).



Structure of
 $[\mu_8\text{-SiCo}_9(\text{CO})_{21}]^{2-}$
 [89, 90]

Figure 1.27

The structure of $[\mu_8\text{-SiCo}_9(\text{CO})_{21}]^{2-}$ (figure 1.27) is that of a capped tetragonal antiprismatic array of cobalt atoms where the silicon atom occupies the cavity within the antiprism [89, 90]. Other known structures of this type include $[\text{Rh}_9(\text{CO})_{21}\text{P}]^{2-}$ [127] in which the phosphorus atom is surrounded by a capped cubic antiprism of rhodium atoms, and $[\text{Co}_8(\text{CO})_{18}\text{C}]^{2-}$ [128] where the carbon atom is encapsulated in a tetragonal antiprismatic structure of cobalt atoms.

It has recently been reported [158] that the reaction of GeCl_4 with $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ provides either $[\text{GeNi}_{12}(\text{CO})_{22}]^{2-}$ or $[\text{GeNi}_{10}(\text{CO})_{20}]^{2-}$ depending on the reaction ratio employed. In both compounds the molecular structure is based on a Ge-centred icosahedral packing of metal atoms. An analogous structure is also found for the related tin compound $[\text{SnNi}_{12}(\text{CO})_{22}]^{2-}$ [159].

1.4. Instrumental techniques for the analysis of group 14-cobalt carbonyl compounds.

1.4.1. Carbonyl Region Infrared Spectroscopy.

Carbonyl region infrared spectroscopy is a valuable tool for the analysis of these compounds. For simplicity, this discussion is divided into structural categories of molecules containing all terminal $\text{Co}(\text{CO})_4$ units, those where a group 14 atom bridges a Co-Co bond, and those where a group 14 atom bridges a plane of cobalt atoms.

1.4.1.1. Carbonyl region infrared spectroscopy of molecules comprising all terminal $\text{Co}(\text{CO})_4$ units.

In the analysis of these simple species carbonyl region infrared spectroscopy is a powerful aid. For compounds of the type $\text{R}_3\text{M}'\text{Co}(\text{CO})_4$ with C_{3v} symmetry, $2a_1 + e$ carbonyl stretching modes are predicted, and generally observed. Replacing M' by a heavier group 14 atom tends to shift bands by $1\text{--}2\text{ cm}^{-1}$ to lower frequency [34]. The replacement of substituents by less electronegative groups also leads to a downward shift of bands, usually more marked than for M' exchange [34]. Unsymmetrically substituted $\text{X}_2\text{YM}'\text{Co}(\text{CO})_4$ compounds are of C_s symmetry. Splitting of the e mode of C_{3v} to $a' + a''$ is often reflected by the appearance of an extra band [20]. Table 1.6 lists the carbonyl region infrared spectra of three examples.

Table 1.6 Carbonyl region infrared spectra of some $\text{R}_3\text{M}'\text{Co}(\text{CO})_4$ compounds.

$\text{Me}_3\text{SnCo}(\text{CO})_4$ [129]	$\text{Me}_3\text{GeCo}(\text{CO})_4$ [129]	$\text{MeGeH}_2\text{Co}(\text{CO})_4$ [35]
2099 m	2101 m	2106 m a'
2028 w-m	2030 m	2046 m-s a'
2001 vs	2004 vs	2017 vs $a' + a''$
		2012 s }

All recorded as gases (cm^{-1}).

The bis-cobalt species, $\text{R}_2\text{M}'[\text{Co}(\text{CO})_4]_2$, with both substituents the same, are of C_{2v} symmetry with $3a_1 + 3b_1 + b_2$ infrared active modes predicted for the carbonyl region. All of these are usually observed. When the substituents differ the symmetry is reduced to C_s with $4a' + 4a''$ vibrations predicted [20]. Table 1.7 gives examples of the carbonyl region infrared spectra of these types of molecules.

Table 1.7. Carbonyl region infrared data for two $R_2M'[Co(CO)_4]_2$ species. (cm^{-1}).

$Me_2Ge[Co(CO)_4]_2$ [20]	$MeClGe[Co(CO)_4]_2$ [35]
2099 w	2109 w
2081 vs	2091 vvs
2032 sh	2049 m
2025 s	2043 m
2019 vs	2031 vs
2007 vs	2025 vs
1997 m	2014 m
	2002 w

Recorded in hexane

The tris- $Co(CO)_4$ molecules are ideally of C_{3v} symmetry with the predicted $3a_1 + 4e$ carbonyl stretching modes generally observed [20]. For example, the carbonyl region infrared spectrum of $MeGe[Co(CO)_4]_3$ [20] is listed in table 1.8.

Table 1.8. Carbonyl region infrared data for $MeGe[Co(CO)_4]_3$ [20]. (cm^{-1}).

2102 w
2084 s-vs
2038 sh, w-m
2030 sh, m
2020 vs
2012 vs
2004 sh, w-m
1997 sh, w

Recorded in hexane

The weak-medium intensity high wavenumber band observed in the spectra of these simple compounds is often a useful indicator of the presence of a terminal $Co(CO)_4$ unit.

The tetrakis-cobalt molecules are ideally of T_d symmetry with $3t_2$ infrared active carbonyl stretching modes predicted. The spectra consist of two very strong bands and two weak bands. This has been explained by a twisting motion of the $Co(CO)_4$ units about the $M'-Co$ axis resulting in the molecule having only T symmetry. This would correspond with the $4t$ bands observed in the carbonyl region. Table 1.9. lists the carbonyl region infrared spectrum of $Ge[Co(CO)_4]_4$ [34].

Table 1.9. Carbonyl region infrared data of $\text{Ge}[\text{Co}(\text{CO})_4]_4$ [34] (cm^{-1}).

2079 s
2032 sh
2020 vs
2000 br

Recorded in hexane

1.4.1.2. Carbonyl region infrared spectra of molecules containing a group
14 atom bridging a Co-Co bond.

Bor [130] has discussed the generalised infrared spectrum expected for the carbonyl stretches of $M_2(CO)_6(\mu-X)_2$ species, of idealised C_{2v} symmetry. This generalised spectrum is shown in figure 1.2b.

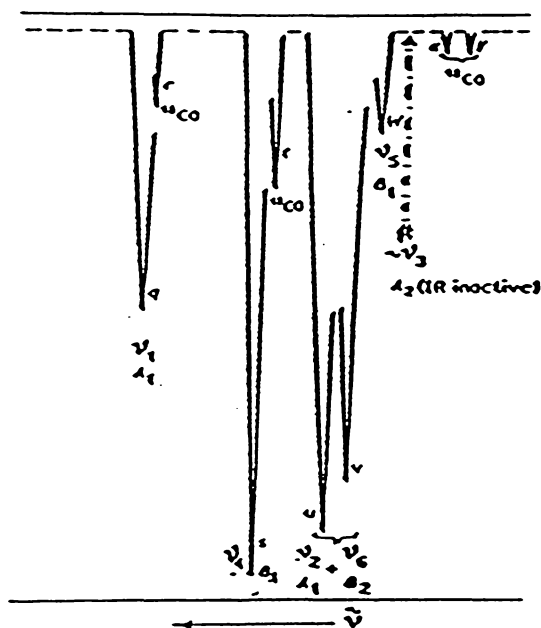


Figure 1.28 [130]

A comparison of the carbonyl region infrared spectra of $\text{Co}_2(\text{CO})_6(\mu\text{-GeR})_2$ and $\text{Co}_2(\text{CO})_7(\mu\text{-GeR}_2)$ with this generalised spectrum shows well resolved main bands as predicted (see table 1.10).

Table 1.10 Carbonyl stretching region infrared data for dimethylgermyl substituted cobalt carbonyl species. (cm^{-1})

Bor symbol [130]	$[\text{Me}_2\text{Ge}]_2\text{Co}_2(\text{CO})_6$ [17](a)	$(\text{Me}_2\text{Ge})\text{Co}_2(\text{CO})_7$ [20](b)
q	2072 s	2088 s
s	2035 vs	2048 vs
u	2014 vs	2026 vs
v	1994 vs	2008 vs
w	1984 m	1998 sh, w
	1964 vw (c)	1965 sh, vw (c)

(a) Recorded as cyclohexane solution

(b) Recorded as hexane solution

(c) Probably ^{13}C satellite peak

From table 1.10 it is also clear that replacement of one bridging carbonyl group by a Me_2Ge group leads to a shift to lower frequency of an average 14 cm^{-1} .

Bor's idealised infrared spectrum is also a useful diagnostic tool for the larger open chain clusters such as $\text{GeCo}_4(\text{CO})_{14}$, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (section 1.3.2.1.). These compounds are structurally related and comprise chains of two, four and six GeCo_2 triangles respectively. Their infrared spectra (table 1.11) are compatible in each case with two, three and four $(\mu\text{-M}')_2\text{Co}_2(\text{CO})_6$ Bor Units [130]. There is an increase in wavenumber of the higher frequency carbonyl stretches of this series, with increasing cluster size.

Table 1.11. Carbonyl region infrared spectra of $\text{GeCo}_4(\text{CO})_{14}$, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$. (cm^{-1})

$\text{GeCo}_4(\text{CO})_{14}$ (a) [18 (b)]	$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (a) [20]	$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (b) [20]
2079 s	2087 s	2094 s
2061 vs	2068 vs	2073 s
	2054 m	2065 vs
2040 m	2050 sh	2053 s
	2040 w	
2032 m	2033 w	2038 m
2023 w	2027 m	2027 m
2005 w	2021 w	2011 sh, w
	2003 w	
1848 m	1848 sh	1853 br, w
	1844 m	

(a) Recorded from hexane solution

(b) Recorded from hexane/dichloromethane solution

Where a cluster contains both terminal $\text{Co}(\text{CO})_4$ groups and bridged $\text{Co}_2(\text{CO})_6$ units analysis of the infrared spectrum becomes very difficult. It is sometimes possible to assign a portion of the bands on the basis of their similarities in intensity and position to those of related, but more simple species, and this process is employed on occasion in the work described in this thesis. Often there is mixing between bands resulting from carbonyl groups situated in different environments which further complicates the analysis, however carbonyl region infrared spectroscopy is still a useful aid in the identification of known compounds through a "fingerprint" comparison.

1.4.1.3. Carbonyl region infrared spectra of molecules containing a group 14 atom bridging a plane of cobalt atoms

For molecules of the form $\text{RM}'\text{Co}_3(\text{CO})_9$, based on C_{3v} molecular symmetry, five infrared active carbonyl stretching modes ($2a_1 + 3e$) are predicted and usually observed. For example, the spectra of two molecules in this series are shown in table 1.12.

Table 1.12. Carbonyl region infrared data for two $\text{RM}'\text{Co}_3(\text{CO})_9$ species. (cm^{-1})

$\text{MeGeCo}_3(\text{CO})_9$, [38]	$(\text{CO})_4\text{CoGeCo}_3(\text{CO})_9$, [50]
2108 m	2112 w
2055 vs	2083 ms
2045 s	2045 vs
2018 m	2029 m
1992 w	2008 w
	1991 vw

Both recorded from hexane solution

For larger molecules, such as the anionic species described in section 1.3.2.2., the analysis of the carbonyl stretching modes becomes difficult. Its use as a fingerprint technique, however, is well illustrated by these anions. Table 1.13. shows the carbonyl region infrared data for the anions $[\text{GeCo}_5(\text{CO})_{16}]^-$, $[\text{GeCo}_7(\text{CO})_{20}]^-$ and $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$. The weak bands at higher wavenumber are very important in distinguishing these species.

Table 1.13. Carbonyl region infrared data for some anionic germanium - cobalt carbonyl clusters (cm^{-1}).

$[\text{GeCo}_5(\text{CO})_{16}]^-$ [28, 29]	$[\text{GeCo}_7(\text{CO})_{20}]^-$ [83]	$[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ [83, 84]
2078 w	2078 w	2064 m
2053 w-m	2048 m	
2025 vs	2022 vs	2024 vs
2000 w	1995 w	2007 m
1963 sh	1968 br, w	1969 w, br
1820 w, br		

All recorded from dichloromethane solution

Related to these germanium-cobalt carbonyl anions is the series of anionic tin species $\{[\text{R}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$, discussed in section 1.3.2.2. [94, 95]. The carbonyl region infrared spectra of each of the molecules are shown in table 1.14.

Table 1.14. Carbonyl region infrared spectra of $\{[\text{R}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ species [94] (cm^{-1}).

$\text{R}_3 = [(\text{CO})_4\text{Co}]_3$	$\text{R}_3 = [(\text{CO})_4\text{Co}]_2\text{Cl}$	$\text{R}_3 = [(\text{CO})_4\text{Co}]\text{Cl}_2$
2082 m, w	2078 s	2094 m
2065 s	2070 s	2087 s
2056 w, sh	2064 s	2069 w
		2052 m
		2034 m
1994 vs, br	2001 vs, br	2010 vs, br
1970 w, sh	1934 m, br	1967 m

All recorded in dichloromethane solution

From table 1.14 it is clear that each replacement of a $\text{Co}(\text{CO})_4$ unit on the tin atoms by a Cl atom results in a shift of the major peaks to higher wavenumber, the shift being of an average 8 cm^{-1} . This may be compared to the shift observed on going from $\text{MeGe}[\text{Co}(\text{CO})_4]_3$ to $\text{MeClGe}[\text{Co}(\text{CO})_4]_2$ (tables 1.7 and 1.8) where replacing a $\text{Co}(\text{CO})_4$ unit by Cl results in the bands again moving to higher wavenumber by an average of 8 cm^{-1} .

The *clos*-hexanuclear clusters, $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$, generally show similar patterns in their carbonyl region infrared spectra. For the carbonyl ligands of the $\text{Co}_4(\text{CO})_{11}$ plane eight infrared active modes are predicted for terminal and semi-bridging carbonyls based on C_{2v} molecular symmetry. The observed spectra, however, often show only five terminal carbonyl stretches

and one fully bridging stretch from this unit. If D_{4h} symmetry is considered for the $\text{Co}_4(\text{CO})_8$ moiety then three infrared active bands are predicted which, together with the two semi-bridging carbonyl stretches, is consistent with the observed spectra. Table 1.15 lists the carbonyl region infrared spectra for two examples from this group.

Table 1.15. Carbonyl region infrared spectra of two $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$ species. (cm^{-1})

$(\text{Me}_2\text{Ge})_2\text{Co}_4(\text{CO})_{11}$ [20]	$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ [20]
	2100 s
	2065 w, sh
	2050 s, sh
2034 vs	2037 vs
2015 s, sh	2014 m
2004 sh, m	2003 sh, w
1990 w	1990 sh, w
1985 vw	
1850 w, br	1844 w, br

Both recorded from dichloromethane solution

1.4.2. Raman Spectroscopy of Group 14-Cobalt Carbonyl Compounds.

As yet, virtually no work has been carried out on the Raman spectra of the more complex molecules of this class. Study in this area has been confined solely to the smaller compounds containing only one or two group 14-cobalt bonds. Even with these simple molecules problems have been found where the samples decompose during the recording of the spectrum, resulting in complicated analysis, particularly of the carbonyl region.

A complete Raman spectrum of $\text{H}_3\text{GeCo}(\text{CO})_4$ as a liquid has been reported [143]. Here the carbonyl region shows the complementary picture to that provided by infrared spectroscopy, giving useful information on the symmetry of the vibrations. Table 1.16 lists the infrared and Raman data obtained for the carbonyl region of this compound, together with the assignments made.

Table 1.16. Infrared and Raman data for the carbonyl vibrations of $\text{H}_3\text{GeCo}(\text{CO})_4$ [143]. (cm^{-1}).

Infrared (solid)	Raman (liquid)	Tentative assignment
2105 vs 2055 vs	2110 vs (p)	$\nu\text{CO } a_1$
2033 vs 1985 vs, br 1962 sh	2059 vs (p) 2040 sh 2010 s	$\nu\text{GeH } a_1$ $\nu\text{CO } a_1$ $\nu\text{CO } e$ $\nu^{13}\text{CO}$

Raman spectroscopy also gives useful information on vibrations of Ge-C and Co-C bonds, although this region - commonly between 800 and 300 cm^{-1} - is often ignored. Finally, perhaps the most interesting data provided by Raman spectroscopy is that of the metal-metal stretching region. Table 1.17 lists some examples of the information obtained using this technique.

Table 1.17. $\text{M}'\text{-Co}$ stretching frequencies and force constants for $\text{R}_3\text{M}'\text{-Co}(\text{CO})_4$ species [12].

$\text{R}_3\text{M}'$	$\nu(\text{M}'\text{-Co})$ (cm^{-1})	$K(\text{M}'\text{-Co})$
H_3Si	315	1.50
Cl_3Si	308	1.45
H_3Ge	223	1.30
Cl_3Ge	242	1.52
Me_3Ge	192	
Cl_3Sn	205	1.30
Me_3Sn	177	

Force constant trends have been rationalized [131] in terms of changes in π -backbonding.

1.4.3. NMR Spectroscopy

^1H NMR Spectroscopy may be used in the identification and characterisation of group 14-cobalt carbonyl species where, of course, there are attached protons contained in the cluster. However, it is a particularly useful technique for following reaction systems involving a group 14 hydride.

This process was employed during studies of the reaction between MeGeH_3 and $\text{Co}_2(\text{CO})_8$. It provided useful information on the nature of the intermediates involved [35]. For example, a number of reactions (ranging

from 2:1 to 1:2 ratios) were carried out at -20°C using SiCl_4 as solvent. These showed a consistent pattern of changes where, initially, the signals were very degraded, suggesting a paramagnetic intermediate. When the signals could be resolved (ca. 1 hr at -20°C) there were present signals arising from $\text{HCo}(\text{CO})_4$, and species giving a triplet at 0.81 δ and a related component at 4.3 δ , a doublet at 1.25 δ with a related component at 5.2 δ , a singlet at 1.6 δ and a second singlet at 1.92 δ . As the reaction proceeded the main change was the increase in intensity of the 1.92 δ singlet which was subsequently identified as arising from the major product of this reaction, $\text{MeGeCo}_3(\text{CO})_{11}$ [35]. The triplet signal observed in the methyl proton region was assigned as $\text{MeGeH}_2\text{Co}(\text{CO})_4$, confirmed by a separate synthesis. The doublet at 1.25 δ was attributed to a species of the form $\text{MeGeHCo}_2(\text{CO})_x$. This species and $\text{MeGeH}_2\text{Co}(\text{CO})_4$ were assumed to be intermediates in the production of $\text{MeGeCo}_3(\text{CO})_{11}$.

Similar studies have been undertaken to follow the reactions of both GeH_4 and Ge_2H_6 with $\text{Co}_2(\text{CO})_8$ [21]. These each showed the production of molecular hydrogen and $\text{HCo}(\text{CO})_4$ during the reaction. Also present in each case was a broad ill-resolved signal centred around 4.8 δ for the GeH_4 reaction, and around 5.0 δ for the Ge_2H_6 reaction. These were attributed to cobalt substituted germanium hydride species which, as these peaks had disappeared by the end of the reaction were plainly intermediates. As can be seen from table 1.18, their direction and magnitude of shift from the original GeH_4 and Ge_2H_6 signals is consistent with dicobalt substitution of germanium hydrides.

Table 1.18. ^1H NMR data for some germanium hydride species.

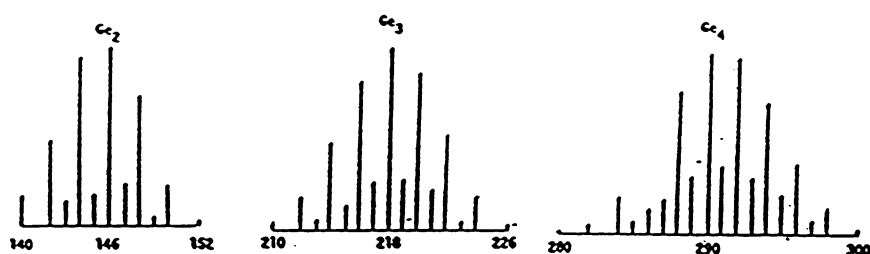
Germanium Hydride	Solvent	Ge-H δ ppm	C-H δ ppm	ref.
GeH_4	C_6H_6	3.20	—	132
$\text{GeH}_3\text{Co}(\text{CO})_4$	C_6H_6	3.73	—	25
MeGeH_3	CS_2	3.45	0.29	133
$\text{MeGeH}_2\text{Co}(\text{CO})_4$	SiCl_4	4.38	0.84	35
$\text{MeGeHCo}_2(\text{CO})_x$	SiCl_4	5.48	1.21	35
Ge_2H_6	C_6H_6	3.08	—	25
$\text{Ge}_2\text{H}_5\text{Co}(\text{CO})_4$	C_6H_6	3.75/3.49	—	25
$[\text{H}_2\text{GeCo}(\text{CO})_4]_2$	C_6H_6	4.31	—	134

A small amount of study has been carried out on ^{13}C and ^{17}O NMR spectroscopy of these clusters. In particular, ^{13}C NMR spectra can give useful information on the environments of individual carbonyl ligands. For example, the low temperature ^{13}C NMR spectrum of $(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ showed two

resonances at 238 δ and 204 δ with relative intensities 1/4 [104]. These were assigned to the pair of bridging CO's and the eight equivalent terminal CO's, respectively, for the cluster core possessing idealised D_{2h} symmetry [104]. As the temperature was raised the two signals merged into a broad singlet at 208 δ indicating a rapid interchange of carbonyl groups over the Co_4 core [104].

1.4.4. Mass Spectroscopy of Group 14-Cobalt Carbonyl Clusters.

Mass spectroscopy is an extremely useful aid in the identification of new compounds. In the case of germanium, which has five reasonably abundant isotopes, a characteristic pattern is observed throughout the spectrum indicating the number of Ge atoms contained in the molecule. The patterns of Ge_2 , Ge_3 and Ge_4 are shown in figure 1.29.



Characteristic isotope patterns for germanium containing species

Figure 1.29.

Most of the clusters so far investigated are of sufficient volatility to allow the recording of good mass spectra without excessive heating which could lead to decomposition. Often, however, the peak arising from the parent ion is of low intensity which may lead to complications in assignment.

A high proportion of the total ion current is generally carried by ions retaining the M'_xM_y skeleton and, commonly, a stepwise loss of CO from the parent ion is observed as a series of envelopes separated by 28 m.u. Where methyl groups are present in the molecule, difficulties may arise as the loss of two methyl groups overlaps with the loss of one carbonyl. However, it is usual that the methyl groups are retained on the metal skeleton until all CO groups are lost.

For the molecule $Ge_2Co_6(CO)_{20}$, where no X-ray crystallographic structure determination was possible, the main basis for proposing the structure as six $GeCo_2$ triangles was the mass spectrum [19, 20]. Here the parent ion plus the fragment ions from the stepwise loss of the twenty CO

groups carried 79% of the total ion current. Other prominent ions were Ge_2Co_4^+ , Ge_2Co_2^+ and GeCo_2^+ which strongly suggested that the structure was based on linked GeCo_2 triangles. The peaks corresponding to Ge_2Co_3^+ and GeCo_3^+ were of very low intensity, unlike those observed in the mass spectra of compounds of the form $\text{RGeCo}_3(\text{CO})$, [49]. No peak corresponding to Ge_2^+ was observed thus it was unlikely that the molecule contained a Ge-Ge bond.

1.5 Overview of the thesis.

The work described in this thesis covers several areas within the field of group 14- cobalt carbonyl chemistry. The first three chapters describe the reactions of germanium hydrides with cobalt carbonyl species. Chapter Two, which is essentially preliminary to the main work of this thesis, extends the research previously carried out on the reactions of germanium polyhydrides and of methylgermane with dicobalt octacarbonyl; Chapter Three covers some studies of the reactions of mono- and dimethylgermane with $\text{GeCo}_4(\text{CO})_{14}$ and $\text{GeCo}_4(\text{CO})_{13}$; and Chapter Four describes the reactions of mono- and dimethylgermane with some more complex germanium-polycobalt clusters. Chapter Five discusses the preliminary studies of the chemistry of the Ge_2Co_4 type clusters which have recently been synthesised at the University of Waikato. These studies include carbonylation reactions and some relatively straightforward ligand substitutions. Chapter Six describes the reactions of germanium-cobalt carbonyl clusters with some transition metal carbonyl anions. Chapter Seven is concerned with the synthesis of some tin-cobalt carbonyl compounds. Finally Chapter Eight brings together some general conclusions applicable to several of the preceding chapters.

Since each chapter is an individual project it is more convenient to include a short experimental section describing the preparation of starting materials within each chapter. Similarly, discussion is mainly confined to the individual chapters. However, instrumental techniques and the purification of solvents, processes which were used in all parts of this work, are described together in Appendix One. Appendix Two gives a brief review of the various preparations of mono and dimethylgermane available in the literature which is intended to be of use to later workers in this area.

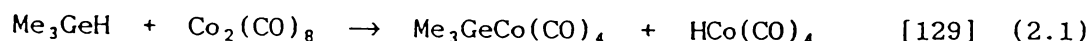
Appendix three contains tables of final positional and anisotropic thermal parameters for the various X-ray crystal structure determinations carried out in this work, together with complete lists of the bond lengths and angles determined for each molecule.

After the references, at the very end of the thesis, is a fold-out section depicting the molecular structures of all the clusters commonly referred to in this work. These are represented in the text by a letter of the alphabet, enclosed in brackets, written after the formula of each cluster.

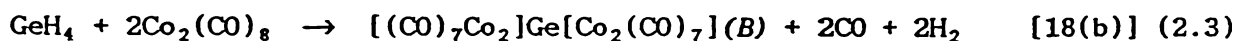
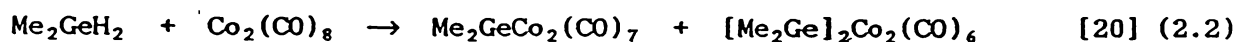
CHAPTER 2: Further Studies of the Reactions of Some Polygermanes and Two Monosubstituted Germanes with Dicobalt Octacarbonyl.

2.1 Background and aim

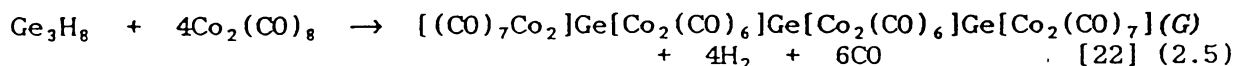
As described in Chapter 1, the reactions of germanium hydrides with dicobalt octacarbonyl are well established. For example, equation 2.1.



In an extension of this type of $\text{Ge-H} + \text{Co}_2(\text{CO})_8$ reaction, where there are two hydrogens attached to the germanium, a bridging carbonyl can be replaced by the R_2Ge group with loss of CO and H_2 . (For example, equations 2.2 and 2.3).



Analogous processes are observed, together with Ge-Ge cleavage, in the reactions of the polygermanes, Ge_2H_6 or Ge_3H_8 , with $\text{Co}_2(\text{CO})_8$ (equations 2.4 and 2.5). These result in the higher homologue of the product obtained in equation 2.3.



The three processes, shown as equations 2.3, 4 and 5, have been well investigated and the optimum reactant ratios leading to these products have been established [20, 21]. In each case it was never possible to obtain a 100% yield of these products and some proportion of the smaller germanium cobalt carbonyl clusters, as well as $\text{Co}_4(\text{CO})_{12}$, was always found.

Various reactant ratios were tried for the reaction of $\text{Co}_2(\text{CO})_8$ with Ge_2H_6 . The best yield of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(E)$ (80 + %) was found for a Ge_2H_6 to $\text{Co}_2(\text{CO})_8$ molar ratio of 1:2.6-2.8 - slightly less than the product stoichiometry [21]. For reactant Ge:Co ratios of 1:3 or higher, substantial amounts of $\text{GeCo}_4(\text{CO})_{14}(B)$ were found leading to low recoveries

of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ due to separation difficulties. In contrast, for a reaction ratio of $\text{Ge}_2\text{H}_6 : \text{Co}_2(\text{CO})_8$ of 1:2, although reasonable yields of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ were obtained, evidence for partially substituted hydride species was also reported [21]. Similar observations have been made for low ratios of $\text{Co}_2(\text{CO})_8$ to GeH_4 , and further substitution of $\text{GeCo}_4(\text{CO})_{14}$ is not favourable [20].

In the reaction of Ge_3H_8 with $\text{Co}_2(\text{CO})_8$ it was found that an initial Ge:Co ratio of 1:2.5-2.65, again slightly less than the product stoichiometry, provided the optimum yield of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$, while higher ratios favoured formation of the smaller homologue, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ [21].

Although the first three members of this series are well established the next homologue, $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$, has not been found, neither in the systems described above nor in a preliminary study of the reaction between Ge_4H_{10} and $\text{Co}_2(\text{CO})_8$ [39].

It was desirable to conduct a further investigation into these systems to determine by how great an extent the products obtained are dependant on the reaction ratio. For example, could a polygermanium hydride starting material of germanium chain length Ge_n produce a Ge_{n+x} polycobalt product ($n = 2,3$; $x = 1,2$) if the appropriate reactant ratio were employed? It was of particular interest to establish whether $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ could be observed in any of these systems, and a further study of the reaction between Ge_4H_{10} and $\text{Co}_2(\text{CO})_8$ has been carried out.

In the previous studies of these systems cobalt carbonyl hydride, $\text{HCo}(\text{CO})_4$, has always been qualitatively observed among the volatile components. However, the quantity of this was never determined due to the difficulty of its separation from solvent. It was, therefore, desirable to make quantitative measurements of this species to evaluate its importance in the reaction pathway.

Also described in this chapter is a detailed study of the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$. This system has previously been investigated by Graham and co-workers [35] who reported the major product to be $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ (figure 2.1).

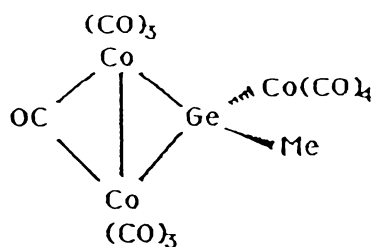


Figure 2.1

The reaction has been studied over molar ratios of MeGeH_3 to $\text{Co}_2(\text{CO})_8$ ranging from 1:2 to 2:1, and at room temperature was found to proceed rapidly. For example, in a ^1H NMR study of a 1:2 mixture, no further reaction was observed after 5 minutes when all the MeGeH_3 was consumed [35]. During the ^1H NMR experiments, several intermediates were observed in the system but not identified. $\text{HCo}(\text{CO})_4$ was always observed among the products but it was not conclusively determined how this was involved in the reaction scheme. Similarly, no analysis of the incondensable gas evolution was made.

It was therefore desirable to undertake an additional examination of this system in an attempt to clarify the reaction process, with particular emphasis on $\text{HCo}(\text{CO})_4$ production and incondensable gas evolution. Also of interest was the effect of a larger ratio of MeGeH_3 to $\text{Co}_2(\text{CO})_8$ and a ^1H NMR study of a 4:1 mixture was undertaken. The effects of longer reaction times and varying concentrations have also been investigated here, and a detailed examination of the vibrational spectrum of $\text{MeGeCo}_3(\text{CO})_{11}$ has been carried out.

The final section of this chapter is a brief study of the reaction between $\text{H}_3\text{GeCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$. The reaction of $\text{H}_3\text{GeMn}(\text{CO})_5$ with $\text{Co}_2(\text{CO})_8$ is known to provide $(\text{CO})_5\text{MnGeCo}_3(\text{CO})_9$ (figure 2.2) as the major product [43] and it was of interest to determine if the analogous reaction would be observed.

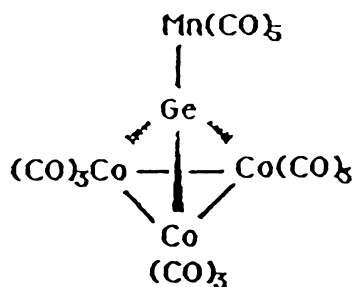


Figure 2.2

2.2 Preparation of starting materials

Monogermane was synthesised by the acid hydrolysis of an aqueous germanate solution with sodium borohydride as described by Jolly [135]. This process also yielded *ca.* 10-20% Ge_2H_6 and *ca.* 5% Ge_3H_8 but these, and Ge_4H_{10} , were more profitably prepared by the action of a silent electric discharge on monogermane [136]. This process yielded *ca.* 50% Ge_2H_6 , 30% Ge_3H_8 and 10% Ge_4H_{10} on the basis of GeH_4 consumed. The Ge_4H_{10} produced in this manner was expected to be of reasonable purity with respect to higher nuclearity germanium hydride species, as these would be too involatile to distil from the vacuum line to the reaction vessel, although it was quite likely that the tetragermane consisted of a mixture of the *n*- and *i*-isomers in unknown proportions.

Methylgermane was prepared by the lithium aluminium hydride reduction of MeGeCl_3 in di-*n*-butyl ether. MeGeCl_3 was supplied by the Laramie Chemical Co. and was found to be of sufficient purity (by ^1H NMR spectroscopy) for use without further treatment. LiAlH_4 was purified by Soxhlet extraction to ensure its highest possible reactivity.

$\text{H}_3\text{GeCo(CO)}_4$ was prepared by the coupling reaction of H_3GeCl and KCo(CO)_4 [12]. H_3GeCl was prepared by passing GeH_4 over a deficit of SnCl_4 [137] and purification was achieved by fractionation of the resulting mixture through baths held at -127 and -96°C . KCo(CO)_4 was produced by the reduction of $\text{Co}_2(\text{CO})_8$ with Na/K alloy in diethyl ether [12].

Dicobalt octacarbonyl was sublimed under vacuum at 30°C to ensure freedom from $\text{Co}_4(\text{CO})_{12}$ and cobalt (II) species, then stored under N_2 at -30°C .

2.3 General experimental techniques

All of the reactions were performed in a similar manner. The hydride (the amount either calculated by volume or by weighing under vacuum) was condensed onto a thoroughly degassed hexane solution of dicobalt octacarbonyl.

In the reactions of the polygermanes with $\text{Co}_2(\text{CO})_8$ the mixture was sealed in a glass ampoule capable of withstanding up to 10 atmospheres pressure. This was stored at room temperature in the dark for the duration of the reaction - generally several months. A rubber sleeve, fitted with a tap adaptor, allowed the ampoule to be opened without loss of gas or contact with the air. At this point, the incondensable gases were removed from the

frozen reaction mixture by a Toepler pump and measured in a gas burette. A full description of this technique is given in Appendix 1.

For those reactions of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ where regular incondensable measurements were made, the reaction mixture was contained within a vessel fitted with a Kontes greaseless tap.

For the ^1H NMR studies of the MeGeH_3 and $\text{Co}_2(\text{CO})_8$ reaction the samples were contained in glass tubes of 5 mm o.d. These tubes could be opened under vacuum and the contents recovered.

All of these reactions were worked up similarly. Any incondensable gases were removed by Toepler pump and measured, then all volatiles were removed from the reaction mixture and fractionated through slush baths at temperatures of -22°C , -63°C , and -127°C to separate any unreacted hydride, solvent and, as far as possible, produced $\text{HCo}(\text{CO})_4$. The various fractions were identified by infrared spectroscopy. Cobalt carbonyl hydride was returned to an ampoule, generally with some solvent from which it could not be separated, and heated to form first $\text{Co}_2(\text{CO})_8$ and H_2 [138], followed by the decarbonylation of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$. The amount of $\text{HCo}(\text{CO})_4$ was determined from the weight of $\text{Co}_4(\text{CO})_{12}$ obtained.

The involatile species were dissolved in dichloromethane and transferred, under N_2 , to a nitrogen-flushed vessel. After removal of solvent these products could be separated by extraction with hexane and/or dichloromethane depending on their solubilities. In most cases this process was sufficient, but on occasion a mixed fraction was obtained where the solubilities of the products were too close to allow complete separation. Here an approximate yield could be determined by comparison with the infrared spectra of standard mixtures.

Since all of the species found are well established, it was possible to characterise them simply by comparison of their infrared active carbonyl stretches. ($\text{Co}_4(\text{CO})_{12}$ [139]; $\text{GeCo}_4(\text{CO})_{14}$ [18(b)]; $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ [19]; $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ [22] and $\text{MeGeCo}_3(\text{CO})_{11}$ [35]).

2.4 Reactions of some polygermanes with dicobalt octacarbonyl

2.4.1. Experimental Details and Results.

The results of these reactions are summarised in Table 2.1 at the end of this section.

2.4.1.1. Reaction of Ge_2H_6 and $\text{Co}_2(\text{CO})_8$ in the ratio for $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$.

Ge_2H_6 (0.255g; 1.70 mmols) and $\text{Co}_2(\text{CO})_8$ (1.55g; 4.53 mmols), ($\text{Ge}:\text{Co} = 1:2.66$) were allowed to react in hexane (10 mls) for sixteen weeks. Incondensable gases (7.71 mmols) were removed, of composition 51% CO , 49% H_2 . No unreacted Ge_2H_6 was found among the volatile components. $\text{HCo}(\text{CO})_4$ (0.24 mmols from its subsequent decomposition to $\text{Co}_4(\text{CO})_{12}$ (0.034g; 0.06 mmols)) was observed.

The infrared spectrum of a solution of the involatile products in $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ (1:2) showed a mixture of $\text{Co}_4(\text{CO})_{12}$, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, a small amount of $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ (the condensation product of $\text{GeCo}_4(\text{CO})_{14}$) and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$. No $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ was observed at this stage but, after partial separation had been achieved, an infrared spectrum of the less soluble fractions showed a trace of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ to be present (characteristic carbonyl band at 2093 cm^{-1} [22]). Repeated washings with a 1:2 mixture of $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ allowed a pure sample of $\text{Ge}_2\text{Co}_6(\text{CO})_{26}$ (0.5502g; 0.52 mmols) to be separated from the mixture. The remaining amount of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was estimated by comparison with the infrared spectra of standard mixtures to be approximately 0.35 mmols. On the basis of consumed Ge_2H_6 this represents a yield of 51% $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$.

The yields of the minor products - $\text{Co}_4(\text{CO})_{12}$, $\text{GeCo}_4(\text{CO})_{14}$, $\text{GeCo}_4(\text{CO})_{13}$ and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ - were not determined since complete separation was not achieved. However, it is possible to state that the amount of each present was: $\text{GeCo}_4(\text{CO})_{14} > \text{Co}_4(\text{CO})_{12} \gg \text{GeCo}_4(\text{CO})_{13} > \text{Ge}_3\text{Co}_8(\text{CO})_{26}$. These products appeared to account for the remaining germanium and cobalt.

2.4.1.2. Reaction of Ge_2H_6 and $\text{Co}_2(\text{CO})_8$ in the ratio for $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$

Ge_2H_6 (0.214g; 1.43 mmols) and $\text{Co}_2(\text{CO})_8$ (1.22g; 3.57 mmols) ($\text{Ge}:\text{Co} = 1:2.5$) were allowed to react in hexane (10 mls) for 23 weeks. Incondensable gases (7.27 mmols) were recovered of composition 53% CO , 47%

H₂. A trace of unreacted Ge₂H₆ (ca. 0.2 mmoles) was observed among the volatile components but could not be separated from solvent. HCo(CO)₄ (0.16 mmoles from 0.023g; 0.04 mmoles Co₄(CO)₁₂) was also observed.

From the infrared spectrum of a solution of the involatile products in CH₂Cl₂/C₆H₁₄ it could, again, be seen that a mixture of Co₄(CO)₁₂, GeCo₄(CO)₁₄(B), GeCo₄(CO)₁₃(I) and Ge₂Co₆(CO)₂₀(E) had been produced. Neither Ge₃Co₈(CO)₂₆(G) nor Ge₄Co₁₀(CO)₃₂ were observed. After the products had been separated as completely as possible a pure sample of Ge₂Co₆(CO)₂₀ (0.402g; 0.38 mmoles) was obtained which, together with the small amount remaining in a mixed fraction, represents an approximate yield of 34% on the basis of consumed Ge₂H₆.

The yields of the minor components were, again, not determined but the amount of each present was in the following order: GeCo₄(CO)₁₄ > Co₄(CO)₁₂ >> GeCo₄(CO)₁₃.

2.4.1.3. Reaction of Ge₃H₈ and Co₂(CO)₈ in the ratio for Ge₄Co₁₀(CO)₃₂.

Ge₃H₈ (0.17g; 0.76 mmoles) and Co₂(CO)₈ (0.975g; 2.85 mmoles) (Ge:Co = 1:2.5) were allowed to react in hexane (10 mls) for 81 weeks. Incondensable gases (8.28 mmoles) were removed of composition 57% CO, 43% H₂. The volatile fraction contained no unreacted Ge₃H₈. HCo(CO)₄ (0.07 mmoles from 0.01g, 0.018 mmoles Co₄(CO)₁₂) was found, while the remainder of the volatile fraction was solvent.

An infrared spectrum of a solution of the involatile products in CH₂Cl₂/C₆H₁₄ showed the major product to be Ge₃Co₈(CO)₂₆(G). The solution also contained a trace of both Co₄(CO)₁₂ and GeCo₄(CO)₁₄(B), together with a larger proportion of Ge₂Co₆(CO)₂₀(E). No new species were observed. After the best possible separation of these products had been achieved a pure sample of Ge₃Co₈(CO)₂₆ (0.666g; 0.47 mmoles) was obtained. This, together with an estimate (ca. 0.05 mmoles) of the amount of Ge₃Co₈(CO)₂₆ remaining as a mixed fraction, represented a yield of 69% on the basis of consumed Ge₃H₈.

The yields of the minor products were not calculated but the amount of each present was in the following order: Ge₂Co₆(CO)₂₀ >> GeCo₄(CO)₁₄ ≈ Co₄(CO)₁₂.

2.4.1.4. Reaction of Ge_4H_{10} and $\text{Co}_2(\text{CO})_8$.

Ge_4H_{10} (0.14g; 0.47 mmol) and $\text{Co}_2(\text{CO})_8$ (0.804g; 2.35 mmol) (Ge:Co = 1:2.5) were allowed to react in hexane (10 ml) for 42 weeks.

Incondensable gases (3.92 mmol) were removed, of composition 55% CO, 45% H_2 . No unreacted Ge_4H_{10} was found. The volatile fraction contained $\text{HCo}(\text{CO})_4$ (0.03 mmol from 0.004g, 0.008 mmol $\text{Co}_4(\text{CO})_{12}$).

An infrared spectrum of the involatile products in a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution showed the major product to be $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (G). Also present were a fair proportion of $\text{GeCo}_4(\text{CO})_{14}$ (B) and a lesser amount of each of $\text{Co}_4(\text{CO})_{12}$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (E). No new species were observed, even in an infrared spectrum of a solid sample taken from the least soluble fraction. After separation by washing, the yield of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (0.580g; 0.41 mmol) was determined as 65% on the basis of consumed germanium.

The yields of the minor products were not calculated but the amount of each present was in the following order: $\text{GeCo}_4(\text{CO})_{14} \gg \text{Ge}_2\text{Co}_6(\text{CO})_{20} \approx \text{Co}_4(\text{CO})_{12}$.

Table 2.1 Summarised reaction conditions and results of the polygermanes/dicobalt octacarbonyl systems

Polygermane (quantity in mmol)	Ratio of poly- germane to $\text{Co}_2(\text{CO})_8$	Ratio of Ge to Co	Duration (weeks)	Inconden- sable gas (mmol)	$\text{HCo}(\text{CO})_4$ (mmol)	Major product (yield)
Ge_2H_6 (1.70)	1:2.7	3:8	16	7.71 (51% CO)	0.212	$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ 51%
Ge_2H_6 (1.43)	1:2.5	4:10	23	7.27 (53% CO)	0.15	$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ 34%
Ge_3H_8 (0.76)	1:3.75	4:10	81	8.28 (57% CO)	0.07	$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ 69%
Ge_4H_{10} (0.47)	1:5	4:10	42	3.92 (55% CO)	0.03	$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ 65%

2.4.2 Discussion of the Reactions of Polygermanes with Dicobalt Octacarbonyl

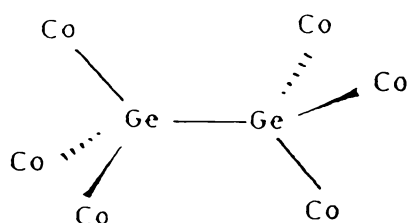
2.4.2.1. Discussion of the reactions of Ge_2H_6 or Ge_3H_8 with $\text{Co}_2(\text{CO})_8$

The first objective of this study was to determine whether, by employing the appropriate reactant ratio, a polygermanium hydride of chain length Ge_n could provide a germanium polycobalt product incorporating Ge_{n+x} in its structure, ($n = 2, 3$; $x = 1, 2$), or if the products were solely dependent on the nuclearity of the germanium hydride starting material. For the reactions of Ge_2H_6 or Ge_3H_8 with $\text{Co}_2(\text{CO})_8$ it appears that the latter is, in fact, the case.

The reactant ratios which lead to the best yield of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ from Ge_2H_6 and $\text{Co}_2(\text{CO})_8$, and to $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ from Ge_3H_8 and $\text{Co}_2(\text{CO})_8$ have been reported as slightly less than the stoichiometric ratios [21]. For example, in the production of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, a Ge_2H_6 to $\text{Co}_2(\text{CO})_8$ ratio of 1:2.6-2.8 is found to be most favourable [21]. The appropriate ratio of Ge_2H_6 to $\text{Co}_2(\text{CO})_8$ for the formation of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$, used in the run described in section 2.4.4.1, is 1:2.7. As this is within the range described as the optimum ratio for $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ formation it is perhaps not surprising that only a trace of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ was observed. A lower Ge:Co ratio of 1:2.5 however appeared to promote cleavage of the Ge-Ge bonds, resulting in a larger proportion of the smaller clusters $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ and $\text{Co}_4(\text{CO})_{12}$ and a significantly lower yield of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$.

Similarly, the appropriate, stoichiometric ratio of Ge to Co for formation of $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ from Ge_3H_8 and $\text{Co}_2(\text{CO})_8$, as used in the run described in section 2.4.1.3, is 1:2.5. This falls just within the lowest end of the range reported as the optimum conditions for $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ formation [21]. Thus it is, again, not surprising that no higher nuclearity products are observed.

It seems clear that the formation of higher nuclearity products is not favoured from these reactions and will only occur to a very limited degree. It is possible that this results from the nature of the intermediates involved in these processes. It is anticipated that the Ge-Ge bonds are retained until the latter stages of reaction since, if this were not the case, a much higher proportion of the smaller cluster, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, would be expected among the products. Thus, an intermediate in the formation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$, from the reaction of Ge_2H_6 with $\text{Co}_2(\text{CO})_8$, could be of the form



When carbonyl groups are taken into consideration as well, this type of intermediate appears very crowded, thus addition of a further GeCo_n fragment would not be favoured.

In any event, from the results of these experiments it may be concluded that the polygermanes Ge_2H_6 and Ge_3H_8 follow the reactivity pattern of GeH_4 in their reactions with $\text{Co}_2(\text{CO})_8$. It is clear that the products obtained from each system are primarily determined by the Ge_n chain length of the starting material, while the yield of the Ge_n polycobalt product is optimised by the use of a slightly less than stoichiometric $\text{Ge}:\text{Co}$ ratio initially.

2.4.2.2. Discussion of the attempted preparation of $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$

The second aim of this study was to establish if the formation of the next homologue of this series, $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$, could be observed. No evidence for the presence of this species was obtained in any of the systems studied, including that of Ge_4H_{10} and $\text{Co}_2(\text{CO})_8$.

As stated in section 2.1.3., it was possible to characterise all of the compounds found by comparison of their infrared active carbonyl stretches. The infrared spectra of the three species, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ are shown in figures 2.3 (a), (b) and (c). It is clear from these that there is a pattern to the vibrational bands of these species. In particular the high wavenumber mode of each (at 2079 cm^{-1} in (a), 2087 cm^{-1} in (b) and 2094 cm^{-1} in (c)) is very characteristic of this series. As an extension of this, it could be expected that the analogous band of $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ would be observed at around 2100 cm^{-1} . Hence, if a peak were found in this area it would be strongly indicative of this higher homologue.

As the solubilities of the established clusters diminish with chain length it was expected that the desired product would be only slightly soluble in dichloromethane. Infrared spectra of the least soluble fractions were, therefore, recorded as nujol mulls. There was no sign of any peak around 2100 cm^{-1} .

As can be seen from figure 2.3. the relative intensity of the high wavenumber band decreases as the number of carbonyl ligands on the cluster increases. It is, therefore, possible that for $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ this band would be of quite low intensity compared to the analogous mode of the smaller clusters. However, it is felt that if at least 5% of the samples used for infrared analysis was $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ then this peak should be at least weakly observed. This was not the case.

It is, of course, possible, that $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ would not follow the vibrational pattern of the smaller homologues, however at no time were any bands found in the infrared spectra of the products which could not be immediately identified as known species.

It therefore seems reasonable to conclude that $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ is not formed in any more than trace amounts through the reactions of any of Ge_2H_6 , Ge_3H_8 or Ge_4H_{10} with $\text{Co}_2(\text{CO})_8$.

This conclusion is not greatly surprising for the reactions of Ge_2H_6 or Ge_3H_8 with $\text{Co}_2(\text{CO})_8$ since it appears that the reaction products are determined primarily by the Ge_n chain length of the starting hydride, and formation of a higher nuclearity species is not favourable. It is more noteworthy that $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ is not formed in the reaction of Ge_4H_{10} with $\text{Co}_2(\text{CO})_8$.

The Ge_4H_{10} used in this study was obtained from silent electric discharge on a sample of monogermane. It was assumed to be free of Ge_1 , Ge_2 and Ge_3 fractions, since these were easily removed due to their relatively high volatility, and free of Ge_5 , or higher, species since these would be too involatile to distil from the discharge apparatus. However no formal attempt was made at characterisation of this fraction and the proportions of n- and i- tetragermane were not known. Statistically, it would be expected that the n- isomer would be present in the higher proportion however the iso form is the more volatile of the two thus this form may have been enriched, relative to the n-isomer, by the distillation from the discharge apparatus into the reaction vessel. According to the original study of this process [136] the yield of the n-isomer of tetragermane was 4-10 times greater than that of the iso-form. However, it was stated that the sensitivity of the detector used was lower for branched chain species, thus the yields of the iso form may have been underestimated. It is also possible that different initial pressures of GeH_4 , and longer periods of discharge will result in different proportions of all isomers.

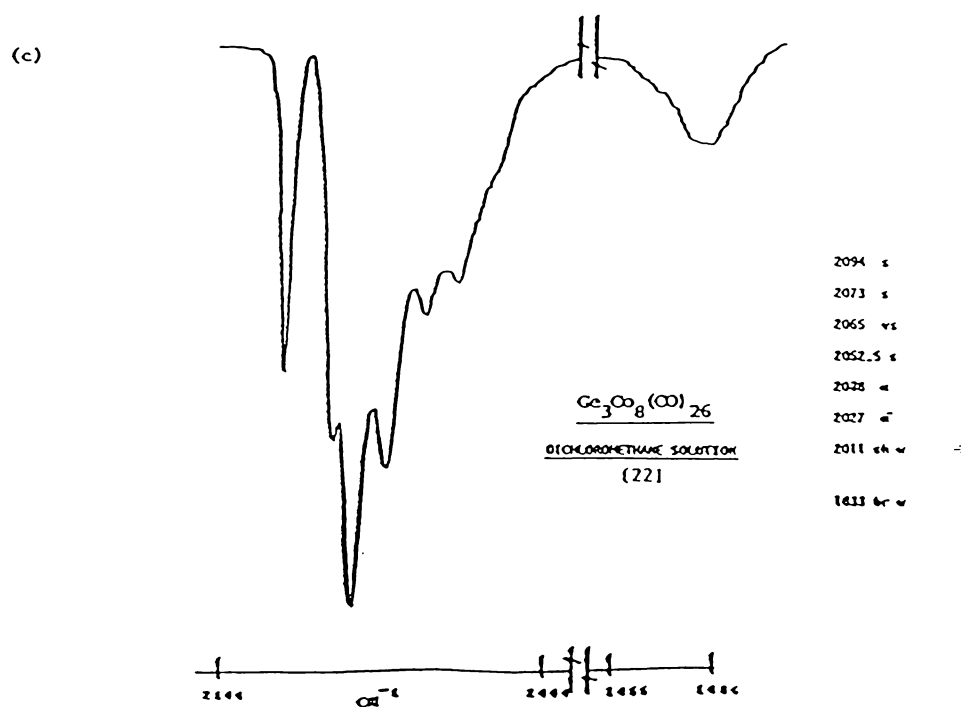
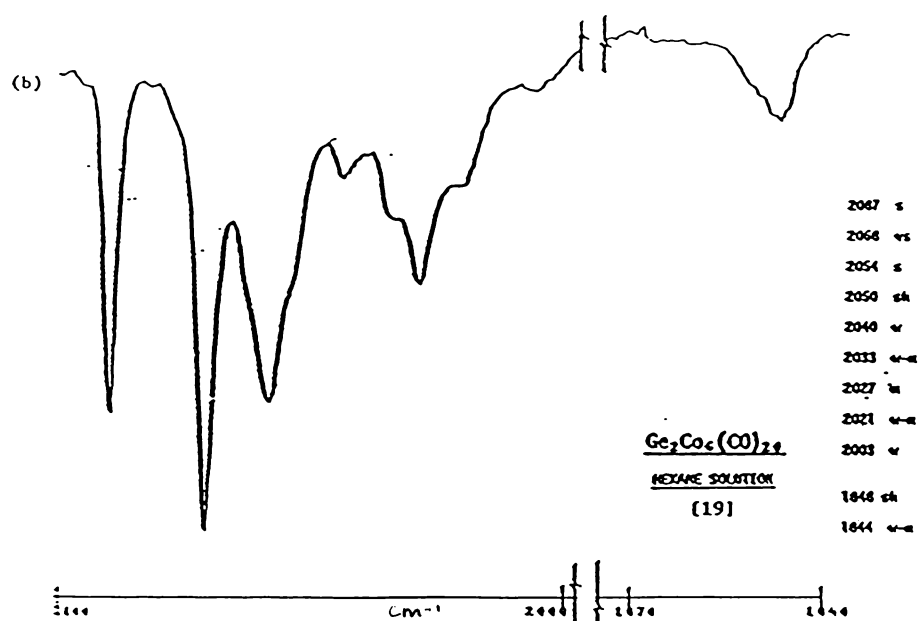
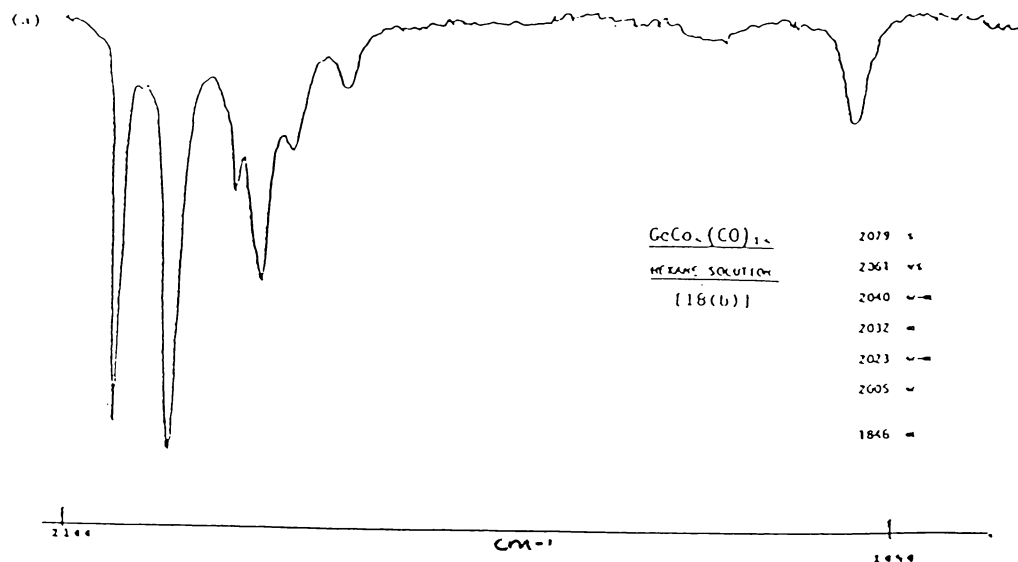
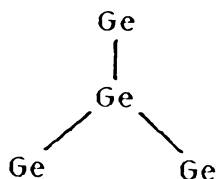


Figure 2.3.

The germanium backbone of iso-tetragermane i.e.



would make it impossible for a straight chain product to form from the reaction of this species with $\text{Co}_2(\text{CO})_8$ thus Ge-Ge cleavage would be expected to occur at an early stage in the reaction. Thus if the iso form were the major component of the tetragermane fraction used in this experiment then the absence of any Ge_4 containing products is not surprising.

The suggestion that the presence of the iso form of tetragermane is largely responsible for the non-formation of $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ is supported by the proportions of the products obtained from this system. The reaction produced a 65% yield of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(G)$ on the basis of consumed Ge_4H_{10} . The remaining germanium was accounted for by the formation of $\text{GeCo}_4(\text{CO})_{14}(B)$ and a trace of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(E)$. Similar results were found in the previous study of this system [39] where the major products were $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ and $\text{GeCo}_4(\text{CO})_{14}$ with only a trace of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ observed. As the proportions of the major products were in an approximately 1:1 ratio it was suggested that the Ge_4H_{10} starting material was breaking down in a 1:3 manner.

If the hydride exists in its straight chain form only, then there is no obvious reason why the cleavage would not also occur between the two central germaniums, resulting in a significant proportion of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ among the products. However, if the hydride is mainly in the iso form, then cleavage of any one Ge-Ge bond will result in a Ge_1 and a Ge_3 fragment, giving the observed products.

Although it may be assumed from the results of this study that the branched isomer dominated the fraction of tetragermane, the straight chain form would still be present in some proportion. As stated for the Ge_2H_6 and Ge_3H_8 systems, it is again possible that small amounts of $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ would not be observed in the infrared spectra of the product mixture. However, it is equally possible that some other factor prevents the formation of this cluster. This could result from steric hindrances within the Ge-Co intermediate involved, or alternatively, the desired product, $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$, may be too sterically crowded for its production from this process to be favoured. It is possible however that the desired cluster could be obtained by an entirely different route. For example, the

reaction of $\text{Fe}(\text{CO})_4(\text{GeMeH}_2)_2$ with $\text{Co}_2(\text{CO})_8$ produces the cluster $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ shown in figure 2.4 [31].

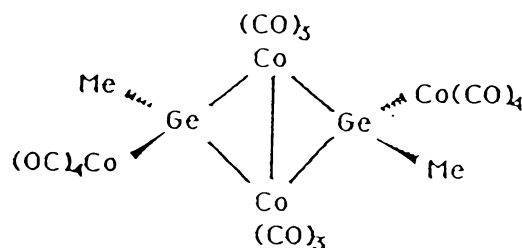


Figure 2.4 [31]

If a species such as $\text{Fe}(\text{CO})_4(\text{Ge}_2\text{H}_5)_2$ were reacted with $\text{Co}_2(\text{CO})_8$ it is conceivable that $\text{Ge}_4\text{Co}_{10}(\text{CO})_{32}$ would be produced. Similarly, it is known that $\text{Me}_2\text{Si}(\text{GeH}_3)_2$ reacts with $\text{Co}_2(\text{CO})_8$ to produce $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(E)$ in almost quantitative yield [20]. It may thus be envisaged that the reaction of a species such as $\text{Me}_2\text{Si}(\text{Ge}_2\text{H}_5)_2$ or $\text{Si}(\text{GeH}_3)_4$ with $\text{Co}_2(\text{CO})_8$ would produce the desired cluster.

2.4.2.3. Discussion of the minor reaction products.

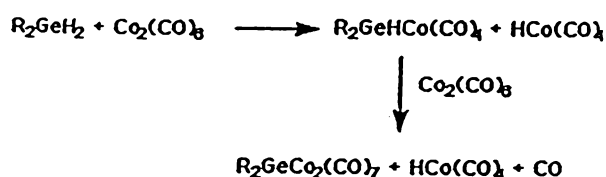
The final objective of this investigation was to survey the lesser reaction products, $\text{HCo}(\text{CO})_4$ and $\text{Co}_4(\text{CO})_{12}$, in a more quantitative manner than has been carried out previously, to determine their importance in the reaction pathway.

The amount of incondensable gases recovered from all of these systems show that H_2 and CO production are a significant part of these reaction processes. These measurements have not been considered in great detail as thorough studies of the incondensable gas evolution have been previously reported [21]. In fact, the amounts of gas found here show slight discrepancies from the expected values, however, this is anticipated to result from errors in measurement, rather than from some secondary process. Fortunately, these results are not of particular importance in this examination and not too much is lost by their unreliability.

The amount of $\text{HCo}(\text{CO})_4$ produced in each system, shows this to be only a minor component. It is possible that a small amount of $\text{HCo}(\text{CO})_4$ may have been lost by decomposition occurring before it was transferred from the vacuum line to a reaction vessel where the process could be monitored. However, this would not markedly affect the results obtained as the decomposition process was observed to take several months to reach completion at room temperature. It is, of course, also possible that, with the long reaction times involved, decomposition of $\text{HCo}(\text{CO})_4$ had already

begun in the reaction vessel. This possibility is emphasised by the fact that the decomposition of $\text{HCo}(\text{CO})_4$ to H_2 and $\text{Co}_2(\text{CO})_8$ is catalysed by $\text{Co}_2(\text{CO})_8$ [153] which would have been present in large proportions at least in the early stages of reaction. However, the presence of large amounts of CO and H_2 resulting from the reaction of the polygermane with $\text{Co}_2(\text{CO})_8$ would be likely to inhibit the decomposition process, and it would be expected that considerably larger amounts of $\text{HCo}(\text{CO})_4$ would be observed at completion of the reaction if this were a by-product of the major reaction pathway.

It therefore seems probable that the observed $\text{HCo}(\text{CO})_4$ is produced in a side reaction and is not formed directly as a result of the mechanisms involved in the formation of the major products. Thus, of the reaction pathways introduced in chapter 1, that involving $\text{HCo}(\text{CO})_4$ formation (scheme 2.1) is not likely to be a favoured route for the production of these germanium polycobalt species and will not occur to any significant degree.



Scheme 2.1

The formation of $\text{Co}_4(\text{CO})_{12}$ in these reactions is commonly observed. Although it has not been possible to measure the exact amount of this species as a result of its very similar solubility to $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ it is certainly only a minor product in these systems. It is unlikely that its formation occurs through decomposition of $\text{HCo}(\text{CO})_4$ for the reasons discussed above. It is more probable that it results from the decarbonylation reaction of the dicobalt octacarbonyl starting material as shown in equation 2.6.



Finally, the overall amounts of the products obtained account reasonably well for the consumed starting material. Although exact quantities of the minor components, such as $\text{GeCo}_4(\text{CO})_{14}$ and $\text{Co}_4(\text{CO})_{12}$, could not be determined as a result of separation difficulties, the total involatile products appeared to correspond well to the consumed germanium.

2.5 Reactions of methylgermane and dicobalt octacarbonyl

2.5.1 Experimental Details and Results

Run 1: MeGeH_3 (0.997 mmol by volume) was allowed to react with $\text{Co}_2(\text{CO})_8$ (0.34g, 0.995 mmol) (1:1 ratio) in hexane (5 ml) for 9 hrs at room temperature. Incondensable gas evolution was monitored at regular intervals and the results of this are shown in table 2.2 and figure 2.5. The total incondensable gas measured was 0.98 mmol. The volatile components were fractionated to yield MeGeH_3 (0.31 mmol) together with a small amount of MeGeH_3 (ca. 0.1 mmol) which could not be separated from the solvent. $\text{HCo}(\text{CO})_4$ (0.44 mmol from its subsequent decomposition to $\text{Co}_4(\text{CO})_{12}$ (0.064g; 0.11 mmol)) was also present.

On workup the involatile products were characterised by carbonyl region infrared spectroscopy to be virtually pure $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ [35] with only a trace of unreacted $\text{Co}_2(\text{CO})_8$. 0.22 mmol of initial $\text{Co}_2(\text{CO})_8$ was found as $\text{HCo}(\text{CO})_4$. This then gives the yield of $\text{MeGeCo}_3(\text{CO})_{11}$ (0.284g; 0.496 mmol) as 96% based on initial $\text{Co}_2(\text{CO})_8$. Based on consumed MeGeH_3 (taken as ca. 0.587 mmol) this gives an approximate yield of 84%.

Table 2.2 Incondensable gas evolution over time from run 1.

Time interval (mins)	Gas evolved (mmol)	%CO	%H ₂	Cumulative time (mins)	Total gas (mmol)
35	0.21	61	39	35	0.21
30	0.13	73	27	65	0.34
30	0.12	97	3	95	0.46
30	0.12	2	98	125	0.58
30	0.08	3	97	155	0.66
40	0.11	60	40	195	0.77
45	0.08	*	*	240	0.85
45	0.07	66	34	285	0.92
60	0.03	42	58	345	0.95
155	0.03	53	47	540	0.98

* Not measured

Run 2: MeGeH_3 (1.96 mmol) and $\text{Co}_2(\text{CO})_8$ (0.667g; 1.95 mmol) (1:1 ratio) were allowed to react in hexane (10 ml) for 13 hrs at 10°C. The incondensable gas evolution was again monitored at regular intervals and the results of this are shown in table 2.3 and figure 2.6. The total incondensable gas measured was 1.99 mmol. Fractionation of the volatiles gave MeGeH_3 (0.78 mmol) with a small amount (ca. 0.2 mmol) remaining

with the solvent. $\text{HCo}(\text{CO})_4$ (0.88 mmol from 0.127g, 0.22 mmol $\text{Co}_4(\text{CO})_{12}$) was also present.

Again, the involatile products, characterised by infrared spectroscopy, were found to consist solely of a trace of unreacted $\text{Co}_2(\text{CO})_8$ and $\text{MeGeCo}_3(\text{CO})_{11}$ (0.509g, 0.89 mmol; 88% yield based on 1.51 mmol $\text{Co}_2(\text{CO})_8$ consumed after $\text{HCo}(\text{CO})_4$ production accounted for; ca. 91% yield based on ca. 0.98 mmol MeGeH_3 consumed).

Table 2.3 Incondensable gas evolution over time from run 2.

Time interval (mins)	Gas evolved (mmol)	%CO	%H ₂	Cumulative time (mins)	Total gas (mmol)
20	0.29	52	48	20	0.29
20	0.17	*	*	40	0.46
20	0.15	67	33	60	0.61
30	0.24	89	11	90	0.85
30	0.17	83	17	120	1.02
45	0.25	51	49	165	1.27
45	0.22	23	77	210	1.49
60	0.18	13	87	270	1.67
60	0.10	38	62	330	1.77
130	0.10	*	*	460	1.87
320	0.12	49	51	780	1.99

* Not measured

Run 3: MeGeH_3 (1.98 mmol) and $\text{Co}_2(\text{CO})_8$ (0.677g, 1.98 mmol) (1:1 ratio) were allowed to react in hexane (5 ml) for 9 hrs at 10°C. The results of monitoring the incondensable gas evolution are shown in table 2.4 and figure 2.7. The total incondensable gas measured was 2.25 mmol. The volatile components were fractionated to yield unreacted MeGeH_3 (0.71 mmol) with a small amount (ca. 0.2 mmol) remaining with the solvent. $\text{HCo}(\text{CO})_4$ (0.88 mmol from 0.124g; 0.22 mmol $\text{Co}_4(\text{CO})_{12}$) was also present.

The involatile products, characterised by infrared spectroscopy, again proved to be a mixture of a trace of unreacted $\text{Co}_2(\text{CO})_8$ and $\text{MeGeCo}_3(\text{CO})_{11}$ (A) (0.516g; 0.902 mmol; 88% yield based on 1.54 mmol consumed $\text{Co}_2(\text{CO})_8$ after $\text{HCo}(\text{CO})_4$ production accounted for; ca. 84% yield based on ca. 1.07 mmol consumed MeGeH_3).

Table 2.4: Incondensable gas evolution over time for run 3.

Time interval (mins)	Gas evolved (mmoles)	%CO	%H ₂	Cumulative time (mins)	Total gas (mmoles)
30	0.49	50	50	30	0.49
30	0.44	55	45	60	0.93
30	0.31	68	32	90	1.24
30	0.22	67	33	120	1.46
45	0.30	35	65	165	1.76
45	0.21	40	60	210	1.97
45	0.15	50	50	255	2.12
60	0.06	*	*	315	2.18
90	0.04	*	*	405	2.22
135	0.03	*	*	540	2.25

* Not measured

The graphs shown as figures 2.5, 6 and 7 depict the results of tables 2.2, 3 and 4 more clearly. Where the percentage composition has not been measured estimated values have been used. These results will be discussed in section 2.5.2.2.

Run 4: MeGeH₃ (0.06 mmoles) was allowed to react with Co₂(CO)₈ (0.05g; 0.15 mmoles) (1:2.5 ratio) in d₆ benzene and the reaction followed by ¹H NMR spectroscopy. All MeGeH₃ could be seen to have reacted within 10 minutes. Unfortunately the spectra obtained from this experiment were ill-resolved and did not yield any useful information. After two hours the reaction mixture was worked up and an infrared spectrum of the involatile products in hexane showed a mixture of MeGeCo₃(CO)₁₁(A), and unreacted Co₂(CO)₈.

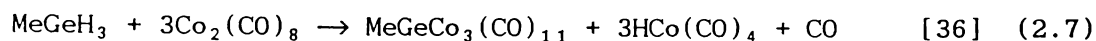
Run 5: MeGeH₃ (0.52 mmoles) and Co₂(CO)₈ (0.04g; 0.12 mmoles) (4:1 ratio) were allowed to react in d₆ benzene at 10°C and the reaction was again followed by ¹H NMR spectroscopy. A complicated series of peaks were observed and several of the spectra obtained are shown in figures 2.9 (a) to (e). These will be discussed in section 2.5.2.3.

After 72 hrs the MeGeCo₃(CO)₁₁ could be seen to have virtually all reacted. Workup confirmed this showing a mixture of involatile products which could not be separated to allow identification as a result of the small amounts involved.

2.5.2. Discussion of the Reactions of MeGeH_3 with $\text{Co}_2(\text{CO})_8$

2.5.2.1 Discussion of the reaction scheme

When $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ was first prepared by the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ [36] the proposed reaction scheme was as shown in equation 2.7.



The results found in the study described here, however, do not appear to be consistent with the above formulation.

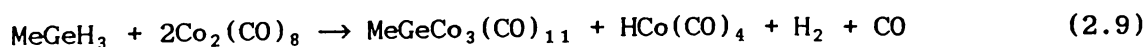
Firstly, the plots of incondensable gas evolution against time (figures 2.5, 6 and 7) clearly indicate that hydrogen evolution is an important part of the reaction process. The amounts involved make it unlikely that this H_2 is produced solely by $\text{HCo}(\text{CO})_4$ decomposition. Observation of this decomposition process, used to determine the amount of $\text{HCo}(\text{CO})_4$ present in product mixtures, has shown it to be extremely slow relative to these reactions at room temperature or lower. Similarly, a separate experiment showed the production of $\text{HCo}(\text{CO})_4$ itself, from H_2 and $\text{Co}_2(\text{CO})_8$, is a slow reaction and any equilibrium of the form shown in equation 2.8 takes an extremely long time to become established under the conditions used here.



The overall quantity of incondensable gas produced in each experiment is approximately 1 mole of gas per mole of $\text{Co}_2(\text{CO})_8$ consumed, and is composed of roughly equal proportions of CO and H_2 . This volume of gas is not accounted for in the formulation proposed by Graham (equation 2.7) [36].

Secondly, the amount of $\text{HCo}(\text{CO})_4$ found in each experiment does not correspond with this scheme. Approximately $\frac{1}{2}$ mole of $\text{HCo}(\text{CO})_4$ is found for each mole of reacting $\text{Co}_2(\text{CO})_8$. As mentioned above, it is unlikely that produced $\text{HCo}(\text{CO})_4$ is breaking down to form H_2 and $\text{Co}_2(\text{CO})_8$ over the relatively short time scale of these reactions.

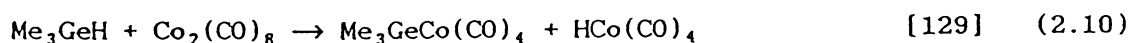
A new scheme consistent with the results of this study is therefore proposed.



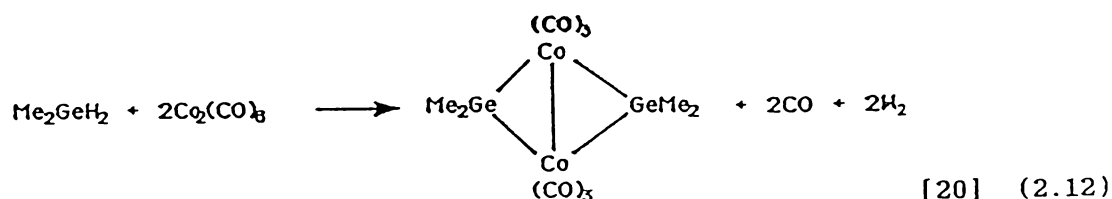
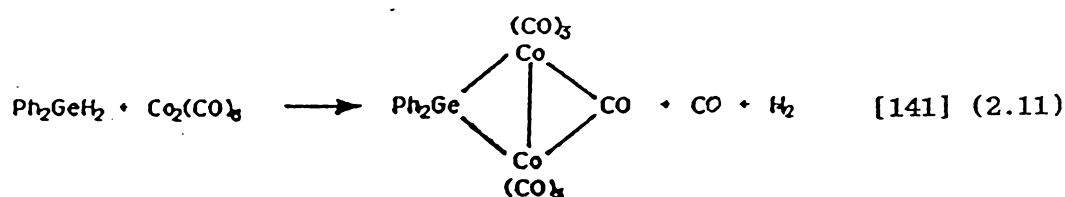
This scheme is particularly interesting in that it suggests the occurrence of two individual pathways. (i) The reaction of a R_2GeH_2 species to replace a bridging carbonyl as observed for Me_2GeH_2 with $Co_2(CO)_8$ [17] and (ii) Cleavage of a Co-Co bond by an R_3Ge-H group to form $R_3GeCo(CO)_4$ and $HCo(CO)_4$ as seen in the reaction of trisubstituted silanes with $Co_2(CO)_8$ [16(a)].

Consider the reactions of various monogermanium hydrides with $Co_2(CO)_8$:

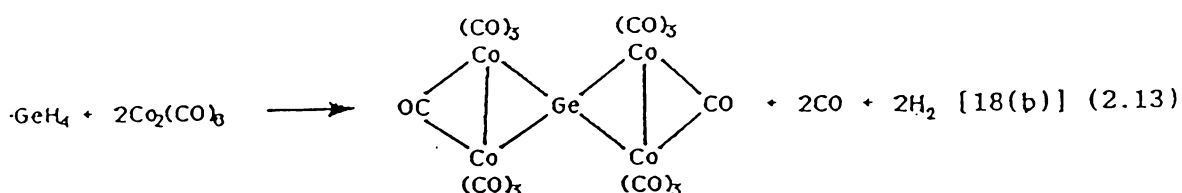
(i) Where there is only one hydrogen attached to the germanium Co-Co bond cleavage is observed, resulting in the formation of $R_3GeCo(CO)_4$ and $HCo(CO)_4$. For example, equation 2.10.



(ii) Where there are two hydrogens attached to the germanium, replacement of a bridging carbonyl results with release of H_2 and CO. For example equations 2.11 and 2.12.



(iii) For four attached hydrogens replacement of a bridging carbonyl is again observed resulting in the formation of two $GeCo_2$ triangles sharing a germanium apex. (equation 2.13) [18(b)]



Now, in the case of $MeGeH_3$, where there are three attached hydrogens, it appears that both the replacement of a bridging carbonyl group to form a $GeCo_2$ triangle with loss of H_2 and CO, and Co-Co bond cleavage with

formation of HCo(CO)_4 and a Co(CO)_4 terminal unit, are occurring together. These observations suggest the following hypothesis: "Where an even number of hydrogens is attached to a germanium group they will react with $\text{Co}_2(\text{CO})_8$ primarily to replace a bridging carbonyl group resulting in the formation of a $\text{GeCo}_2(\text{CO})_7$ unit. Where an odd number of hydrogen atoms is attached to a germanium group Co-Co bond cleavage will also occur, resulting in the formation of Co(CO)_4 terminal groups".

Clearly this is a generalised statement and several factors may influence this. For example, in the reaction of $\text{MeGeH}_2\text{Co(CO)}_4$ with $\text{Co}_2(\text{CO})_8$, according to the above hypothesis this hydride should react directly with the Co-Co bond replacing the bridging carbonyl to form a GeCo_2 triangle giving $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, with release of H_2 and CO. However, although this cluster is the major product of the reaction [35], it is also reported that 80% of the released hydrogen is found as HCo(CO)_4 . Additionally, the fully open form of this cluster, $\text{MeGe[Co(CO)}_4\text{]}_3$, is observed among the products. Although the latter feature of this reaction may be explained by subsequent addition of evolved CO to $\text{MeGeCo}_3(\text{CO})_{11}$, it is clear that the major production of HCo(CO)_4 may only be rationalised by this reaction proceeding primarily via Co-Co bond cleavage. This may be attributed to the original presence of both the methyl group and the Co(CO)_4 unit which could sterically hinder the substitution reaction. Thus, if the above statement is qualified by the addition of "where there is no steric effect" it should stand.

These observations contrast with the germanium halide coupling reactions with $[\text{Co(CO)}_4]^-$ [12] which result, at least initially, in the formation of only terminal Co(CO)_4 units. However, since an entirely different mechanism is involved in these processes it is not surprising that different products are observed.

2.5.2.2. Discussion of the incondensable gas evolution and the effect of reaction conditions.

The plots of incondensable gas evolution against time shown in figures 2.5 and 2.6, are very similar. Clearly CO is released predominantly in the early stages of the reaction, while H_2 evolution takes over later. Towards the reaction end, overall gas production diminishes with both H_2 and CO being released in similar quantities.

Gas evolution over time for run 1

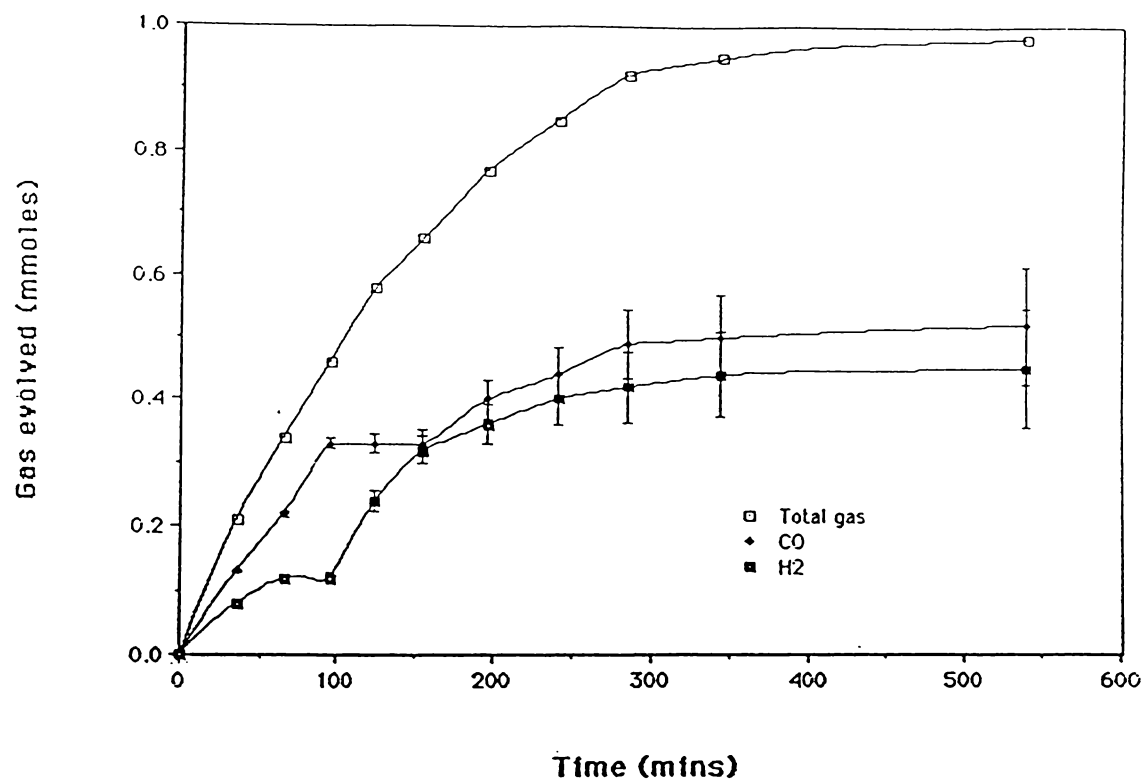


Figure 2.5.

"Gas evolution - Run 2"

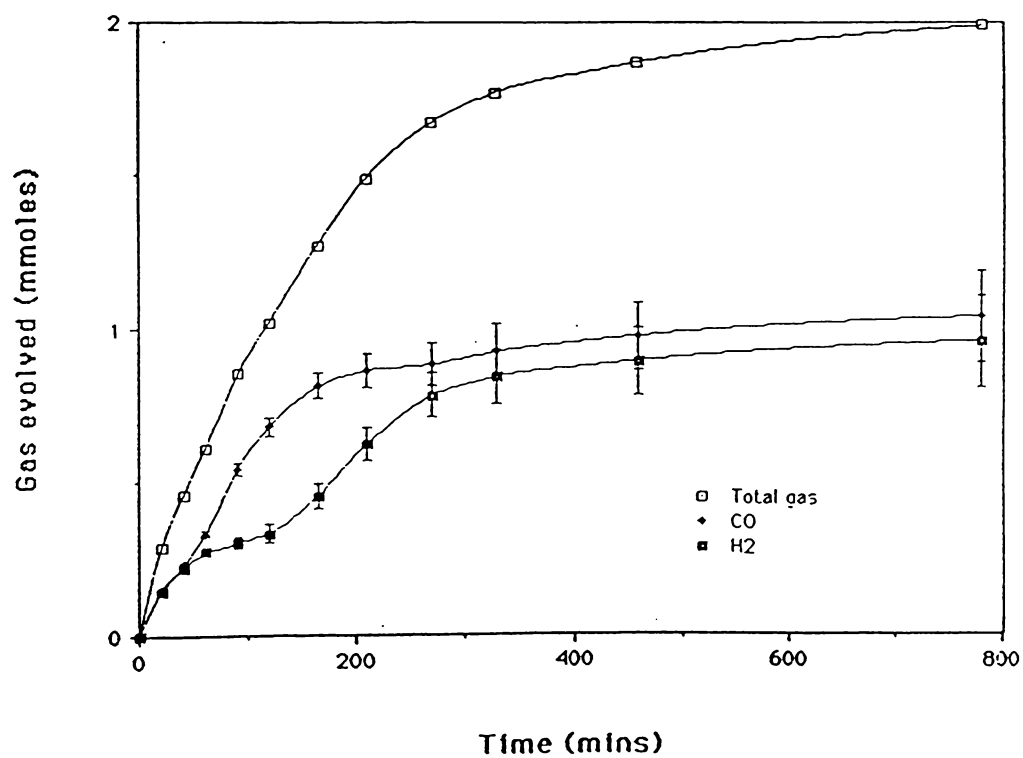


Figure 2.6.

"Gas evolution - Run 3"

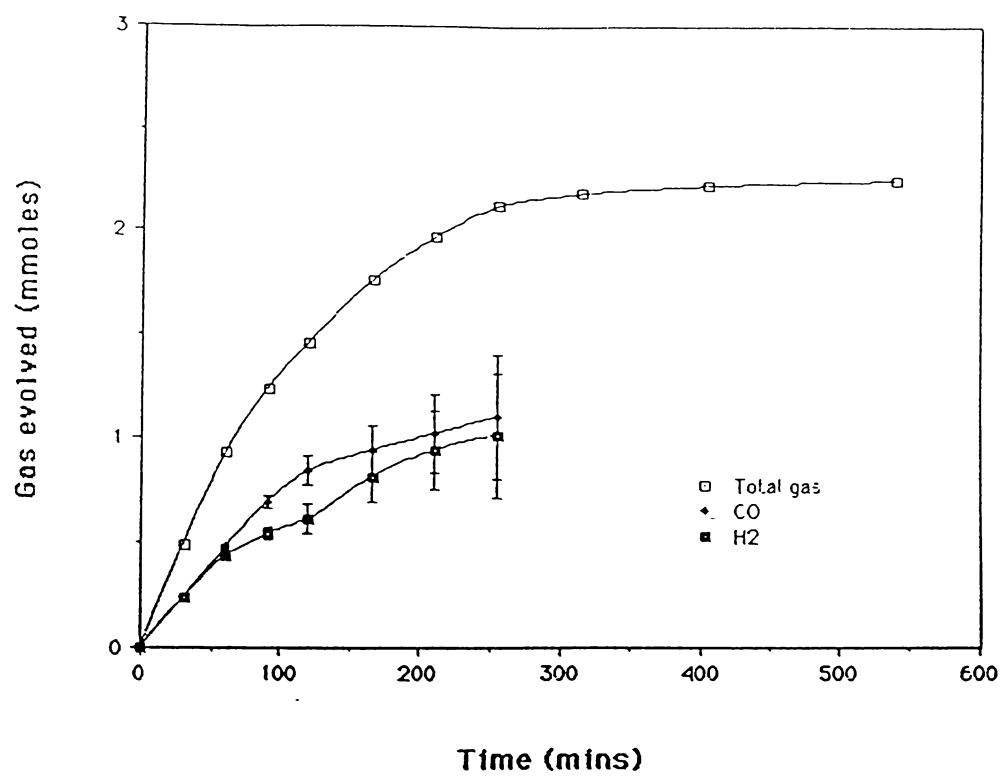


Figure 2.7.

Comparison of gas evolution of runs 1,2 +3.

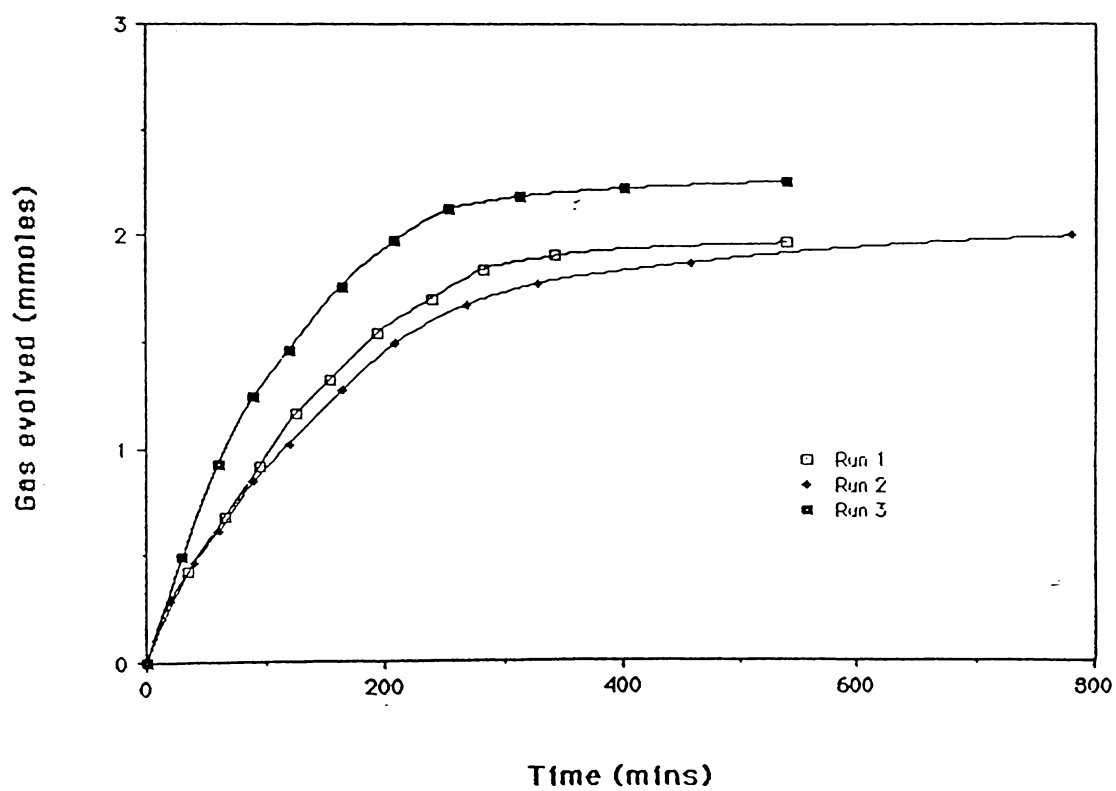
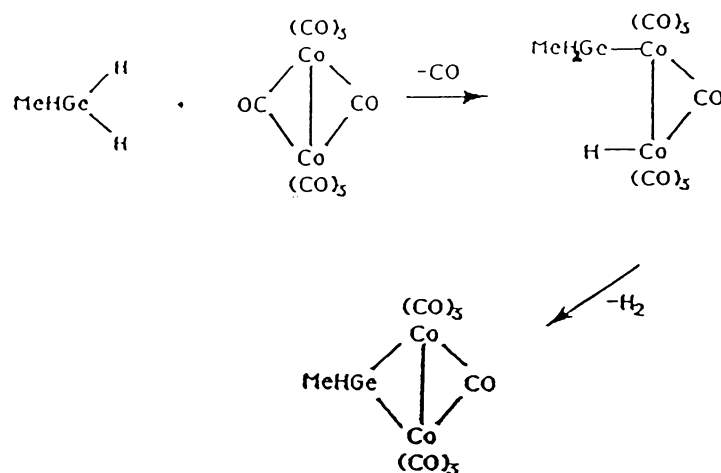


Figure 2.8.

These results suggest that the process of formation of the GeCo_2 triangle begins with the release of the bridging carbonyl ligand before the hydrogens from the methylgermane are removed. For example, this could be of the form shown in scheme 2.2



Scheme 2.2.

The point at which the single $\text{Co}(\text{CO})_4$ unit becomes attached to the germanium atom, with formation of $\text{HCo}(\text{CO})_4$, cannot be discerned from this study.

Although the incondensable gas figures from runs 1 and 2 correspond very well with the values expected from scheme 2.2, those of run 3 give a total gas value somewhat higher than anticipated. Although it is possible that some decomposition reaction was occurring in run 3 which would result in the additional gas this seems unlikely since no other products were observed on work-up. More probable is that there may have been an error in one of the readings. Unfortunately, time did not permit a repeat of this study, however as the value is only slightly above that anticipated it may be assumed that this does not affect the overall picture provided by this experiment.

It is of interest to compare the gas evolution profiles of runs 1 and 2. If the measurements from run 1 are doubled to allow for the fact that approximately double the quantities of MeGeH_3 and $\text{Co}_2(\text{CO})_8$ used here were used in run 2 - although the overall concentrations were the same - then, as shown in figure 2.8, only a very small reduction in the speed of gas evolution is observed as a result of the lower reaction temperature of run 2. Clearly, this lower temperature does not affect the activity of the reacting species to any large extent. This observation is, perhaps, not too surprising when it is considered that, at least in the early stages of

run 1, the reaction mixture was frequently frozen down in liquid nitrogen to allow the gas measurements to be made, thus it would have been at lower than room temperature for much of the time.

Runs 2 and 3 were conducted under identical conditions, other than a concentration difference. From figure 2.8 it is clear that doubling the concentration from run 2 to that in run 3 results in a dramatic increase in the rate of the reaction. However, the slight discrepancy in the incondensable gas measurements of run 3 makes it impossible to state if this effect is directly proportional to the concentration increase.

The overall reaction duration in these studies is much longer than those of the previous investigations [35]. At that time small amounts of partially substituted hydrides were also observed in the product mixture. Despite using an excess of MeGeH_3 in the studies described here, at no time was any species other than $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ found as a product (apart from in the ^1H NMR experiments which will be discussed in the following section) and the excess MeGeH_3 was quantitatively recovered. It seems likely that the longer reaction times employed here allow complete conversion to $\text{MeGeCo}_3(\text{CO})_{11}$, particularly since the evolved gas is removed during the reaction, the presence of which might inhibit its formation to some extent, while the lesser substituted species previously observed were intermediates in this process rather than the products of side reactions.

2.5.2.3. Discussion of the ^1H NMR experiments.

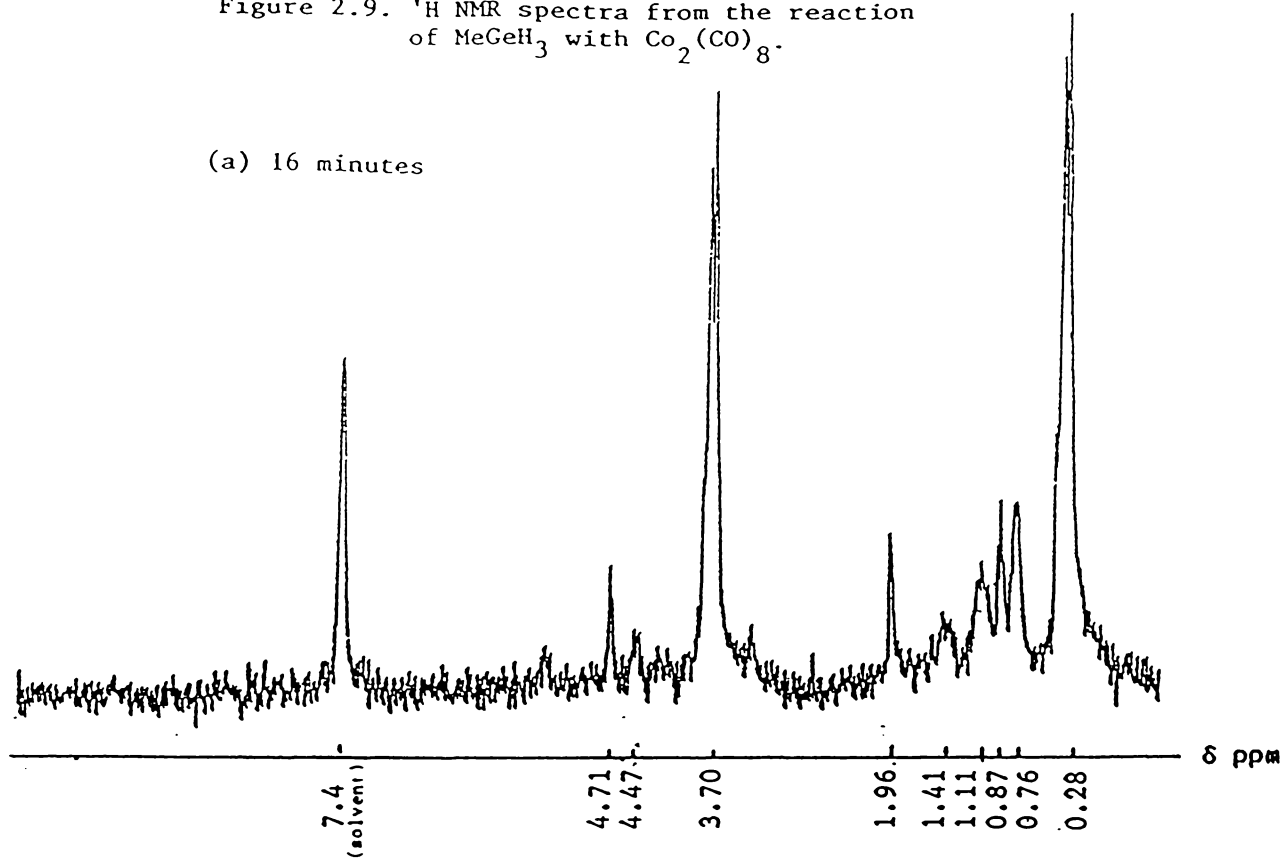
Run 5, where MeGeH_3 and $\text{Co}_2(\text{CO})_8$ were reacted in a 4:1 ratio, was carried out to determine the effect of a high ratio of hydride to $\text{Co}_2(\text{CO})_8$. Several of the ^1H NMR spectra obtained from this experiment are shown as figures 2.9 (a) to (e). It is clear from these that this is a rather more complicated reaction than might be anticipated.

The previous studies of this system [35] covered only the first, rapid period of reaction - approximately up to 2 hrs for reaction ratios ranging from 2:1 to 1:2. The first stage of reaction was difficult to observe as the signals were ill-resolved due to paramagnetic intermediates, but as the reaction proceeded a similar pattern of signals to those seen here emerged.

The quartets at 0.28 δ and 3.7 δ ($J=4.15$ Hz) clearly result from unreacted MeGeH_3 . According to the previous studies [35] the protons from $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ are observed at 1.92 δ while in this survey the singlet at 1.96 δ is attributed to the $\text{MeGeCo}_3(\text{CO})_{11}$ protons. This discrepancy is due to the different solvents used - SiCl_4 in the original study and d_6 benzene here. For reference, in a 5% solution of TMS in

Figure 2.9. ^1H NMR spectra from the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$.

(a) 16 minutes



(b) 1 hour

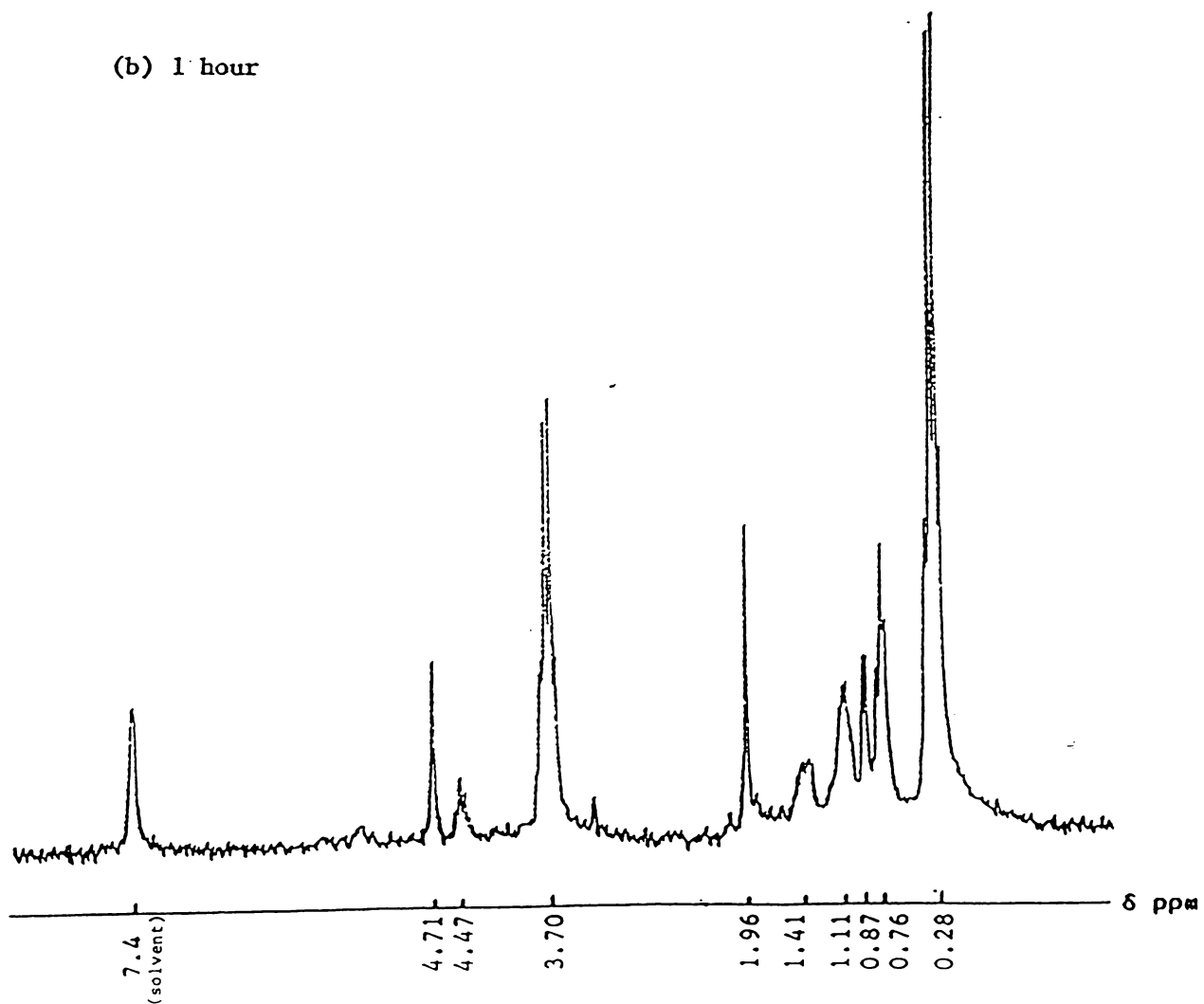
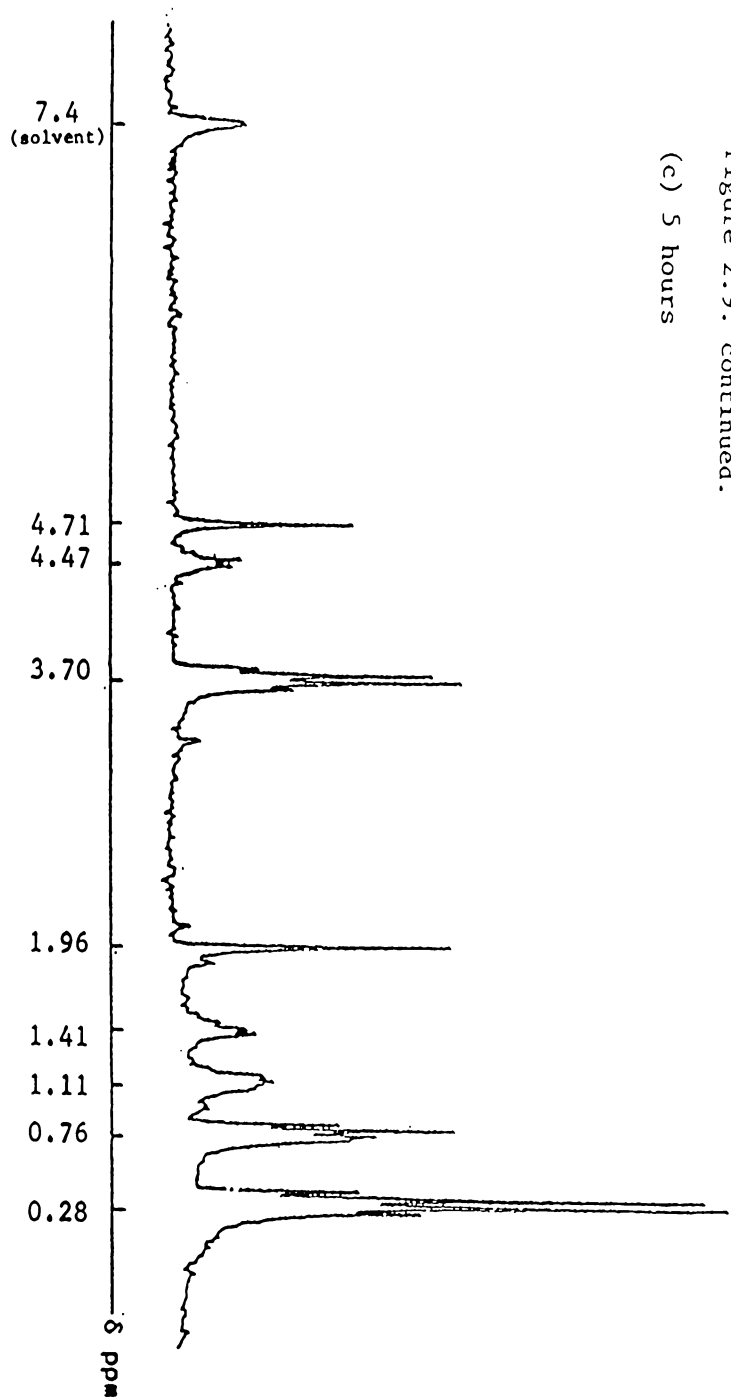


Figure 2.9. continued.

(c) 5 hours



(d) 30 hours

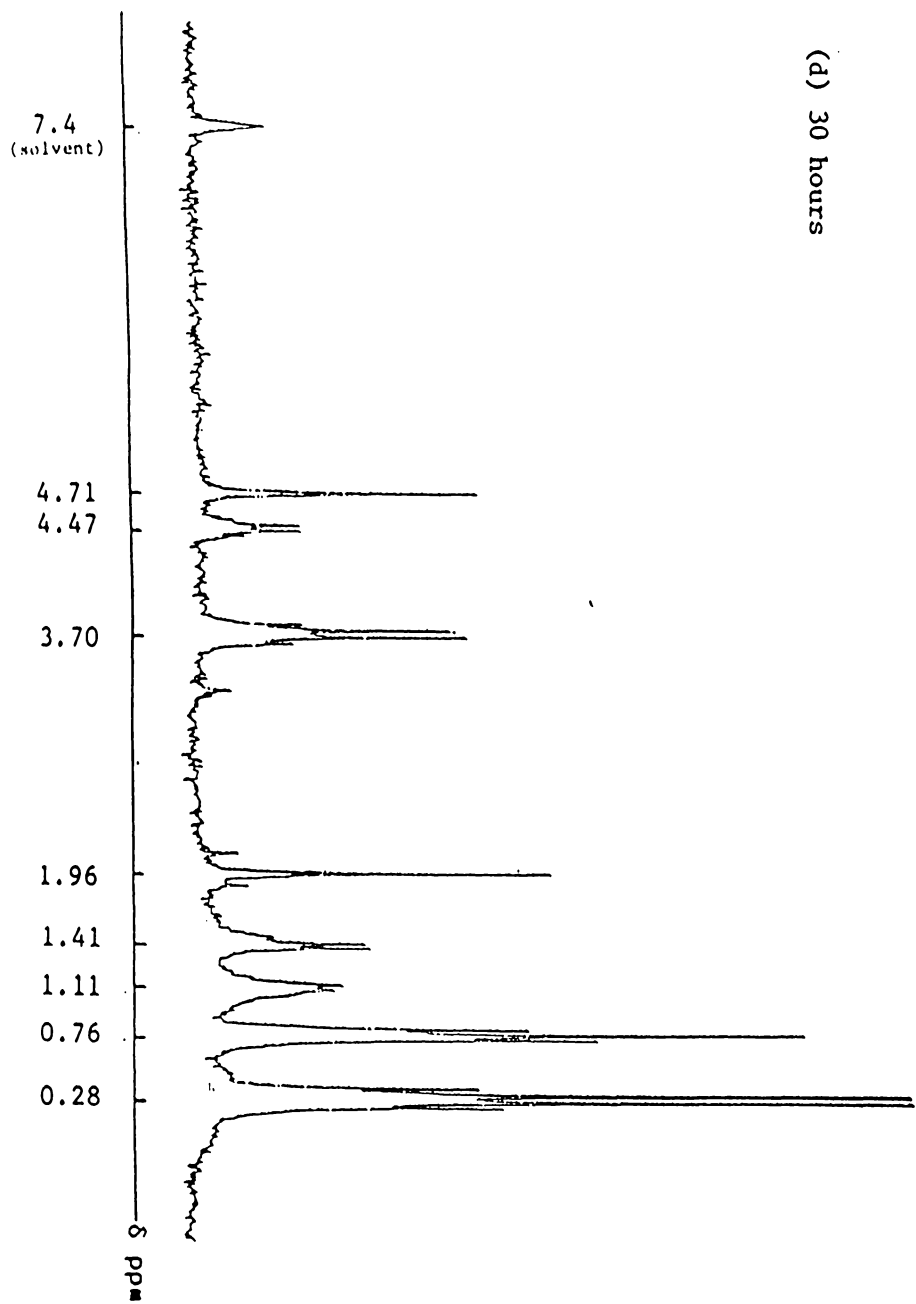
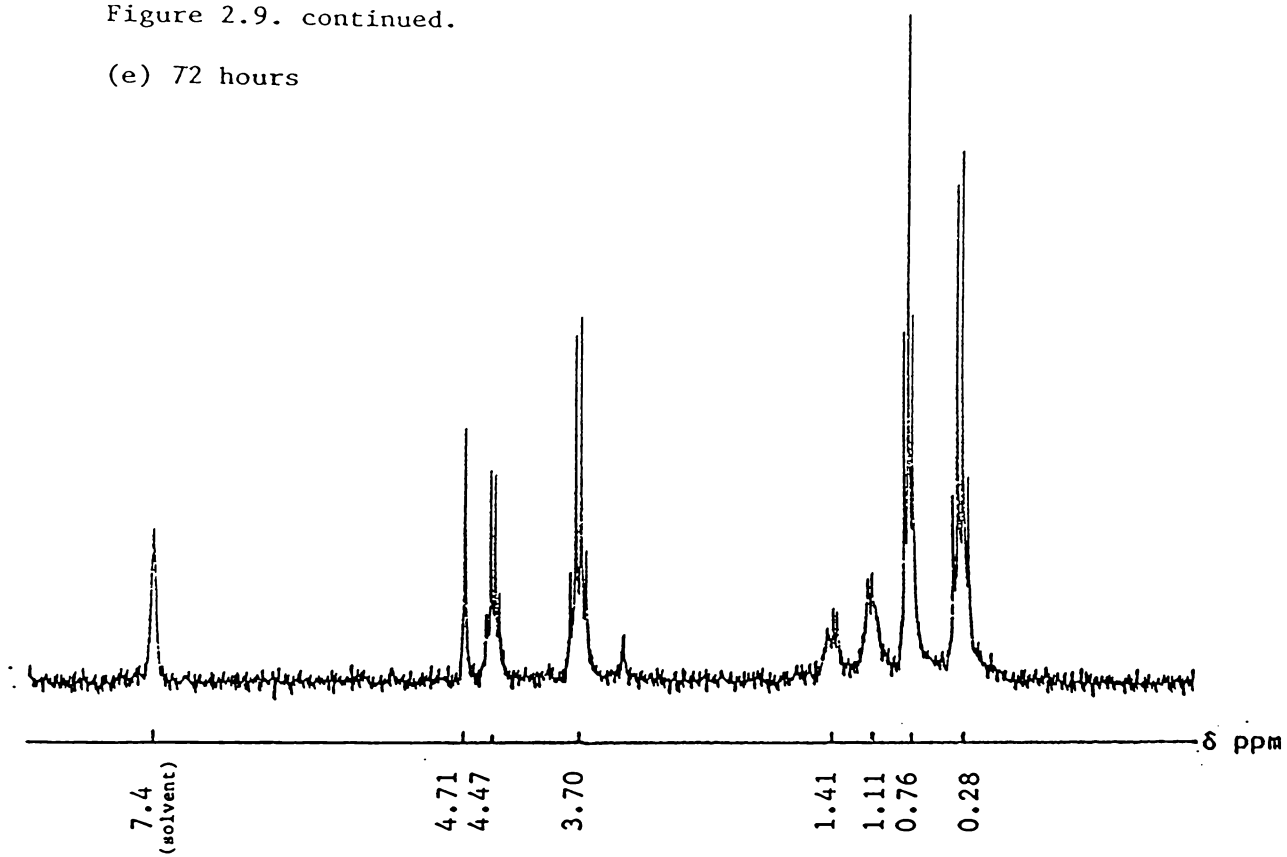


Figure 2.9. continued.

(e) 72 hours

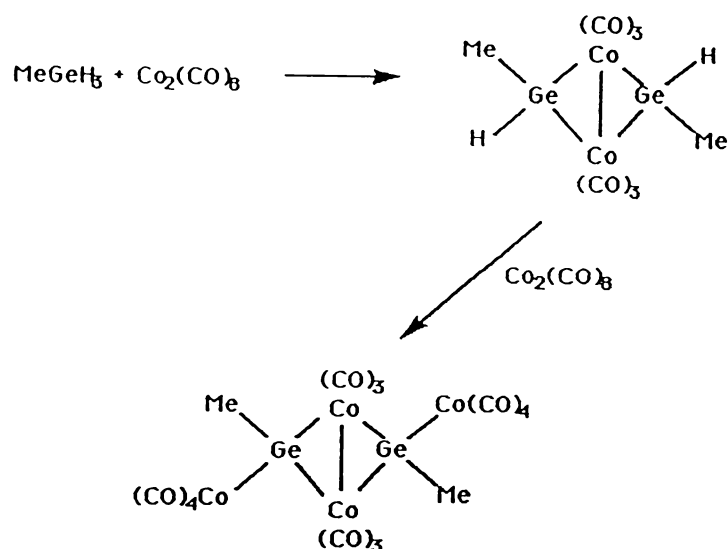


benzene the protons are observed at 7.12 δ , while in a 5% solution of benzene in TMS the signal arises at 7.17 δ [132]. This shift shows the magnitude of the difference that is likely to be observed in other comparative signals. The singlet at 4.71 δ is attributed to evolved hydrogen while that at -11.6 δ arises from the HCo(CO)_4 proton.

The triplet at 0.76 δ and the quartet at 4.47 δ ($J=3.42$ Hz) are assigned to $\text{MeGeH}_2\text{Co(CO)}_4$ (Lit. values 0.81 δ and 4.3 δ ; $J=3.3$ Hz (solvent = SiCl_4) [35]). There is also a doublet at 1.11 δ with the same J value of 3.42 Hz, but decoupling of these signals showed that this doublet is not connected with the other peaks and this was purely coincidental. This doublet is likely to have arisen from a $\text{MeGeH[Co}_2(\text{CO})_x]$ species ($x = 7$ or 8) where the quartet from the single proton is of too low an intensity to be observed. In the original study [35] a doublet at 1.25 δ was assigned to $\text{MeGeH[Co(CO)}_4]_2$ while a doublet at 1.4 δ was assigned to $\text{MeGeHCo}_2(\text{CO})_7$. Thus it is likely that the doublet at 1.11 δ results from $\text{MeGeH[Co(CO)}_4]_2$ while that at 1.41 δ results from $\text{MeGeHCo}_2(\text{CO})_7$. Here, again, the single proton must give rise to a multiplet of too low an intensity to be observed.

This assignment is supported by the fact that as the reaction proceeds the intensity of the $\text{MeGeHCo}_2(\text{CO})_7$ peak increases with respect to that of $\text{MeGeH[Co(CO)}_4]_2$ which is consistent with the decarbonylation of the latter to form $\text{MeGeHCo}_2(\text{CO})_7$ over the longer reaction time.

A third doublet is observed at 0.87 δ ($J=2.44$ Hz) which is almost as large as the methyl signal from $\text{MeGeH}_2\text{Co(CO)}_4$ at 5 minutes, is still substantial at 1 hour of reaction, and has not completely gone after 5 hrs. It is possible that as a result of the very large excess of MeGeH_3 a species such as $[\text{MeGeH}]_2\text{Co}_2(\text{CO})_6$ is forming in the early stages and the single hydrogens are then slowly displaced to form Ge-Co(CO)_4 units as shown in scheme 2.3.



Scheme 2.3

The final product of this sequence is known to be formed from this reaction [32] and this may account for one of the many methyl singlets that are observed in the latter stages of reaction. These singlets may also arise from $\text{MeGeCo}_3(\text{CO})_9(H)$, the condensation product of $\text{MeGeCo}_3(\text{CO})_{11}(A)$; $\text{MeGeCo}_3(\text{CO})_{12}$, the fully open relation of $\text{MeGeCo}_3(\text{CO})_{11}$; and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(J)$, the condensation product of the final product of scheme 2.3. However, there are so many low intensity singlets and distortions of the major peaks in the latter stages of reaction it is impossible to assign these with any certainty.

Table 2.5 shows the assignments which have been made.

Table 2.5 Summarised assignments from the ^1H NMR spectra of Run 5.

Signal (δ ppm)	Multiplicity	J_{HH} Hz	Assignment
0.28 3.70	4 4	4.15	MeGeH_3
1.96	1		$\text{MeGeCo}_3(\text{CO})_{11}$
0.76 4.47	3 4	3.42	$\text{MeGeH}_2\text{Co}(\text{CO})_4$
1.11 ?	2 4	3.42	$\text{MeGeH}[\text{Co}(\text{CO})_4]_2$
1.41 ?	2 4	3.17	$\text{MeGeHCo}_2(\text{CO})_7$
0.87 ?	2 4	2.44	$(\text{MeGeH})_2\text{Co}_2(\text{CO})_6$
4.71	1		H_2
-11.60	1		$\text{HCo}(\text{CO})_4$

The intensity of the singlet arising from $\text{HCo}(\text{CO})_4$ gradually diminishes to zero once $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ has been completely formed - after about 8 hours. While this occurs the intensity of the singlet due to evolved H_2 increases, thus it seems likely that the $\text{HCo}(\text{CO})_4$ is breaking down to form H_2 and $\text{Co}_2(\text{CO})_8$. As discussed in section 2.5.2.1. this process is usually very slow, thus here it is probably promoted by some other species in solution. In particular, at this stage no unreacted $\text{Co}_2(\text{CO})_8$ remained thus the breakdown of $\text{HCo}(\text{CO})_4$ could be required so that further reaction with MeGeH_3 may occur.

It is possible that $\text{HCo}(\text{CO})_4$ is reacting directly with a Ge-H species, however it has recently been reported [142] that in the reaction of R_3SiH species with $\text{Co}_2(\text{CO})_8$ the addition of $\text{HCo}(\text{CO})_4$ does not affect the reaction rate and is not observed to react directly with the silane.

Once the $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, singlet has reached its highest intensity it also starts to diminish to reach virtually zero after 72 hours. Clearly, from the corresponding decrease in the MeGeH_3 peaks it is reacting with the excess hydride in some manner. This may possibly form a species such as that shown in figure 2.10.

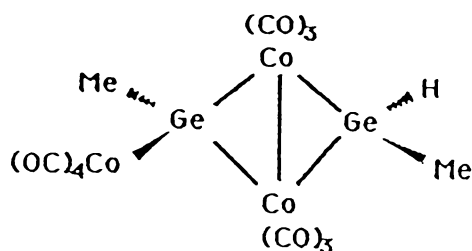


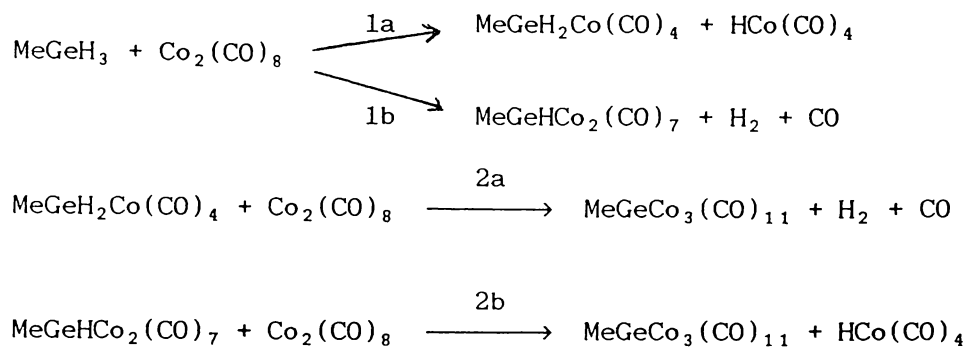
Figure 2.10

This could then react further with $\text{Co}_2(\text{CO})_8$ returned to solution by the decomposition of $\text{HCo}(\text{CO})_4$. $\text{MeGeCo}_3(\text{CO})_{11}$ may also react with $\text{MeGeH}_2\text{Co}(\text{CO})_4$ to form either $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ or $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ (see section 3.8). As the peaks arising from $\text{MeGeH}_2\text{Co}(\text{CO})_4$ appear to remain at much the same intensity it seems that reaction with the hydride is preferred.

Both $\text{MeGeH}_2\text{Co}(\text{CO})_4$ and $\text{MeGeHCo}_2(\text{CO})_7$ may be considered as intermediates in the formation of $\text{MeGeCo}_3(\text{CO})_{11}$. They would, therefore, be expected to decrease in concentration as the $\text{MeGeCo}_3(\text{CO})_{11}$ is produced. With the large excess of MeGeH_3 present in this experiment, however, the quantities of each would be regularly replenished until all $\text{Co}_2(\text{CO})_8$ had reacted, at which point there would be no further depletion of either of these two species.

The formation of $\text{MeGeH}[\text{Co}(\text{CO})_4]_2$, prior to that of $\text{MeGeHCo}_2(\text{CO})_7$, contradicts the proposal made in section 2.5.2.1. that two reaction pathways are being observed within this reaction i.e. both replacement of a bridging carbonyl by the germanium with loss of H_2 , and Co-Co bond cleavage with formation of $\text{HCo}(\text{CO})_4$. However, since the peak assigned to $\text{MeGeHCo}_2(\text{CO})_7$ is present even at the start of this reaction, and H_2 evolution is clearly of importance even before large scale $\text{HCo}(\text{CO})_4$ decomposition begins, it seems likely that the formation of $\text{MeGeHCo}_2(\text{CO})_7$ from $\text{MeGeH}[\text{Co}(\text{CO})_4]_2$ is only a minor route. It is also possible that the addition of the terminal $\text{Co}(\text{CO})_4$ unit to $\text{MeGeHCo}_2(\text{CO})_7$ is fast, resulting in the low concentration of this species at all times.

From these ^1H NMR observations, together with the information obtained from the other experiments, a proposal for a full reaction scheme for this process may be made. That is

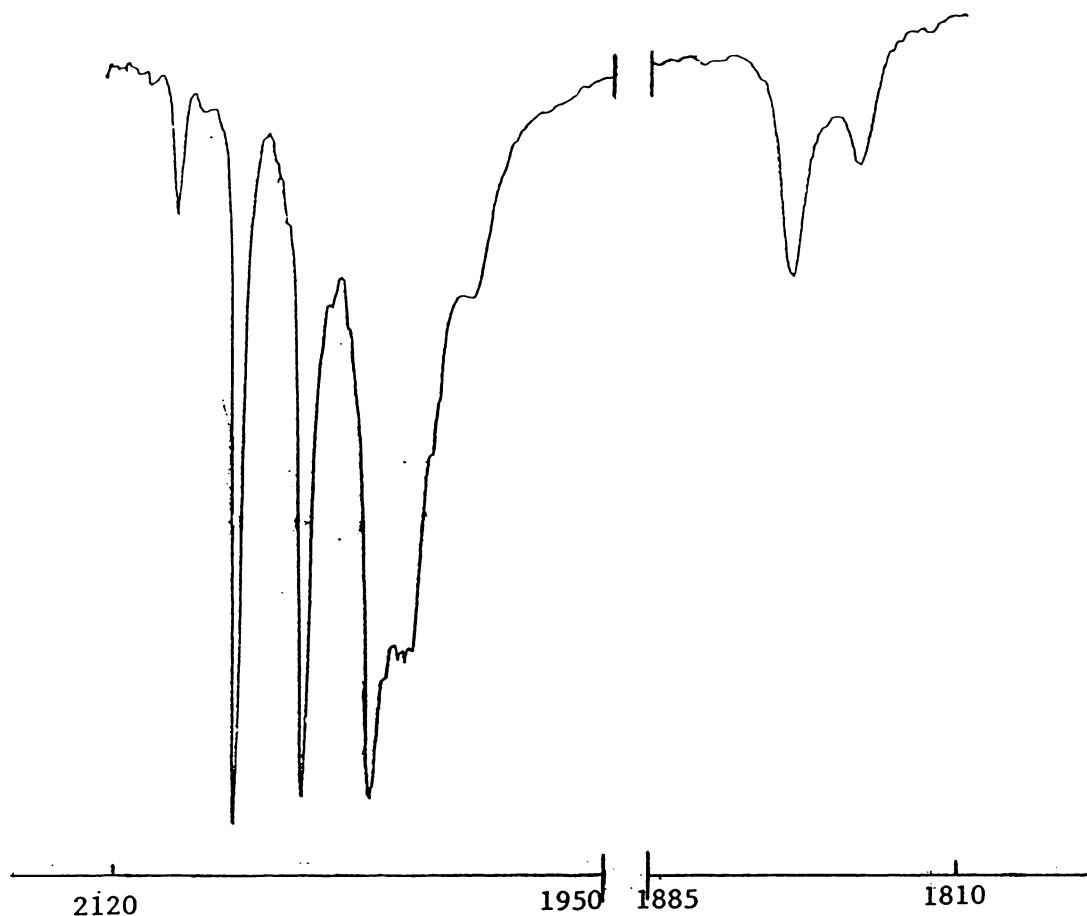


Scheme 2.4

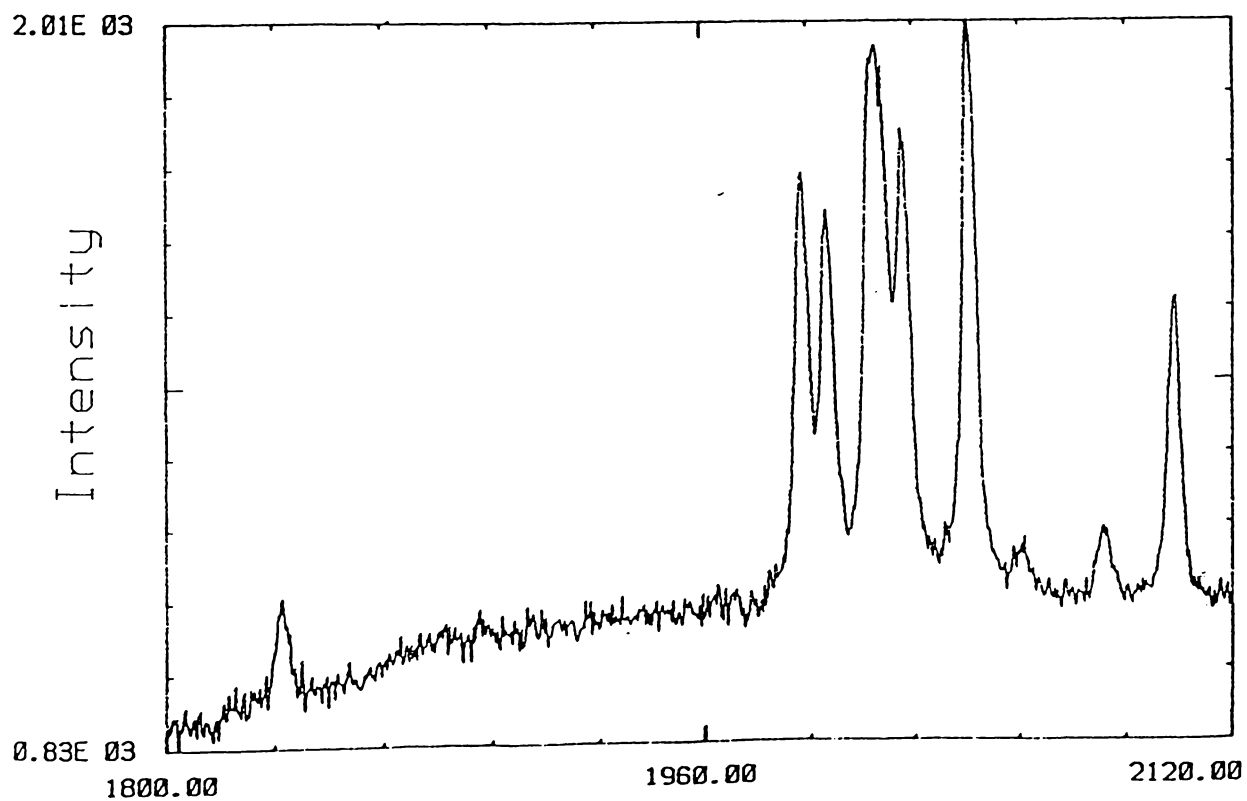
2.5.2.4. Discussion of the vibrational spectra of $\text{MeGeCo}_3(\text{CO})_{11}$.

The infrared and Raman spectroscopy data for $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, are recorded in table 2.6 while some of the spectra are shown in figures 2.11(a) to (d).

Figure 2.11. Vibrational spectra of $\text{MeGeCo}_3(\text{CO})_{11}$.



(a) Infrared spectrum between 2120 and 1810 cm^{-1}



(b) Raman spectrum between 2120 and 1800 cm^{-1}

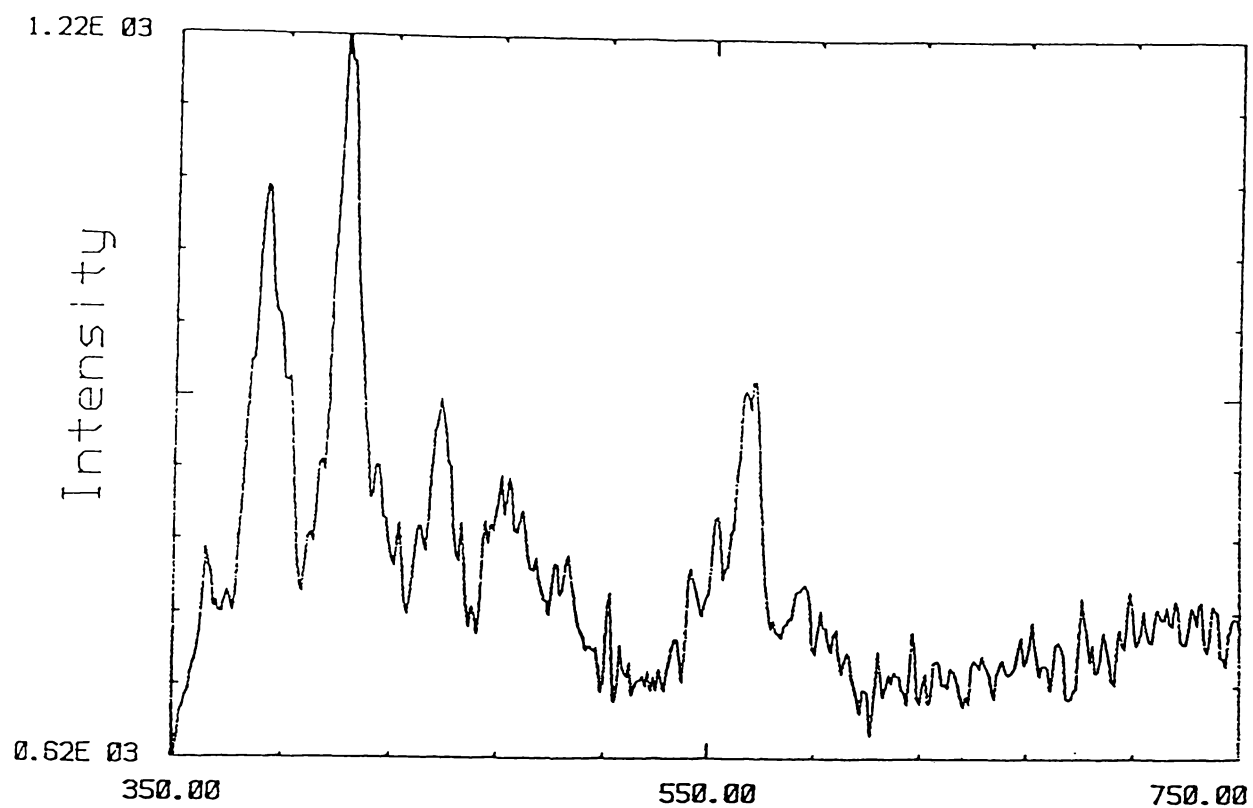
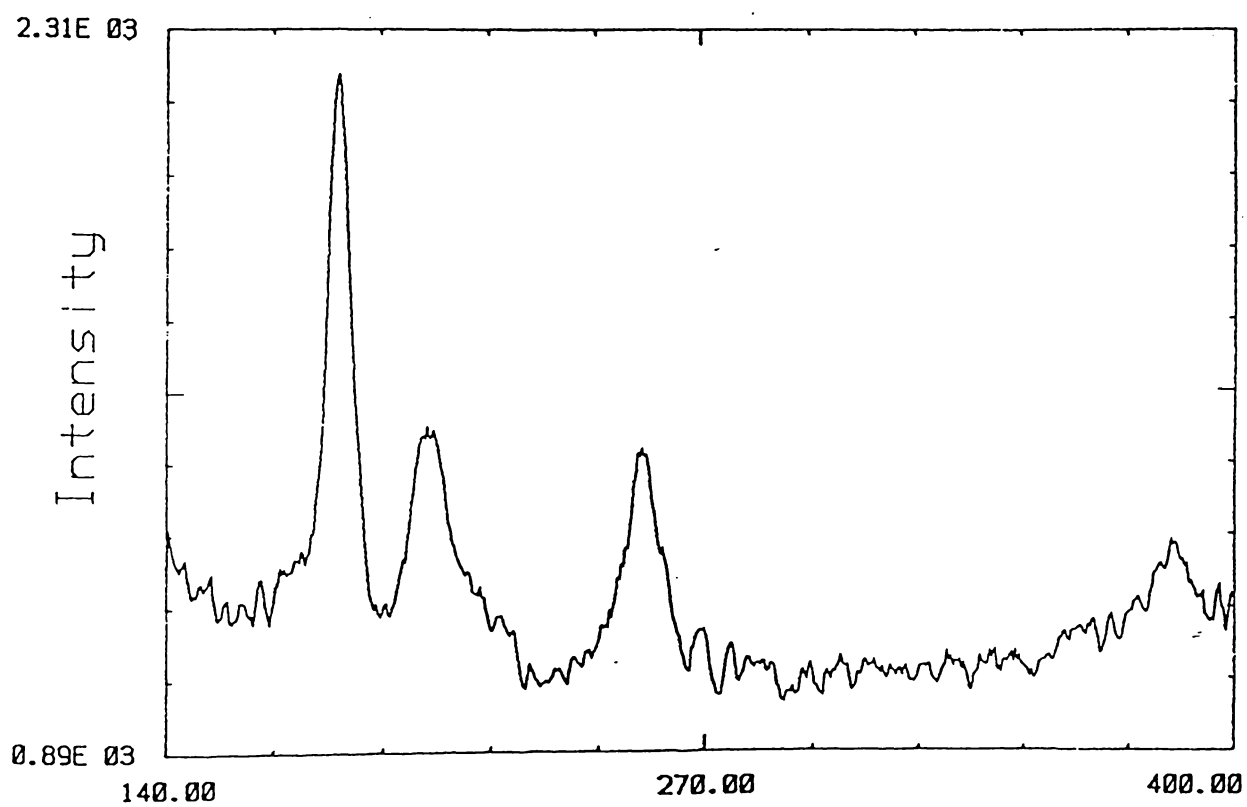
(c) Raman spectrum between 350 and 750 cm^{-1} (d) Raman spectrum between 140 and 400 cm^{-1}

Table 2.6 Vibrational spectroscopy data for $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$.

(C ₆ H ₁₄ solution)[35]	Infrared (cm ⁻¹)		Raman (cm ⁻¹) (powdered solid)
		(nujol mull)	
2105 m		2103 w	2103 m
2082 s		2080 s	2081 w
2056 s		2053 s	2057 w
2046 w, sh			
2030 s		2032 s	2040 s
2020-5 m		2022 s	2021 s
2017 m		2017 m	2013 s
2007 w		2010 m	
2003 w, sh		2001 w, sh	
1998 w			1997 s
		1993 w, sh	1990 w
1850 m		1843 m, br	
1838 w		1833 m, br	1834 w
		577 w	585 w
		555 w	565 m
		529 m	
			495 w
			473 m
			448 m
			413 s
			383 s
			363 w
			255 w
			204 w
			182 m
			103 s
			80 w

$\text{MeGeCo}_3(\text{CO})_{11}$ may be assumed to have C_s symmetry and will possess 84 fundamental modes of vibration. The C-H vibrations were not examined since these modes are of little interest for this molecule. 76 fundamental modes would then be predicted. Clearly, not all of these vibrations are observed.

This is one of the few cases where both infrared and Raman data are available for a fairly complex germanium - cobalt carbonyl cluster. Thus the analysis, although fairly tentative since there is little background for reference, is treated in some detail.

The most easily assigned vibrational mode of this molecule is the stretching vibration of the bridging carbonyl. This results in the two peaks observed at 1850 cm⁻¹ and 1838 cm⁻¹ in the solution infrared spectrum, at 1843 cm⁻¹ and 1833 cm⁻¹ in the solid infrared spectrum, and in one peak, at 1834 cm⁻¹, in the Raman. The observation of two peaks suggests that two possible isomers exist for this species as shown in figure 2.12.

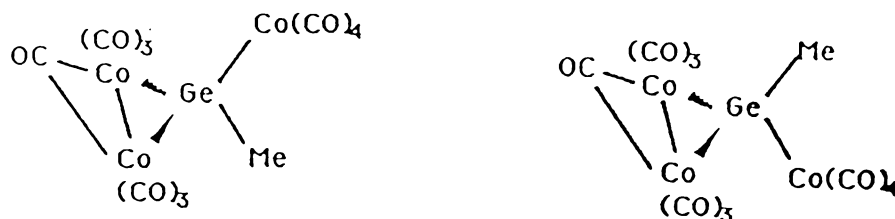


Figure 2.12

Two peaks are not observed in the Raman spectrum but this mode would be expected to be weak here.

In the ^1H NMR spectra (figures 2.9(a) to (e)) only one signal was observed to result from the methyl protons of $\text{MeGeCo}_3(\text{CO})_{11}$ (at 1.96 δ). Clearly an interchange between the two isomers must occur in solution which is too rapid to be observed under NMR examination (timescale $\sim 10^{-3}$ s), but is seen in the infrared experiment (timescale $\sim 10^{-10}$ s).

A similar observation is reported for the bridging carbonyl vibrations of the phenyl equivalent of this molecule, $\text{PhGeCo}_3(\text{CO})_{11}$ [37], where two bands, at 1850 cm^{-1} and 1835 cm^{-1} , are observed in the infrared spectrum as a result of these modes.

There is no other evidence from vibrational spectroscopy for the presence of these isomers suggesting that the terminal carbonyl energies are very similar for each.

There are two possible approaches to the analysis of the terminal carbonyl vibrations. If the individual cobalt carbonyl moieties interact across the germanium then analysis becomes very complicated; however, if coupling across the germanium is assumed to be moderate, then the terminal $\text{Co}(\text{CO})_4$ unit and the $\text{Co}_2(\text{CO})_7$ unit may be considered separately.

Of the known species containing a terminal $\text{Co}(\text{CO})_4$ unit $\text{MeGeH}_2\text{Co}(\text{CO})_4$ is the most appropriate simple compound for a comparison with $\text{MeGeCo}_3(\text{CO})_{11}$ (see Table 2.7).

Table 2.7. Carbonyl region infrared data for $\text{MeGeH}_2\text{Co}(\text{CO})_4$. (cm^{-1}).

2106 (s)	}	
2047 (vs)	}	
2017 (vs)	}	3 a' and a''
2012 (vs)	}	
1982 (m)	}	(^{13}CO)

Recorded from the gas [36].

This might suggest that the bands observed at 2105 cm^{-1} and 2046 cm^{-1} , for $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ arise directly from the a' vibrations of the $\text{Co}(\text{CO})_4$ unit carbonyls.

Similarly an interpretation of the $\text{Co}_2(\text{CO})_6$ group carbonyl stretches may be made with reference to other, simpler, bridged $\text{Co}_2(\text{CO})_6$ species. Bor [130] has discussed the generalised infrared spectrum of the carbonyl groups of $\text{Co}_2(\text{CO})_6(\mu_2\text{-X})_2$ compounds with idealised C_{2v} symmetry (see section 1.4.1.2.). The carbonyl region infrared data of $\text{Co}_2(\text{CO})_6(\mu_2\text{-CO})_2$, $\text{Co}_2(\text{CO})_6(\mu_2\text{-CO})(\mu_2\text{-GeMe}_2)$ and $\text{Co}_2(\text{CO})_6(\mu_2\text{-GeMe}_2)_2$ are shown in table 2.8.

Table 2.8. Carbonyl region infrared data for some $\text{Co}_2(\text{CO})_6(\mu_2\text{-X})_2$ species. (cm^{-1}).

Bor symbol [130]	$\text{Co}_2(\text{CO})_8$ [130]	$\text{Me}_2\text{GeCo}_2(\text{CO})_7$ [20]	$(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ [17]
q (A_1)	2111.8	2088	2072
s (B_1)	2071.0	2048	2035
u (A_1)	2044.0	2026	2014
v (B_2)	2042.4	2008	1994
w (B_1)	2034.8*	1998	1984
		1965	1964

* Calculated value [130]

These three compounds exhibit clearly resolved Bor spectra.

$\text{Me}_2\text{GeCo}_2(\text{CO})_7$ may be considered as containing a $\text{Co}_2(\text{CO})_6$ unit closely related to that of $\text{MeGeCo}_3(\text{CO})_{11}$. Thus the bands at 2082 and 2056 cm^{-1} for $\text{MeGeCo}_3(\text{CO})_{11}$ may be considered as resulting directly from the vibrations of the $\text{Co}_2(\text{CO})_6$ unit. These would then be Bor's q and s modes.

The remainder of the spectrum in this region may be considered as overlapping of the lower frequency modes.

This analysis appears to work reasonably well, however it does assume that there is little interaction between the various carbonyl ligands across the germanium, which may well not be the case. Although the positions of the bands of $\text{MeGeH}_2\text{Co}(\text{CO})_4$ match very well with those of the $\text{Co}(\text{CO})_4$ unit of $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, the intensities do not correspond so closely. This however, may be a result of a moderate interaction and it is felt that this model gives a reasonable assignment of at least some of the terminal carbonyl bands.

In either case, 10 terminal carbonyl modes are expected for this molecule. The new Raman data shows the two bands at 1997 cm^{-1} and 1990 cm^{-1} are likely to be fundamentals. Previously, when only the infrared spectra were available, these were assumed from their weak intensity to result from ^{13}CO vibrations [36]. Eleven bands are observed in total in the terminal carbonyl stretching region, hence one probably does

result from a ^{13}CO vibration. The two weakest bands in the infrared are at 2047 cm^{-1} and at 2003 cm^{-1} . Since the band at 2047 cm^{-1} corresponds so well with position of an a' mode of $\text{MeGeH}_2\text{Co}(\text{CO})_4$ it is probable that it is the band at 2003 cm^{-1} which is due to the presence of ^{13}CO .

The carbonyl stretching region of the infrared spectrum of the phenyl equivalent of this molecule, $\text{PhGeCo}_3(\text{CO})_{11}$ [37], compares very well with the data for $\text{MeGeCo}_3(\text{CO})_{11}$. All the bands are represented other than the weak shoulder at 2003 cm^{-1} which supports the suggestion that this could result from a ^{13}CO vibration.

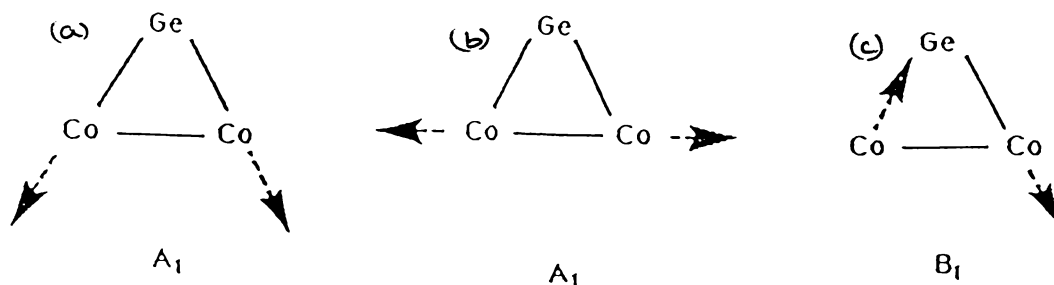
For the lower frequency modes, it has only been possible to make very tentative assignments due to the very small amount of comparative data for these types of molecules.

The band observed at 585 cm^{-1} in the Raman spectrum is assigned to Ge-C stretching. It is probable that the band at 577 cm^{-1} in the infrared spectrum arises from the same vibration as there is commonly a shift observed between the two techniques. For example, the Ge-C stretch of $\text{MeGeH}_2\text{Co}(\text{CO})_4$ is assigned to bands at 587 cm^{-1} in the infrared and 594 cm^{-1} in the Raman spectrum [36].

The bands from $565\text{--}363\text{ cm}^{-1}$ are attributed to Co-C-O deformations and Co-C stretching. Again, $\text{MeGeH}_2\text{Co}(\text{CO})_4$ is the most convenient molecule for comparison. For this bands ranging from $549\text{--}542\text{ cm}^{-1}$ were assigned to Co-C-O deformations while those from $504\text{ to }413\text{ cm}^{-1}$ were attributed to Co-C stretching [36].

The three bands observed at 255 cm^{-1} , 204 cm^{-1} and 182 cm^{-1} are assigned to metal-metal stretching modes. For comparison, the Ge-Co stretch of $\text{H}_3\text{GeCo}(\text{CO})_4$ is reported to arise at 220 cm^{-1} [143] while the Co-Co stretch of $\text{Co}_2(\text{CO})_8$ is observed at 230 cm^{-1} [145].

The metal-metal stretching vibrations of $\text{MeGeCo}_3(\text{CO})_{11}$ must really be considered to arise through motions of the whole molecule. If the GeCo_2 triangle is considered first this ideally has C_{2v} symmetry which predicts three vibrations ($2A_1 + B_1$). These modes are depicted schematically in figure 2.13.



Schematic representation of the $2A_1 + B_1$ modes
predicted for the GeCo_2 triangle of $\text{MeGeCo}_3(\text{CO})_{11}$

Figure 2.13.

From figure 2.13 it can be seen that while (a) is essentially a stretching mode of the Ge-Co bonds it will also involve Co-Co stretch. Similarly, the vibrations shown as (b) and (c), while considered as stretching modes, will also require deformation about the Co-Ge-Co and/or Ge-Co-Co bond angle. Thus these metal triangle vibrations cannot be considered simply as stretching or bending modes.

It is noticeable that the range of frequencies over which the metal-metal vibrations of $\text{MeGeCo}_3(\text{CO})_{11}$ are observed is greater than the observed range of $240\text{--}210\text{ cm}^{-1}$ found for the Ge-M stretching modes of $\text{R}_3\text{GeM}(\text{CO})_n$ compounds [7]. It is thus apparent that the metal skeleton of $\text{MeGeCo}_3(\text{CO})_{11}$ undergoes vibrations of both higher and lower energy than those observed for simpler species.

When the $\text{Co}(\text{CO})_4$ unit is included the modes are further complicated. It may be anticipated that the highest energy band observed would result from symmetric stretch of the entire metal framework of the molecule, as shown in figure 2.14.

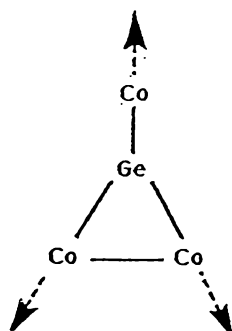


Figure 2.14.

The band observed at 255 cm^{-1} is, therefore, assigned to this vibration.

The Raman spectrum of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ has been recorded (see section 3.4.2.3.) and the lower frequency peaks are shown in table 2.9.

Table 2.9 Raman spectrum of $\text{GeCo}_4(\text{CO})_{14}$ from 220 - 93 cm^{-1} .

220 (s)
201 (w)
181 (w)
148 (m)
136 (m)
93 (w)

Recorded from a solid sample.

Two of the bands observed for this molecule, at 201 cm^{-1} and 181 cm^{-1} , correspond quite closely to the bands assigned as metal framework vibrations of $\text{MeGeCo}_3(\text{CO})_{11}$. However, the two mutually perpendicular GeCo_2 triangles of $\text{GeCo}_4(\text{CO})_{14}$ would be expected to give rise to a more complicated spectrum, as observed.

The two lower bands of $\text{MeGeCo}_3(\text{CO})_{11}$, at 103 cm^{-1} and 80 cm^{-1} are thought to arise through motions of the metal framework, such as twisting about the germanium.

Table 2.10 repeats the vibrational data for $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ showing the assignments that have been made in this analysis.

Table 2.10 Vibrational data for $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ with assignments.

Band (cm^{-1})	Activity	Assignment
2105	IR(m) R(m)	a' of $\text{Co}(\text{CO})_4$ unit CO stretch
2082	IR(s) R(w)	q mode of $\text{Co}_2(\text{CO})_7$ unit CO stretch*
2056	IR(s) R(w)	s mode of $\text{Co}_2(\text{CO})_7$ unit CO stretch*
2046	IR(w)	a' mode of $\text{Co}(\text{CO})_4$ unit CO stretch
2030	IR(s) R(s)	}
2020-5	IR(s) R(s)	} Overlapping modes
2017	IR(m) R(s)	} Terminal CO stretching.
2007	IR(m)	}
2003	IR(w)	^{13}CO vibration
1998	IR(w) R(s)	} Overlapping modes
1993	IR(w) R(w)	} Terminal CO stretching

Table 2.10 continued

1850	IR(m)	}	Bridging carbonyl stretch of two isomers.
1838	IR(m) R(w)	}	
585	R(w)	}	Ge-C stretch.
577	IR(w)	}	
565	R(m)	}	Co-C-O deformation +
555	IR(w)	}	
529	IR(m)	}	Co-C stretch
495	R(w)	}	
473	R(m)	}	
448	R(m)	}	
413	R(s)	}	
383	R(s)	}	
363	R(w)	}	
255	R(w)	}	
204	R(w)	}	Metal-metal vibrations
182	R(m)	}	
103	R(s)	}	Skeletal deformation modes e.g. twisting
80	R(w)	}	

* From [130]

2.6 Reaction of germyl cobalt tetracarbonyl with dicobalt octacarbonyl

2.6.1. Experimental Details and Results

Run 1: $\text{H}_3\text{GeCo}(\text{CO})_4$ (ca. 0.19 mmol from volume of ClGeH_3 used in its preparation - see section 2.2) and $\text{Co}_2(\text{CO})_8$ (0.018g; 0.55 mmol) (1:3 ratio) were allowed to react in hexane (5 ml) for 5 weeks. Incondensable gas (0.65 mmol) was removed, of composition 75% CO, 25% H_2 . Fractionation of the volatile components showed no unreacted $\text{H}_3\text{GeCo}(\text{CO})_4$, however $\text{HCo}(\text{CO})_4$ (0.16 mmol, based on its subsequent decomposition to $\text{Co}_4(\text{CO})_{12}$ (0.029g; 0.04 mmol)) was observed.

A carbonyl region infrared spectrum of the involatile products in hexane solution showed a mixture of unreacted $\text{Co}_2(\text{CO})_8$, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ and a lesser amount of $\text{Co}_4(\text{CO})_{12}$. These products could not be separated due to their similar solubilities and their presence in similar quantities.

Run 2: $\text{H}_3\text{GeCo}(\text{CO})_4$ (ca. 0.54 mmol) and $\text{Co}_2(\text{CO})_8$ (0.342g; 1.00 mmol) (1:2 ratio) were allowed to react in hexane (5 ml) for 4 weeks. Incondensable gases (1.51 mmol) were measured, of composition 67% CO, 33% H_2 . Fractionation of the volatiles yielded only solvent and $\text{HCo}(\text{CO})_4$ (0.50 mmol, from $\text{Co}_4(\text{CO})_{12}$ (0.071g; 0.125 mmol)).

The involatile products were kept at 10°C at all times to stabilise any open species which might have formed, such as $[(\text{CO})_4\text{Co}_2]_2\text{GeCo}_2(\text{CO})_7$. A carbonyl region infrared spectrum of these products in hexane solution showed the major product to be $\text{GeCo}_4(\text{CO})_{14}(\text{B})$. A small amount of unreacted $\text{Co}_2(\text{CO})_8$ was also observed, together with a trace of $\text{Co}_4(\text{CO})_{12}$. $\text{GeCo}_4(\text{CO})_{14}$ was separated from the mixture as far as possible, by fractional crystallisation from hexane solution at -15°C, which gave 0.336g, 0.48 mmoles pure $\text{GeCo}_4(\text{CO})_{14}$, an 89% yield on the basis of consumed $\text{H}_3\text{GeCo}(\text{CO})_4$.

2.6.2. Discussion of the Reaction of $\text{H}_3\text{GeCo}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$.

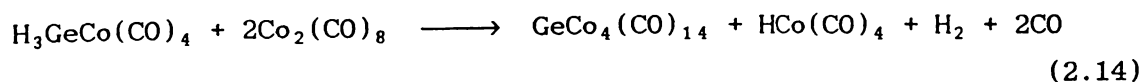
From the results described above, it appears that the reaction between $\text{H}_3\text{GeCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$ follows a similar path to that of MeGeH_3 and $\text{Co}_2(\text{CO})_8$.

The second run provided a good yield of the major product, $\text{GeCo}_4(\text{CO})_{14}$, and only a small amount of unreacted $\text{Co}_2(\text{CO})_8$ remained. This run was carried out using a $\text{Ge}:\text{Co}_2$ reactant ratio of 1:2 which is the likely reactant ratio of the $\text{MeGeH}_3/\text{Co}_2(\text{CO})_8$ system.

H_2 and CO evolution are clearly an important part of this reaction process. In run 2 approximately 3 moles of gas were evolved for each mole of reacting $\text{H}_3\text{GeCo}(\text{CO})_4$ - that is, one mole of H_2 and two of CO. In run 1 the proportional amount of gas was much higher, which is likely to result from decarbonylation of unreacted $\text{Co}_2(\text{CO})_8$ to give $\text{Co}_4(\text{CO})_{12}$. The amounts of both unreacted $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ were much higher in run 1 than in run 2, and this rationalisation of the higher gas evolution measurement for run 1 is also supported by the increased proportion of CO.

The quantity of $\text{HCo}(\text{CO})_4$ produced in each run also correlates with the reaction pathway of MeGeH_3 and $\text{Co}_2(\text{CO})_8$. For every mole of reacting $\text{Co}_2(\text{CO})_8$, approximately $\frac{1}{2}$ mole of $\text{HCo}(\text{CO})_4$ is observed. Although $\text{Co}_4(\text{CO})_{12}$ was observed in comparatively large quantities in run 1, it was only present in a trace amount in run 2, thus this species is most likely to result from an unrelated side reaction - the decarbonylation of unreacted $\text{Co}_2(\text{CO})_8$ - rather than as a direct result of the overall reaction pathway.

These results suggest the formulation shown in equation 2.14.



Other than an extra CO among the products this is identical to the reaction scheme proposed for the $\text{MeGeH}_3/\text{Co}_2(\text{CO})_8$ system. The additional CO is likely to result from decarbonylation of an initially formed intermediate to give $\text{GeCo}_4(\text{CO})_{14}$.

As was the case for the MeGeH_3 and $\text{Co}_2(\text{CO})_8$ reaction, two individual pathways are apparently occurring together. Replacement of a bridging carbonyl ligand on $\text{Co}_2(\text{CO})_8$ by a GeH_2 group to form a GeCo_2 triangle with release of CO and H_2 , and Co-Co bond cleavage to form $\text{HCo}(\text{CO})_4$ and a $\text{Ge-Co}(\text{CO})_4$ unit. This supports the hypothesis put forward in section 2.5.2.1. which stated that, on reaction with $\text{Co}_2(\text{CO})_8$, the presence of two attached hydrogens on a germanium group will give rise to a GeCo_2 triangle while a single Ge-H unit will result in the formation of a $\text{Ge-Co}(\text{CO})_4$ terminal group and $\text{HCo}(\text{CO})_4$.

The only germanium containing product found in this system was $\text{GeCo}_4(\text{CO})_{14}$ (figure 2.15).

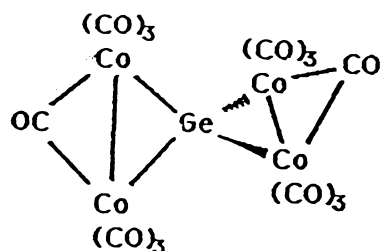


Figure 2.15

As a $\text{Co}(\text{CO})_4$ terminal unit was already present in the germanium hydride starting material it was possible that a semi-open species might be obtained, such as $\text{GeCo}_4(\text{CO})_{15}$ shown in figure 2.16.

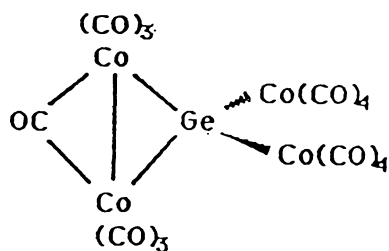
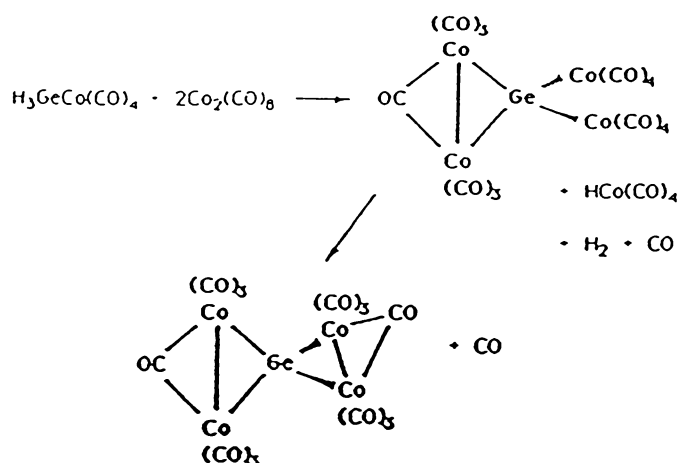


Figure 2.16

Carbonyl region infrared spectroscopy would be expected to indicate the presence of this type of species. Characteristic of the terminal $\text{Co}(\text{CO})_4$ groups are intense bands at relatively high wave number, arising through an a' vibration of this unit (see Section 1.4.1.1.). However, no such band was observed. In fact, no bands were found which could not immediately be

assigned to known species. This form of a GeCo_4 species is obviously not favoured.

Although $\text{GeCo}_4(\text{CO})_{15}$ does not appear to be stable enough to be observed as a product of this reaction, it is presumably formed as an intermediate in the production of $\text{GeCo}_4(\text{CO})_{14}$ as depicted in scheme 2.5.



Scheme 2.5

The reaction of $\text{H}_3\text{GeMn}(\text{CO})_5$ with $\text{Co}_2(\text{CO})_8$ produced $[(\text{CO})_5\text{Mn}]\text{GeCo}_3(\text{CO})_9$ as the major product [43]. Also observed among the involatile products of the reaction was a species whose carbonyl region infrared spectrum suggested that it could be of the form $[(\text{CO})_7\text{Co}_2]\text{GeXY}$ and it was suggested to be the open-skeleton analogue of $[(\text{CO})_5\text{Mn}]\text{GeCo}_3(\text{CO})_9$, that is $[(\text{CO})_5\text{Mn}]\text{Ge}[\text{Co}_2(\text{CO})_7][\text{Co}(\text{CO})_4]$ (figure 2.16).

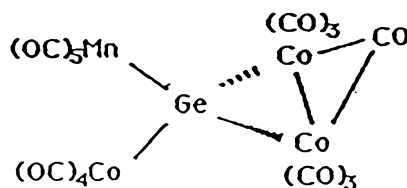
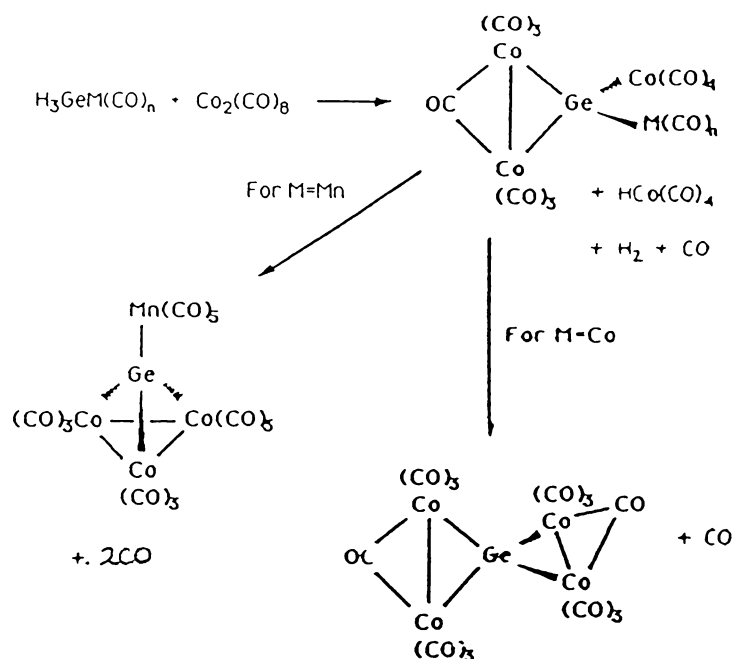


Figure 2.17

In this study of the $\text{H}_3\text{GeCo}(\text{CO})_4/\text{Co}_2(\text{CO})_8$ reaction the fully closed species, $[(\text{CO})_4\text{Co}]\text{GeCo}_3(\text{CO})_9$, was not observed. It is likely that while the first steps of these reactions are identical, the final product is dependent on the metal carbonyl group attached to the germanium hydride starting material, as depicted in scheme 2.6.



Scheme 2.6

In the $\text{H}_3\text{GeCo(CO)}_4$ system a bond is easily formed between the two Co(CO)_4 terminal groups giving $\text{GeCo}_4(\text{CO})_{14}$ as product. However, in the $\text{H}_3\text{GeMn(CO)}_5$ reaction, an equivalent species is not possible since it is not favourable for manganese to be involved in the metal framework of the cluster. Thus, the open intermediate condenses in the alternative sense.

2.7 Conclusion

This chapter has mainly been concerned with further investigations of established systems. In the polygermane and $\text{Co}_2(\text{CO})_8$ reactions it has been found that the products are primarily determined by the nuclearity of the starting germane. Altering the reactant ratio from the optimum situation will promote cleavage of the Ge-Ge bonds resulting in an increased proportion of the smaller clusters, lowering the yield of the larger germanium polycobalt species.

In the reactions of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ the detailed study of the incondensable gas evolution, HCo(CO)_4 production and the ^1H NMR experiment have allowed a new proposal for the reaction pathway - that is



This in turn has suggested the hypothesis that "where there is no steric effect, if an even number of hydrogens is attached to a germanium group this will react with $\text{Co}_2(\text{CO})_8$ primarily to replace a bridging carbonyl group resulting in the formation of a $\text{GeCo}_2(\text{CO})_7$ unit with evolution of H_2 and CO ; where there is an odd number of hydrogens attached Co-Co bond cleavage will also occur, resulting in the formation of terminal $\text{Co}(\text{CO})_4$ groups and $\text{HCo}(\text{CO})_4$ ".

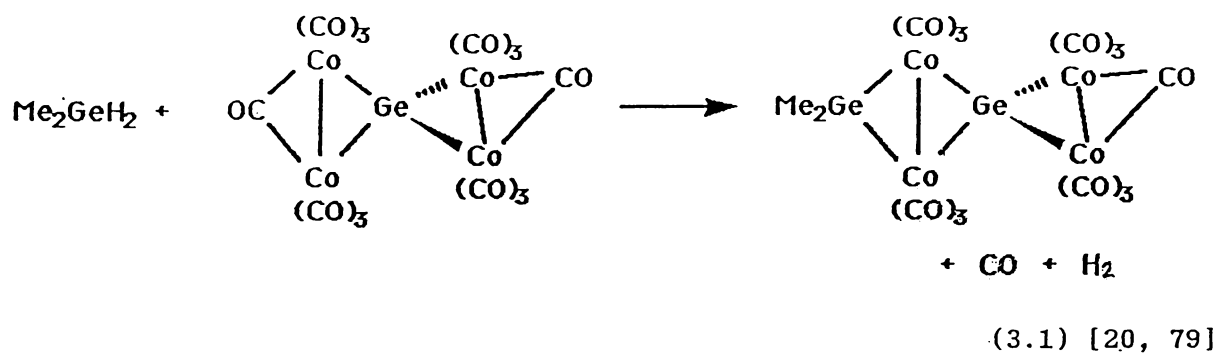
This statement is supported by the results of the reaction between $\text{H}_3\text{GeCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$ which follows a very similar route to that of MeGeH_3 and $\text{Co}_2(\text{CO})_8$. That is



CHAPTER 3: Reactions of Mono- and Dimethylgermane with $\text{GeCo}_4(\text{CO})_{14}$ and Related Systems

3.1. Background and aim

The reaction of dimethylgermane and $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ in a low molar ratio has been examined by Foster [20,79]. It was reported that the hydride replaces a bridging carbonyl ligand on the cluster in an analogous manner to that observed in the reactions of germanium hydrides with $\text{Co}_2(\text{CO})_8$ [79]. The reaction process, which yields $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ as the major product, is depicted in equation 3.1



Only one of the available bridging carbonyl ligands was observed to be replaced and, at that time, this was attributed to a contraction of the Co-Co bond across the central germanium when the opposite Co-Co bond had been bridged by a large group [20].

Similarly, the reaction of monomethylgermane with $\text{GeCo}_4(\text{CO})_{14}$ produced the monosubstituted cluster $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ [20]. Also observed as a product of this reaction was the new *closo*-hexanuclear cluster, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (figure 3.1) [20, 87].

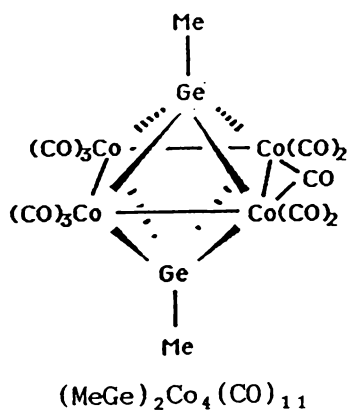


Figure 3.1. [20, 87]

It was of interest to study both of these reactions further to determine if the monosubstituted species were the sole extended chain product, or if the second bridging carbonyl could be replaced by the use of higher molar ratios of hydride to cluster.

Secondly, it was desirable to clarify the MeGeH_3 reaction to establish how the formation of the closed cluster, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, occurs.

3.2. Preparation of starting materials.

$\text{GeCo}_4(\text{CO})_{14}(\text{B})$ was prepared by the room temperature reaction of GeH_4 with $\text{Co}_2(\text{CO})_8$ in hexane for ten days [34]. It was purified by fractional crystallisation from a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution stored at -15°C .

MeGeH_3 and Me_2GeH_2 were produced by the lithium aluminium hydride reduction of MeGeCl_3 and Me_2GeCl_2 respectively, in di-n-butyl ether. The Me_2GeCl_2 , supplied by the Laramie Chemical Co., had, on occasion, to be separated from ca. 10% MeGeCl_3 by fractionation on a vacuum line. Other sources of Me_2GeCl_2 and Me_2GeH_2 are discussed in appendix 2.

CO was produced by the addition of 80% formic acid to concentrated sulphuric acid [146]. Before use this was slowly passed through two traps immersed in liquid nitrogen to remove CO_2 , H_2O and volatile acids.

3.3. General experimental details.

Experiments were carried out in the same manner as those described in chapter 2 (see Section 2.3).

3.4. Reactions of excess dimethyl- or monomethylgermane with $\text{GeCo}_4(\text{CO})_{14}(\text{B})$.

The following reactions between Me_2GeH_2 or MeGeH_3 and $\text{GeCo}_4(\text{CO})_{14}$ were carried out to determine if substitution of both bridging carbonyl ligands on the cluster could be achieved by the use of a large excess of hydride.

3.4.1. Experimental Details and Results

These experiments are summarised in table 3.3

Run 1: Me_2GeH_2 (0.9 mmol by volume) and $\text{GeCo}_4(\text{CO})_{14}$ (0.063 g; 0.09 mmol) (10:1 ratio) were allowed to react in hexane (10 ml) at room temperature. After 3 weeks the vessel was opened to yield incondensable gas (0.14 mmol) of composition 68% CO, 32 % H_2 . The volatile components were removed to a vacuum line and an infrared spectrum was recorded of the involatile species in hexane solution. This showed a mixture of products, indicating the reaction was not complete. Both the volatile and involatile species were returned to a vessel where regular incondensable gas measurements could be taken. The results of these measurements are shown in table 3.1. After a further 12 weeks the reaction seemed complete. Total incondensable gases measured were 0.33 mmol, of composition 59% CO, 41% H_2 . Me_2GeH_2 (0.67 mmol) was recovered on fractionation of the volatiles with a trace (ca. 0.05 mmol) not separated from the solvent.

All of the involatile products were soluble in hexane other than a trace of dark-coloured material which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a decomposition product and was discarded. An infrared spectrum of the soluble fraction in hexane showed only one carbonyl containing species which was subsequently identified as the disubstituted compound, $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. Its characterisation, by infrared, Raman, ^1H NMR and mass spectroscopy and by an X-ray crystal structure determination will be discussed in section 3.5.

Table 3.1 Incondensable gas evolution over time from run 1.

Time interval (days)	Gas evolved (mmol)	% CO	% H_2	Cumulative time (days)	Total gas evolved (mmol)
27	0.144	68	32	27	0.144
14	0.065	60	40	41	0.209
14	0.055	45	55	55	0.264
14	0.029	50	50	69	0.293
14	0.015	51	49	83	0.308
14	0.015	47	53	97	0.323
14	0.008	*	*	111	0.331

* Not measured

Run 2: Me_2GeH_2 (0.65 mmol) and $\text{GeCo}_4(\text{CO})_{14}$ (0.065 g; 0.093 mmol) (7:1 ratio) were allowed to react in hexane (10 ml) for 20 weeks at room temperature. Incondensable gases (0.343 mmol) were measured, of composition 52% CO , 48% H_2 . Unreacted Me_2GeH_2 (0.47 mmol) was recovered from the volatile components the remainder of which was solvent.

The involatile products showed only a trace of the insoluble decomposition product and an 86% yield (0.068 g; 0.08 mmol) of $(\text{MeGe})_2\text{GeCo}_4(\text{CO})_{12}$ on the basis of initial $\text{GeCo}_4(\text{CO})_{14}$.

Run 3: Me_2GeH_2 (0.040 mmol) and $\text{GeCo}_4(\text{CO})_{14}$ (0.011 g; 0.016 mmol) (2.5:1 ratio) were allowed to react in d_6 benzene (2 ml) at room temperature. The reaction was followed by ^1H NMR spectroscopy and some of the spectra obtained are shown in figures 3.6(a) to (f). These will be discussed in section 3.4.3.2. After 38 days the reaction seemed complete and the system was worked up. The incondensable gases were not measured. Examination of the volatile species showed a trace of remaining Me_2GeH_2 but this was not separated from the solvent.

The involatile products were all soluble in hexane other than a trace of an insoluble decomposition product. A carbonyl region infrared spectrum of the soluble species in hexane showed the major carbonyl containing species to be $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, but also present was a minor amount of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$. These products could not be separated. No unreacted $\text{GeCo}_4(\text{CO})_{14}$ was observed. The total weight of the soluble products was 0.012g.

Run 4: MeGeH_3 (0.5 mmol) and $\text{GeCo}_4(\text{CO})_{14}$ (0.019 g, 0.03 mmol) (16.5:1 ratio) were allowed to react in hexane (10 ml) for 8 weeks at 10°C . Incondensable gases were removed but not measured. MeGeH_3 (0.3 mmol) was recovered on fractionation of the volatiles with a small amount (ca. 0.15 mmol) remaining with the solvent.

The involatile products were all soluble in hexane and an infrared spectrum of the hexane solution showed a mixture of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ [20] and a new compound, later characterised by comparison with the dimethylgermyl equivalent as $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$. This will be discussed in section 3.5. These products could not be separated.

Run 5: MeGeH_3 (0.45 mmol) and $\text{GeCo}_4(\text{CO})_{14}$ (0.063 g; 0.09 mmol) (5:1 ratio) were allowed to react in hexane (10 ml) for 13 weeks at room temperature. Incondensable gas evolution was monitored at regular intervals and the results of this are shown in table 3.2. The total amount of

incondensable gas measured was 0.30mmoles, of composition 54% CO, 46% H₂. Unreacted MeGeH₃ (0.2 mmoles) was recovered from the volatiles while a small amount (ca. 0.05 mmoles) could not be separated from the solvent.

The involatile products showed a trace of an insoluble decomposition product, while the remainder was soluble in hexane. An infrared spectrum of the soluble fraction in hexane showed only one carbonyl containing species, (MeHGe)₂GeCo₄(CO)₁₂. On the basis of initial GeCo₄(CO)₁₄ the yield was 82% (0.061 g; 0.074 mmoles).

Table 3.2. Incondensable gas evolution over time from run 5.

Time interval (days)	Gas evolved (mmoles)	%CO	%H ₂	Cumulative time (days)	Total gas evolved (mmoles)
3	0.10	60	40	3	0.10
10	0.05	55	45	13	0.15
7	0.02	15	85	20	0.17
14	0.04	80	20	34	0.21
14	0.03	15	85	48	0.24
11	0.02	70	30	59	0.26
17	0.03	*	*	76	0.29
14	0.01	*	*	90	0.30

* Not measured

Table 3.3. summarises the results of these experiments.

Table 3.3 Summarised reaction conditions and results for the reactions of Me_2GeH_2 or MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$.

Run	Duration (weeks)	Temp.	Initial ratio of hydride to cluster	mmoles of cluster reacted	Reacting ratio of hydride to cluster	Incondensable gas evolved (mmoles)	Yield of disubstituted product
1	15	R.T.	10:1	0.09	ca. 2:1	0.33 (59% CO)	Ca. 80%
2	20	R.T.	7:1	0.09	2:1	0.34 (52% CO)	86%
3	5	R.T.	2.5:1	0.02	-	-	Ca. 75%
4	8	10°C	17:1	0.03	ca. 1.7:1	-	Ca. 50%
5	13	R.T.	5:1	0.09	ca. 2.2:1	0.30 (54% CO)	82%

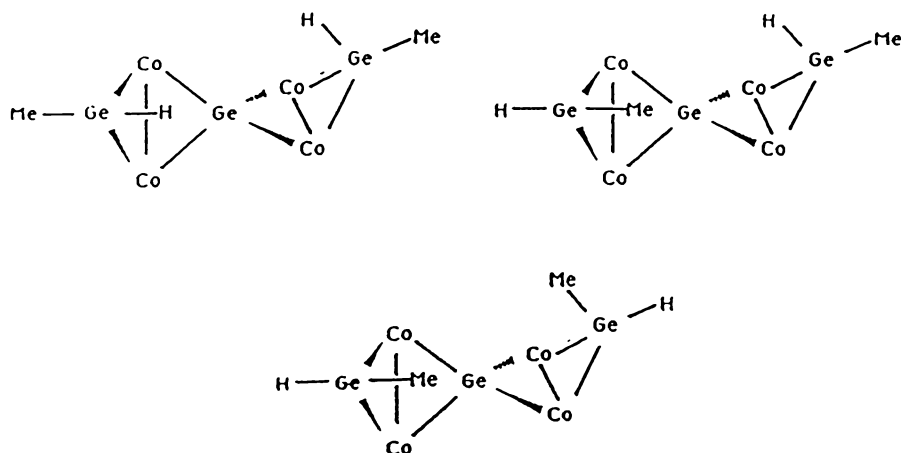
3.4.2. Characterisation of the New Clusters $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}(D)$.

3.4.2.1. Handling of $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(D)$.

These compounds are very similar in their handling characteristics. They are both bright orange solids which are stable at room temperature in the absence of air. In the presence of oxygen decomposition will occur, however they may be handled in air for short periods with little appreciable decomposition.

Their solubility in non-polar solvents, such as hexane, is much greater than that of the parent cluster, $\text{GeCo}_4(\text{CO})_{14}$, which may be attributed to the addition of hydrocarbon groups. Naturally, they are both very soluble in more polar solvents such as dichloromethane.

The only physical difference between these two compounds which is easily observed is their ability to crystallise. $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ readily crystallises from hexane solution cooled to -15°C , while $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ was not observed to crystallise from solution under any of the conditions attempted. Solid that came down from solution tended to be of the form of coagulated powder. This may be attributed to the number of isomers available for $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ resulting from the various orientations of the unsymmetrical bridging germanium groups. These isomers are shown in figure 3.2.



Isomers of $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$
(Carbonyls omitted for clarity)

Figure 3.2

The existence of isomers in unsymmetrically substituted clusters of this type has been observed in low temperature ^1H NMR studies of species such as $[\text{MeGeH}]\text{GeCo}_4(\text{CO})_{13}$ and $[\text{MeGeCl}]\text{GeCo}_4(\text{CO})_{13}(\text{C})$ [32]

3.4.2.2. Infrared spectra of $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$.

These two clusters show very similar patterns in the carbonyl region of the infrared spectrum, while individual peaks are shifted by an average of 4 cm^{-1} to lower frequency on replacement of Ge-H by Ge-Me. This corresponds well with the change observed for the monosubstituted species $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ where a shift of 3 cm^{-1} to lower frequency is observed on replacement of Ge-H by Ge-Me [20].

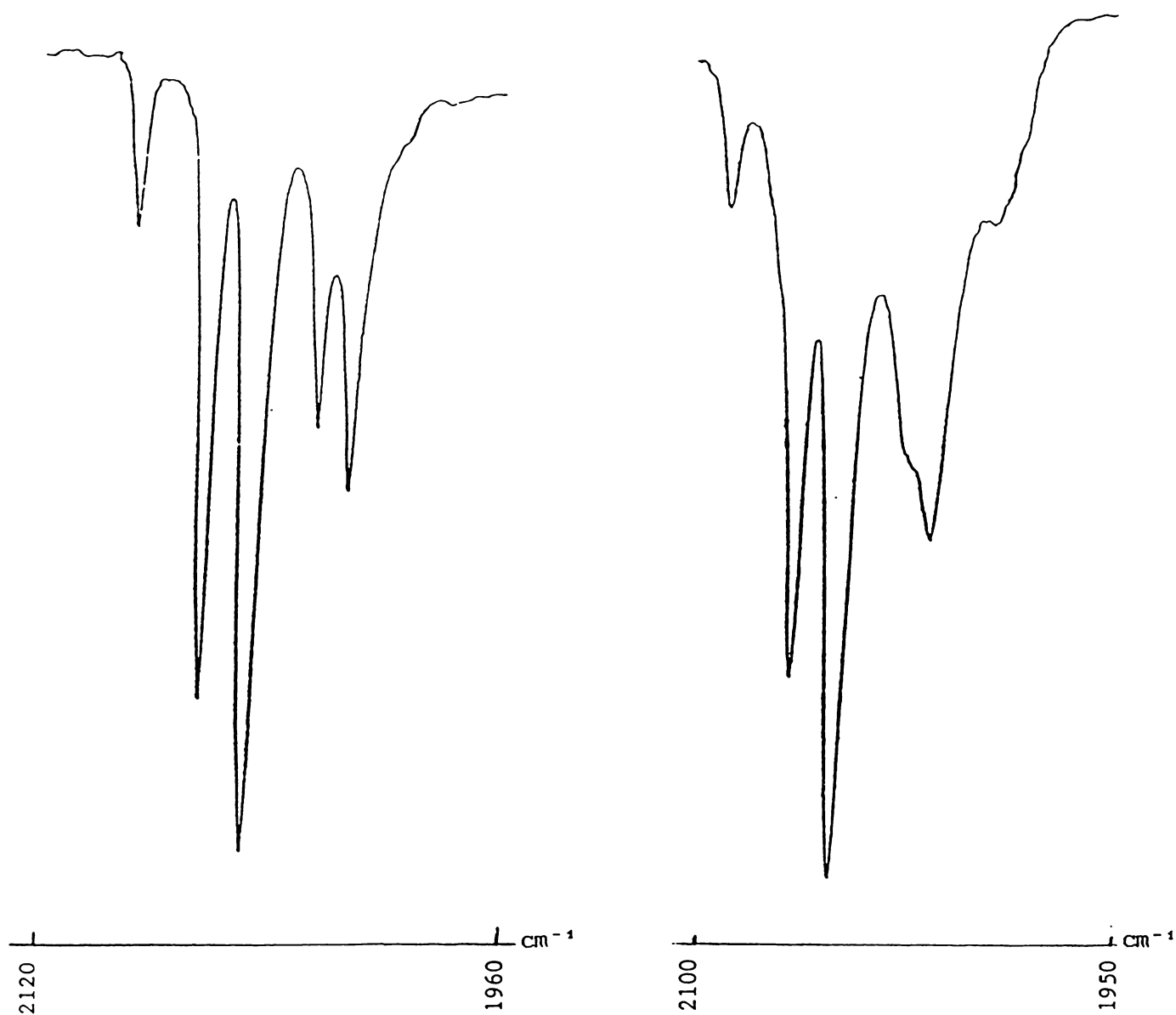
Figures 3.3 (a) and (b) show the infrared active carbonyl stretches recorded for each compound in hexane solution. The absence of any band arising from bridging carbonyl stretches was a strong indicator that these were the disubstituted species. A detailed discussion of the carbonyl region of the vibrational spectra will be given in section 3.6.

For $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ solid phase infrared spectra of both the carbonyl region and the region between 900 and 400 cm^{-1} were also recorded. These spectra are shown in figures 3.3 (c) and (d).

While the solution carbonyl spectrum shows only five bands, up to ten bands are resolved from the solid state spectrum. $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ has idealised C_2 symmetry where the two fold axis passes through the central germanium and bisects the angle between the two bridging Me_2Ge units. This symmetry predicts 12 carbonyl bands ($6\text{A} + 6\text{B}$) and, together with the modes observed in the Raman spectrum (see following section), these are all observed.

The lower region - between 900 and 400 cm^{-1} - consists mainly of bands resulting from Ge-C and Co-C stretching vibrations and various deformation modes. Very little comparative data from this region is available for molecules of this type, however the gas phase infrared spectrum of $\text{Me}_2\text{GeHCo}(\text{CO})_4$ has been reported [152]. Bands between 900 and 700 cm^{-1} are assigned to methyl rock, bands between 630 and 580 cm^{-1} are assigned to Ge-C stretching while those below 580 cm^{-1} are ascribed to various Co-C stretching vibrations and Co-C-O bending modes.

Figure 3.3. Infrared spectra of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$
and $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$.



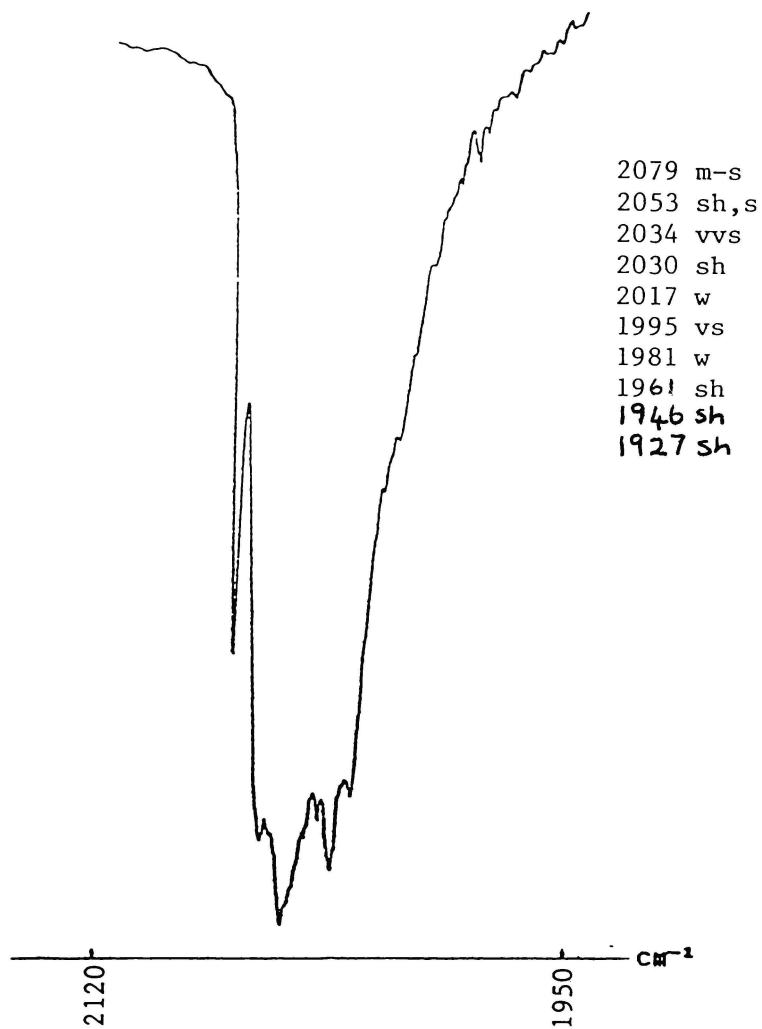
(a) $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ in hexane:
Infrared active carbonyl stretches.

2081 w
2054 vs
2037 vs
2015 m
2002 m

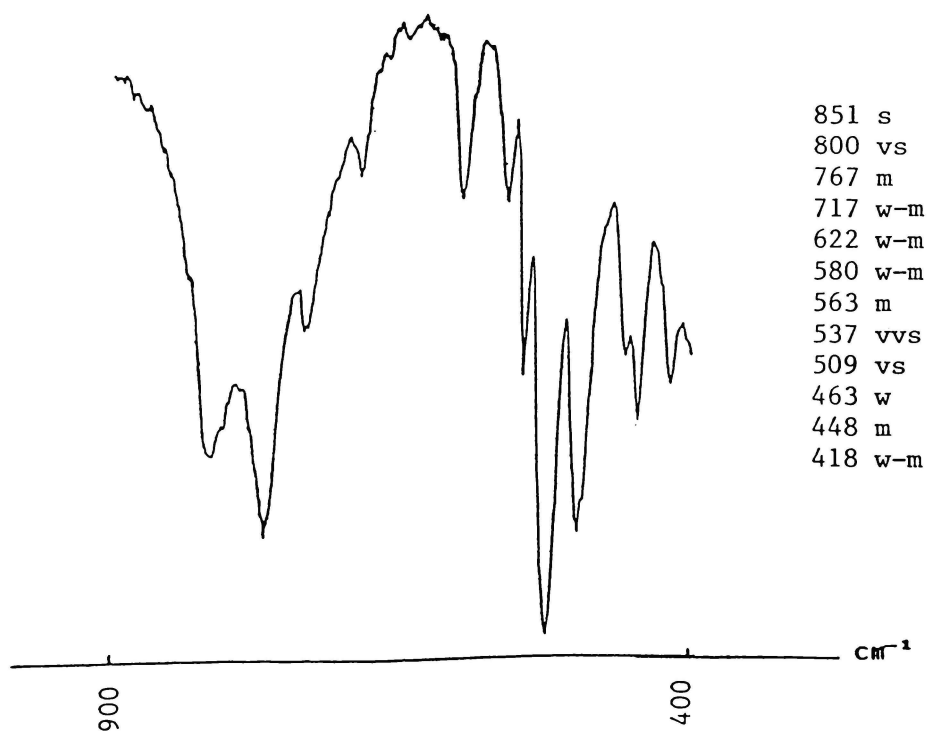
(b) $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ in hexane:
Infrared active carbonyl
stretches.

2085 w
2057 vs
2041 vvs
2012 sh,m
2007 m
1986 sh.w

(c) $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ as a nujol mull
between 2120 and 1950 cm^{-1}



(d) $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ as a nujol mull
between 900 and 400 cm^{-1}



3.4.2.3. Raman spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$.

The Raman spectra shown in figures 3.4 (a) and (b) were recorded from a crystal of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. The carbonyl region will be fully discussed in section 3.6.

The lower region - below 650 cm^{-1} - contains bands resulting from Ge-C stretching, Co-C stretching, metal-metal stretching modes and various deformation modes. These bands are listed in table 3.4 together with the same region of the Raman spectrum of the parent cluster, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$. Tentative assignments have been made by comparison with the vibrational spectra of some other germanium-cobalt carbonyl species.

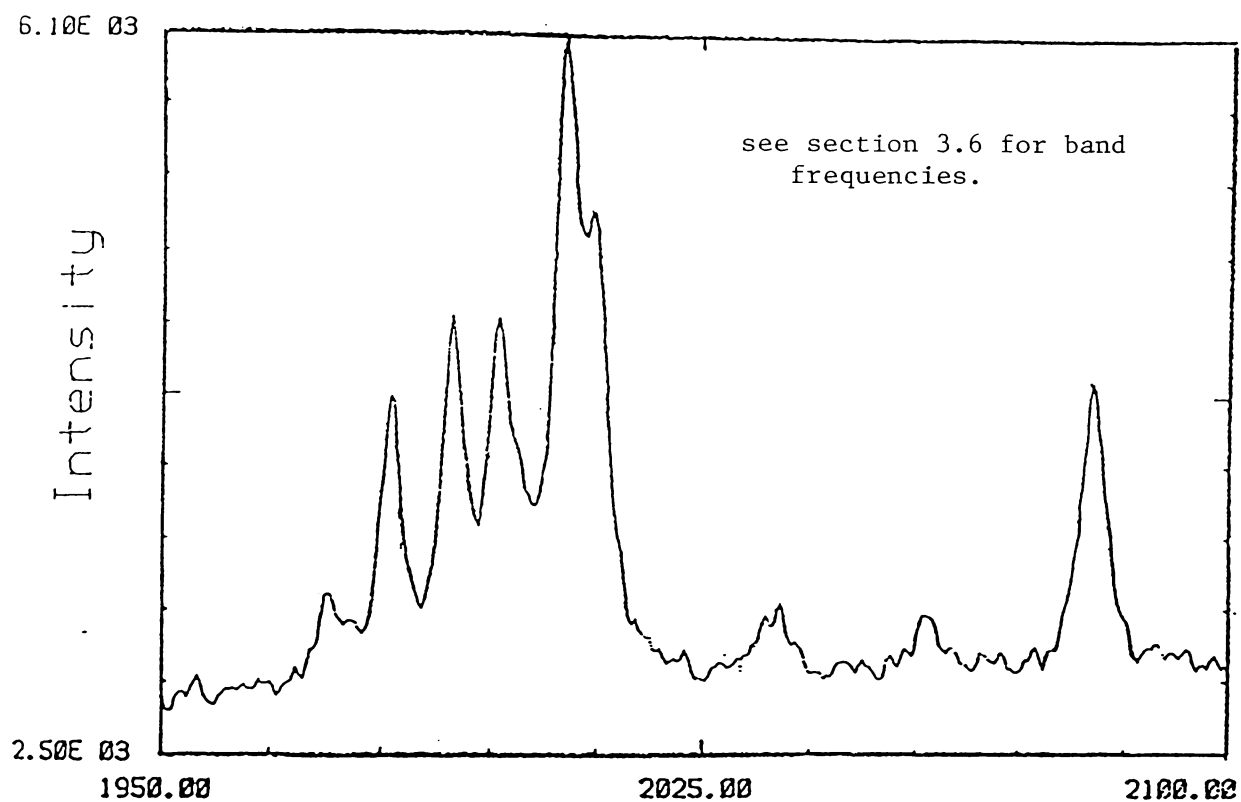
Table 3.4. Raman spectra of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$ from $650\text{--}150\text{ cm}^{-1}$

$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$		$\text{GeCo}_4(\text{CO})_{14}$
585 w	Ge-C stretch	
570 m	Co-C-O deformation	
520 w		
470 m	Co-C stretch	
420 w		382 w
265 s	Metal-metal	
230 s	stretching	221 s
200 vs	modes	201 w
180 m		181 w
120 m	Deformations of	148 m
110 s	metal framework	136 m
90 vs	eg. twisting	93 w
75 s		
60 m		

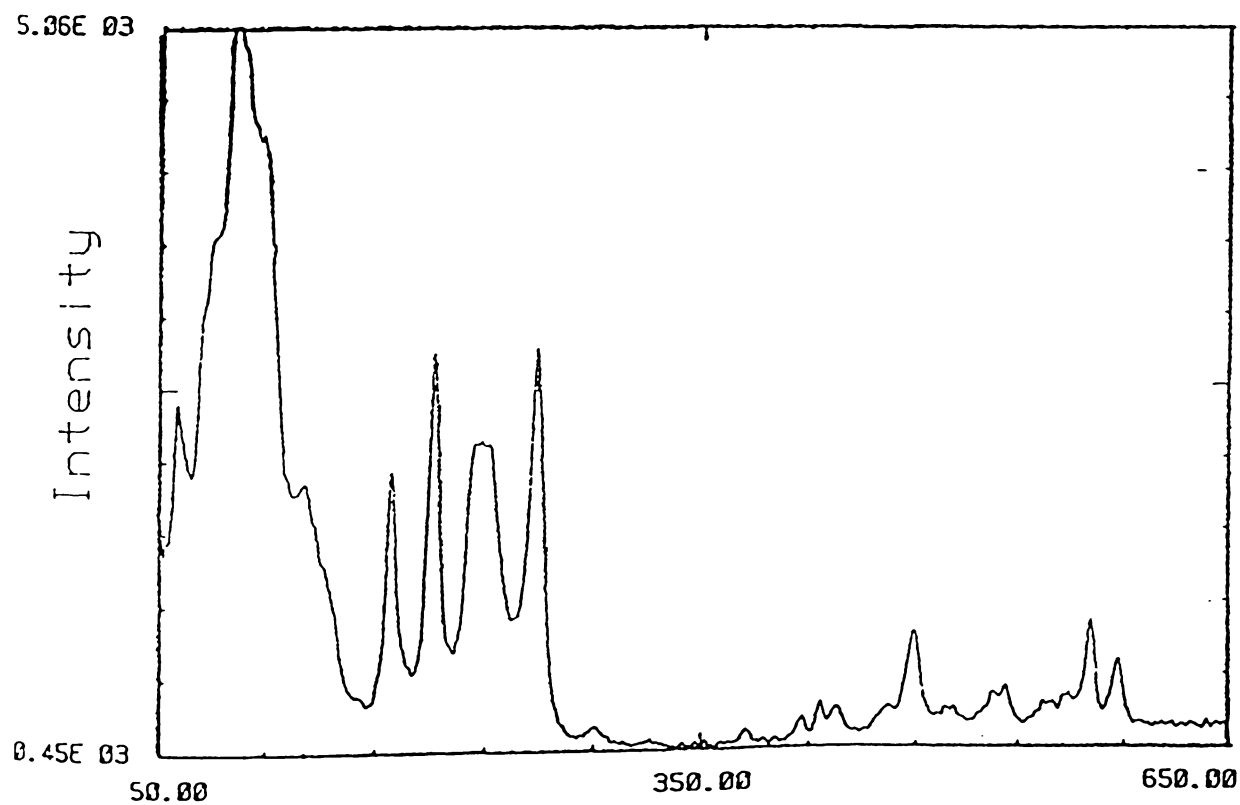
Both recorded from the solid phase

The assignments made for metal-carbon stretching and deformation modes of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ have been made by comparison with the vibrational spectra of $\text{MeGeH}_2\text{Co}(\text{CO})_4$ [36]. These bands compare very well and are thus assigned unambiguously (see also the infrared analysis of this region in the previous section).

(a) Between 1950 and 2100 cm^{-1}

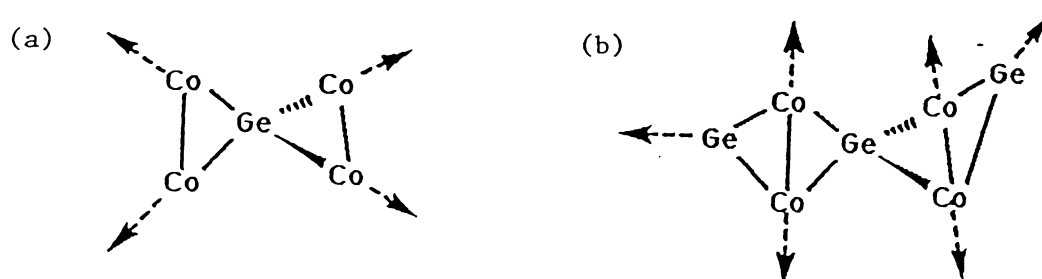


(b) Between 50 and 650 cm^{-1}



The assignment of the various metal-metal stretches and deformations within the two GeCo_2 triangles of each molecule must be carried out by considering the entire metal framework. For comparison, the Co-Co stretch of $\text{Co}_2(\text{CO})_8$ is observed at 230 cm^{-1} [145] and the Ge-Co stretch of $\text{H}_3\text{GeCo}(\text{CO})_4$ arises at 220 cm^{-1} [143]. The Raman spectrum of $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ has been discussed (section 2.5.2.4.). The GeCo_2 triangle was considered as having C_{2v} symmetry where $2\text{A}_1 + \text{B}_1$ modes were predicted and it was found that each of these vibrations would contain elements of both stretching and bending. Now, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, containing two mutually perpendicular GeCo_2 triangles, may be considered as ideally having D_{2d} symmetry. Seven Raman active vibrations of the metal framework are predicted ($2\text{A}_1 + \text{B}_1 + 2\text{B}_2 + 2\text{E}$). Where the symmetry is reduced to C_2 the two E modes will split giving nine possible bands. Of these, six would be expected to arise at the high energy end of the metal-metal stretching region while three would result from low frequency modes such as twisting about the germanium. It is clear from table 3.4. that not all of these modes have been observed.

In the case of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ the two additional GeCo_2 triangles would be expected to further complicate the spectrum and, as can be seen from table 3.4, three extra bands are observed in this region. As suggested for $\text{MeGeCo}_3(\text{CO})_{11}$ (section 2.5.2.4.) the highest frequency band is likely to arise from a symmetric stretch of the entire metal framework. Thus the bands at 265 cm^{-1} in the spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and at 221 cm^{-1} for $\text{GeCo}_4(\text{CO})_{14}$ are anticipated to arise from this type of mode. These are depicted schematically in figure 3.5.



Schematic representation of highest frequency vibration of the metal framework of (a) $\text{GeCo}_4(\text{CO})_{14}$ and (b) $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

Figure 3.5.

3.4.2.4. Mass Spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$.

The significant peaks of the mass spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ are listed in table 3.5. These showed the characteristic intensity pattern of Ge_3 containing ions. No peak corresponding to $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}^+$, which would arise at $m/e = 844-854$, was observed. The highest mass observed was at $m/e = 833-844$ but from this a stepwise series from the loss of 12 CO units was clear. Approximately 65% of the total ion current was carried by this series. The high mass peak at $m/e = 833-844$ corresponds to the parent ion after loss of one methyl group. Ions corresponding to the loss of further methyl groups were only of significant intensity when most of the CO had been lost. The Ge_3Co_4 skeleton remains whole with only one cobalt loss of sufficient intensity to be observed.

Alternative fragmentations are through the loss of CH_2 or CH_4 moieties, and this process may account for the few moderate intensity peaks observed very close to the higher intensity peaks shown in table 3.5. For example peaks with highest intensity bands at $m/e = 652, 660, 613, 519$, and 448 were noted, and these may, presumably, be accounted for by different fragmentation patterns of the methyl groups.

It should be noted that the mass spectrometer used to record this spectrum is rather old and it is possible that instead of an initial Me loss the calibration was actually 15 m.u. too low. However, the overall pattern of the spectrum is still clear.

The mass spectrum of the monosubstituted compound, $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ [20] shows a similar pattern to that observed here, except that a peak corresponding to the parent ion $[\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{13}]^+$ is also found. Peaks corresponding to loss of Co and Ge from the metal skeleton were also of sufficient intensity to be observed for this molecule.

Table 3.5. Mass spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

m/e	relative intensity	Assignment
883-844	48	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_{12}^+$
808-820	41	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_{11}^+$
780-791	69	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_{10}^+$
754-765	76	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_9^+$
728-742	61	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_8^+$
701-714	74	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_7^+$
674-687	100	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_6^+$
645-660	80	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_5^+$
616-630	94	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_4^+$
587-602	50	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_3^+$
573-587	26	$\text{Me}_2\text{Ge}_3\text{Co}_4(\text{CO})_3^+$
558-574	36	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_2^+$
544-557	17	$\text{Me}_2\text{Ge}_3\text{Co}_4(\text{CO})_2^+$
530-545	12	$\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})^+$
503-517	41	$\text{Me}_2\text{Ge}_3\text{Co}_4(\text{CO})^+$
489-503	9	$\text{MeGe}_3\text{Co}_4(\text{CO})^+$
475-487	54	$\text{Me}_2\text{Ge}_3\text{Co}_4^+$
463-474	59	$\text{MeGe}_3\text{Co}_4^+$
448-459	81	Ge_3Co_4^+
402-414	20	$\text{MeGe}_3\text{Co}_3^+$
389-399	34	Ge_3Co_3^+

3.4.2.5. ^1H NMR spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$.

The ^1H NMR spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ in d_6 benzene was recorded and showed one singlet at 0.76 δ . This has been assigned to the protons of the four methyl groups.

3.4.2.6. X-Ray crystallographic study of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$.

Single crystals of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ suitable for study were grown from a hexane solution slowly cooled to -15°C . A bright orange oblong crystal was mounted in Araldite on a glass fibre. Preliminary precession photography indicated triclinic symmetry. Intensity data was collected at the University of Canterbury on a Nicolet P3 diffractometer. Table 3.6. records the crystal data for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$.

Table 3.6. Crystal Data for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$.

Formula: $\text{C}_{16}\text{H}_{12}\text{Co}_4\text{Ge}_3\text{O}_{12}$
 Mr: 849.77
 Spacegroup: Triclinic, $\text{P}\bar{1}$.

$a = 9.607 (3) \text{ \AA}$ $b = 14.796 (4) \text{ \AA}$ $c = 9.476 (3) \text{ \AA}$
 $\alpha = 95.83 (2)^\circ$ $\beta = 91.94 (2)^\circ$ $\gamma = 98.83 (2)^\circ$

$U = 1322.4 (6) \text{ \AA}^3$

$D_{\text{calc}} = 2.14 \text{ g cm}^{-3}$

$Z = 2$

$F(000) = 816$

$T = 293 \text{ K}$

$D_{\text{obs}} = \text{Not measured}$

$\mu(\text{Mo-K}\alpha) = 57 \text{ cm}^{-1}$

$\lambda(\text{Mo-K}\alpha) = 0.7107$

A total of 5192 unique reflections in the range $4^\circ < 2\theta < 45^\circ$, with $0 < h < 11$, $-16 < k < 16$, $-11 < l < 11$, were collected. Of these, the 3353 having $I > 2\sigma(I)$ were used in all calculations. The intensity data were corrected for Lorentz, polarisation and absorption effects (based on a series of ϕ scans). The transmission factors were Max = 0.949 and Min = 0.736.

Solution of the structure was achieved by direct methods. The heavy atoms of the unique molecule were found with ease while subsequent refinements and difference maps gave the positions of all of the carbonyl groups and the methyl carbons. The hydrogen atoms were included in calculated positions and all atoms were made anisotropic. Full matrix least squares refinement to convergence gave $R = 0.044$, $RW = 0.0399$ with $w = (\sigma^2 F + 0.000325 F^2)^{-1}$. At this point the largest parameter shift not involving hydrogen atoms was 0.1σ , while the final difference map showed no new peak having greater than 0.5 electrons $\text{\AA}^{-3}$.

The final positional and anisotropic thermal parameters of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ are given in Appendix 3 together with a complete list of the bond lengths and angles determined for this molecule. The observed and calculated structure factors have been archived by the University of Waikato.

3.4.3. Discussion of the Reactions of Excess Mono- and Dimethylgermane with $\text{GeCo}_4(\text{CO})_{14}(\text{B})$.

3.4.3.1. General discussion of these reactions.

The new clusters $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ appear to be produced almost quantitatively from the reactions of $\text{GeCo}_4(\text{CO})_{14}$ with a large excess of MeGeH_3 or Me_2GeH_2 respectively.

The incondensable gas evolution monitored in runs 1 and 5 show similar results for the two hydrides, where gas release is fast in the early stages but slows down towards the reaction end. The values for percentage CO and H_2 in each case appear to be somewhat random. Since the amount of gas measured at each stage of these reactions was very small, particularly towards the reaction end, it is possible that these figures are unreliable. However, these results may indicate that there are different stages during the reaction where CO release predominates over H_2 evolution and vice versa. This may be compared with the results for the reactions of $MeGeH_3$ with $Co_2(CO)_8$ described in Chapter 2, where CO release was observed to dominate in the early stages of reaction while later H_2 evolution took over. This suggested the release of the bridging carbonyl prior to the loss of hydrogen from the germanium group. The results from the incondensable gas monitoring of run 1, in the reaction of Me_2GeH_2 and $GeCo_4(CO)_{14}$ show a similar pattern, although this is not as clear as in the reaction of $Co_2(CO)_8$ with $MeGeH_3$.

Overall, the incondensable gas measurements for these reactions give values which appear to be somewhat low. For example, in run 2 0.34 mmoles of gas were measured where at least 0.36 mmoles would have been anticipated, since all the $GeCo_4(CO)_{14}$ was observed to have reacted. However the values obtained are within reasonable experimental error.

In all of these reactions the overall composition of the gas seems reasonable, since a slightly higher percentage of CO relative to H_2 would be expected as a result of the small amount of decomposition product obtained.

In run 2, where all unreacted Me_2GeH_2 was recovered from the volatile components, it was found that 0.18 mmoles of Me_2GeH_2 had reacted with 0.09 mmoles of $GeCo_4(CO)_{14}$. This corresponds exactly with the product of this system being $(Me_2Ge)_2GeCo_4(CO)_{12}$. In runs 2 and 5 the exact amount of reacted hydride could not be determined since some was not separated from the solvent. However the estimated values are consistent with the observed product.

In run 1 the reaction duration was 15 weeks while that of run 5 was 13 weeks. These may be considered as very similar reaction times since run 1 had no incondensable gases removed for the first 3 weeks of reaction which would be likely to inhibit it [20]. As run 1 had an initial ratio of hydride to cluster of 10:1 while that of run 5 was only 5:1 it appears that as long as a sufficient excess of hydride is present to allow the formation of the disubstituted species, any further excess of hydride will not result in a faster reaction.

Any comparison between the reactivities of MeGeH_3 and Me_2GeH_2 is not possible from this study and would require a further examination of these systems.

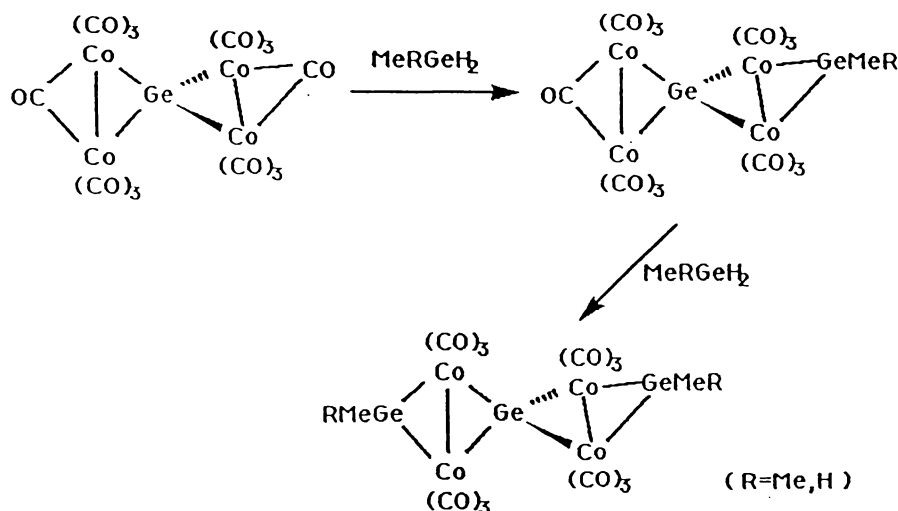
3.4.3.2. Discussion of the formation of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{MeHGe})_2\text{Co}_4(\text{CO})_{12}(D)$.

The earlier studies of the reactions of MeGeH_3 and Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}(B)$ [20] suggested that only the monosubstituted clusters, $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(C)$ respectively, could be obtained from these systems. This observation was rationalised by the suggestion that once one Co-Co bond had been bridged by a larger group the second Co-Co bond would contract preventing further substitution [20]. However, in these studies only low ratios of hydride to cluster were employed which would not have been high enough to promote formation of the disubstituted clusters, $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{12}(D)$. Clearly, it is the initial ratio of hydride to cluster which primarily determines which of the two possible products is formed.

It is possible that the earlier rationalisation is, at least, partially true since in the previous studies of the reactions of these hydrides with $\text{GeCo}_4(\text{CO})_{14}$ only the monosubstituted products were observed, rather than a mixture of the disubstituted species and unreacted $\text{GeCo}_4(\text{CO})_{14}$. It may thus be concluded that the new clusters $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ will only form where there is sufficient hydride to push the reaction past the monosubstituted stage.

It seems likely that the disubstituted product is formed subsequent to the monosubstituted species, since the product mixtures of runs 1 and 4, observed before the completion of reaction, showed the presence of both the mono- and disubstituted compounds.

This suggestion is also supported by a brief study of the reaction of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ with excess Me_2GeH_2 which showed the product to be $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ [32]. Hence, the monosubstituted compounds may be considered as intermediate in the formation of the disubstituted species, as shown in scheme 3.1.



Scheme 3.1.

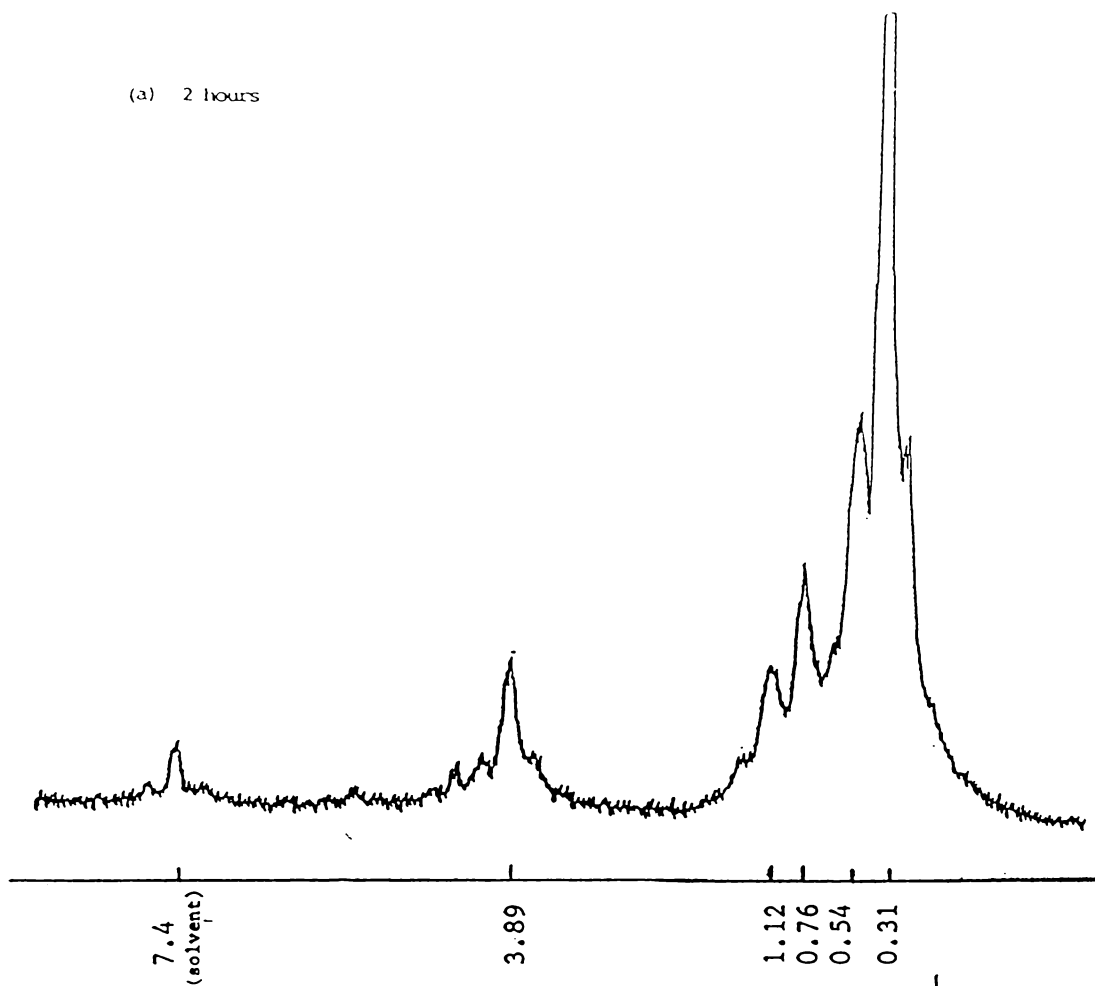
It is apparent that formation of the monosubstituted species occurs faster than that of the disubstituted product. If this were not so, it would be unlikely that the monosubstituted compounds would be observed. This again supports the original hypothesis that after one Co-Co bond is bridged by a large group then the opposite Co-Co bond contracts, causing the second substitution to occur comparatively slowly.

This type of process is also observed for the reactions of phenyl- and ethylgermane with $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ [32], where, at low molar ratios of hydride to cluster the major product is the monosubstituted species - $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ respectively - while at higher than a 2:1 ratio of germane to cluster the major product is the disubstituted compound - $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$.

Further evidence for the monosubstituted compounds being intermediates in the production of the disubstituted species was obtained from run 3 where the reaction between Me_2GeH_2 and $\text{GeCo}_4(\text{CO})_{14}$ (2.5:1 ratio) in d_6 benzene was followed using ^1H NMR spectroscopy. Some of the spectra obtained from this experiment are shown in figures 3.6(a) to (f). The triplet observed at 0.31 δ with a second component at 3.89 δ ($J = 3.81$ Hz) are assigned to the protons of Me_2GeH_2 while the singlet at 4.71 δ is attributed to molecular H_2 . Over the duration of the reaction the peaks resulting from Me_2GeH_2 diminish to almost zero intensity while that of H_2 gradually increases, reflecting the consumption of Me_2GeH_2 by reaction with $\text{GeCo}_4(\text{CO})_{14}$, which, in turn, produces H_2 .

Figure 3.6. ^1H NMR spectra from the reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$.

(a) 2 hours



(b) 24 hours

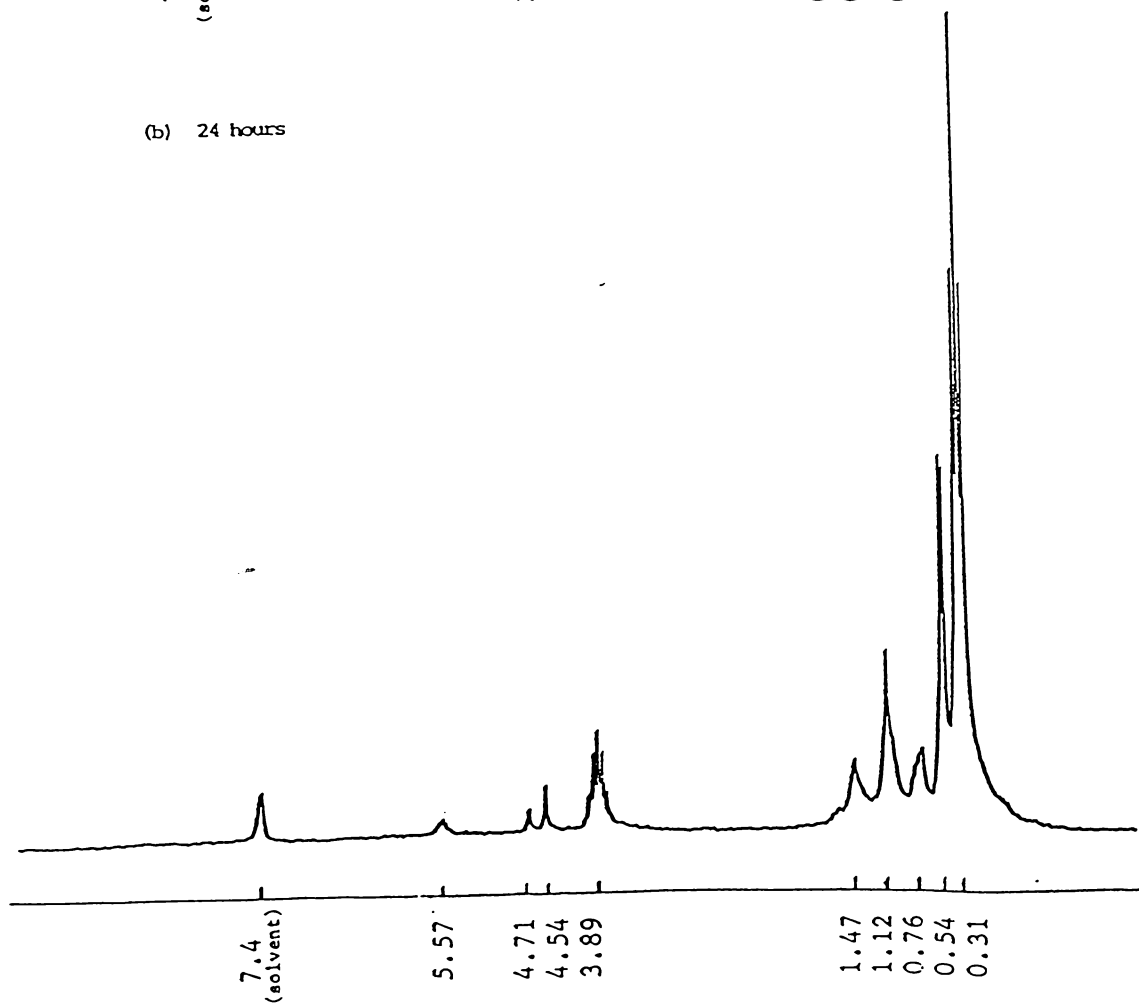
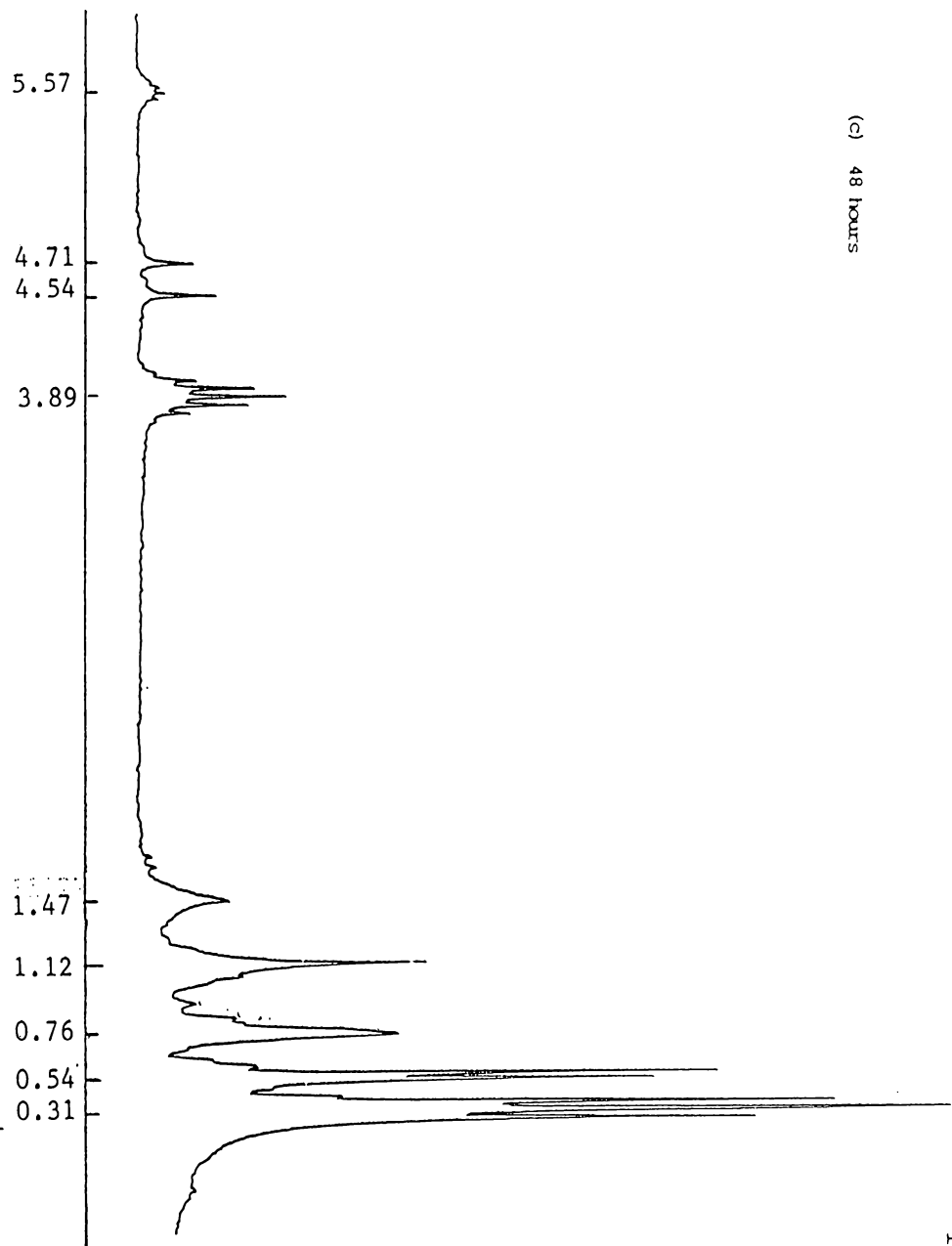


Figure 3.6. continued.

(c) 48 hours



(d) 75 hours

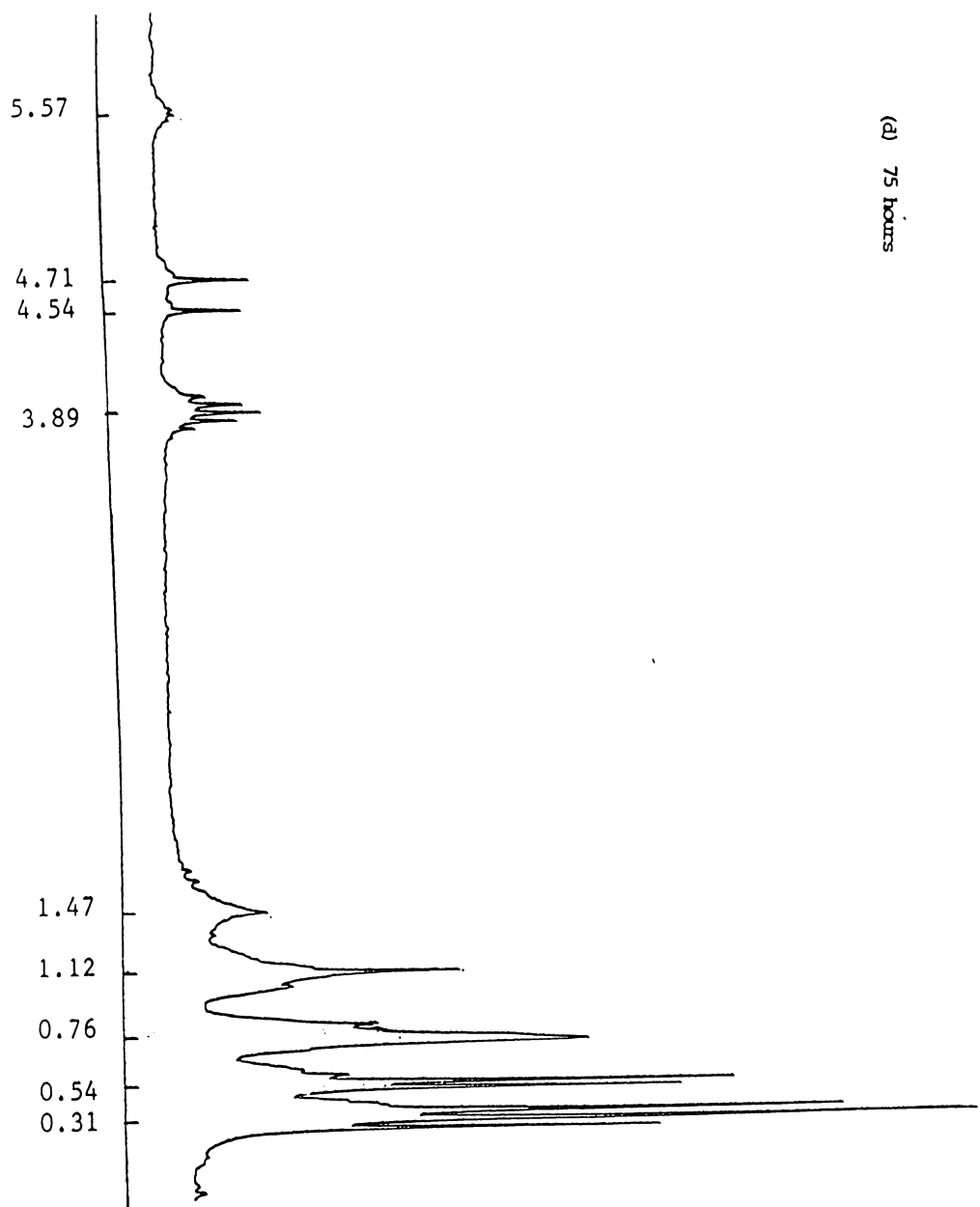
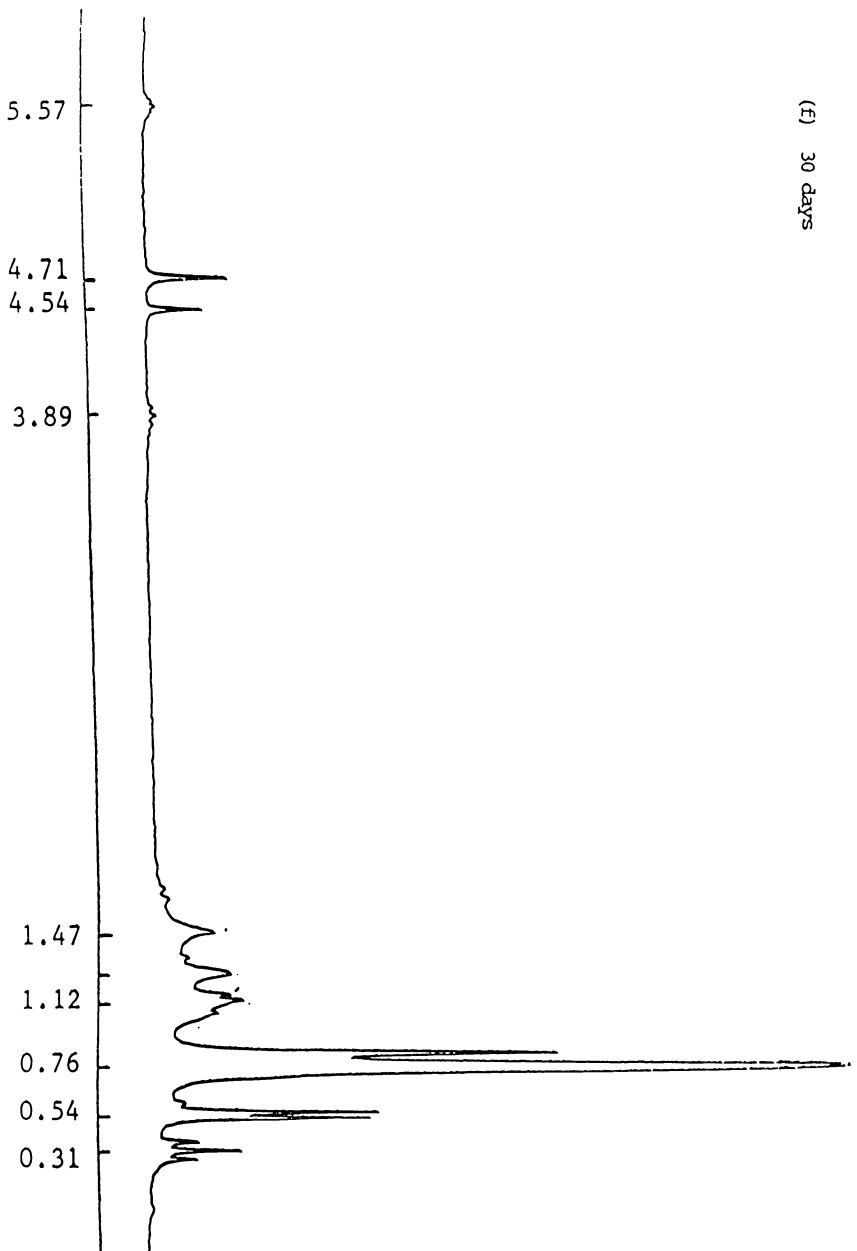
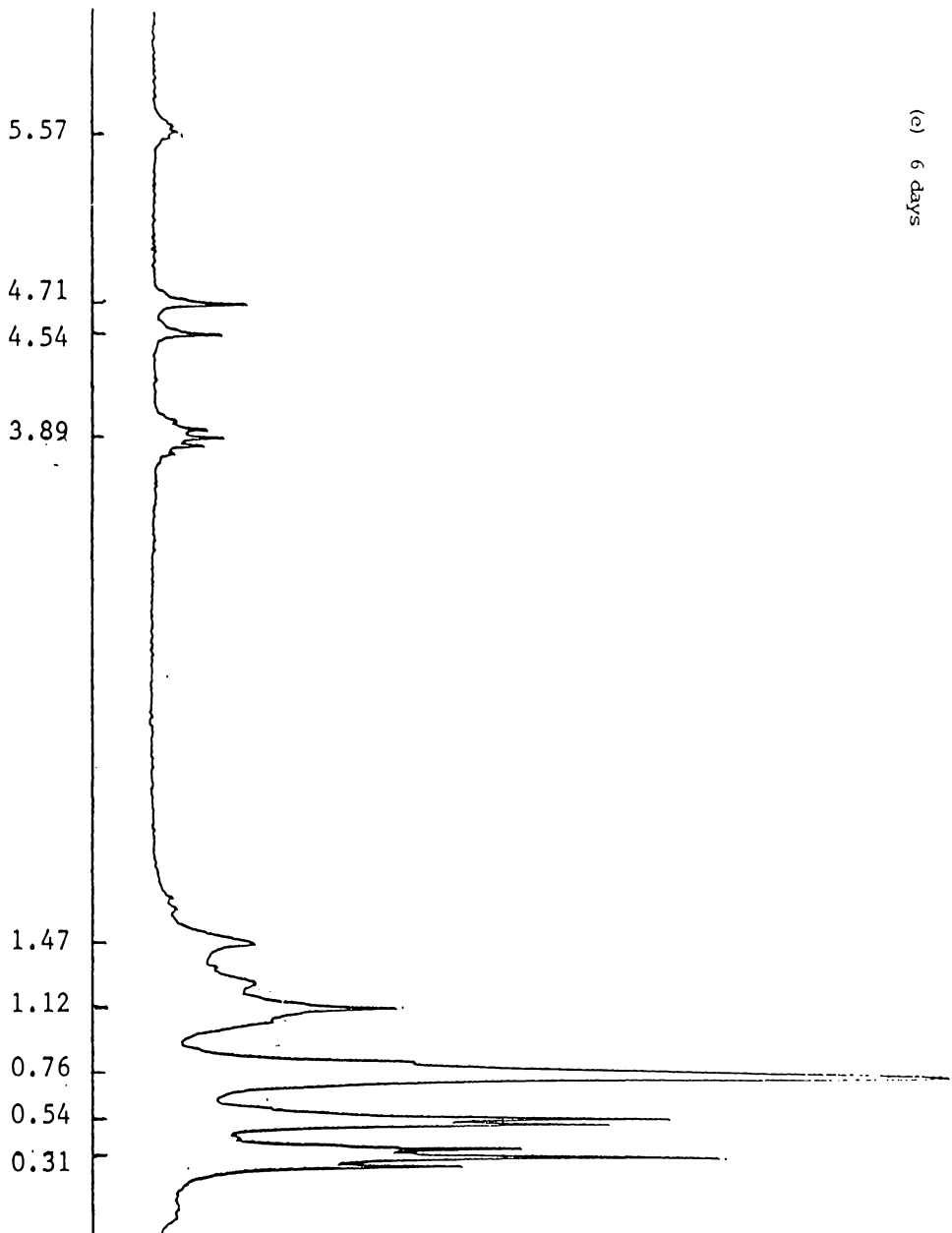


Figure 3.6. continued.

(f) 30 days



(e) 6 days



From an early stage in the reaction a singlet is observed at 1.12 δ . This is the observed position of the methyl protons of the monosubstituted species $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$, in d_6 benzene which was recorded separately. This peak remains at much the same intensity until near the reaction end where it diminishes to almost zero. A second singlet at 0.76 δ increases in intensity to become by far the strongest peak in the spectrum by the end of the reaction. This second singlet results from the methyl protons of the disubstituted product, $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$. This ^1H NMR experiment thus supports the suggestion that the formation of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ is a stepwise process, proceeding *via* the initial formation of the monosubstituted compound, $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$.

Several other peaks are observed in the ^1H NMR spectra of this reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$. A medium intensity doublet at 0.54 δ with a second component at 5.57 δ ($J = 2.64$ Hz) is observed. The signals attain reasonable resolution and remain at much the same intensity throughout the reaction. These peaks presumably result from the C-H and Ge-H protons of a species of the form Me_2GeHX . At the end of the reaction the intensity of the doublet at 0.54 δ is much greater than the singlet resulting from $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$. A trace of the latter was observed in the carbonyl region infrared spectrum of the involatile product mixture recorded after work-up, thus it is likely that the species giving rise to the doublet either contains no carbonyl groups or is a volatile species which was pumped away when the volatiles were removed from the reaction mixture. The fact that the intensity of these peaks remains the same throughout the reaction suggests that these result from an impurity which is either not involved in the reaction at all, or forms very quickly in the early stages and then takes no further part. For example, if a small amount of $\text{Co}_2(\text{CO})_8$ were present among the $\text{GeCo}_4(\text{CO})_{14}$ starting material this could possibly react with Me_2GeH_2 to produce $\text{Me}_2\text{GeHCo}(\text{CO})_4$ which would give the observed pattern of signals. This is unlikely however, since the $\text{GeCo}_4(\text{CO})_{14}$ was very carefully purified before use to ensure its freedom from any impurities. Also, the ^1H NMR spectrum of $\text{Me}_2\text{GeHCo}(\text{CO})_4$ has been recorded in SiCl_4 [152] and the peaks are observed at 1.06 δ and 4.97 δ with $J = 3.2$ Hz. Although some shift would be expected because of the different solvent used, it would be unlikely to be this large. A more reasonable assignment of these peaks is to Me_2GeHCl . This species could be present as a result of incomplete reduction of Me_2GeCl_2 by LiAlH_4 during the preparation of Me_2GeH_2 . The ^1H NMR spectrum of Me_2GeHCl recorded in CCl_4 solution shows a doublet at 0.8 δ and a septet at 5.55 δ with $J = 2.70$ Hz [154]. Once allowance is made for solvent shift these signals correspond very well with those observed here.

The presence of Me_2GeHCl would explain the fact that although a small excess of Me_2GeH_2 over $\text{GeCo}_4(\text{CO})_{14}$ (2.5:1) was used, at the time of workup the Me_2GeH_2 was almost completely consumed while a small amount (Ca. 10%) of the monosubstituted product, $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, still remained.

It is interesting that Me_2GeHCl does not appear to react with $\text{GeCo}_4(\text{CO})_{14}$ itself. It seems that replacement of the bridging carbonyl is the favoured reaction and since this path is not available to Me_2GeHCl , as it has only one attached hydrogen, it takes no part in the reaction process. It has been observed that an attached Cl does not become involved in this type of neutral substitution reaction. For example, in the reaction of MeGeH_2Cl with $\text{GeCo}_4(\text{CO})_{14}$ the major products are $[\text{Me}(\text{Cl})\text{Ge}]\text{GeCo}_4(\text{CO})_{13}$ or $[\text{Me}(\text{Cl})\text{Ge}]_2\text{GeCo}_4(\text{CO})_{12}$, depending on the initial reaction ratio [32]. It is also possible that the presence of the Cl atom on Me_2GeHCl makes this species too hindered to allow an approach to the cluster. In any event, it is clear that reaction of $\text{GeCo}_4(\text{CO})_{14}$ with Me_2GeH_2 is much preferred to reaction with Me_2GeHCl .

Also observed in the ^1H NMR spectra recorded of this reaction are comparatively low intensity singlets at 1.47 δ and 4.54 δ . Again, these remain at much the same intensity throughout the reaction and it is anticipated that these also arise from some minor impurities present in the reaction mixture although the exact nature of these is unknown.

Table 3.7. lists the observed peaks with assignments and shows the relative intensity of each during the reaction.

Table 3.7. ^1H NMR data from the reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$.

Signal (δ ppm)	$J_{\text{H-H}}$ (Hz)	Multiplicity	Assignment	Approximate Relative Intensity		
				24 hrs	75 hrs	31 days
0.31		triplet				
3.89	3.81	septet	Me_2GeH_2	8.0	4.5	0.8
4.71	-	singlet	H_2	0.1	0.3	0.6
1.12	-	singlet	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	1.5	1.5	0.9
0.76	-	singlet	$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	0.4	2.0	9.5
0.54	2.64	doublet	Me_2GeHCl	2.5	2.5	2.5
5.57		septet				
1.47	-	singlet	?	0.4	0.4	0.4
4.54	-	singlet	?	0.2	0.2	0.2

Also clear from table 3.8. is that replacement of one CO by GeMe₂ in (I) results in shifts to lower frequency of between 17 and 35 cm⁻¹ (average 28 cm⁻¹) and on the second replacement, in (II), a further shift of between 16-21 cm⁻¹ (average 18 cm⁻¹) is observed.

Since the new clusters (MeRGe)₂GeCo₄(CO)₁₂(D) (R = H, Me) have become available it is of interest to compare the vibrational spectra of these, and that of the parent cluster, GeCo₄(CO)₁₄(B), with Bor's idealised system. If these compounds are written as {(μ-X)Co₂(CO)₆}₂Ge where X = CO(III) or GeRMe(IV) then it is obvious that these are related to the molecules discussed above. In fact they may be considered as "Double-Bor" systems where (III) is analogous to (I) and (IV) to (II). If the coupling of the two Co₂(CO)₆ units through the central germanium is moderate, then it is possible to regard the resultant vibrational modes as the in- and out-of-phase combinations of the Bor modes. In Chapter 2 it was shown that interpretation of the carbonyl vibrations of the infrared spectrum of MeGe[Co(CO)₄]Co₂(CO)₇(A) is possible in terms of the Co(CO)₄ and the Co₂(CO)₇ units.

Of further help in this analysis is the fact that if the bridging X groups are neglected and all Ge-Co distances regarded as equal then the Ge[Co₂(CO)₆]₂ unit has D_{2d} symmetry. Although the molecular symmetry in the solid is only C₂, the selection rules for the higher symmetry should give a guide to intensities.

The correlation found is shown in table 3.9. Since the two Co₂(CO)₆ units are mutually perpendicular the local x and y axes exchange so that, in the local C_{2v} symmetry, a B₁ mode in one unit is a B₂ mode in the other. This reconciles the B₁ + B₂ (in C_{2v}) with E (in D_{2d}) correlation.

Table 3.9. Correlation between $M_2(CO)_6(\mu-X)_2$ and $[(\mu-X)M_2(CO)_6]_2(\mu_4-E)$ carbonyl vibrations.

Bor symbols	Bor Unit Vibrations Symmetry and Activity	Double-Bor Symbol	Unit Vibrations Symmetry and Activity**
ν_1 q	A_1 (IR, R)	q'	A_1 (R) ν_1
ν_4 s	B_1 (IR, R)	q''	B_2 (IR, R) ν_5
ν_2 u	A_1 (IR, R)	s'	E (IR, R) ν_7
ν_6 v	B_2 (IR, R)	u'	A_1 (R) ν_2
ν_5 w	B_1 (IR, R)	u''	B_2 (IR, R) ν_6
ν_3 z*	A_2 (R)	v'	E (IR, R) ν_8
		w'	E (IR, R) ν_9
		z'	A_2 (inactive) ν_3
		z''	B_1 (R) ν_4

* The infrared inactive A_2 mode was not designated by Bor [130] and the symbol z is introduced. r, t, x and y were used to denote ^{13}CO modes.

** Based on idealised D_{2d} symmetry.

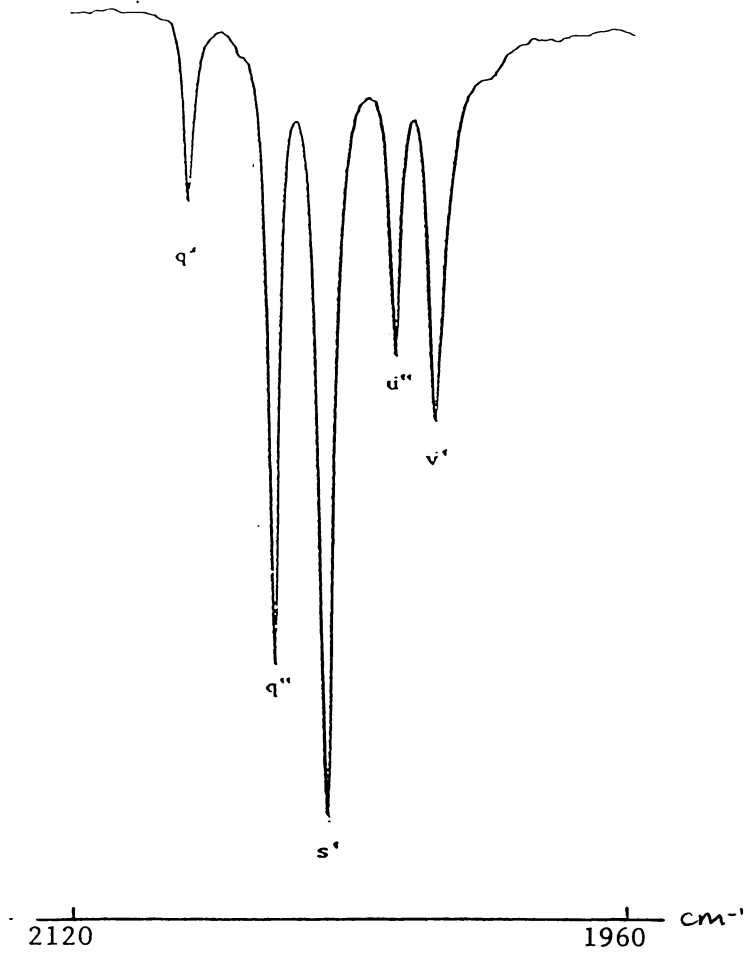
The carbonyl region of the vibrational spectra of (III) and $(Me_2Ge)_2GeCo_4(CO)_{12}$ are depicted in figures 3.8 (a) to (d) with the "Double Bor" modes assigned.

It is clear from table 3.9. and from the resulting assignments on the spectra shown in figure 3.8 that the analysis leads to a consistent correlation where the lower true symmetry leads to the following effects:

- (i) The A_1 modes appear in the infrared spectra, but only weakly.
- (ii) The A_2 mode is very weak or absent with the observed mode due to ^{13}CO .
- (iii) The B_1 mode is absent from the infrared spectra.
- (iv) The B_2 modes are stronger in the infrared than in the Raman spectra.

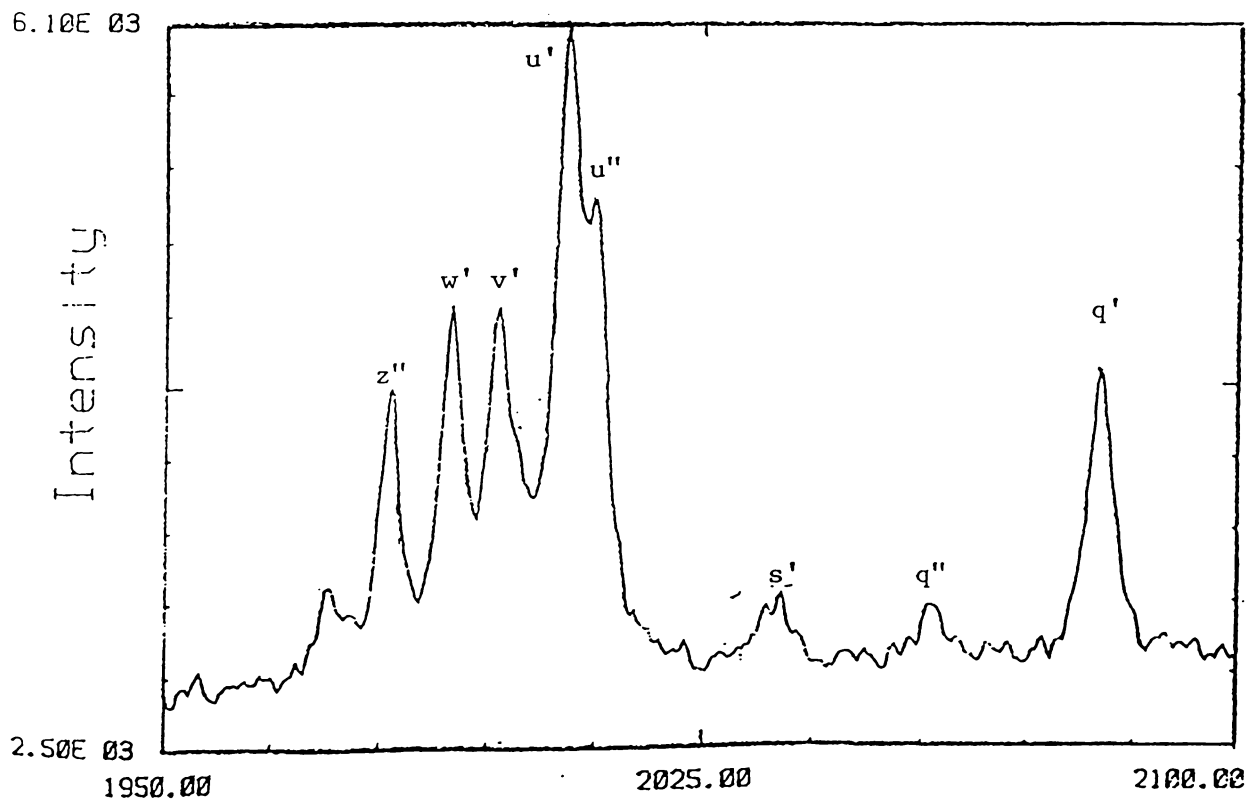
Any splitting of the E modes is very small but the main anomaly arises for these in that: s' is very strong in the infrared for both compounds while v' and w' vary between the two molecules but at least one is much stronger in the Raman than in the infrared. Since the Bor unit parent

Figure 3.8. Carbonyl region vibrational spectra of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$ depicting the "Double Bor" modes.

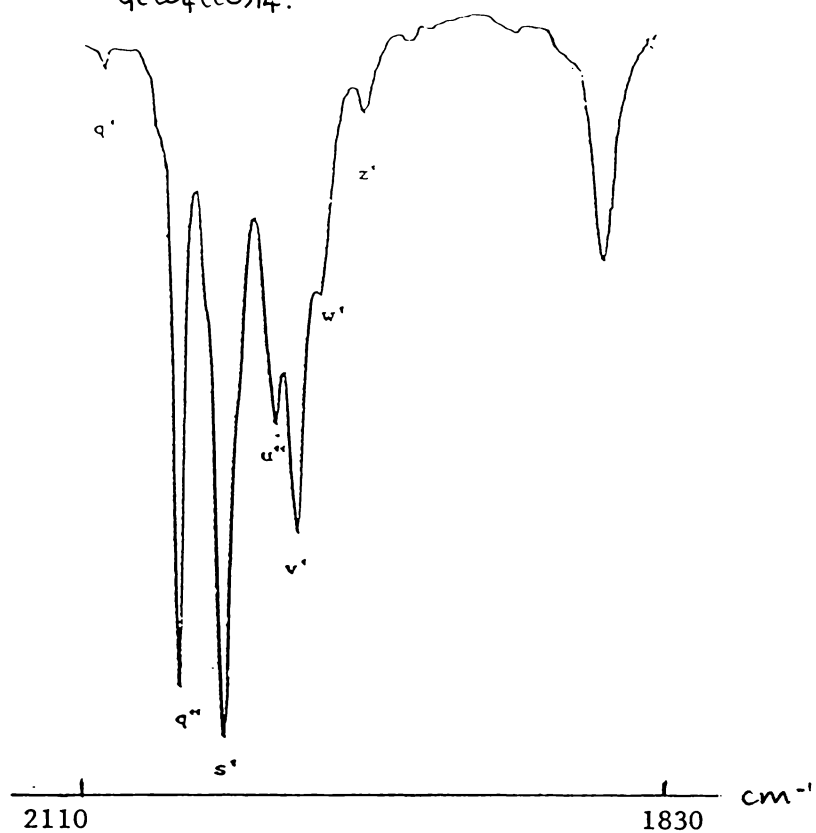


(a) Carbonyl region infrared spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$.

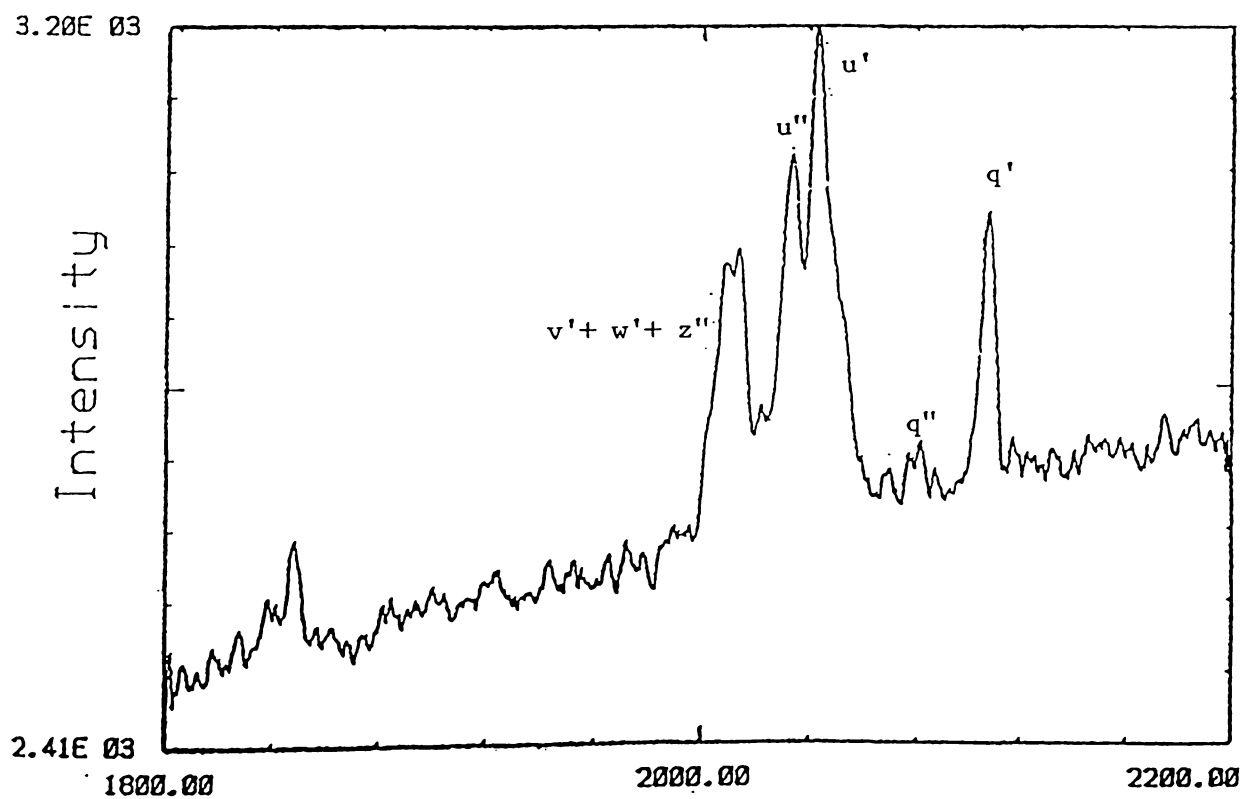
(b) Carbonyl region Raman spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$.



(c) Carbonyl region infrared spectrum of $\text{GeCo}_4(\text{CO})_{14}$.



(d) Carbonyl region Raman spectrum of $\text{GeCo}_4(\text{CO})_{14}$.



modes, $\nu(B_2)$ and $w(B_1)$, are very close and of quite different intensities it is not surprising that the simplified approach breaks down in this region.

A comparison of the frequencies of the infrared active carbonyl vibrations of the molecules $\text{GeCo}_4(\text{CO})_{14}$, $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, listed in table 3.10, shows replacement of $\mu\text{-CO}$ by $\mu\text{-GeMe}_2$ leads to shifts to lower frequency of between 18 and 7 cm^{-1} (average 13 cm^{-1}) and on the second replacement shifts of between 17 and 10 cm^{-1} (average 14 cm^{-1}) to lower frequency are observed. These are comparable with those found in the substitution of $\text{Co}_2(\text{CO})_8$.

Table 3.10 Terminal carbonyl infrared stretches of $\text{GeCo}_4(\text{CO})_{14}$, $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. (cm^{-1}).

$\text{GeCo}_4(\text{CO})_{14}(\text{a})$	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{b})$	$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$
	2096 m	2081 m
2080 s	2064 vs	2054 vs
2061 vs	2054 vs	2037 vs
	2043 vs	
2040 m	2027 m	2015 m
	2021 sh, w	
2032 m	2016 s	2002 m
2020 w	2002 w	
2004 w	1987 w	

(a) [34] (b) [20]

All recorded in hexane solution.

3.4.3.4. Discussion of the structure of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

The asymmetric unit contains a discrete molecule of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. A perspective view of the structure is given in figure 3.9 while a stereo view of the molecule is depicted in figure 3.10.

As expected the molecule comprises a central GeCo_4 unit where each Co-Co bond has been bridged by a Me_2Ge unit, which replaces the original bridging carbonyl ligands. This results in the cluster containing four GeCo_2 triangles linked by Co-Co edges and germanium apices.

The bond lengths and angles of the metal skeleton of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ are shown in table 3.11 together with those recorded for the two unique molecules of the parent cluster, $\text{GeCo}_4(\text{CO})_{14}$ [18(b)]. Figure 3.11 depicts the molecular structure of each showing the labelling system used. In each

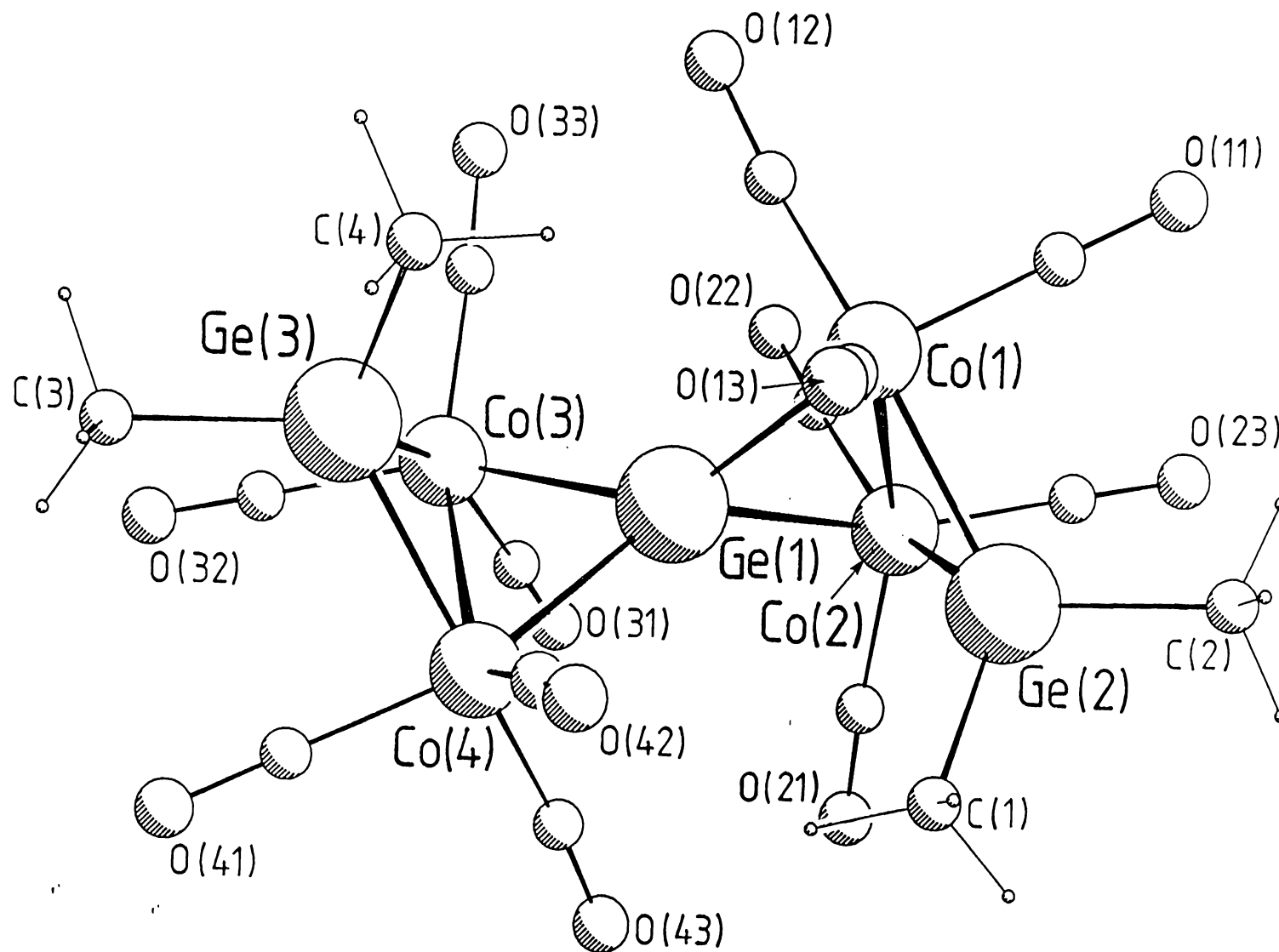
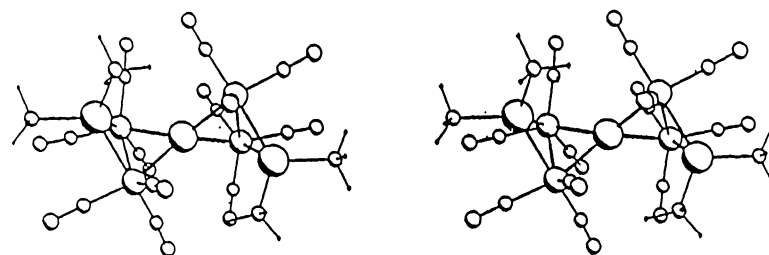


Figure 3.9. Perspective view of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$.



Stereo view of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

Figure 3.10.

structure Co_1 and Co_4 are closer to the bridging group of the opposite Co-Co bond than Co_2 or Co_3 .

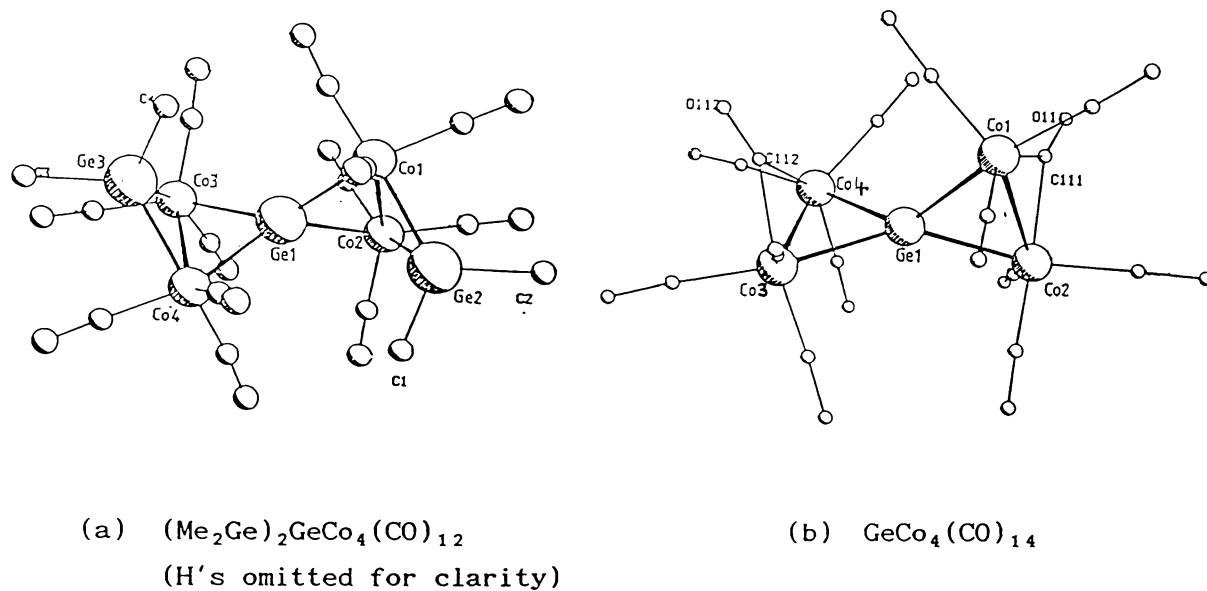


Figure 3.11

Table 3.11 Selected bond lengths and angles for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$

Bond (Å)	$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	$\text{GeCo}_4(\text{CO})_{14}$	
		1	2
$\text{Ge}_1\text{-Co}_1$	2.367 (1)	2.372 (3)	2.379 (3)
$\text{Ge}_1\text{-Co}_2$	2.387 (1)	2.344 (2)	2.341 (3)
$\text{Ge}_1\text{-Co}_3$	2.383 (1)	2.348 (2)	2.339 (2)
$\text{Ge}_1\text{-Co}_4$	2.372 (1)	2.381 (3)	2.387 (2)
$\text{Ge}_2\text{-Co}_1$	2.378 (1)		
$\text{Ge}_2\text{-Co}_2$	2.349 (1)		
$\text{Ge}_3\text{-Co}_3$	2.363 (1)		
$\text{Ge}_3\text{-Co}_4$	2.372 (1)		
$\text{Co}_1\text{-Co}_2$	2.639 (1)	2.570 (3)	2.559 (3)
$\text{Co}_3\text{-Co}_4$	2.644 (1)	2.564 (3)	2.552 (3)
Bond Angles ($^\circ$)			
$\text{Co}_1\text{Ge}_1\text{Co}_2$	67.5 (1)	66.0 (1)	65.7 (1)
$\text{Co}_1\text{Ge}_1\text{Co}_3$	138.3 (1)		
$\text{Co}_1\text{Co}_2\text{Ge}_1$	55.9 (1)	57.5 (1)	57.9 (1)
$\text{Co}_2\text{Co}_1\text{Ge}_1$	56.6 (1)	56.5 (1)	56.4 (1)
$\text{Co}_1\text{Ge}_2\text{Co}_2$	67.9 (1)		
$\text{Ge}_2\text{Co}_1\text{Ge}_1$	82.6 (1)		
$\text{Ge}_2\text{Co}_2\text{Ge}_1$	82.8 (1)		
Dihedral Angles			
$\text{Ge}_1\text{Co}_1\text{Co}_2\text{-Ge}_1\text{Co}_3\text{Co}_4$	101.07	96	97
$\text{Ge}_1\text{Co}_1\text{Co}_2\text{-Ge}_2\text{Co}_1\text{Co}_2$	105.39		
$\text{Ge}_1\text{Co}_3\text{Co}_4\text{-Ge}_3\text{Co}_3\text{Co}_4$	105.32		

As would be anticipated, the replacement of the bridging carbonyl ligands of $\text{GeCo}_4(\text{CO})_{14}$ by the much larger GeMe_2 units to provide $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, lengthens the Co-Co bonds quite markedly. The observed lengthening is of an average $0.081(2) \text{ \AA}$. For comparison, in the molecule $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$, which may be considered as a central $\text{GeCo}_4(\text{CO})_{12}$ unit where each Co-Co bond is bridged by a $\text{GeCo}_2(\text{CO})_7$ group, the Co-Co bond lengths of the two inner triangles are $2.664(2) \text{ \AA}$ [22, 23], slightly greater than that observed for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ at $2.642(1) \text{ \AA}$. Presumably the larger groups attached to the bridging germanium in $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ result in this slight increase in Co-Co bond length. In the anion $\{[(\text{CO})_4\text{CoHg}]\text{GeCo}_4(\text{CO})_{13}\}^-$, the Co-Co bond bridged by the mercury atom is further enlarged at $2.751(2) \text{ \AA}$ [80] which reflects the increased size of the bridging group.

In $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, a corresponding opening of the Co-Ge₁-Co bond angles to compensate for this Co-Co bond lengthening is also found but this is surprisingly small, at an average of only 1.6° (1). This may be explained by the observation that the Ge₁-Co bond lengths are also enlarged relative to those of both the parent cluster (by an average $0.016 \text{ \AA}$) and the outer Ge-Co bond lengths of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (by average $0.012 \text{ \AA}$), which presumably arises to avoid steric strains which would be promoted by the opening of the Co-Ge₁-Co bond angles. A similar situation is observed for $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ where the Co-Ge₁-Co angles are larger than those of $\text{GeCo}_4(\text{CO})_{14}$ by an average of only 2° while the Ge₁-Co bonds are considerably lengthened by an average $0.019 \text{ \AA}$ [22, 23].

The dihedral angle between the two inner GeCo_2 triangles of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ is also larger than that of the parent compound by an average of 4.5° . This is likely to result from the large size of the bridging groups requiring the cluster to open out slightly so that these may be kept at a distance from one another.

The dihedral angles between the inner and outer GeCo_2 triangles of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ are almost identical at 105.39° and 105.32° . In the molecule $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ the dihedral angles between the inner and outer GeCo_2 triangles are 120.4° [22,23], larger than those observed here. Clearly the methyl groups attached to the bridging germanium of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ exert less steric influence on the molecule than attached $\text{Co}_2(\text{CO})_7$ units, thus smaller dihedral angles are possible.

For both of the clusters $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ the central GeCo_2 triangles are clearly asymmetric, although for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ this effect is less pronounced, and the long and short Ge-Co bonds are the opposite way round from the case of the parent cluster.

That is, in $\text{GeCo}_4(\text{CO})_{14}$, Ge_1Co_1 and Ge_1Co_4 are relatively long bonds while Ge_1Co_2 and Ge_1Co_3 are relatively short, however for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, $\text{Ge}_1\text{-Co}_1$ and $\text{Ge}_1\text{-Co}_4$ are the relatively short bonds and $\text{Ge}_1\text{-Co}_2$ and $\text{Ge}_1\text{-Co}_3$ are relatively long.

In order to rationalise these observations it is necessary to consider the bonding within these types of molecules. A discussion has been reported [148] of the bonding within $(\mu\text{-Me}_2\text{Ge})_3\text{Fe}_2(\text{CO})_6$. In the D_{3h} point group, where the Fe-Fe bond of a GeFe_2 triangle is taken as the z direction, the main bonding interactions are (i) a_1' and e' combinations of the metal d_{z^2} and the d_{xz} , d_{yz} pair with an inward-pointing hybrid orbital on each germanium; (ii) an e'' interaction between one p orbital on each germanium and the d_{xz} orbital on each iron so that the two irons are antibonding towards each other, but bonding to the germanium. The latter is shown in figure 3.12 for one GeFe_2 triangle.

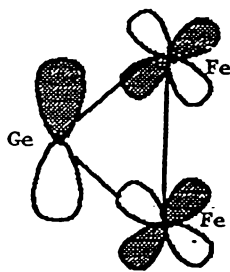
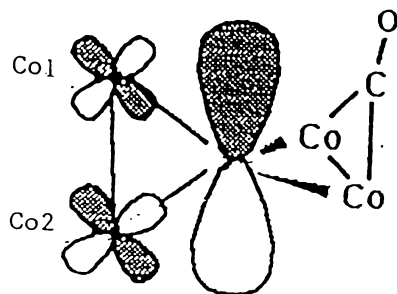


Figure 3.12

The a_1' and e' effects stabilise orbitals bonding between the $\text{Fe}(\text{CO})_3$ fragments, while the e'' contribution stabilises orbitals which are Fe-Fe antibonding. Hence, instead of a clear division of orbitals into Fe-Fe and Fe-Ge bonds there is an overall distribution of electron density throughout the Fe_2Ge units, involving centrally and peripherally directed elements. In the general case, the precise contribution of each interaction depends particularly on the M-M'-M angle and the M-M distance.

Now, for the two clusters under study here it may be considered that a significant contribution to the bonding of the central GeCo_2 triangles of $\text{GeCo}_4(\text{CO})_{14}$ will be as shown in figure 3.13.



For clarity the bonding of only one GeCo_2 triangle is shown and most CO groups have been omitted.

Figure 3.13

This may be considered as equivalent to the e'' interaction in a D_{3h} treatment as described above. The second GeCo_2 triangle would bond in this manner through a second germanium p orbital perpendicular to that shown, i.e. that coming out of the page.

From this diagram it becomes clear that the bridging carbonyl unit is close enough, and in the correct orientation for a filled $p\pi$ or $p\pi^*$ orbital to interact with the p orbital of the central germanium. This interaction would, in turn, reduce the interaction between the germanium and Co_1 , causing this bond to be lengthened relative to $\text{Ge}_1\text{-Co}_2$. Similarly, the bonding between Ge_1 and Co_4 would be weakened by an interaction between the germanium p orbital and the bridging carbonyl coming out of the page, causing $\text{Ge}_1\text{-Co}_4$ to be lengthened relative to $\text{Ge}_1\text{-Co}_3$.

In the case of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ the same bonding diagram of the GeCo_2 triangles may be applied, as in figure 3.14.

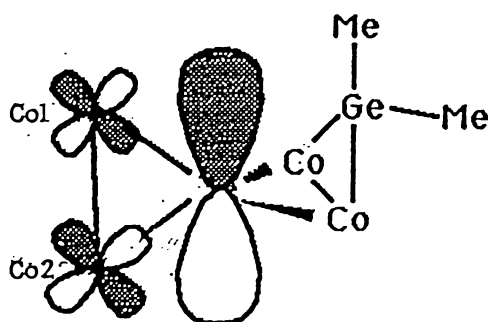


Figure 3.14

Here, however, the bridging Me_2Ge group is a saturated species thus it may not contribute electron density to the central germanium p orbital as is suggested for a bridging carbonyl unit. In fact it is perhaps more likely

that the bridging germanium unit may have a $d\pi$ or an antibonding orbital in the correct orientation to accept electron density from the central germanium p orbital. This would allow the bond between Ge_1 and Co_1 to be strengthened, resulting in the comparative shortness of this bond with respect to $\text{Ge}_1\text{-Co}_2$. Again, an identical effect will be observed for the perpendicular Ge_1 p orbital and the GeMe_2 orbital coming out of the page, resulting in $\text{Ge}_1\text{-Co}_4$ being shortened relative to $\text{Ge}_1\text{-Co}_3$.

This postulate, although only suggested tentatively to explain the observed asymmetry, is supported for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ by two features. Firstly, the $\text{Ge}_1\text{-Ge}_2$ and $\text{Ge}_1\text{-Ge}_3$ non bonding distances are 3.132 Å, well within the sum of their Van der Waals radii of 4.20 Å, which clearly indicates that an interaction exists between them. A comparison with $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ shows that the analogous Ge-Ge non-bonding distances of this molecule are longer by 0.1 Å [23], although it should be noted that $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ is a much more sterically strained molecule. Further evidence for this explanation comes from the fact that if the bridging germanium groups were accepting electron density into an antibonding orbital orientated towards the central germanium p orbital, then it would be expected that the bond between the bridging germanium and the exo methyl carbon, opposite this antibonding orbital, would be lengthened relative to that of the second methyl carbon. Although the standard deviations preclude any definite judgements, the bond lengths do suggest a lengthening of $\text{Ge}_2\text{-C}_2$ relative to $\text{Ge}_2\text{-C}_1$ and of $\text{Ge}_3\text{-C}_3$ relative to $\text{Ge}_3\text{-C}_4$.

The outer GeCo_2 triangles also show a degree of asymmetry but in the opposite sense to that of the inner GeCo_2 triangles. That is $\text{Ge}_2\text{-Co}_1$ and $\text{Ge}_3\text{-Co}_4$ are long while $\text{Ge}_2\text{-Co}_2$ and $\text{Ge}_3\text{-Co}_3$ are short. Clearly, if it is assumed that Co_1 and Co_4 are bonding more strongly with Ge_1 than are Co_2 and Co_3 , then as a result, they will not be able to bond as strongly with the outer germanium atoms than will Co_2 and Co_3 . Asymmetry is also observed in the Co_2CO triangles of $\text{GeCo}_4(\text{CO})_{14}$. This is in the opposite sense to that of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ which is again explained by the effect of the different bridging group.

3.5. The Reactions of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ with low molar ratios of MeGeH_3 .

3.5.1. General

As stated in section 3.1, the original study of the reaction of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ with MeGeH_3 provided the monosubstituted species $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{13}(\text{C})$ together with a new cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ [87]. It was of interest to study this reaction more closely in order to obtain some insight into the formation of the latter species, as this seemed to involve a very complex rearrangement which was difficult to rationalise. At the same time, it was desirable to optimise the yield of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ obtained through this route, thus several experiments under varying reaction conditions were carried out.

3.5.2. Experimental Details and Results.

The results of these experiments are summarised in table 3.12 at the end of this section.

Run 1: MeGeH_3 (0.3 mmol by volume) and $\text{GeCo}_4(\text{CO})_{14}$ (0.252 g; 0.36 mmol) (1:1.2 ratio) were allowed to react in hexane (10 ml) for 120 hours at 43°C. Incondensable gases (0.306 mmol) were measured, of composition 64% CO, 36% H_2 . Fractionation of the volatile components yielded unreacted MeGeH_3 (0.1 mmol) and solvent.

All of the involatile products were soluble in hexane. An infrared spectrum of the product mixture in hexane showed carbonyl stretches resulting from $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ [20] and $\text{GeCo}_4(\text{CO})_{13}$, the condensation product of $\text{GeCo}_4(\text{CO})_{14}$ [49]. These could not be separated by either extraction or fractional crystallisation. Chromatography was attempted but $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ was found to decompose on the silica gel.

Run 2: MeGeH_3 (0.2 mmol) and $\text{GeCo}_4(\text{CO})_{14}$ (0.049 g; 0.07 mmol) (2.8:1 ratio) were allowed to react in hexane (10 ml) for 240 hrs at 35°C. Incondensable gases (0.17 mmol) were measured of composition 79% CO, 21% H_2 . Unreacted MeGeH_3 (0.06 mmol) was recovered from the volatiles while a small amount (ca. 0.01 mmol) could not be separated from the solvent.

Again, all of the involatile products were soluble in hexane. An infrared spectrum of the solution showed the major product to be $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$. Also present were small amounts of $\text{GeCo}_4(\text{CO})_{13}$ and the disubstituted product $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$. These could not be separated.

Run 3: MeGeH_3 (0.11 mmoles) and $\text{GeCo}_4(\text{CO})_{14}$ (0.077 g; 0.11 mmoles) (1:1 ratio) were allowed to react in hexane (10 mls) for 96 hrs at 40°C. Incondensable gases (0.10 mmoles) were measured of composition 64% CO, 36% H_2 . Fractionation of the volatile components yielded only solvent.

The involatile products were separated into two fractions. The first of these was hexane soluble and, using infrared spectroscopy, was shown to be a mixture of mainly $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ and a lesser proportion of $\text{GeCo}_4(\text{CO})_{13}$. These, again, could not be separated. The second fraction was only slightly soluble in hexane but was fairly soluble in dichloromethane. This compound was not characterised at this stage as such a small amount of it was obtained.

Run 4: MeGeH_3 (0.17 mmoles) and $\text{GeCo}_4(\text{CO})_{14}$ (0.07 g; 0.1 mmoles) (1.7:1 ratio) were allowed to react in hexane (10 mls) for 360 hrs at 10°C. Incondensable gases (0.218 mmoles) were measured of composition 64% CO, 36% H_2 . A trace of unreacted MeGeH_3 (ca. 0.04 mmoles) was observed among the volatiles but could not be separated from the solvent.

An infrared spectrum of the involatile products in hexane showed mainly $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ and a trace of the disubstituted compound $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$. These, again, could not be separated. Also found among the involatile products was a dark-coloured, insoluble material. This showed no carbonyl vibrations in the infrared spectrum and was assumed to be a decomposition product. This may have been present in the original sample of $\text{GeCo}_4(\text{CO})_{14}$ as this had been prepared several months before its use here.

Run 5: MeGeH_3 (0.6 mmoles) and $\text{GeCo}_4(\text{CO})_{14}$ (0.042 g; 0.062 mmoles) (10:1 ratio) were allowed to react in hexane (10 mls) for 16 weeks at room temperature under 1 atmosphere of CO pressure. This system showed no reaction and all starting materials were recovered.

Table 3.12 summarises the results of these experiments.

Table 3.12. Summarised reaction conditions and results for the reactions of MeGeH_3 and $\text{GeCo}_4(\text{CO})_{14}$.

<u>Run</u>	<u>Duration</u>	<u>Temp.</u> (°C)	<u>Initial ratio of</u> <u>hydride to cluster</u>	<u>Reacting ratio of</u> <u>hydride to cluster</u>	<u>Incondensable</u> <u>gas evolved</u> (mmoles)	<u>Approximate yield</u> <u>of involatile products</u>
1	120 hrs	43	1:1.2	1:1.25	0.306 (64% CO)	70% $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ + 30 % $\text{GeCo}_4(\text{CO})_{13}$
2	240 hrs	35	2.8:1	Ca. 1.86:1	0.17 (79% CO)	80% $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ + 10% $\text{GeCo}_4(\text{CO})_{13}$ + 10% $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$
3	96 hrs	40	1:1	1:1	0.10 (64% CO)	70% $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ + 20% $\text{GeCo}_4(\text{CO})_{13}$ + 10% unidentified species
4	360 hrs	10	1.7:1	Ca. 1.4:1	0.218 (64% CO)	70% $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ + 10% $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}$ + 20% decomposition product
5	16 weeks Under 1 atm of CO pressure	R.T.	10:1	No reaction		

3.5.3. Discussion of the Reactions of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ with MeGeH_3 in Low Molar Ratios.

None of the reactions between MeGeH_3 and $\text{GeCo}_4(\text{CO})_{14}$ described above provided a pure sample of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}(\text{C})$. The various conditions employed seem to promote the formation of secondary products in varying proportions but did not seem to affect the yield of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$. Since the purification techniques available did not allow the separation of this compound from the product mixtures it is apparent that the preparation of pure $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ via the reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ is not promising.

Table 3.12 shows summarised results for these systems. The incondensable gas measurements correspond qualitatively fairly well with the observed products, in that a higher proportion of CO to H_2 is expected as a result of the decarbonylation of $\text{GeCo}_4(\text{CO})_{14}$ to $\text{GeCo}_4(\text{CO})_{13}$. The overall incondensable gas measurements for runs 1 and 3 appear to be rather low with respect to the observed products. Presumably a comparatively large experimental error was incurred during these measurements. Fortunately this does not affect the overall picture of these reactions.

$\text{GeCo}_4(\text{CO})_{13}(\text{I})$ is observed as a product of these systems on three occasions. As these occasions were all runs conducted at relatively high temperatures it seems likely that this was produced through the known decarbonylation reaction of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ shown in figure 3.15.

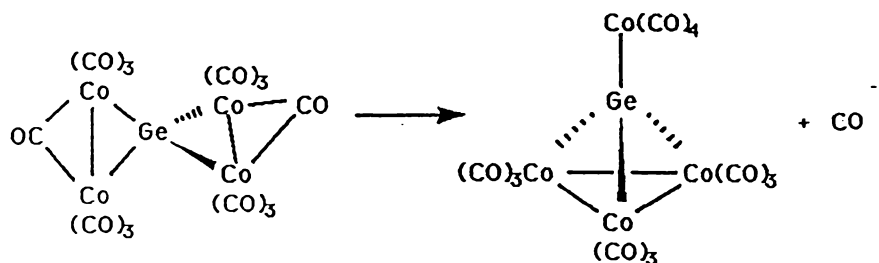


Figure 3.15 [18(b)]

However, there was an alternative possibility that $\text{GeCo}_4(\text{CO})_{13}$ was involved in the formation of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ thus a study of the reaction of $\text{GeCo}_4(\text{CO})_{13}$ with MeGeH_3 was carried out and is described in section 3.6.

In run 3 a small amount of a compound soluble only in a relatively polar solvent such as dichloromethane was observed. This was not identified at the time of work-up but has since been characterised, through

a comparison of the carbonyl region infrared spectrum, as the cluster $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (figure 3.16) [32, 39].

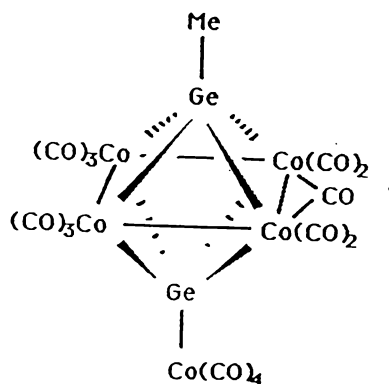


Figure 3.16 [32, 39]

This cluster has been found in the reaction of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}(\text{C})$ with $\text{Co}_2(\text{CO})_8$ [32]. It is probable that the $\text{GeCo}_4(\text{CO})_{14}$ starting material had not been thoroughly purified and contained a small amount of $\text{Co}_2(\text{CO})_8$, thus allowing the formation of this species.

The disubstituted product, $(\text{MeHGe})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$, was observed to form where there was an excess of MeGeH_3 available (other than Run 5). Clearly its formation occurs readily, although for these low molar ratios of MeGeH_3 to $\text{GeCo}_4(\text{CO})_{14}$ the monosubstituted product is still preferred.

For the run conducted under 1 atmosphere of carbon monoxide pressure no reaction was observed. This is consistent with release of CO from $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ being inhibited by the presence of the introduced gas, thus preventing the reactants from forming the necessary intermediates. This observation corresponds with the results of section 3.4. where the experiments having the incondensable gases removed at regular intervals were observed to reach completion sooner than those where the evolved gases remained within the vessel for the duration of the reaction.

None of the systems described here showed similar results to those reported by Foster when the system was first explored [20]. For example, the cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ was never observed, even in the runs conducted under higher temperatures where it might be expected to form. Foster also reported the presence of $\text{Co}_4(\text{CO})_{12}$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ among the products which was never the case here. A recent investigation by a co-worker at Waikato [32] has shown that MeGeH_3 and $\text{Co}_4(\text{CO})_{12}$ react together readily producing $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. It is possible that the $\text{GeCo}_4(\text{CO})_{14}$ starting material used in the original study had not been thoroughly

purified and contained small amounts of $\text{Co}_4(\text{CO})_{12}$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$. The reaction between MeGeH_3 and $\text{Co}_4(\text{CO})_{12}$ would then account for the observed formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

Some other routes to the cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ are described in section 3.8.

3.6 Reactions of $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ with MeGeH_3 .

3.6.1. General

Although the presence of $\text{GeCo}_4(\text{CO})_{13}$ among the products of the reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 was likely to result from the relatively high temperatures under which these experiments were conducted, causing the decarbonylation of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ to $\text{GeCo}_4(\text{CO})_{13}$, there was an alternative possibility that $\text{GeCo}_4(\text{CO})_{13}$ might be a necessary intermediate in the reaction process. Thus the following reactions between $\text{GeCo}_4(\text{CO})_{13}$ and MeGeH_3 were carried out in order to clarify this situation.

3.6.2. Experimental Details and Results.

Run 1: MeGeH_3 (0.27 mmoles by volume) and $\text{GeCo}_4(\text{CO})_{13}$ (0.054 g; 0.08 mmoles) (3.4:1 ratio) were allowed to react in hexane (10 mls) at room temperature. After approximately 12 weeks the colour of the solution was clearly changing from the original deep purple to orange. After a total of 16 weeks reaction the vessel was opened and incondensable gases (0.086 mmoles) were removed of composition 13% CO , 87% H_2 . Unreacted MeGeH_3 (0.16 mmoles) was recovered from the volatiles with a trace (0.03 mmoles) remaining with the solvent fraction.

An infrared spectrum of the soluble involatile products in hexane showed pure $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ [20]. Also present was a trace of dark coloured, insoluble material which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a decomposition product and was discarded. The yield of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$, on the basis of consumed $\text{GeCo}_4(\text{CO})_{13}$, was 87% (0.053 g; 0.07 mmoles).

Run 2: MeGeH_3 (0.3 mmoles) and $\text{GeCo}_4(\text{CO})_{13}$ (0.067 g; 0.1 mmoles) (3:1 ratio) were allowed to react in hexane (10 mls) for 20 weeks at room temperature. Incondensable gases (0.091 mmoles) were measured of composition 11% CO , 89% H_2 . MeGeH_3 (0.1 mmoles) was recovered from the volatiles with a small amount (ca. 0.05 mmoles) remaining in the solvent fraction.

The solid products proved to be a trace of a decomposition product and a yield of 88% $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ (0.067 g; 0.09 mmols) on the basis of consumed $\text{GeCo}_4(\text{CO})_{13}$.

3.6.3. Discussion of the Reactions of $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ and MeGeH_3 .

From the results shown above it is clear that $\text{GeCo}_4(\text{CO})_{13}$ will react slowly with MeGeH_3 at room temperature to provide the cluster $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}(\text{C})$.

The incondensable gas measurements qualitatively correspond well with the values expected for the observed products, where the high proportion of hydrogen is accounted for by the reacting methylgermane, and the observed CO is likely to arise from the decomposition causing the dark insoluble product found in each experiment. In run 1, 0.075 mmols of evolved H_2 were observed with only 0.07 mmols of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ obtained. In run 2, the difference is in the opposite sense where only 0.081 mmols of H_2 are observed compared to 0.09 mmols of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$. These values are within reasonable experimental error.

These experiments were carried out to establish if the cluster $\text{GeCo}_4(\text{CO})_{13}$, observed as a product in the reactions of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ with MeGeH_3 in low molar ratios, was actually an intermediate in that process or if it was merely produced as a side-product of the heat applied to the system. Although it has been observed that $\text{GeCo}_4(\text{CO})_{13}$ will indeed react with MeGeH_3 to provide the same product as $\text{GeCo}_4(\text{CO})_{14}$ it is thought unlikely that it is an intermediate in that process since the reaction times here were so much longer than those of the $\text{GeCo}_4(\text{CO})_{14}$ and MeGeH_3 reactions. It seems more probable that the two clusters react independently with MeGeH_3 and this must be by very different mechanisms. This will be discussed in section 3.6.4.

It has been observed that under CO pressure of up to 100 atmospheres $\text{GeCo}_4(\text{CO})_{13}$ will not take up a CO ligand to yield $\text{GeCo}_4(\text{CO})_{14}$ [149]. Clearly the equilibrium shown in figure 3.17 lies very much to the right.

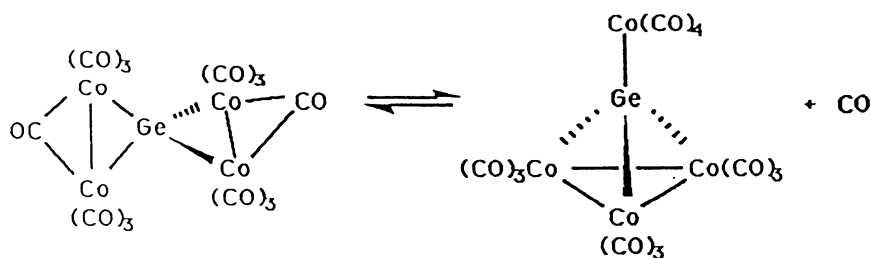


Figure 3.17

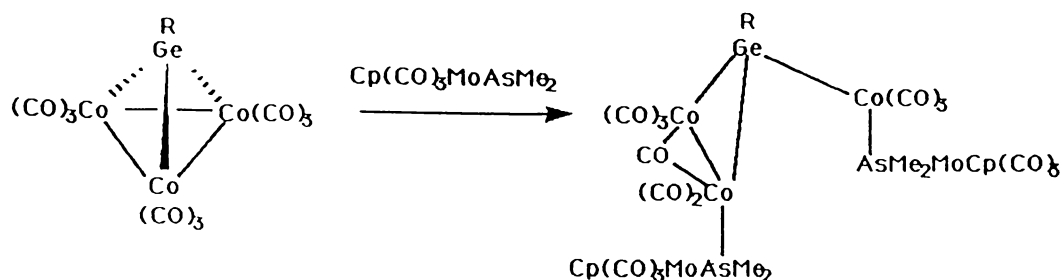
It could, at first sight, be thought surprising that $\text{GeCo}_4(\text{CO})_{13}$ will react with MeGeH_3 to form an open-skeleton derivative while it does not react similarly with CO . If the relative bond energies of each are considered, however, this may be understood. Table 3.13 shows the bonds involved in each of these reactions.

Table 3.13 Bonds involved in the equilibria between $\text{GeCo}_4(\text{CO})_{13}$ and $\text{GeCo}_4(\text{CO})_{14}$, and between $\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$.

$\text{GeCo}_4(\text{CO})_{13} + \text{CO} \rightleftharpoons \text{GeCo}_4(\text{CO})_{14}$	
4 (Ge-Co)	4 (Ge-Co)
3 (Co-Co)	2 (Co-Co)
13 (Co-C)	14 (Co-C)
$\text{GeCo}_4(\text{CO})_{13} + \text{MeGeH}_3 \rightleftharpoons (\text{MeHGe})\text{GeCo}_4(\text{CO})_{13} + \text{H}_2$	
4 (Ge-Co)	6 (Ge-Co)
3 (Co-Co)	2 (Co-Co)
13 (Co-C)	13 (Co-C)
1 (Ge-C)	1 (Ge-C)
3 (Ge-H)	1 (Ge-H)
	1 (H-H)

In the equilibrium between $\text{GeCo}_4(\text{CO})_{13}$ and $\text{GeCo}_4(\text{CO})_{14}$ the slight energy gain in Co-C bonding does not compensate for the loss of Co-Co bonding energy thus the equilibrium lies heavily to the left. In the second case, however, the increase in Ge-Co bonding energy, and formation of molecular hydrogen will push the equilibrium to the right.

The reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{13}$ to provide $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ increases the nuclearity of the metal skeleton from 5 to 6. This may be compared with the reactions carried out by Vahrenkamp [44], where cluster opening is the first step in the formation of new metal skeletons. For example:



(R = Me, Ph)

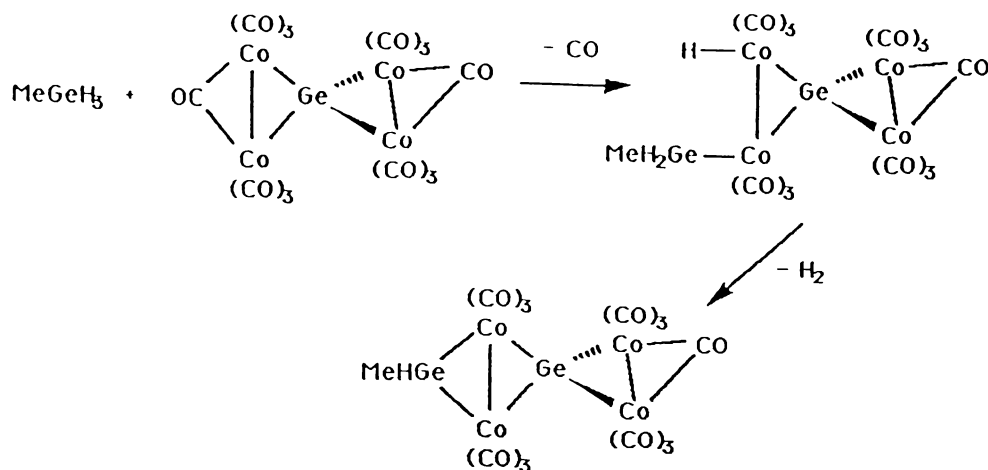
Figure 3.18 [44]

Thermolysis of this product results in condensation to the tetrahedral structure with elimination of the organometalarsenide. Often a cobalt carbonyl group of the original cluster has been replaced by a $\text{Mo(CO)}_2\text{Cp}$ group [44]. Thus, attack at a cobalt carbonyl group of the GeCo_3 tetrahedron, resulting in cluster opening is not unprecedented.

3.6.4. A Comparison of the Reactions of $\text{GeCo}_4(\text{CO})_{14}$ (*B*) and $\text{GeCo}_4(\text{CO})_{13}$ (*I*) with MeGeH_3 .

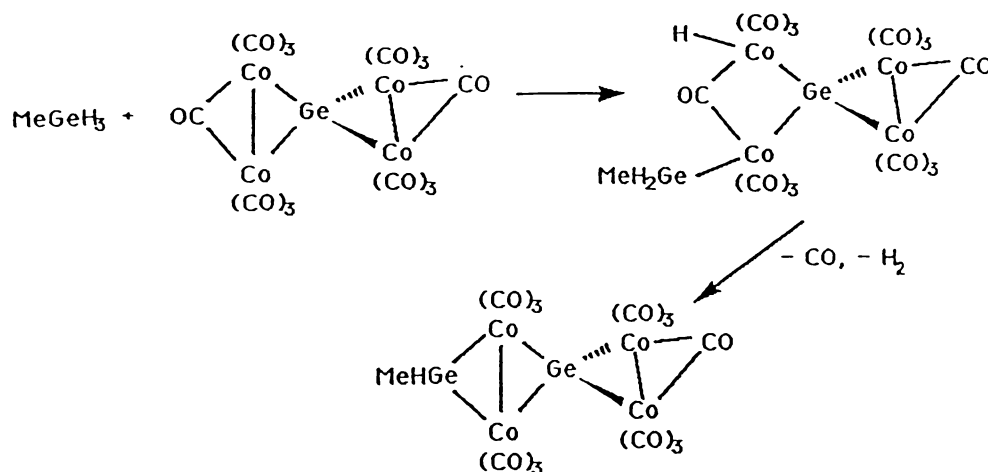
The clusters $\text{GeCo}_4(\text{CO})_{14}$ and $\text{GeCo}_4(\text{CO})_{13}$ both react with MeGeH_3 to provide the same species, $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ as the major product. In the reactions of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 held at relatively high temperatures $\text{GeCo}_4(\text{CO})_{13}$ was also observed to be present among the products. However, in those reactions conducted at room temperature or lower, $\text{GeCo}_4(\text{CO})_{13}$ was not observed. Also, the reactions of $\text{GeCo}_4(\text{CO})_{13}$ with MeGeH_3 took much longer to reach completion than those of $\text{GeCo}_4(\text{CO})_{14}$. It is thus unlikely that $\text{GeCo}_4(\text{CO})_{13}$ is an intermediate in the production of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ from $\text{GeCo}_4(\text{CO})_{14}$ and MeGeH_3 . It seems more probable that the two species react independently with MeGeH_3 and follow very different pathways.

For $\text{GeCo}_4(\text{CO})_{14}$, it is anticipated that the hydride will react to replace one bridging carbonyl of the cluster in a similar manner to that observed in the reactions of MeGeH_3 with $\text{Co}_2(\text{CO})_8$, discussed in Chapter 2. This could provide a pathway of the form shown in scheme 3.2 which is similar to that suggested in section 1.3.



Scheme 3.2.

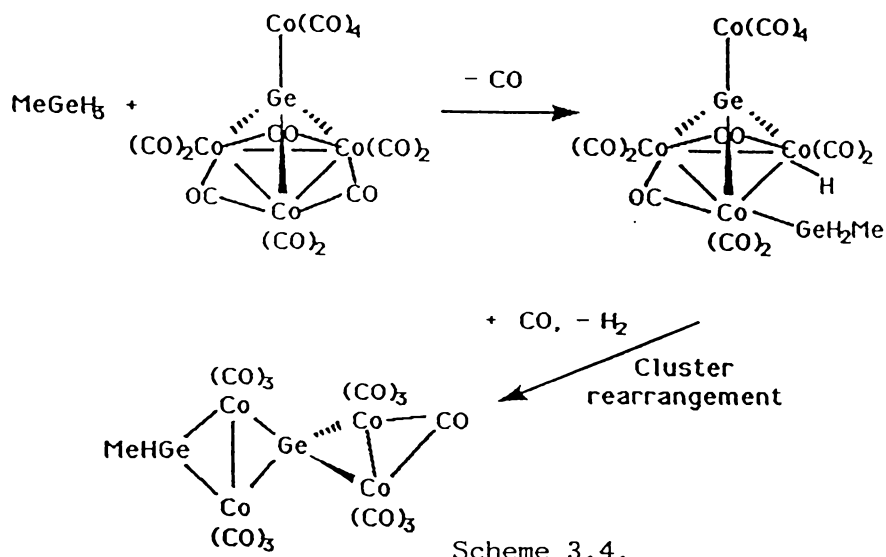
Alternatively, the process could follow the route shown in scheme 3.3 which is related to the pathway suggested for the reaction of Ph_2GeH_2 with $\text{Co}_2(\text{CO})_8$ (Scheme 1.1) [1].



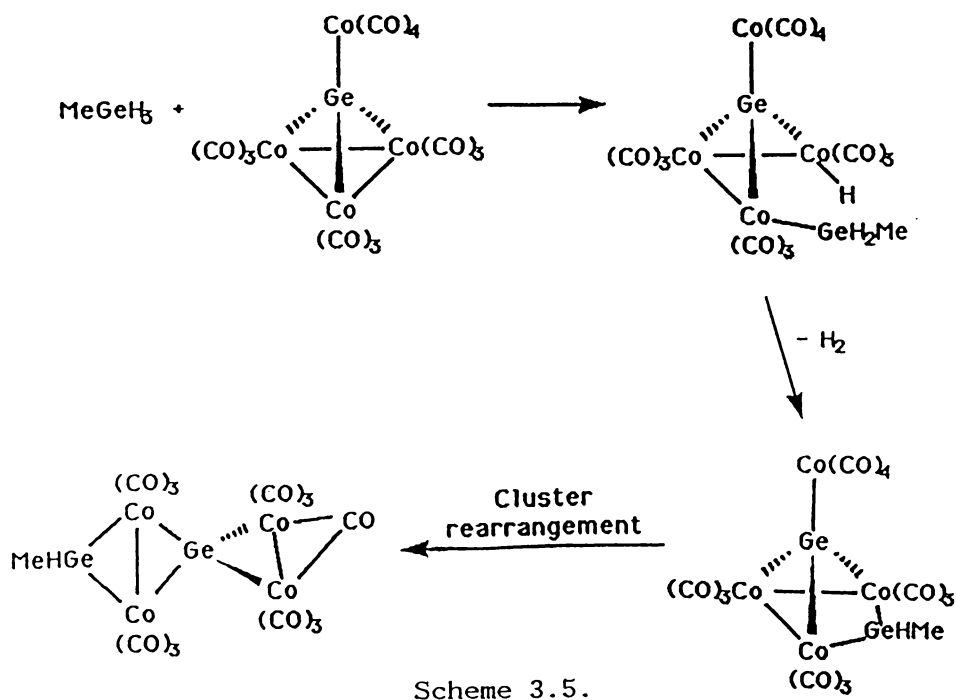
Scheme 3.3.

It is not possible at this stage to distinguish between the above two pathways. However it seems likely that the important step in the reactions of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 is replacement of a bridging carbonyl by the MeGeH unit.

Although $\text{GeCo}_4(\text{CO})_{13}$ is known to have no bridging carbonyls in the solid state [49] it is possible that these are present in solution. A very rapid exchange of terminal and bridging carbonyl groups would account for the absence of any bands arising through bridging carbonyl vibrations in the infrared spectrum. This could then suggest the pathway shown in scheme 3.4.



This pathway seems unlikely since, once the MeGeH group has bridged a Co-Co bond, there is no necessity for the cluster to take up the CO group again to open out. An alternative route is depicted in scheme 3.5. This ignores the possibility of bridging carbonyl groups, and suggests an early Co-Co bond cleavage.



This pathway is consistent with the very low proportion of CO found in the incondensable gases evolved during this reaction, and it also explains the comparatively long reaction duration for the $\text{GeCo}_4(\text{CO})_{13}$ system since

the necessary Co-Co bond cleavages would make this process extremely slow compared to that of $\text{GeCo}_4(\text{CO})_{14}$.

Although it is not possible to define the reaction pathways of these two clusters with MeGeH_3 with any certainty, it is highly probable that they proceed through quite different routes.

3.7. Exploratory carbonylation reactions of $\text{Ge}[\text{Co}_2(\text{CO})_7]_2(B)$, $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}(C)$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(C)$.

3.7.1. Experimental Details and Results.

Run 1: $\text{Ge}[\text{Co}_2(\text{CO})_7]_2(B)$ (0.03 g; 0.04 mmoles) in hexane (5 mls) was sealed in a high pressure bomb for 24 hours under CO pressure of 30 atm. Before the pressure was released the bomb was cooled in ice water to help to preserve any labile products. A carbonyl region infrared spectrum was recorded of the hexane solution immediately after opening. This showed a mixture of $\text{GeCo}_4(\text{CO})_{14}$ and the fully open species $\text{Ge}[\text{Co}(\text{CO})_4]_4$ [34]. The observed bands and assignments are listed in table 3.14. On standing at atmospheric temperature and pressure for 5 minutes $\text{Ge}[\text{Co}(\text{CO})_4]_4$ had completely reverted to $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$.

Table 3.14. Carbonyl region infrared data for the products of run 1, together with that for $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$, $\text{Ge}[\text{Co}(\text{CO})_4]_4$ and $\text{Sn}[\text{Co}(\text{CO})_4]_4$. (cm^{-1}).

$\text{Ge}[\text{Co}_2(\text{CO})_7]_2$ [34]	Products of Run 1	$\text{Ge}[\text{Co}(\text{CO})_4]_4$ [34]	$\text{Sn}[\text{Co}(\text{CO})_4]_4$ [150]
2079 s	2079 s	2079 s	2079 vs
2061 vs	2061 s		
2040 mw	2040 sh, w		
2032 m	2032 m	2032 sh	2032 m
2023 mw	2021 s	2020 vs	2018 vs
2004 w	2002 vw	2000 w, br	1999 w, sh 1994 w
1848 m	1848 m		

All recorded in hexane.

Run 2: $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ (0.04g; 0.05 mmoles) in hexane (5 mls) was sealed in a high pressure bomb for 16 hours under CO pressure of 30 atm. The bomb was cooled in icewater before the pressure was released and a carbonyl region infrared spectrum of the hexane solution was recorded immediately after opening. This is shown in figure 3.19 and listed in

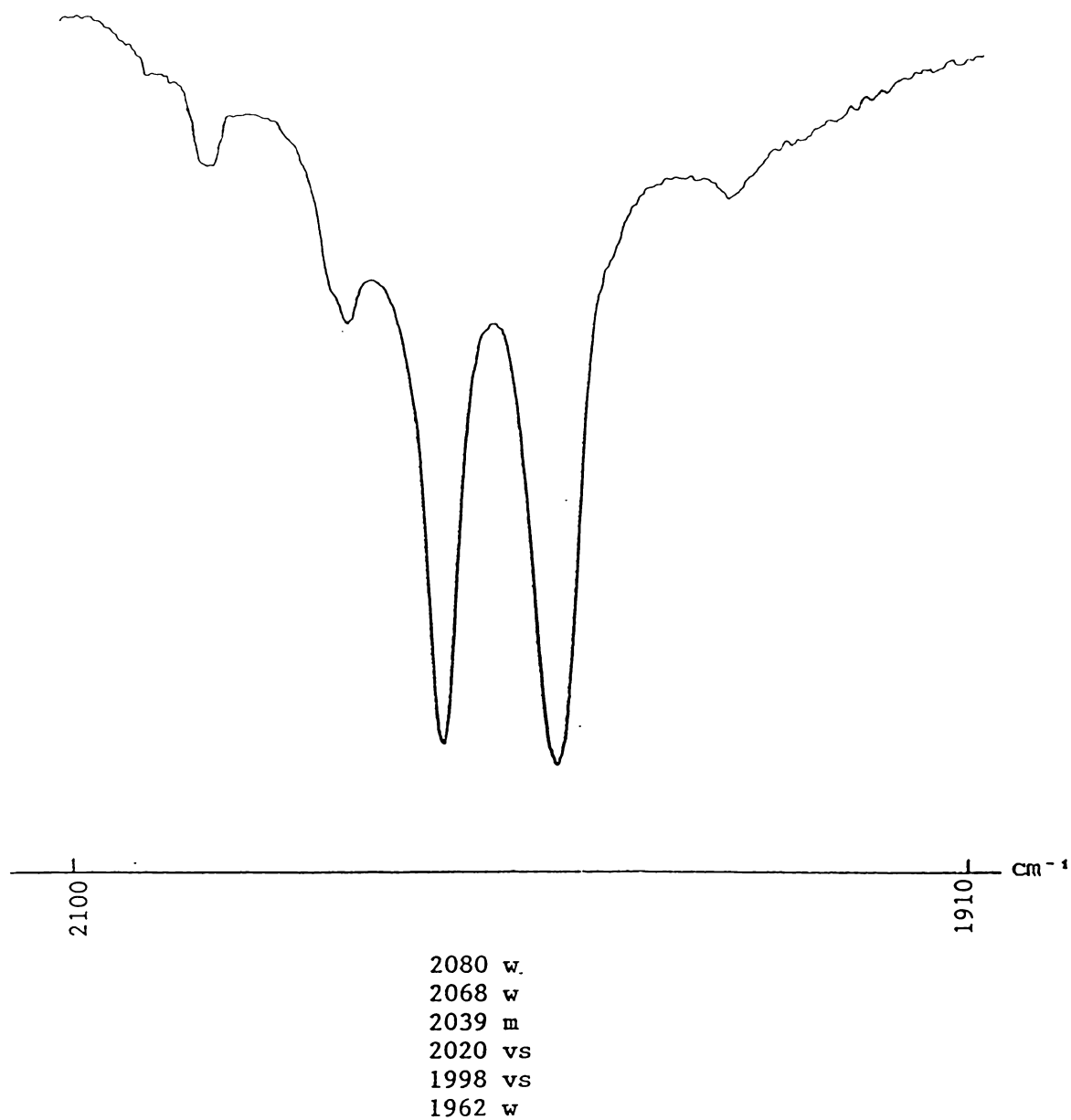


Figure 3.19. Infrared active carbonyl stretches of the carbonylation product of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$.

table 3.15 and it can be seen that all the $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ had been converted to some new species. Solvent was removed by pumping under vacuum, and an infrared spectrum was recorded of the solid as a nujol mull. This showed complete reconversion of the sample to $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$.

Run 3: $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (0.036g; 0.046 mmoles) in hexane (5 mls) was sealed in a high pressure bomb for 24 hours under 30 atmospheres of CO pressure. Before the pressure was released the bomb was cooled in ice water and an infrared spectrum of the hexane solution was recorded immediately after opening. This showed a mixture of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and a new species. Table 3.15 lists the observed bands.

This mixture was then placed as quickly as possible in a vessel fitted with a Kontes greaseless tap and was heated at 35°C for 72 hours. Incondensable gas evolution was noted, but was not measured. An infrared spectrum of the solution was then recorded which showed the mixture to have reverted to pure $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$. Also present was a small amount of a dark decomposition product.

Table 3.15. Carbonyl region infrared data for the products of runs 2 and 3, $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$. (cm^{-1}).

$(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ [20] [79,20]	Products of Run 2	Products of Run 3	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2097 m	2080 w 2068 w	2080 w 2070 w, sh 2066 m 2055 m	2095 m 2064 vs 2054 s
2067 vs		2044 s	2043 vs
2046 vs	2039 m	2022 vs	2025 m
2029 m	2020 vs		2019 sh 2015 m-s
	1998 vs 1962 w	1999 vs 1962 w	
1841 m		1843 w	1843 m

All recorded in hexane solution

3.7.2. Discussion of the Carbonylation Reactions of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}(\text{C})$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$.

These exploratory experiments were carried out to determine if the open-skeleton derivatives of each compound could be obtained by using high pressures of CO as a forcing condition.

The infrared data obtained from run 1 is shown in table 3.14. From this it is clear that the products are a mixture of $\text{Ge}[\text{Co}_2(\text{CO})_7]_2(B)$ and $\text{Ge}[\text{Co}(\text{CO})_4]_4$. The latter species has previously been observed in the reactions of GeX_4 species ($X = \text{halogen}$) with $\text{NaCo}(\text{CO})_4$ [34] and is reported to rapidly decarbonylate at room temperature yielding $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$ [84]. From the results obtained above, this decarbonylation reaction is clearly reversible. Interestingly, this is not the case for the further condensation reaction of $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$ to $[(\text{CO})_4\text{Co}]_2\text{Ge}[\text{Co}_3(\text{CO})_9](I)$. This cluster has been subjected to CO pressures of up to 100 atmospheres with no change in its structure [149]. The various steps of these interconversions are depicted in figure 3.20.

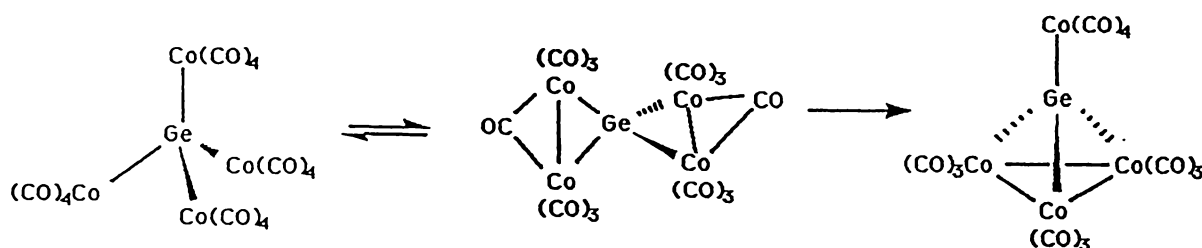
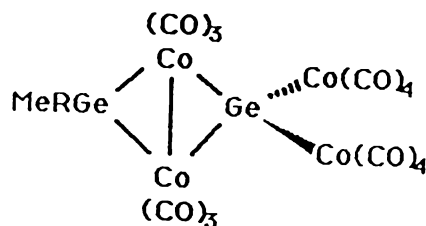


Figure 3.20.

This latter result is surprising since the alkyl clusters $\text{PhGeCo}_3(\text{CO})_9$ and $\text{MeGeCo}_3(\text{CO})_9$ carbonylate to give the more open $\text{RGeCo}_3(\text{CO})_{11}$ ($R = \text{Ph}, \text{Me(A)}$) when subjected to high CO pressure [44]. This closed relation of the tetracobalt cluster is therefore particularly stable compared to the alkyl tricobalt analogues.

The product mixture of run 1 showed only $\text{Ge}[\text{Co}_2(\text{CO})_7]_2(B)$ and $\text{Ge}[\text{Co}(\text{CO})_4]_4$. No bands were observed which could be attributed to $[(\text{CO})_4\text{Co}]_2\text{Ge}[\text{Co}_2(\text{CO})_7]$ containing two terminal $\text{Co}(\text{CO})_4$ units and a $\text{GeCo}_2(\text{CO})_7$ triangle. It seems likely from this result, and that of section 2.6. where the reaction of $\text{H}_3\text{GeCo}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$ provided only $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$, that $[(\text{CO})_4\text{Co}]_2\text{Ge}[\text{Co}_2(\text{CO})_7]$ is not favoured, although it is presumably an intermediate in these carbonylation/decarbonylation reactions.

Since $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$ is observed to open out to $\text{Ge}[\text{Co}(\text{CO})_4]_4$, with addition of CO ligands and cleavage of Co-Co bonds, the clusters $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ may follow a similar path on carbonylation to form $(\text{MeRGe})[\text{Co}_2(\text{CO})_6]\text{Ge}[\text{Co}(\text{CO})_4]_2$ ($R = \text{H}, \text{Me}$ respectively) with the structure shown in figure 3.21.



(R = H, Me)

Figure 3.21.

The absence of any bridging carbonyl modes in the infrared spectra of these products (table 3.15) supports this formulation. However, further analysis of the carbonyl vibrations should help to strengthen this suggestion.

As discussed in section 3.4.3.3., Bor has studied the generalised infrared spectra of $M_2(CO)_6(\mu-X)_2$ species of idealised C_{2v} symmetry [130]. The two new clusters may be considered as $Co_2(CO)_6(\mu-GeMeR)[\mu-Ge(Co(CO)_4)_2]$ species, thus the infrared vibrations of the carbonyl ligands of the $Co_2(CO)_6$ unit may be analysed using Bor's generalised spectrum (figure 3.7).

The $Co_2(CO)_6$ unit could thus be expected to give rise to four main carbonyl vibrations with the pattern m, vs, vs, s. It is often observed for these species that the u and v modes, being quite close in energy, overlap to provide only one very strong band.

The two terminal $Co(CO)_4$ units, although not identical in $(MeHGe)[Co_2(CO)_6]Ge[Co(CO)_4]_2$, may be assumed to be of close enough energy to be analysed together. These would then be expected to result in up to seven infrared modes ($R_2Ge[Co(CO)_4]_2$ species have $3a_1 + 3b_1 + b_2$ carbonyl stretching modes predicted, although these are not always all observed). The infrared spectrum of $Me_2Ge[Co(CO)_4]_2$ [20] is listed in table 3.16. where only five of the possible bands are observed.

Table 3.16. Infrared active carbonyl stretches of $Me_2Ge[Co(CO)_4]_2$. (cm^{-1}).

2099 (w)
2081 (vs)
2027 (vs)
2006 (vs)
1996 (m)

Recorded in hexane solution.

Some of these lower frequency vibrations could be expected to overlap with bands arising through the vibrations of the $\text{Co}_2(\text{CO})_6$ unit of these molecules. Table 3.17 lists the carbonyl region infrared spectrum of the carbonylation product of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ with possible assignments made with reference to Bor's generalised infrared spectrum and the expected bands of the terminal $\text{Co}(\text{CO})_4$ units.

Table 3.17. Carbonyl region infrared data for the carbonylation product of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ with possible assignments.

(cm^{-1})	
2080 w	a_1 mode of $\text{Co}(\text{CO})_4$ units
2068 w	a_1 mode of $\text{Co}(\text{CO})_4$ units
2039 m	"q" mode of $\text{Co}_2(\text{CO})_6$ unit
2020 vs	"s" mode of $\text{Co}_2(\text{CO})_6$ unit
1998 vs	"u+v" mode of $\text{Co}_2(\text{CO})_6$ unit
1962 w	mode of $\text{Co}(\text{CO})_4$ units

The infrared spectrum of the carbonylation product of $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ (figure 3.9) shows very strong but broad lower frequency bands indicating overlapping modes.

Thus the carbonyl region infrared spectra, although clearly not conclusive, are reasonably consistent with the postulated structures for these carbonylation products.

All of the open species are unstable at even moderate temperatures under atmospheric pressure and the equilibrium shown in figure 3.22 must lie completely on the left hand side at room temperature and atmospheric pressure.

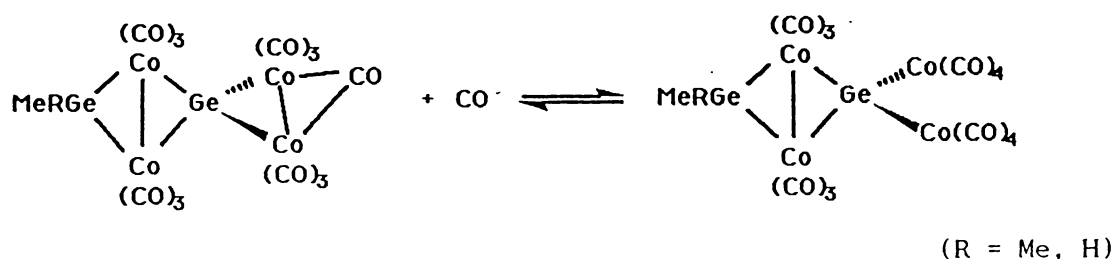


Figure 3.22.

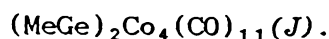
The reversion to the closed form proceeded almost quantitatively for all of the clusters, although the process was somewhat faster for $\text{Ge}[\text{Co}(\text{CO})_4]_4$ which had completely reverted to the condensed species simply on standing at room temperature and pressure for 5 minutes. The dimethylgermyl substituted cluster appeared to decarbonylate rapidly to an equilibrium point - as observed from the carbonyl region infrared spectrum of the product mixture recorded immediately after opening, which showed a

mixture of the open and closed-skeleton species. The monomethylgermyl substituted compound seemed to have a slower rate of decarbonylation since the carbonylated product remained the only species in solution for several hours at room temperature and pressure until pumping under vacuum to remove the solvent also removed the added CO.

Clearly, although there are different decarbonylation rates, these clusters are unstable under atmospheric conditions and the closed form is much preferred.

This preliminary study has suggested that the carbonylation product of $(\text{MeRGe})[\text{Co}_2(\text{CO})_6]\text{Ge}[\text{Co}_2(\text{CO})_7]$ is $(\text{MeRGe})[\text{Co}_2(\text{CO})_6]\text{Ge}[\text{Co}(\text{CO})_4]_2$. Further work is needed before a definite conclusion can be drawn. It would be useful to measure CO evolved on reconversion to the starting cluster and it should be possible to obtain more data on the new species by working at lower temperatures.

3.8. A brief survey of possible new routes to the cluster



3.8.1. General.

Since it was found in section 3.5 that the cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ is not formed in the reaction between $\text{GeCo}_4(\text{CO})_{14}$ and MeGeH_3 as first believed [20] it was desirable to identify a new route to this species. Preferably this route would be straightforward, giving a high yield of the cluster and would use readily prepared starting materials.

Three methods have been examined. The first is the reaction of $\text{MeGeH}_2\text{Co}(\text{CO})_4$ with $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, to determine if the hydride will replace the bridging carbonyl of $\text{MeGeCo}_3(\text{CO})_{11}$ to form the open cluster $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ which is known to decarbonylate to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ as shown in figure 3.23 [31].

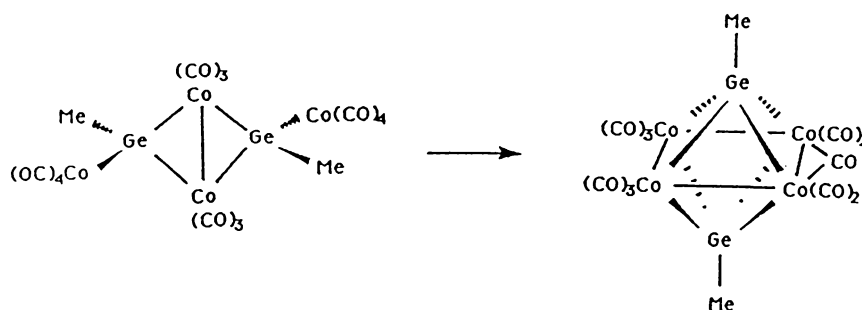


Figure 3.23 [31]

The second reaction was that of $\text{MeGeH}_2\text{GeH}_2\text{Me}$ with $\text{Co}_2(\text{CO})_8$. Monosubstituted digermanes, RGe_2H_5 are known to react with $\text{Co}_2(\text{CO})_8$ ($\text{R} = \text{Me}, \text{Et}, \text{Co}(\text{CO})_4, \text{Mn}(\text{CO})_5$) to yield the clusters $(\text{RGe})[(\text{CO})_4\text{CoGe}]\text{Co}_4(\text{CO})_{11}$ as major products [39]. It was anticipated that a similar reaction might occur for disubstituted digermanes, $\text{RGeH}_2\text{GeH}_2\text{R}$ with $\text{Co}_2(\text{CO})_8$, to yield the $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ clusters, although the increased steric hindrance of the additional R group might lead to Ge-Ge cleavage and the formation of monogermanium products.

The third route examined was the thermolysis of $\text{MeGeCo}_3(\text{CO})_{11}$. This followed up the observation made during a preparation of $\text{MeGeCo}_3(\text{CO})_9$ by heating $\text{MeGeCo}_3(\text{CO})_{11}$ [37] that a minor product was only slightly soluble in hexane solution and gave an infrared spectrum similar to that of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [20, 87].

3.8.2. Preparation of Starting Materials.

$\text{MeGeH}_2\text{Co}(\text{CO})_4$ was prepared by the coupling reaction of MeGeH_2Cl and $\text{KCo}(\text{CO})_4$ [36]. MeGeH_2Cl was produced by passing MeGeH_3 over a slight deficit of SnCl_4 [137] and purification of the products was achieved by fractionation through baths at -83°C and -64°C . $\text{KCo}(\text{CO})_4$ was prepared by reduction of $\text{Co}_2(\text{CO})_8$ over Na/K alloy [12] in diethyl ether.

$\text{MeGeCo}_3(\text{CO})_{11}$ was produced by the reaction of MeGeH_3 and $\text{Co}_2(\text{CO})_8$ in hexane for 24 hours [36]. This was purified, when necessary by fractional crystallisation from hexane solution at -10°C .

$\text{MeGeH}_2\text{GeH}_2\text{Me}$ was prepared by reaction of Ge_2H_6 with SnCl_4 in a 1:2 ratio, then reaction of the produced $\text{Cl}_2\text{Ge}_2\text{H}_4$ with an excess of MeMgBr to yield Me_2GeH_4 . It is known [151] that direct di-halogenation of Ge_2H_6 results in a 90% yield of the $1,2\text{-X}_2\text{Ge}_2\text{H}_4$ species. This was then purified by fractionation through traps held at -83°C and -64°C .

3.8.3. Experimental Techniques.

The two long duration experiments were contained within glass ampoules capable of withstanding high gas pressures. These were set up in a similar manner to that described in section 3.2 and work up was also similar.

The thermolysis experiment was carried out by refluxing a solution of the starting cluster in hexane under N_2 . Work up of the products was then as described in section 3.2.

3.8.4. Experimental Details and Results.

Run 1: $\text{MeGeCo}_3(\text{CO})_{11}$ (0.143g; 0.25 mmol) and $\text{MeGeH}_2\text{Co}(\text{CO})_4$ (0.06g; 0.24 mmol) (1:1 ratio) were allowed to react in hexane (5 ml) for 8 weeks at room temperature. Incondensable gases (0.93 mmol) were measured of composition 72% CO, 28% H_2 . Fractionation of the volatile components yielded only solvent.

A carbonyl region infrared spectrum of the involatile products in a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution showed $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [20] to be the major product, with a lesser amount of the open-skeleton relation, $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ [31], also present. A small amount of unreacted $\text{MeGeCo}_3(\text{CO})_{11}$ was also observed. After conversion of $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, by heating at 40°C for 7 days, the unreacted $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{MeGeCo}_3(\text{CO})_9$ [38] which had now formed to some extent by decarbonylation of $\text{MeGeCo}_3(\text{CO})_{11}$ was removed by fractional crystallisation from a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution cooled to -10°C . This provided an 83% yield of pure $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.143 g; 0.20 mmol) on the basis of consumed $\text{MeGeH}_2\text{Co}(\text{CO})_4$.

Run 2: $\text{Co}_2(\text{CO})_8$ (0.112g; 0.33 mmol) and $\text{MeGeH}_2\text{GeH}_2\text{Me}$ (0.027 g; 0.15 mmol) (2.2:1 ratio) were allowed to react in hexane (10 ml) for 15 months. Incondensable gases (0.68 mmol) were measured of composition 74% CO, 26% H_2 . Fractionation of the volatiles yielded only solvent.

A carbonyl region infrared spectrum of the involatile products in a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution showed a mixture of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, unreacted $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ [139] and $\text{MeGeCo}_3(\text{CO})_{11}$ [35]. After fractional crystallisation from hexane solution cooled to -15°C a 31% yield of pure $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.033 g; 0.047 mmol) was obtained based on $\text{MeGeH}_2\text{GeH}_2\text{Me}$ consumed.

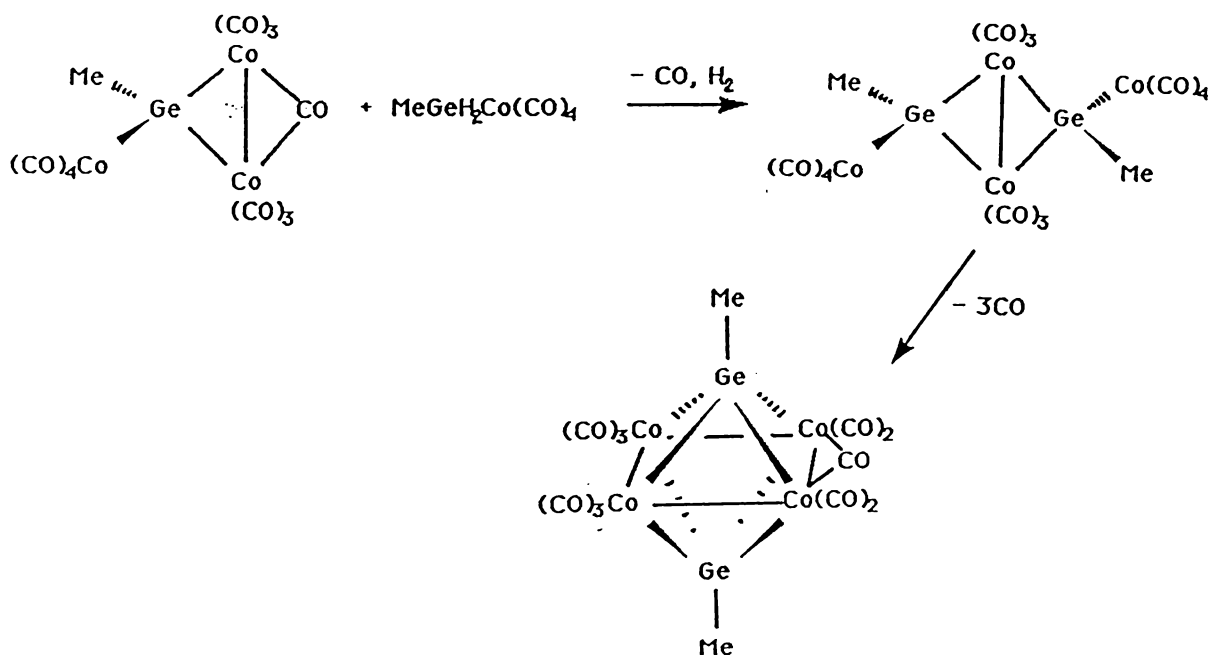
Run 3: $\text{MeGeCo}_3(\text{CO})_{11}$ (0.05 g; 0.09 mmol) in hexane (10 ml) was refluxed for 8 hours under N_2 . Decomposition of the starting material was observed by the appearance of black deposits on the flask at the surface of the solution. Characterisation of these insoluble species was not pursued. An infrared spectrum of the hexane solution showed the only carbonyl containing product to be $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. Recrystallisation from $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution gave a 17% yield of pure $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.011 g; 0.024 mmol) on the basis of consumed $\text{MeGeCo}_3(\text{CO})_{11}$.

3.8.5. Discussion of the New Routes to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$.

The three experiments described above were carried out in the hope of providing at least one new route to the cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. In fact, all three pathways provide the desired product and the benefits and drawbacks of each will be discussed later in this section.

The reaction between $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ and $\text{MeGeH}_2\text{Co}(\text{CO})_4$ produced a mixture of $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. The former species has been observed in the reaction of $\text{Fe}(\text{CO})_4(\text{GeH}_2\text{Me})_2$ with $\text{Co}_2(\text{CO})_8$ [31] and was found to readily decarbonylate to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

This reaction provided 0.93 mmols of incondensable gas. Assuming the reaction follows the pathway shown in scheme 3.6 then 2 moles of incondensable gas would be evolved for every mole of $\text{MeGeH}_2\text{Co}(\text{CO})_4$ reacting to give $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$, and then a further 3 moles of CO would be released on condensation to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

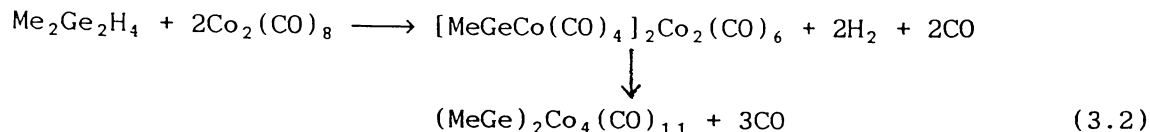


Scheme 3.6.

As 0.24 mmols of $\text{MeGeH}_2\text{Co}(\text{CO})_4$ reacted this should provide 0.24 mmols of H_2 . 0.26 mmols of H_2 were measured, agreeing within experimental error. 0.24 mmols of CO would be released by $\text{MeGeCo}_3(\text{CO})_{11}$ reacting with the $\text{MeGeH}_2\text{Co}(\text{CO})_4$ which, in total, accounts for 0.48 mmols of the evolved gas. The further 0.45 mmols of CO would result from the decarbonylation of some of the produced $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. As 3 mmols of CO should be released per mole of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ formed, this

0.45 mmols of CO would correspond to 0.15 mmols of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, leaving 0.09 mmols of $[\text{MeGeCo}(\text{CO})_4]\text{Co}_2(\text{CO})_6$. This corresponds very well with the observed product mixture.

The reaction between $\text{Me}_2\text{Ge}_2\text{H}_4$ and $\text{Co}_2(\text{CO})_8$ may be anticipated to follow equation 3.2.



Although $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ was not observed among the products, it is assumed to be involved as RGe_2H_5 species reacting with $\text{Co}_2(\text{CO})_8$ generally formed both $[\text{RGeCo}(\text{CO})_4]\text{Co}_2(\text{CO})_6$ and $[\text{RGe}]\text{Co}_4(\text{CO})_{11}$ [39]. It is likely that the long duration of this experiment allowed complete conversion of $[\text{MeGeCo}(\text{CO})_4]\text{Co}_2(\text{CO})_6$ to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (*J*).

In this reaction between $\text{MeGeH}_2\text{GeH}_2\text{Me}$ and $\text{Co}_2(\text{CO})_8$, 1.05 mmols of incondensable gas would be expected for 0.15 mmols of $\text{MeGeH}_2\text{GeH}_2\text{Me}$ reacting. In fact, only 0.68 mmols of incondensable gases were measured although all of the $\text{MeGeH}_2\text{GeH}_2\text{Me}$ had reacted. The composition of the gas is qualitatively reasonable with respect to equation 3.2. thus it is possible that the amount of $\text{MeGeH}_2\text{GeH}_2\text{Me}$ in the reaction mixture was less than stated. This suggestion is supported by the amount of unreacted $\text{Co}_2(\text{CO})_8$ observed which would not be expected if the amount of $\text{MeGeH}_2\text{GeH}_2\text{Me}$ were correct. It is also possible that the ~~$\text{MeGeH}_2\text{GeH}_2\text{Me}$~~ had not been thoroughly purified before use and contained small portions of other substituted digermanes such as $\text{MeGe}_2\text{H}_4\text{Cl}$ which might react quite differently. The studies of the reaction of MeGe_2H_5 with $\text{Co}_2(\text{CO})_8$ also showed the formation of $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{GeCo}_4(\text{CO})_{14}$ as minor products [39]. A small amount of $\text{MeGeCo}_3(\text{CO})_{11}$ was observed in the carbonyl region infrared spectrum of the product mixture obtained here and as little attention was paid to the lighter fractions, it is possible that other monogermanium species had also been produced. Clearly, in addition to the production of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ some cleavage of the starting hydride occurs during the reaction, resulting in the formation of smaller clusters.

Of the three experiments conducted here, the best yield of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (*J*) was obtained in the reaction between $\text{MeGeCo}_3(\text{CO})_{11}$ (*A*) and $\text{MeGeH}_2\text{Co}(\text{CO})_4$. This is a straightforward process and both starting materials are readily prepared. The yield obtained here (83%), and the duration of the reaction (8 weeks) is comparable to the route found by a co-

worker at Waikato [32] where MeGeH_3 and $\text{Co}_4(\text{CO})_{12}$ were allowed to react together to provide $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. This route is also interesting as varying the group attached to either of the germanium-cobalt carbonyl starting materials should allow the formation of new $[\text{R}'\text{Ge}]\text{Co}_4(\text{CO})_{11}[\text{GeR}]$ *closo*-hexanuclear clusters.

Thermolysis of $\text{MeGeCo}_3(\text{CO})_{11}$, although providing a poor yield of the desired cluster, does have the benefit of a very short reaction time, and may be useful on some occasions.

Preparation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ via the reaction of $\text{Co}_2(\text{CO})_8$ with $\text{MeGeH}_2\text{GeH}_2\text{Me}$ does not really seem worthwhile, since other routes provide a better yield of the cluster and $\text{MeGeH}_2\text{GeH}_2\text{Me}$ is prepared by a relatively complicated process. However, this reaction is interesting in its own right as a preparative route to other clusters. As in the reaction of $\text{RGeCo}_3(\text{CO})_{11}$ with $\text{RGeH}_2\text{Co}(\text{CO})_4$, the use of different R groups, such as organometallic fragments, is possible and mixed $\text{R}^1\text{GeH}_2\text{GeH}_2\text{R}^2$ hydrides could be expected to provide some interesting products.

3.9. Conclusion to Chapter 3.

The reaction of a large excess of either dimethyl- or monomethylgermane with $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ provides the new clusters $(\text{MeRGe})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ ($\text{R} = \text{Me}, \text{H}$ respectively). The dimethylgermyl cluster, $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ has been characterised by infrared, Raman, mass and ^1H NMR spectroscopy, and by an X-ray crystal structure determination. The latter showed the molecule to comprise of four GeCo_2 triangles connected by Ge apices and Co-Co edges.

The carbonyl region vibrational spectra of the new compounds, together with that of the parent cluster, $\text{GeCo}_4(\text{CO})_{14}$, have been discussed with reference to Bor's generalised infrared spectra of doubly bridged $\text{M}_2(\text{CO})_6$ species of idealised C_{2v} symmetry [130]. A good correlation has been obtained by considering these compounds as "Double Bor" systems of idealised D_{2d} symmetry.

The speculation that the *closo*-hexanuclear cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ is formed in the reaction of MeGeH_3 and $\text{GeCo}_4(\text{CO})_{14}$ has been disproved and it is suggested that the $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ observed in the original study resulted from the reaction of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$.

MeGeH_3 and $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ react together to provide $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}(\text{C})$. This process is postulated to occur via

attack by the methylgermane on the tetrahedral GeCo_3 unit, that is, by a different mechanism from that involved in the $\text{MeGeH}_3/\text{GeCo}_4(\text{CO})_{14}$ system.

High CO pressures on $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ or $(\text{MeHGe})\text{GeCo}_4(\text{CO})_{13}$ appears to result in scission of a Co-Co bond providing semi-open forms of these clusters. The products are unstable at moderate temperatures and pressures.

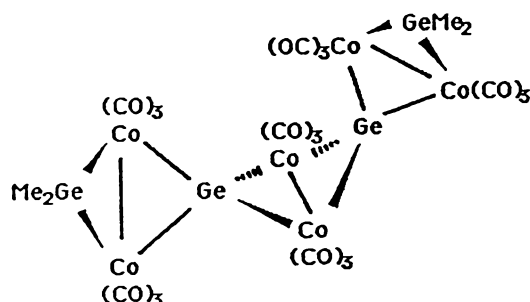
Three new routes to the cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ have been found, each with particular advantages.

CHAPTER 4: Reactions of Mono- and Dimethylgermane with Other Germanium-Cobalt Carbonyl Clusters.

4.1 Background and aim

The reactions of mono- and dimethylgermane with $\text{GeCo}_4(\text{CO})_{14}$ (*B*) (Chapter 3) provided some interesting new products. It was, therefore, desirable to examine the reactions of these hydrides with other available germanium-cobalt carbonyl clusters.

The reaction between Me_2GeH_2 and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) has been briefly studied by Foster [20]. The major product was proposed to be the disubstituted species, $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$, having the structure shown in figure 4.1.



Proposed structure of the major product of reaction between Me_2GeH_2 and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ [20].

Figure 4.1.

This suggestion was supported only by infrared evidence and it was of importance to study this system further. This chapter thus describes a more detailed investigation of the reaction of Me_2GeH_2 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ covering incondensable gas evolution and attempts at characterisation of the major product. A study of the reaction of MeGeH_3 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ is also described here.

The reaction between Me_2GeH_2 and the next homologue of this series, $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (*G*), has also been studied previously [23]. It was reported that the cluster breaks down during the reaction to provide a mixture of products. The infrared spectrum suggested that this included $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (*C*) and the proposed species $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (*F*). The analogous reaction of MeGeH_3 with $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ has now been examined and is reported here.

As described in Chapter 2, a ^1H NMR study was carried out to follow the reaction between excess MeGeH_3 and $\text{Co}_2(\text{CO})_8$. During the reaction it was observed that the product, $\text{MeGeCo}_3(\text{CO})_{11}$ (*A*), was reacting further with the excess MeGeH_3 but the experiment was conducted on too small a scale for the

products of this reaction to be characterised. It was therefore of interest to investigate the reaction of $\text{MeGeCo}_3(\text{CO})_{11}$ with both MeGeH_3 and Me_2GeH_2 and these experiments are described here.

Also included in this chapter is a study of the reactions of Me_2GeH_2 and MeGeH_3 with the three *clos*o clusters, $\text{MeGeCo}_3(\text{CO})_9(H)$, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(J)$ and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(K)$, carried out to determine if these would react with the hydrides in a similar manner to the open-skeleton clusters, or if a different type of process would occur for these species.

4.2. Preparation of starting materials.

The germanium hydrides were prepared as described in section 3.2.

$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was prepared by the reaction of Ge_2H_6 (2.00 mmols by volume) with $\text{Co}_2(\text{CO})_8$ (1.78 g; 5.20 mmols) (1:2.7 ratio) in hexane (20 mls) for 4 weeks [21]. The resulting product mixture, which also contained approximately 10% $\text{GeCo}_4(\text{CO})_{14}$ and 5% $\text{Co}_4(\text{CO})_{12}$ was purified by repeated washings with $\text{CH}_2\text{Cl}_2/\text{hexane}_{(1:1)}$ to provide a 70% yield of pure $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (1.48 g; 1.40 mmols). Purity was checked by comparison of the carbonyl in the infrared spectrum of a hexane solution (2087 (s), 2068 (vs), 2054 (s), 2050 (sh), 2040 (w), 2033 (mw), 2027 (m), 2003 (w), 1848 (sh), 1844 (mw) cm^{-1} [19,20]).

$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ was produced by the reaction of Ge_3H_8 (0.246 g; 1.1 mmols) with $\text{Co}_2(\text{CO})_8$ (0.94 g; 2.75 mmols) (1:2.5 ratio) in hexane (20 mls) for 6 weeks [21]. Again, the resultant product mixture, containing approximately 10% $\text{GeCo}_4(\text{CO})_{14}$, 10% $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and 5% $\text{Co}_4(\text{CO})_{12}$, was purified by washing with $\text{CH}_2\text{Cl}_2/\text{hexane}_{(2:1)}$ to provide a 65% yield of pure $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (1.00 g; 0.71 mmols). Purity was checked by comparison of the carbonyl stretches in the infrared spectrum of a $\text{CH}_2\text{Cl}_2/\text{hexane}_{(1:1)}$ solution (2094 (s), 2073 (s), 2065 (vs), 2053 (s), 2038 (m), 2027 (m), 2011 (sh, w), 1853 (br, w) cm^{-1} [21]).

$\text{MeGeCo}_3(\text{CO})_{11}$ was obtained from the reaction of MeGeH_3 (1.05 mmols by volume) with $\text{Co}_2(\text{CO})_8$ (0.67 g; 1.95 mmols) (1:2 ratio) in hexane (10 mls) for 12 hours. Purification, if necessary, was carried out by fractional crystallisation from a hexane solution cooled to -15°C . This provided a 91% yield of pure $\text{MeGeCo}_3(\text{CO})_{11}$ (0.57 g; 1.0 mmols). Purity was checked by comparison of the carbonyl stretches in the infrared spectrum of a hexane solution (2105 (w), 2082 (s), 2056 (s), 2046 (w, sh), 2030 (s), 2020-5 (m), 2017 (m), 2007 (w), 2003 (w, sh), 1998 (w), 1850 (m), 1838 (w) cm^{-1} [35]).

$\text{MeGeCo}_3(\text{CO})_9$ was produced by heating a solution of $\text{MeGeCo}_3(\text{CO})_{11}$ (0.50 g; 0.87 mmol) in hexane (10 ml) at 50°C for 3 days [38]. $\text{MeGeCo}_3(\text{CO})_{11}$ readily decarbonylates under these conditions to quantitatively provide $\text{MeGeCo}_3(\text{CO})_9$, which needs no purification. Completion of the condensation reaction could be checked by infrared spectroscopy (2108 (m), 2055 (vs), 2045 (s), 2018 (m), 1992 (w) cm^{-1} [38]).

$(\text{Me}_2\text{Ge})\text{Co}_4(\text{CO})_{11}$ was prepared by the reaction of MeGeH_3 (5.5 mmol by volume) with $\text{Co}_4(\text{CO})_{12}$ (0.69 g; 1.2 mmol) (5:1 ratio) in hexane (15 ml) for 8 weeks [32]. Purification was achieved by fractional crystallisation from a hexane solution cooled to -15°C providing a 75% yield of pure $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.65 g; 0.90 mmol). Purity was checked by comparison of the carbonyl stretches in the infrared spectrum of a CH_2Cl_2 /hexane solution (2034 (vs), 2016 (m), 2004 (sh), 1853 (w, br) cm^{-1} [87]).

$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ was prepared by heating a solution of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.76 g; 0.72 mmol) in hexane (10 ml) at 50°C for one week [19, 20]. $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ readily decarbonylates under these conditions to quantitatively provide the closed species. The extent of the condensation could be checked by infrared spectroscopy (2100 (s), 2065 (w, sh), 2050 (s), 2037 (vs), 2014 (m), 2003 (w, sh), 1990 (w, sh), 1844 (w, br) cm^{-1} [19, 20]).

4.3. General experimental techniques

The experiments described in this chapter were carried out in the manner discussed in section 2.3.

4.4. Reactions of Me_2GeH_2 and MeGeH_3 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(E)$.

4.4.1. Experimental Details and Results.

The results of these experiments are summarised in table 4.4 at the end of this section.

Run 1: Me_2GeH_2 (0.82 mmol by volume) and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.043 g; 0.04 mmol) (20:1 ratio) were allowed to react in hexane (10 ml) for 7 weeks at room temperature. Incondensable gases (0.22 mmol) were measured, of composition 43% CO , 57% H_2 . Unreacted Me_2GeH_2 (0.69 mmol) was recovered on fractionation of the volatiles while a trace (ca. 0.02 mmol) remained with the solvent fraction.

The involatile products were separated into two fractions. The first (0.039 g) was soluble in hexane and, as shown in section 4.4.2, the most

reasonable formulation for this species is $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$. Assuming this characterisation, this corresponds to 0.032 mmol, 79% on the basis of initial $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$. The second fraction (0.006 g) was only soluble in CH_2Cl_2 . An infrared spectrum of the carbonyl region of this species in CH_2Cl_2 /hexane showed a broad ill-resolved band centred on 2040 cm^{-1} . This product has not been identified.

Run 2: Me_2GeH_2 (0.50 mmol) and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.099 g; 0.094 mmol) (5:1 ratio) were allowed to react in hexane (15 ml) for 6 weeks at room temperature. Regular incondensable gas evolution measurements were taken and the results of this are shown in table 4.1. The total incondensable gases measured were 0.41 mmol of composition 48% CO, 52% H_2 . Unreacted Me_2GeH_2 (0.30 mmol) was recovered on fractionation of the volatile components.

The involatile products were separated into two fractions. The first was soluble in hexane and was, again, assumed to be $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (0.092 g; 0.08 mmol; 81% yield based on initial $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$). The second (0.015 g) was soluble only in CH_2Cl_2 and showed the same broad ill-resolved band at 2040 cm^{-1} in the carbonyl region infrared spectrum as the unknown species obtained from run 1. This has still not been identified.

Table 4.1. Incondensable gas evolution over time from run 2.

Time interval (days)	Gas evolved (mmol)	%CO	% H_2	Total time (days)	Total gas (mmol)
3	0.115	70	30	3	0.115
4	0.090	55	45	7	0.205
5	0.076	30	70	12	0.281
5	0.045	25	75	17	0.326
7	0.038	35	65	24	0.364
10	0.032	45	55	34	0.396
10	0.014	*	*	44	0.410

* Not measured

Run 3: Me_2GeH_2 (0.05 mmol) and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.010 g; 0.01 mmol) (5:1 ratio) were allowed to react in CDCl_3 (2 ml) at room temperature and the reaction was followed by ^1H NMR spectroscopy. This will be discussed in section 4.4.3.2. After 5 weeks, when the reaction seemed complete, work-up was performed. Incondensable gases were not measured. Unreacted Me_2GeH_2 was observed in the volatiles but was not separated.

The involatile species comprised a hexane soluble fraction (ca. 90%) assumed to be $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ by comparison of the carbonyl stretches in the infrared spectrum, and the same CH_2Cl_2 soluble product (ca. 10%) as observed on the previous two runs.

Run 4: MeGeH_3 (0.71 mmol by volume) and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.104 g; 0.098 mmol) (7:1 ratio) were allowed to react in hexane (10 ml) for 10 weeks at room temperature. Incondensable gases (0.46 mmol) were measured, of composition 51% CO, 49% H_2 . Unreacted MeGeH_3 (0.48 mmol) was recovered from the volatiles with a small amount (ca. 0.01 mmol) remaining with the solvent fraction.

The involatile products were separated into two fractions. The first was soluble in hexane and, as shown in section 4.4.2, the most reasonable formulation of this species is $(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (0.092 g; 0.078 mmol; 80% yield based on initial $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$). The second fraction (0.015 g) was soluble only in CH_2Cl_2 and a carbonyl region infrared spectrum of this species in CH_2Cl_2 /hexane showed a broad, ill-resolved band centred around 2040 cm^{-1} . This product has not been identified.

Run 5: MeGeH_3 (0.55 mmol) and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.058 g; 0.055 mmol) (10:1 ratio) were allowed to react in hexane (10 ml) for 7 weeks at room temperature. Regular incondensable gas measurements were made and the results of this are shown in table 4.2. The total incondensable gases measured were 0.241 mmol, of composition 57% CO, 43% H_2 . Unreacted MeGeH_3 (0.41 mmol) was recovered on fractionation of the volatiles while a small amount (ca. 0.01 mmol) remained with the solvent fraction.

The involatile products yielded three fractions. The first was soluble in hexane and was assumed to be $(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (0.047 g; 0.04 mmol, 72% yield on the basis of initial $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$). The second fraction (0.007 g) was only soluble in CH_2Cl_2 and a carbonyl region infrared spectrum of this species in CH_2Cl_2 /hexane showed the same broad ill-resolved band as observed for the minor product of run 4. This species has still not been identified. The third product (0.006 g) was a dark coloured material, insoluble in both hexane and CH_2Cl_2 , which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a decomposition product and its characterisation was not pursued.

Table 4.2. Incondensable gas evolution over time from run 5.

Time interval (days)	Gas evolved (mmoles)	%CO	%H ₂	Total time (days)	Total gas (mmoles)
3	0.060	80	20	3	0.060
4	0.015	75	25	7	0.075
8	0.084	40	60	15	0.159
5	0.021	35	65	20	0.180
8	0.024	45	55	28	0.204
10	0.017	*	*	38	0.221
15	0.020	85	15	53	0.241

* Not measured

Run 6: MeGeH₃ (0.08 mmoles) and Ge₂Co₆(CO)₂₀ (0.085 g; 0.08 mmoles) (1:1 ratio) were allowed to react in hexane (5 mls) for 34 weeks at room temperature. Incondensable gases (0.228 mmoles) were measured, of composition 51% CO, 49% H₂. Fractionation of the volatile components yielded only solvent.

The involatile products were separated into two fractions. The first (0.003 g) was a dark coloured insoluble material which was assumed to be a decomposition product. The second fraction (0.087 g) was soluble in hexane. An infrared spectrum of this species in hexane was recorded and showed carbonyl stretches corresponding to a mixture of unreacted Ge₂Co₆(CO)₂₀, the product assumed to be (MeGeH)₂Ge₂Co₆(CO)₁₈ and a new species which has been tentatively identified as (MeGeH)Ge₂Co₆(CO)₁₉. The bands, with assignments, are listed in table 4.3. These species could not be separated.

Table 4.3. Carbonyl region infrared data for the product mixture from run 6.

(cm ⁻¹)	
2103 vw	
2097 w-m	
2091 vw	
2086 m	Ge ₂ Co ₆ (CO) ₂₀
2078 w	
2067 w	Ge ₂ Co ₆ (CO) ₂₀ + (MeGeH) ₂ Ge ₂ Co ₆ (CO) ₁₈
2063 vs	
2055 s	
2050 s	
2038 s, br	(MeGeH) ₂ Ge ₂ Co ₆ (CO) ₁₈
2035 sh, s	
2026 m-s	Ge ₂ Co ₆ (CO) ₂₀
2017 m	Ge ₂ Co ₆ (CO) ₂₀
2003 w	Ge ₂ Co ₆ (CO) ₂₀
1844 w, sh	Ge ₂ Co ₆ (CO) ₂₀
1841 m, br	

Recorded in hexane solution

Table 4.4. Summarised results for the reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with Me_2GeH_2 or MeGeH_3 .

Run	Initial ratio	Duration	mmoles of hydride reacted	mmoles of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ consumed	Reacting ratio	Incondensable gas (mmoles)	Yield of involatile products
1 (Me_2GeH_2)	20:1	7 weeks	ca. 0.11	0.04	ca. 2.75:1	0.22 (43% CO)	79 % (Me_2Ge) $_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ 0.006 g CH_2Cl_2 sol. species
2 (Me_2GeH_2)	5:1	6 weeks	0.20	0.094	2.1:1	0.41 (48% CO)	81% (Me_2Ge) $_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ 0.015 g CH_2Cl_2 sol. species
3 (Me_2GeH_2)	5:1	5 weeks	-	0.01	-	-	ca. 90% (Me_2Ge) $_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ ca. 10% CH_2Cl_2 sol. species
4 (MeGeH_3)	7:1	10 weeks	ca. 0.22	0.098	ca. 2.2:1	0.46 (51% CO)	80% (MeGeH) $_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ 0.015 g CH_2Cl_2 sol. species
5 (MeGeH_3)	10:1	7 weeks	ca. 0.13	0.055	ca. 2.4:1	0.24 (57% CO)	72% (MeGeH) $_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ 0.007 g CH_2Cl_2 sol. species 0.006 g decomp. product
6 (MeGeH_3)	1:1	34 weeks	0.08	-	-	0.228 (51% CO)	0.087 g of mixture containing $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, (MeGeH) $_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ + unidentified species 0.003 g decomp. product

4.4.2. The Properties and Tentative Characterisation of the Hexane Soluble Products of the Reaction Between $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and Me_2GeH_2 or MeGeH_3 .

4.4.2.1. Handling

The hexane soluble products obtained from reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with Me_2GeH_2 or MeGeH_3 are both bright orange solids which are stable indefinitely in the absence of air at room temperature. In the presence of oxygen decomposition will occur, however they may be handled in air for short periods with little appreciable decomposition.

The solubility of these two clusters in non-polar solvents such as hexane is much greater than that of the parent cluster, which may be attributed to the addition of hydrocarbon groups. They are, naturally, both very soluble in more polar solvents such as dichloromethane.

The only difference between these two species which was readily observed was their ease of crystallisation. The product of the Me_2GeH_2 system crystallised readily from hexane solution cooled to -30°C . The crystals were, unfortunately, always found to be badly twinned and were thus not suitable for an X-ray crystal structure determination. The product of the MeGeH_3 system, however, was not observed to crystallise from solution under any of the conditions attempted. Any solid which came down from solution tended to be as aggregates of powder. This effect may be attributed to the unsymmetrical nature of the reacting germyl group resulting in the possibility of different isomers and was also observed for $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ (section 3.4.2.1.).

4.4.2.2. Analytical data and possible formulation of the major product of the reactions of Me_2GeH_2 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*).

a) Evidence from the reaction.

Although a large excess of hydride to cluster was used in these reactions most of the Me_2GeH_2 was retrieved at the reaction end. In run 1 the apparent reaction ratio of hydride to cluster was 2.75:1 but the separation of solvent from unreacted hydride may not have been complete. In run 2, where this separation was more rigorous, the reaction ratio was found to be 2.1:1.

The incondensable gas measurements show that hydrogen evolution during the reaction resulted in an average 2.7 mmols of H_2 per mole of cluster reacted.

These values, although somewhat high, could suggest that the major pathway involved in the reaction of Me_2GeH_2 with $Ge_2Co_6(CO)_{20}$ is disubstitution.

b) Electron probe analysis.

The atomic percentage values obtained from the hexane soluble product of the reactions of $Ge_2Co_6(CO)_{20}$ with Me_2GeH_2 were obtained by electron probe analysis. The values are shown in table 4.5.

Table 4.5. Atomic percentage values for the major product of reaction between Me_2GeH_2 and $Ge_2Co_6(CO)_{20}$.

Element	Shell	Atomic percentage
Ge	K	41.8
Co	K	58.2

These values give a Ge:Co ratio of $2:3 \pm 0.13$ which is, again, consistent with disubstitution of the cluster by Me_2GeH_2 .

c) CO content.

A sample of the hexane soluble product from the reaction of Me_2GeH_2 with $Ge_2Co_6(CO)_{20}$ (0.131 g) was heated at $110^\circ C$ for 24 hours, and the evolved CO was measured as 1.81 mmols. An insoluble purple residue remained which could not be removed from the tube.

d) 1H NMR spectroscopy.

The 1H NMR spectrum of the hexane soluble product from the reaction of $Ge_2Co_6(CO)_{20}$ with Me_2GeH_2 showed one singlet at 0.62δ in $CDCl_3$ and at 0.77δ in d_6 benzene. This indicated that all of the protons are in the same average environment and no protons are situated as Ge-H or Co-H in this molecule.

e) Conclusions from the above evidence.

It was unfortunate that this product proved too involatile to allow mass spectroscopy to be employed in its characterisation, however this feature in itself suggests a comparatively high molecular weight. A sample was sent to the University of Adelaide in the hope of obtaining a fast atom bombardment mass spectrum but the compound did not survive transport. Without evidence of a molecular weight or a crystal structure determination it is not possible to characterise this species definitely, however it is certainly possible to propose a reasonable formulation.

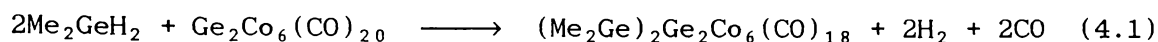
In the previous chapter the reactions of excess Me_2GeH_2 with the smaller homologue of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ yielded $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$. It could thus be anticipated that disubstitution of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ would be the most likely reaction with this hydride.

The evidence from the reaction - reacting ratio and H_2 evolution - and the electron probe analysis suggest that 2 moles of Me_2GeH_2 reacted for each mole of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ consumed. These results are then consistent with the original proposal [20] for the formulation of this species as $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (see section 4.1).

0.131 g of this species decomposed to yield 1.81 mmols of CO. Using the above formulation of the product this corresponds to 16.6 mmols of CO released per mole of $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ decomposing. This value is slightly lower than the expected 18 moles of CO, however a degree of carbide and oxide formation in the residue could be expected. It has been reported [192] that Ca. 90% of CO is evolved during slow heating to decomposition, compared to flow pyrolysis, for transition metal carbonyl silicon compounds. Although this result is not conclusive, as a species containing 17 or 19 CO would be equally possible, it is consistent with the product being $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$.

The ^1H NMR spectrum of this species showed only one singlet indicating that all protons were in the same average environment. Also, no signal corresponding to hydrogen attached directly to a germanium were observed thus only Me_2Ge groups can be present. It is interesting that in d_6 -benzene the resonance was found at 0.77 δ which is exactly the same position as the signal arising for the protons of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ in this solvent. This could suggest that this product is of a similar nature and thus the ^1H NMR spectrum is also consistent with formulation this species as $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$.

As stated earlier, without further evidence no definite conclusions on the structure of this species can be made. It could be useful to attempt these reactions using a different hydride, such as Ph_2GeH_2 , where the larger phenyl groups might help the crystallisation of the product, thus enabling an X-ray crystal structure determination to be carried out. Similarly, further efforts should be made to obtain a fast atom bombardment mass spectrum which would give a molecular weight for this species. However, at this stage, the most reasonable formulation for this product appears to be $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$ which could be formed by the process shown in equation 4.1.



4.4.2.3. Analytical data and possible formulation of the major product from reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ with MeGeH_3 .

a) Evidence from the reaction.

As in the reactions of Me_2GeH_2 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ discussed above, where an excess of MeGeH_3 was employed in reaction with this cluster, the excess hydride was recovered at the reaction end. The reacting ratio of MeGeH_3 to $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was found on average to be 2.1:1. Similarly, the incondensable gas measurements showed hydrogen evolution to be an average 2.1 mmols of H_2 per mole of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ consumed.

These results again suggest disubstitution of the cluster by hydride to be the most likely reaction.

b) Electron probe analysis.

The atomic percentage values obtained from electron probe analysis of the hexane soluble product from the reactions of MeGeH_3 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ are shown in table 4.6.

Table 4.6. Atomic percentage values for the major product of reaction between $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and MeGeH_3 .

Element	Shell	Atomic percentage
Ge	K	39.6
Co	K	60.4

These values give a Ge:Co ratio of $2:3 \pm 0.15$ which again suggests the reaction of 2 moles of MeGeH_3 with one mole of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$.

c) Conclusions from the above evidence.

It was, unfortunately, not possible to obtain as much information on this product as for that obtained from Me_2GeH_2 and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$. However, from the above data it would appear that the reactions proceed analogously giving major products of a similar nature. It was observed in the previous chapter that Me_2GeH_2 and MeGeH_3 reacted very similarly with the smaller homologue of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, to provide $[\text{MeGeR}]_n\text{GeCo}_4(\text{CO})_{14-n}$ ($\text{R} = \text{Me}, \text{H}$ respectively; $n = 1, 2$ depending on initial ratio of hydride to cluster). It thus seems reasonable to suggest that the major product of the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with MeGeH_3 is $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$.

4.4.2.4. Mass balance of these reactions.

If the above characterisations of the major products of these reactions are assumed then it may be stated that $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ reacts with Me_2GeH_2 or MeGeH_3 over a period of weeks to provide $[\text{MeGeR}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$ ($\text{R} = \text{Me}, \text{H}$ respectively) (equation 4.2) in approximately 80% yields.



Table 4.4., which lists summarised results for all of these experiments, shows a reasonable correlation between the reactants consumed and the products obtained. For example, in run 2 0.20 mmols of Me_2GeH_2 was observed to react with 0.094 mmols of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.099 g) producing 0.41 mmols of incondensable gas, of which 52% was H_2 . An 81% yield of $(\text{Me}_2\text{Ge})_2\text{GeCo}_6(\text{CO})_{18}$ (0.092 g) was obtained which corresponds to 0.076 mmols of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.08 g) and 0.15 mmols of Me_2GeH_2 reacting and 0.30 mmols of incondensable gas produced. The remaining 0.018 mmols of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.019 g) and 0.05 mmols of Me_2GeH_2 are likely to have reacted to form the 0.015 g of the CH_2Cl_2 soluble product and the further 0.11 mmols of incondensable gas. The slightly higher ratio of hydrogen to CO in the incondensable gas may arise through this latter reaction, although it is also possible that this is a result of experimental error. A similar mass balance is observed for run 1.

In the MeGeH_3 experiments the amount of reactants consumed also corresponded reasonably with the products obtained. For example, in run 4 0.098 mmols of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.104 g) reacted with approximately 0.22

mmoles of MeGeH_3 producing 0.46 mmoles of incondensable gas of which 49% was H_2 . An 80% yield of $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (0.092 g) was obtained which corresponds to 0.078 mmoles of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.082 g) and 0.16 mmoles of MeGeH_3 reacting and to 0.31 mmoles of produced incondensable gas. The remaining 0.02 mmoles of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.021 g) and 0.06 mmoles of MeGeH_3 are likely to have reacted to produce the 0.015 g of the CH_2Cl_2 soluble product and the further 0.15 mmoles of incondensable gas. A similar mass balance was found for run 5 although a higher ratio of CO to H_2 was observed. This may be accounted for by the small amount of decomposition product obtained from this run.

The fact that these analyses show such good correspondence between the reactants used and the products obtained supports the scheme shown as equation 4.2. It may be stated that even if this formulation is incorrect the products must be of a similar molecular weight to that of the proposed species or the mass balance of these reactions would not be consistent.

4.4.2.5. Carbonyl stretches in the infrared spectra of $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and $(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$.

The carbonyl stretching region of the infrared spectra of $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and $(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ are shown in figure 4.2. The bands are also listed in table 4.7. together with those for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$.

Table 4.7. Carbonyl region infrared data for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and $(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$. (cm^{-1}).

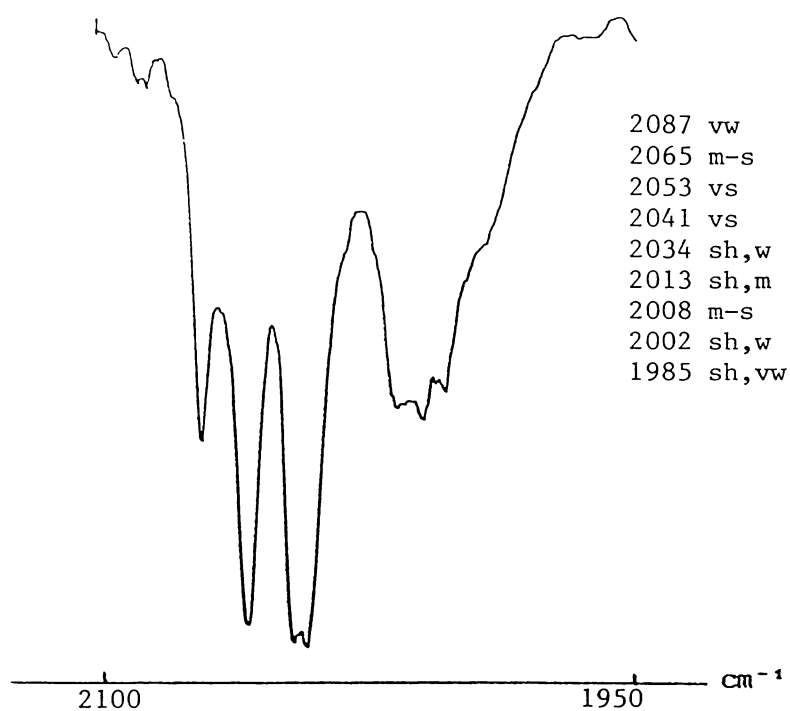
$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	$(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$	$(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$
2081 m	2087 vw	2086 w
	2065 m-s	2071 m-s
2054 vs	2053 vs	2055 vs
2037 vs	2041 vs	2038 vvs
	2034 sh, w	
	2013 sh, m	2022 sh, w
2015 m	2008 m-s	2010 s
2002 m-s	2002 sh, w	2003 sh, w
	1985 sh, vw	1985 sh, vw

All recorded in hexane.

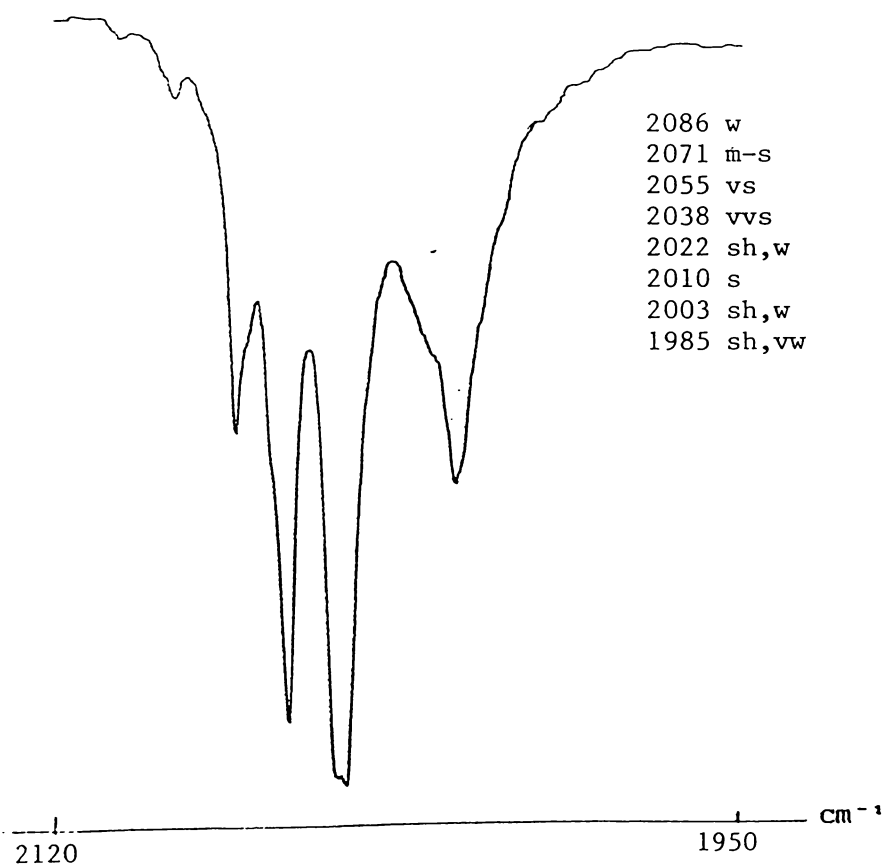
It should be noted that the $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ obtained in this work gave an identical carbonyl region infrared spectrum to that found in the previous study [20].

Figure 4.2. Infrared active carbonyl stretches of
 $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and $(\text{MeHGe})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$.

(a) $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ in hexane.



(b) $(\text{MeHGe})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ in hexane.



The absence of any bands corresponding to bridging carbonyl modes in the infrared spectra of both of these products strongly indicates that the two bridging carbonyl ligands of the parent cluster, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(E)$, have been replaced by germyl groups.

The carbonyl region infrared spectra compare very well with that obtained for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(D)$ thus these products may be anticipated to have a similar structure, as shown in figure 4.3.

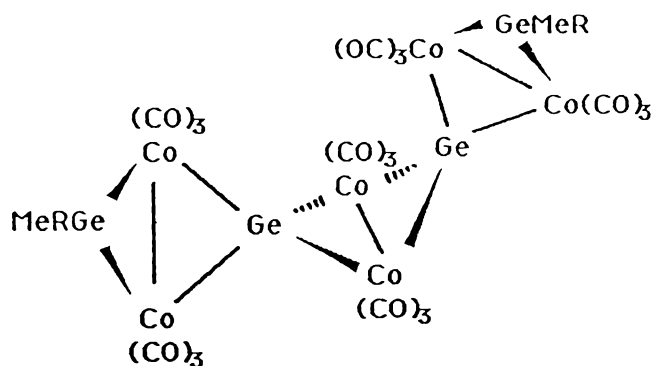
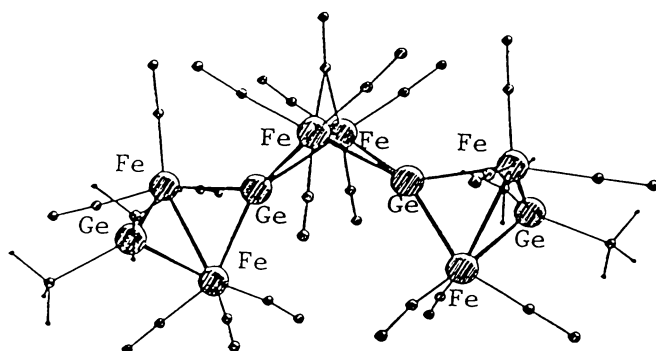


Figure 4.3.

This structure would, ideally, have C_{2v} symmetry where 14 infrared active modes ($5a_1 + 5b_1 + 4b_2$) are predicted. Alternatively these clusters may be of C_s , or lower, symmetry where 18 infrared active modes ($9a' + 9a''$) would be expected. A maximum of 9 bands are observed in the solution spectra, however the major peaks are all quite broad and it is possible that other bands are obscured by overlap.

Further support for the formulation of these species as $(\text{MeGeR})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ may be obtained by comparison of their carbonyl region infrared spectra with that of the recently prepared $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Fe}_6(\text{CO})_{19}$ [82]. This compound has been crystallographically characterised and comprises the expected six GeFe_2 triangles, as depicted in figure 4.4.



Structure of
 $(\text{Me}_2\text{Ge})_2\text{Fe}_6(\text{CO})_{19}$ [82]

Figure 4.4.

The carbonyl stretching vibrations of $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Fe}_6(\text{CO})_{19}$ are listed in table 4.8.

Table 4.8. Carbonyl stretching region infrared data for $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Fe}_6(\text{CO})_{19}$, [82]. (cm^{-1}).

$(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$	$(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Fe}_6(\text{CO})_{19}$
2087 vw	2083 vw
2065 s-vs	2063 s
2053 vs	2045 vs
2041 vs	2035 vs
2034 sh, w	
2013 sh, m	2012 w
2008 m-s	1996 m
2002 sh, w	1989 sh, w
1985 sh, vw	

Both recorded in hexane solution

The very similar pattern of the bands in these two spectra strongly suggests that these two compounds have the same arrangement of carbonyl groups over a similar metal framework.

Replacement of Ge-H by Ge-Me results in a shift to lower frequency by an average 2 cm^{-1} . This corresponds with the direction of the shift observed on moving from $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ to $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ (section 3.4.2.2.), although the magnitude is slightly smaller.

4.4.3. Discussion of the Reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ with Me_2GeH_2 or MeGeH_3 .

4.4.3.1. General

As discussed in the previous section, the best formulation for the major product of the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with Me_2GeH_2 or MeGeH_3 is $[\text{MeGeR}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$ ($\text{R} = \text{Me}, \text{H}$ respectively). As these species are the higher homologues of the products obtained from reactions of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ with an excess of Me_2GeH_2 or MeGeH_3 , $[\text{MeGeR}]_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$, it could be anticipated that the reactions follow a similar path.

The incondensable gas evolution from runs 2 and 5 was followed by regular measurements. The values obtained from this are shown in tables 4.1. and 4.2. In both cases, the typical pattern for overall gas release is observed where evolution is fast in the early stages but slows down towards the reaction end. Also in both cases, it appears that CO release predominates at first while H₂ evolution takes over later. This effect was observed in the reaction of MeGeH₃ and Co₂(CO)₈ (see section 2.5.2.2.) and has been explained by release of the bridging carbonyl group before the hydrogens are lost from the replacing germyl species. The results from run 5 show that CO evolution again seems to dominate at the end of the experiment. This is probably a result of decomposition of (MeGeH)₂Ge₂Co₆(CO)₁₈ to yield the observed dark, insoluble material.

In run 6, which used a 1:1 ratio of MeGeH₃ to Ge₂Co₆(CO)₂₀(E), the products consisted of a mixture of unreacted Ge₂Co₆(CO)₂₀, (MeGeH)₂Ge₂Co₆(CO)₁₈(F) and a new species. This will be discussed in the following section.

On several runs a species insoluble in hexane but soluble in CH₂Cl₂ was observed as a minor product. This compound has not been identified although it is possible that it is a condensation product of (MeGeR)₂Ge₂Co₆(CO)₁₈ (R = Me, H). This would be consistent with its lower solubility compared to (MeGeR)₂Ge₂Co₆(CO)₁₈. The analysis of the mass balance of these reactions (section 4.4.2.3.) showed that, once the (MeGeR)₂Ge₂Co₆(CO)₁₈ species had been accounted for, approximately 3 moles of hydride reacted with 1 mole of cluster to provide the CH₂Cl₂ soluble species. This may indicate the addition of a further germanium group although as this would be expected to increase the solubility of the product some degree of condensation may still have occurred. It should be noted, however, that no significant difference in the product proportions was observed between the open and sealed tube reactions.

The disubstitution of Ge₂Co₆(CO)₂₀ occurs at a faster rate than that of its smaller homologue, GeCo₄(CO)₁₄(B). For example, using an initial ratio of Me₂GeH₂ to Ge₂Co₆(CO)₂₀ of 5:1 the reaction took 6 weeks to reach completion while a reaction of Me₂GeH₂ with GeCo₄(CO)₁₄ having an initial ratio of 10:1 took 15 weeks. Both of these systems were held at room temperature and had similar concentrations. It has been suggested [20] that disubstitution of GeCo₄(CO)₁₄ is not favourable since replacement of one bridging carbonyl by a larger germanium group would expand the substituted Co-Co bond resulting in a contraction of the opposite Co-Co bond. For Ge₂Co₆(CO)₂₀, however, such an expansion by substitution of the bridging carbonyl on one end of the molecule is likely to result in a

contraction of the central Co-Co bond which in turn would encourage lengthening of the third Co-Co bond. This would then promote disubstitution of this cluster.

4.4.3.2. Discussion of the ^1H NMR experiment including evidence for a monosubstituted species $[\text{MeGeR}]\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ ($\text{R} = \text{Me}, \text{H}$).

It is unfortunate that several of the ^1H NMR spectra obtained from run 3 are ill-resolved, however most of the information is still clear. Four of the spectra recorded after 10 minutes, 4 days, 1 week and 5 weeks are shown in figure 4.5(a) to (d).

The large triplet at 0.28δ with a second component at 3.64δ ($J = 3.90 \text{ Hz}$) is attributed to Me_2GeH_2 [154] while the singlet at 4.61δ is assigned to molecular hydrogen.

As a result of the use of CDCl_3 as solvent for this experiment the slow production of Me_2GeHCl was observed during the reaction (doublet at 0.80δ , multiplet at 5.65δ , $J = 2.64 \text{ Hz}$). As also noted in the ^1H NMR experiment between $\text{GeCo}_4(\text{CO})_{14}$ (*B*) and Me_2GeH_2 (section 3.4.3.2.), Me_2GeHCl had no observed effect on the reaction between $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and Me_2GeH_2 and these signals persisted throughout. It is possible that a slow reaction between Me_2GeHCl and the cluster would occur if this were the only reactant present, however it is apparent that reaction with a R_2GeH_2 species is preferred. Alternatively, the presence of Cl may deactivate the germanium group, although MeGeH_2Cl has been observed to react with $\text{GeCo}_4(\text{CO})_{14}$ (*B*) in much the same manner as Me_2GeH_2 [32].

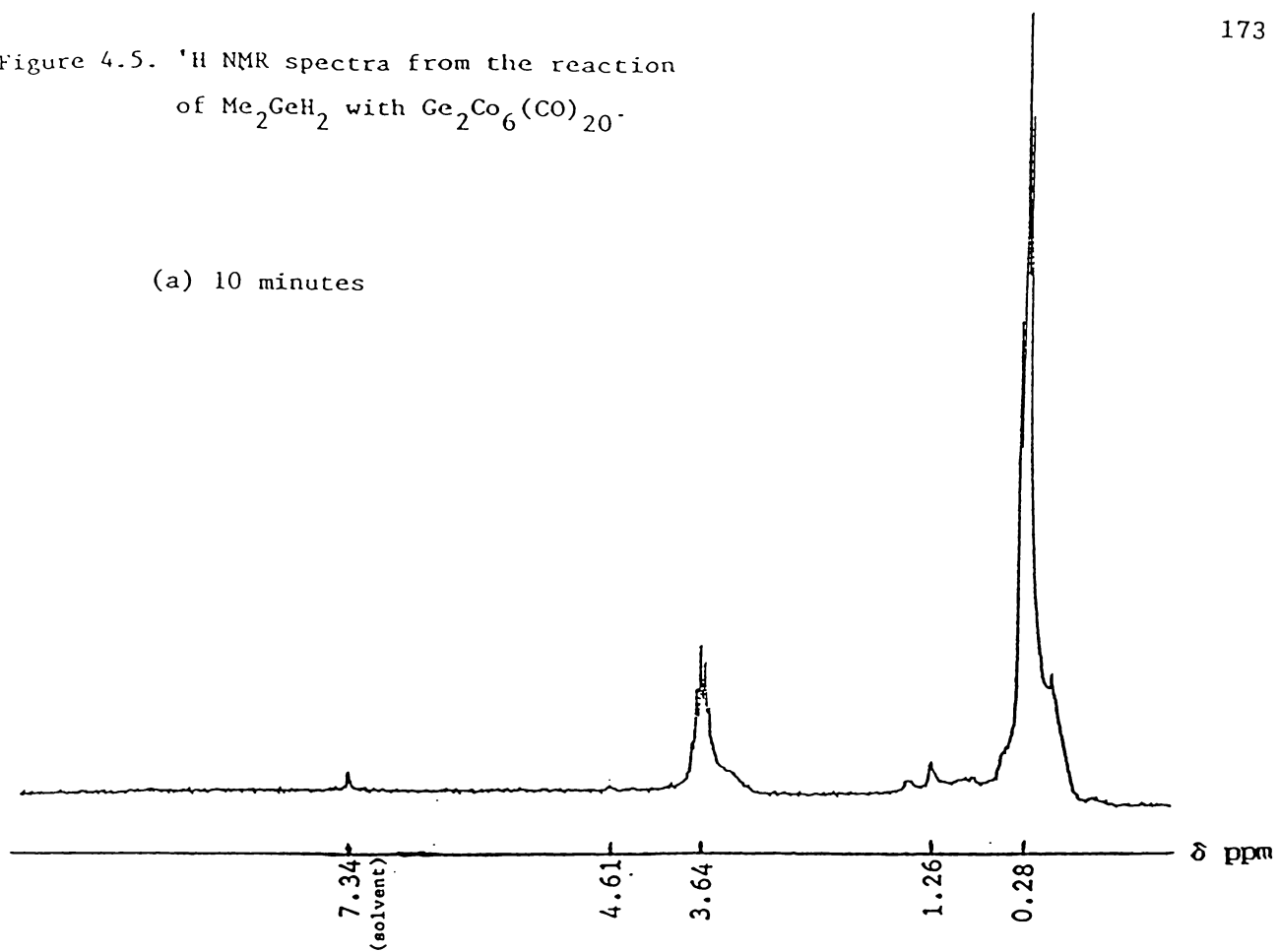
In the final spectrum, recorded after 5 weeks, there are some low intensity singlets in the $\delta\text{C-H}$ region. These presumably result from the products of minor side reactions such as the CH_2Cl_2 soluble species observed on other runs. The low concentration of these, however, makes their characterisation impossible at this stage.

The most important change observed over the course of this experiment was the production of a species giving rise to the singlet at 0.62δ . The ^1H NMR spectrum of $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (*F*) in CDCl_3 was recorded separately and showed a singlet at 0.62δ , thus this peak is assigned to $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (*F*).

Also observed from an early stage in the reaction, although after H_2 production had started, was a low intensity singlet at 1.26δ . The intensity of this did not appear to change during the reaction and it is possible that this peak results from an impurity. It is also possible, however, that this resonance arises from a steady-state concentration of the

Figure 4.5. ^1H NMR spectra from the reaction
of Me_2GeH_2 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$.

(a) 10 minutes



(b) 4 days

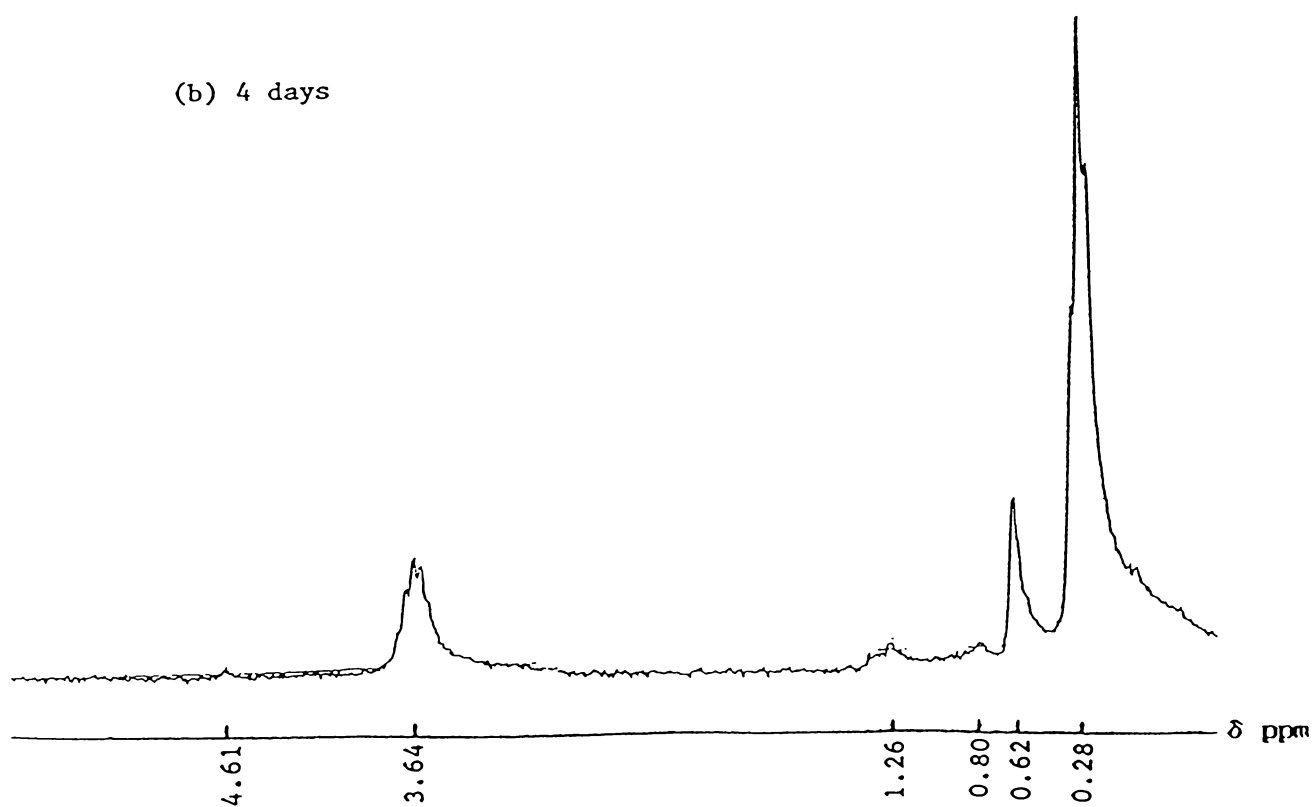
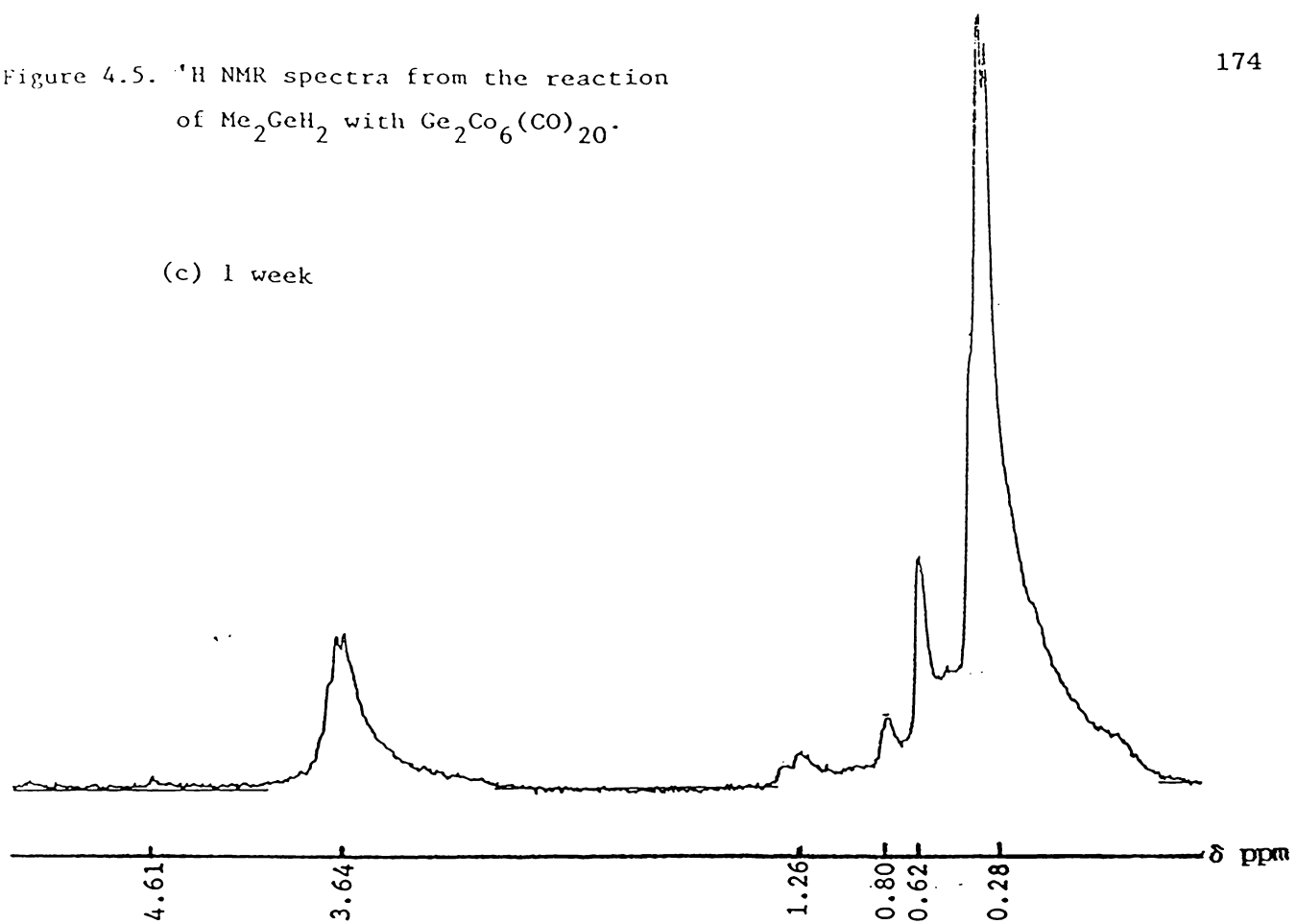
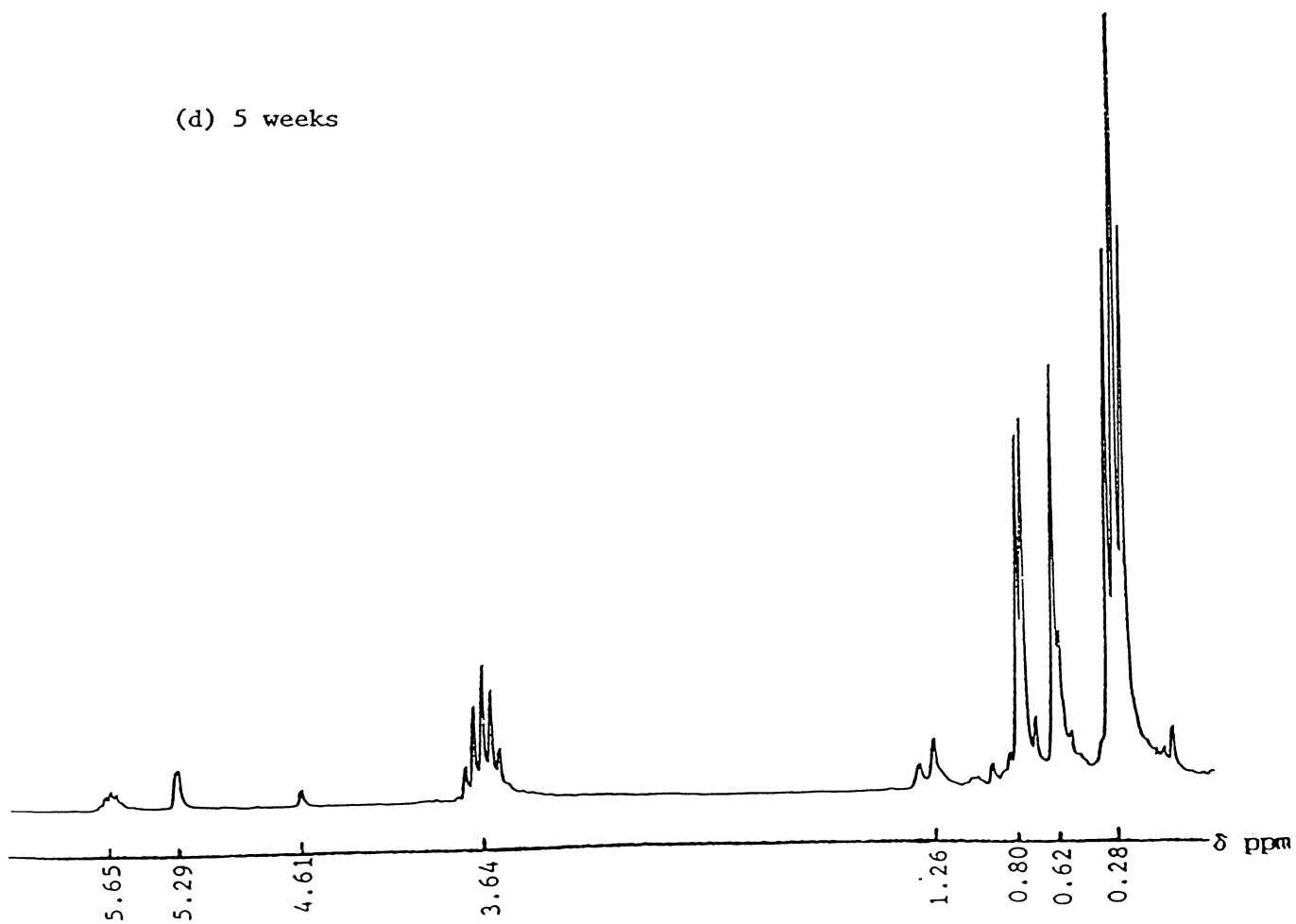


Figure 4.5. ^1H NMR spectra from the reaction
of Me_2GeH_2 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$.

(c) 1 week



(d) 5 weeks



monosubstituted species, $(\text{Me}_2\text{Ge})\text{Ge}_2\text{Co}_6(\text{CO})_{19}$, which is continuously converted to $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$. On workup of the products only $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ was observed but as any other species would only be present as a comparatively small proportion, and as the carbonyl stretching modes of $(\text{Me}_2\text{Ge})\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ are likely to be quite close to those of $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ it is not surprising that this was not noticed. In the ^1H NMR study of the reaction between $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ and Me_2GeH_2 , conducted in d_6 benzene, the monosubstituted derivative, $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$, gave rise to a singlet at 1.13 δ while the methyl protons of the disubstituted species, $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$, were observed at 0.77 δ . Thus the singlet at 1.26 δ in this experiment is in the right region to correspond to $(\text{Me}_2\text{Ge})\text{Ge}_2\text{Co}_6(\text{CO})_{19}$.

Table 4.9 lists the ^1H NMR data obtained from this experiment giving the assignments which have been made.

Table 4.9. ^1H NMR data obtained from run 3.

Signal (δ ppm)	Multiplicity	$J_{(\text{H H})}$ (Hz)	Assignment
0.28 3.64	triplet septet	3.90	Me_2GeH_2 [133]
4.61	singlet	-	H_2
0.80 5.65	doublet septet	2.64	Me_2GeHCl [133]
0.62	singlet	-	$[\text{Me}_2\text{Ge}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$
1.26	singlet	-	$[\text{Me}_2\text{Ge}]\text{Ge}_2\text{Co}_6(\text{CO})_{19}$
0.40	singlet	-	?
0.75	singlet	-	?
0.57	singlet	-	?
5.29	singlet	-	?

In the reaction of $\text{GeCo}_4(\text{CO})_{14}$ with Me_2GeH_2 , the peak arising from $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ gained in intensity at first but, when disubstitution began to predominate, the intensity of this peak was reduced to virtually zero by the reaction end. The singlet arising from $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ increased to become the most intense peak in the spectrum. This suggested a stepwise reaction where the Me_2GeH_2 reacted with $\text{GeCo}_4(\text{CO})_{14}$ to produce

mainly $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ then once little $\text{GeCo}_4(\text{CO})_{14}$ remained in solution the second substitution took place giving $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. Thus the first substitution occurred more readily than the second.

In this experiment, between $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ and Me_2GeH_2 , the very low intensity of the peak attributed to $(\text{Me}_2\text{Ge})\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ at all times suggests that once monosubstitution has occurred the second replacement is very favourable, thus the concentration of the monosubstituted species is never able to build up. These observations are consistent with the earlier suggestion [20] that in $\text{GeCo}_4(\text{CO})_{14}$ disubstitution is less favourable than monosubstitution, while for $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ disubstitution is the favoured process. This effect has been rationalised by changes in bond lengths as described in the previous section. This increased rate of reaction may also be explained by the greater accessibility of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, compared to $\text{GeCo}_4(\text{CO})_{14}$, where the two ends of the molecule may be considered as independent.

Evidence for the formation of a monosubstituted species $[\text{MeGeR}]\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ was also obtained from run 6 where a 1:1 ratio of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ to MeGeH_3 was used. This experiment provided a mixture of unreacted $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and a new species which, unfortunately, could not be separated. The carbonyl region infrared spectrum recorded of the mixture in hexane is shown in figure 4.6. The bands are listed in table 4.10. together with those of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and $[\text{MeGeH}]\text{GeCo}_4(\text{CO})_{13}$.

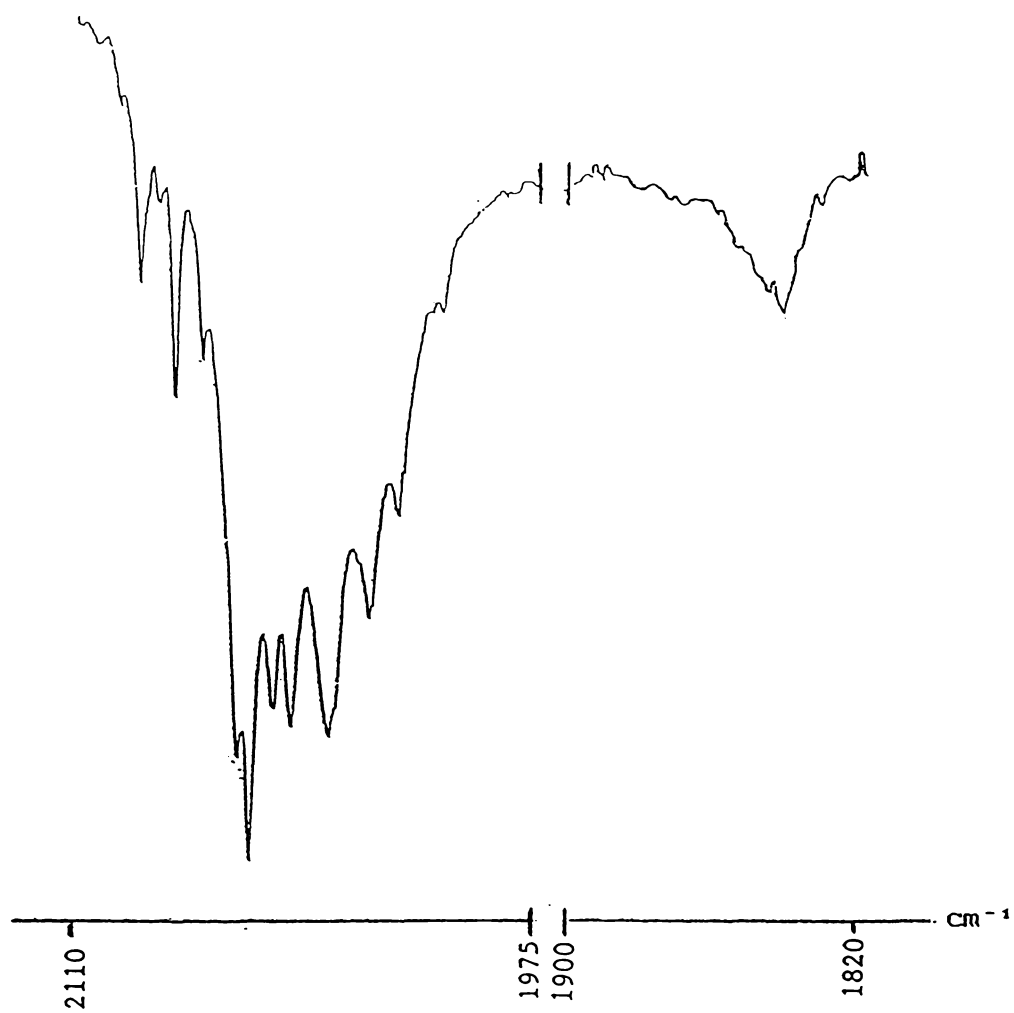


Figure 4.6. Carbonyl region infrared spectrum of the product mixture from run 6.

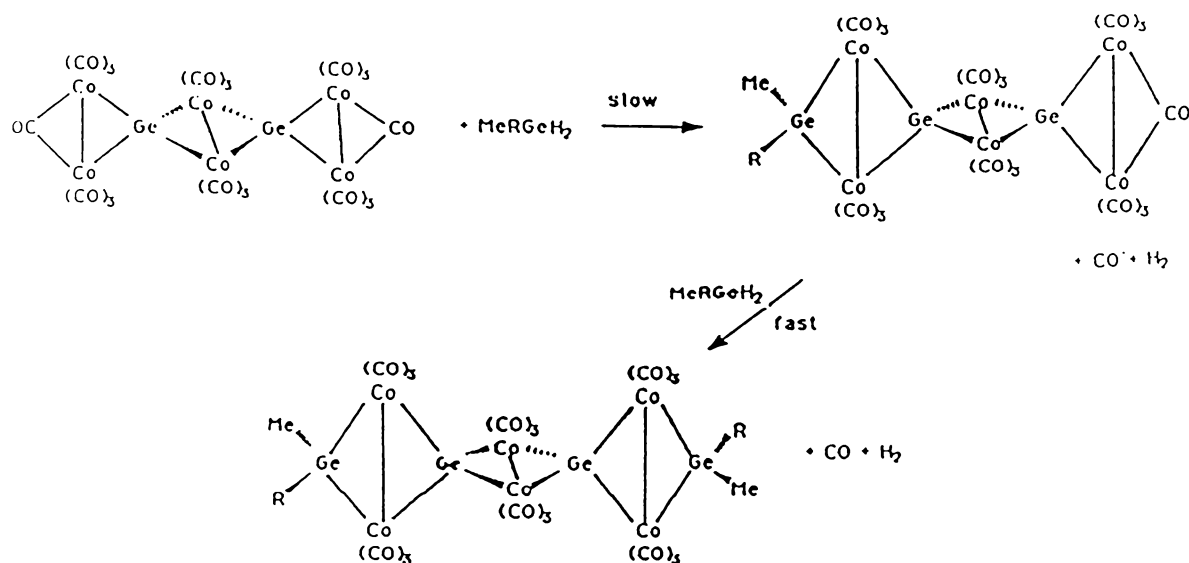
Table 4.10. Carbonyl region infrared data for the product mixture obtained from run 6 together with that for $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ [19, 20], $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and $[\text{MeGeH}]\text{GeCo}_4(\text{CO})_{13}$ [20]. (cm^{-1}).

$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$	$[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$	Product Mix	$[\text{MeGeH}]\text{GeCo}_4(\text{CO})_{13}$
		2097 m	2097 m
		2091 w	
2087 sh		2086 w	
	2086 w	2078 w	
2068 vs		2067 s	2067 vs
	2071 m-s	2063 vs	
2054 s	2054 vs	2055 s	
2050 s		2050 s	
2040 w			2046 vs
2033 mw	2039 vvs	2038 s	
2027 m	2022 vw	2026 m-s	2029 m
	2010 s	2017 m	
2003 w	2003 sh	2003 w	
	1985 sh		
1848 sh			
1844 mw		1844 sh	
		1841 m, br	1841 m

From table 4.10. it is clear that once the bands corresponding to $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ are assigned there are still several not accounted for. These show a reasonable correlation with those of $[\text{MeGeH}]\text{GeCo}_4(\text{CO})_{13}$ [20], the monosubstituted derivative of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$. Thus, the unassigned bands are consistent with this new species being $[\text{MeGeH}]\text{Ge}_2\text{Co}_6(\text{CO})_{19}$.

This reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with MeGeH_3 differs somewhat from the analogous process of $\text{GeCo}_4(\text{CO})_{14}$. For the latter cluster, reaction with MeGeH_3 or Me_2GeH_2 in a 1:1 ratio provided the monosubstituted compound $[\text{MeGeR}]\text{GeCo}_4(\text{CO})_{13}$ as the major product with no disubstitution observed. This resulted in the suggestion that for $\text{GeCo}_4(\text{CO})_{14}$, unless there is sufficient hydride to drive disubstitution, monosubstitution will occur. For $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ however, disubstitution is preferred, even when using comparatively low ratios of hydride to cluster.

These observations allow a pathway for the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with $\text{Me}(\text{R})\text{GeH}_2$ ($\text{R} = \text{H}, \text{Me}$) to be suggested. This is shown in scheme 4.1.



Scheme 4.1.

4.5. Reactions of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ with MeGeH_3 .

4.5.1. Experimental Details and Results.

Run 1: MeGeH_3 (0.57 mmol by volume) and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (0.081 g; 0.06 mmol) (9.5:1 ratio) were allowed to react in CH_2Cl_2 (5 ml) for 45 weeks at room temperature. Incondensable gases (0.38 mmol) were measured, of composition 55% CO , 45% H_2 . Unreacted MeGeH_3 (0.33 mmol) was recovered on fractionation of the volatiles, the remainder of which was solvent.

The involatile components were separated into three fractions. The first (0.035 g) was soluble in hexane giving an orange solution. The second fraction (0.025 g) was insoluble in hexane but fairly soluble in CH_2Cl_2 giving a dark brown solution. The third product (0.026 g) was a dark-coloured material insoluble in both hexane and CH_2Cl_2 . An infrared spectrum of this species recorded as a nujol mull showed no carbonyl vibrations. This was assumed to be a decomposition product and its characterisation was not pursued.

Run 2: MeGeH_3 (0.95 mmol) and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (0.256 g; 0.19 mmol) (5:1 ratio) were allowed to react in CH_2Cl_2 (10 ml) for 16 weeks at 35°C . Incondensable gases (0.92 mmol) were measured, of composition 60% CO , 40% H_2 . Unreacted MeGeH_3 (0.40 mmol) was recovered from the volatiles with a small amount (ca. 0.05 mmol) remaining with the solvent fraction.

The involatile products were as above although present in slightly different proportions. That is, the hexane soluble fraction (0.056 g), the CH_2Cl_2 soluble product (0.11 g) and the insoluble decomposition product (0.11 g).

4.5.2. Tentative Characterisation of the Hexane Soluble Product of the Reaction Between $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ and MeGeH_3 .

4.5.2.1. Handling

The hexane soluble product of these reactions is a dark coloured solid which is stable at room temperature in the absence of air. In the presence of oxygen it will decompose but it may be handled in air for short periods without appreciable decomposition.

This product is fairly soluble in hexane while the parent cluster, $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$, is only slightly soluble in non-polar solvents. This difference may be attributed to the addition of hydrocarbon groups. It is naturally very soluble in dichloromethane.

No success was found in obtaining crystals of this species from any of CH_2Cl_2 solution, CH_2Cl_2 /hexane solution, $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution, or by slow diffusion of hexane into CH_2Cl_2 solution all held at -30°C . It was also found impossible to obtain a mass spectrum of this product as a result of its involatility.

4.5.2.2. Electron probe analysis.

The atomic percentage values obtained for this product by electron probe analysis are shown in table 4.11.

Table 4.11. Atomic percentage for the hexane soluble product from the reaction of MeGeH_3 and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$.

Element	Shell	Atomic Percentage
Ge	K	38.3
Co	K	61.7

These values give a germanium to cobalt ratio of 5:8 which, although not conclusive, is consistent with disubstitution of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ by MeGeH_3 .

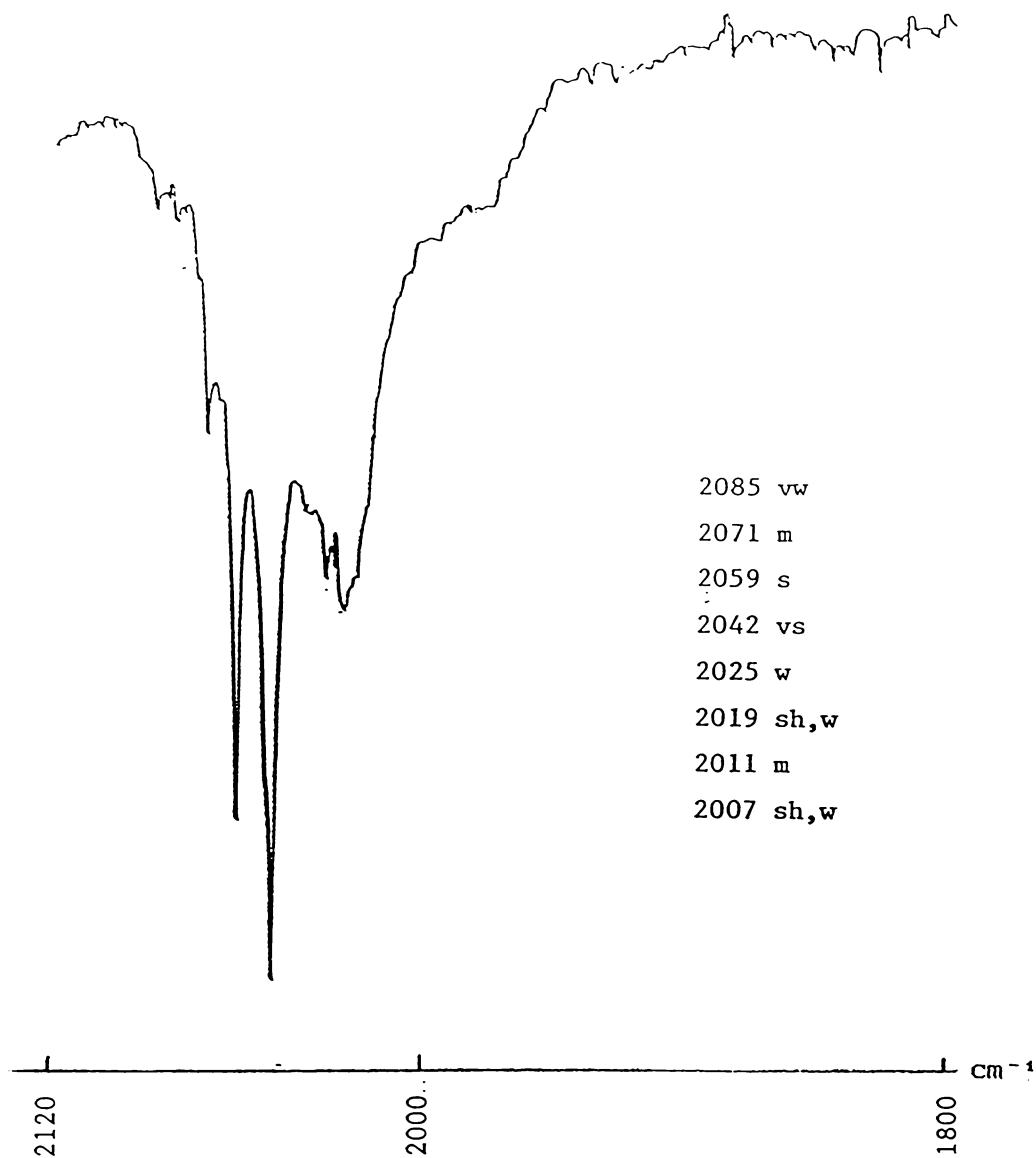


Figure 4.7. Carbonyl region infrared spectrum of the hexane soluble product from the reaction of MeGeH_3 with $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$. Recorded from hexane solution.

4.5.2.3. Carbonyl stretches in the infrared spectrum.

The carbonyl stretches in the infrared spectrum of the hexane soluble product of these experiments are shown in figure 4.7. The bands are listed in table 4.12. together with those of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ and the hexane soluble product obtained from the reaction of MeGeH_3 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$, assumed to be $(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$.

Table 4.12. Carbonyl region infrared data for $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$, $(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ and the hexane soluble product from the reaction of MeGeH_3 with $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$. (cm^{-1}).

$(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$	$(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$	hexane soluble product
2085 w	2086 w	2085 vw
	2071 vs	2071 m
2057 s	2055 vs	2059 s
2041 vs	2038 vvs	2042 vs
2009 sh, w-m	2022 sh, w	2025 w
		2019 sh, w
2007 m	2010 s	2011 m
	2003 sh, w	2007 sh, w
1985 vw	1985 sh, vw	

The study made of the reaction between Me_2GeH_2 and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ [23] reported that the cluster broke down to form a mixture of products including $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$ and $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$. This does not appear to be the case here. The carbonyl region infrared spectrum is not identical with that of any of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$, $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ or $(\text{MeGeH})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$. It is, however, quite similar in pattern and it seems reasonable to suggest that this species is the next homologue in the series - that is, $(\text{MeGeH})_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$.

4.5.2.4. Mass balance of these reactions.

If the above formulation of the hexane soluble product of the reaction between MeGeH_3 and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ is assumed for the moment then the yield of $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ from run 1 was 38% while that from run 2 was 19%, both based on initial $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$.

In run 1 0.06 mmols of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ reacted with 0.24 mmols of MeGeH_3 producing 0.38 mmols of incondensable gas, of which 45% was H_2 . The 38% yield of $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ accounts for 0.023 mmols of the $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$

and 0.046 mmol of MeGeH_3 , and would produce 0.09 mmol of incondensable gas. This then leaves 0.037 mmol (0.052 g) of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ and 0.194 mmol (0.017 g) of MeGeH_3 which must be present in some form in the 0.025 g of the CH_2Cl_2 soluble fraction and the 0.026 g of the insoluble material. This analysis gives a reacting ratio of hydride to cluster of approximately 5:1 in the formation of the latter two species. This seems very high and it is possible that the initial amount of MeGeH_3 was overestimated or some remained with the solvent during fractionation of the volatiles. It is also possible that some may have decomposed during the reaction and the remaining germanium was present among the insoluble material.

The amount of incondensable gas evolved from run 1 is lower than would be anticipated if the insoluble residue were completely carbonyl free. 0.046 mmol of CO would be produced in the formation of $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ which leaves 0.163 mmol of CO to be accounted for. This corresponds to less than 3 moles of CO released per mole of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ reacting to provide the insoluble residue and the CH_2Cl_2 soluble material, thus although no carbonyl vibrations were found in the infrared spectrum of the insoluble product some must have been present and were merely of too low an intensity to be observed.

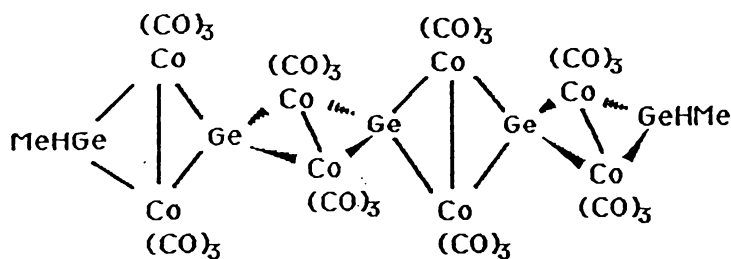
Hydrogen evolution from run 1 resulted in 0.171 mmol of H_2 , of which 0.046 mmol were produced in the formation of $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$. A further 0.194 mmol of MeGeH_3 were found to have reacted although, as stated above, this figure may have been overestimated. If it is accepted at present, however, then at least some of the reacted MeGeH_3 must be present in the CH_2Cl_2 soluble fraction and/or the insoluble material as MeGeH_2 . The comparatively low solubility of these products suggests they may be condensation products and it is possible that the hydrogen released from the reacting MeGeH_3 is involved in the cluster interstitially or as a bridging group.

The overall mass balance of run 2 is again reasonable although the products were obtained in somewhat different proportions. Approximately 0.4 mmol of MeGeH_3 and 0.19 mmol of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ reacted to provide 0.92 mmol of incondensable gas, of which 40% was H_2 . After accounting for the 19% yield of $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$, 0.33 mmol of MeGeH_3 and 0.154 mmol of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$, a total of 0.25 g, remained in the form of the 0.11 g of the CH_2Cl_2 soluble fraction and the 0.11 g of the insoluble material. This gives an approximate reactant ratio of hydride to cluster of 2:1 which is much lower than that found for run 1.

Presumably as a result of the higher temperature under which this run was conducted, a proportionally larger amount of incondensable gas was found compared to that for run 1. After accounting for the gas produced in the formation of $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ then 0.298 mmols of H_2 and 0.482 mmols of CO must be evolved during the reaction between the remaining MeGeH_3 and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ to form the CH_2Cl_2 soluble product and the insoluble material. The amount of evolved H_2 corresponds to the remaining 0.33 mmols of reacted MeGeH_3 which, although to a lesser degree than in the previous run, again suggests the presence of hydrogen other than the expected MeGeH groups within these products. The amount of produced CO relates to the remaining 0.154 mmols of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ again giving approximately 3 moles of CO released for each mole of reacting $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$.

4.5.3. Discussion of the Reactions of MeGeH_3 with $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$

On the basis of the results of electron probe analysis and carbonyl region infrared spectroscopy and the similar handling characteristics to $[\text{MeGeH}]_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ and the product tentatively characterised as $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$, the hexane soluble product obtained from the reaction of MeGeH_3 with $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ has been tentatively formulated as $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$. This species is the higher homologue in the series of these disubstituted germanium-cobalt carbonyl clusters and is suggested to arise through replacement of the two bridging carbonyls by MeGeH groups giving the structure shown in figure 4.8.



Proposed structure of hexane soluble product
obtained from reaction of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ with MeGeH_3 .

Figure 4.8.

The CH_2Cl_2 soluble fraction was not identified, however the discussion of the mass balance of these reactions led to the proposal that some hydrogen other than the expected MeGeH groups was involved in the product.

The lower solubility of this species could suggest that it has a *closo* structure which might arise through condensation of $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ or of some other species. This could then be a hydrido cluster which would account for the remaining hydrogen. The carbonyl stretches in the infrared spectrum of the CH_2Cl_2 soluble fraction are listed in table 4.13.

Table 4.13. Carbonyl stretches in the infrared spectrum of the CH_2Cl_2 soluble fraction from the reaction of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ with MeGeH_3 (cm^{-1}).

2084 w
2052 s
2038 s
2013 m
2005 w, sh

Recorded in CH_2Cl_2 /hexane.

The simplicity of this spectrum supports the suggestion that this product has a *closo*-structure.

The nature of the insoluble species is unknown at this stage.

It should be noted that the use of CH_2Cl_2 as the solvent for these reactions may have introduced some complications as chlorinated hydrocarbon solvents are known to exchange chlorine with hydrogen on germanium hydrides [147]. CH_2Cl_2 does not donate chlorine as readily as CCl_4 or CHCl_3 , however it is possible that MeGeCl , MeGeHCl or MeGeCl_2 groups are present in the products. The electron probe analysis of the hexane soluble product did not show the presence of chlorine thus the characterisation of this species as $(\text{MeGeH})_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ seems the most likely. The dichloromethane soluble product, however, may well contain chlorine.

These experiments have given different results from those of the previous study of the $\text{Me}_2\text{GeH}_2/\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ system [23]. This could be due to the use of the different hydride, although it is possible that the hexane soluble material observed in the original study, which was characterised by infrared spectroscopy as a mixture of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$ and $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$, was in fact a mixture of $(\text{Me}_2\text{Ge})_2\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ and a second species which gave a carbonyl region infrared spectrum similar to the former mixture.

Clearly, further study of both of these systems is required to clarify the reaction process and fully characterise the products. It would be worthwhile to attempt these reactions using a different hydride, for example Ph_2GeH_2 , which could aid in the crystallisation of the resulting products

thus allowing X-ray crystallography to be utilised in their characterisation.

At this stage, however, it may be stated that $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ appears to react with MeGeH_3 to provide $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$, the higher homologue of $[\text{MeGeH}]_2\text{GeCo}_4(\text{CO})_{14}$ (*D*) and $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (*F*), in low yield, together with some other products suggested to be *closo* species.

4.6. Reactions of Me_2GeH_2 and MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_{11}$ (*A*)

4.6.1. Reaction of Me_2GeH_2 with $\text{MeGeCo}_3(\text{CO})_{11}$ (*A*)

4.6.1.1. Experimental details and results.

Me_2GeH_2 (0.45 mmol by volume) and $\text{MeGeCo}_3(\text{CO})_{11}$ (0.091 g; 0.159 mmol) (3:1 ratio) were allowed to react in hexane (5 ml) for 22 weeks at room temperature. Incondensable gases (0.493 mmol) were measured, of composition 34% CO , 66% H_2 . Unreacted Me_2GeH_2 (0.28 mmol) was recovered on fractionation of the volatiles, the remainder of which was solvent.

Removal of solvent from the involatile products left an oil. This was dissolved in hexane giving a bright yellow-orange solution. A carbonyl region infrared spectrum of this solution was recorded which showed a mixture of products but no unreacted $\text{MeGeCo}_3(\text{CO})_{11}$. The solvent was removed and the mixture pumped under vacuum through liquid nitrogen for 24 hours. A carbonyl region infrared spectrum in hexane was again recorded which showed a slight lowering of intensity of some of the peaks. A volatile species was found in the liquid nitrogen trap and was characterised by infrared spectroscopy as $\text{Me}_2\text{GeHCo}(\text{CO})_4$ (0.011 g; 0.04 mmol) [152]. From the infrared spectrum of the product mixture it appeared that a small amount of this species still remained and the mixture of products still appeared as an oil. These could not be separated by either extraction or fractional crystallisation. Table 4.14. lists the observed bands of the product mixture together with those reported for $\text{Me}_2\text{GeHCo}(\text{CO})_4$ [152], $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ [17] and $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ [20].

Table 4.14. Carbonyl region infrared data for the products of reaction between Me_2GeH_2 and $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ together with those of $\text{Me}_2\text{GeHCo}(\text{CO})_4$, $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ and $\text{Me}_2\text{GeCo}_2(\text{CO})_7$. (cm^{-1}).

Product Mixture (a)	Volatile sample (b)	Remaining mixture (a)	$\text{Me}_2\text{GeHCo}(\text{CO})_4$ [152] (b)	$(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ [17] (c)	$\text{Me}_2\text{GeCo}_2(\text{CO})_7$ [20] (a)
2097 s	2097 s	2093 s	2097 s		2088 s
2082 w		2082 w			
2071 m		2071 m		2072 m	
2064 s		2065 s			
2052 m		2053 m			2048 s
2036 sh, vs	2045 vs	2037 sh, vs	2045 vs		
2034 vvs, br		2034 vvs, br		2035 vs	2026 vs
2013 vvs, br	2015 vvs	2014 vvs, br	2013 vvs	2014 vs	
2009 vvs, br	2008 vvs	2009 vvs, br	2008 vvs		2008 vs
1993 vs, br		1993 vvs		1994 vs	1998 sh, w
		1997 m	1997 m	1984 m	1965 sh, w
	1965 w		1968 m	1964 vw	
1840 w		1840 w			1841 m-s

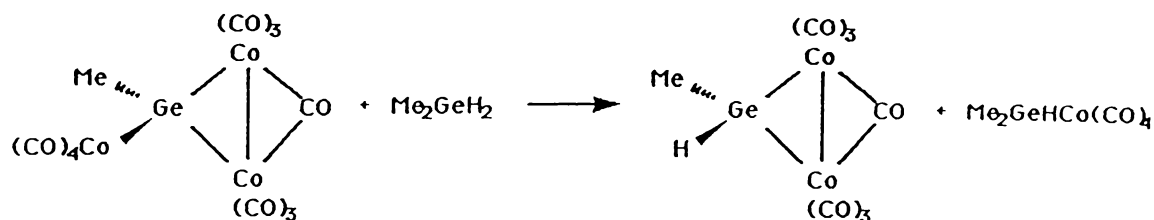
- (a) Recorded from hexane solution
 (b) Recorded as a gas
 (c) Recorded from cyclohexane solution

4.6.1.2. Discussion of the product mixture obtained from the reaction of Me_2GeH_2 with $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$.

From table 4.14. it can be seen that a complicated mixture of product was obtained from the reaction of Me_2GeH_2 with $\text{MeGeCo}_3(\text{CO})_{11}$. The only species which was at least partially separated from this mixture was $\text{Me}_2\text{GeHCo}(\text{CO})_4$ (0.011 g; 0.04 mmoles) which was removed by pumping under vacuum into a liquid nitrogen trap. The infrared spectrum of the remaining mixture showed little change thus it may be assumed that $\text{Me}_2\text{GeHCo}(\text{CO})_4$ contributed little to the first spectrum. The product mixture must, therefore, contain an involatile $\text{Ge-Co}(\text{CO})_4$ species to account for the strong band at 2097 cm^{-1} which is likely to result from an a' mode of this group (see section 1.4.1.1.).

The carbonyl stretches of $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ [17] and $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ [20] are shown in table 4.14 and it can be seen that these match some bands of the product mixture quite closely and it is thus possible that these are both produced to some degree in the reaction of Me_2GeH_2 with $\text{MeGeCo}_3(\text{CO})_{11}$.

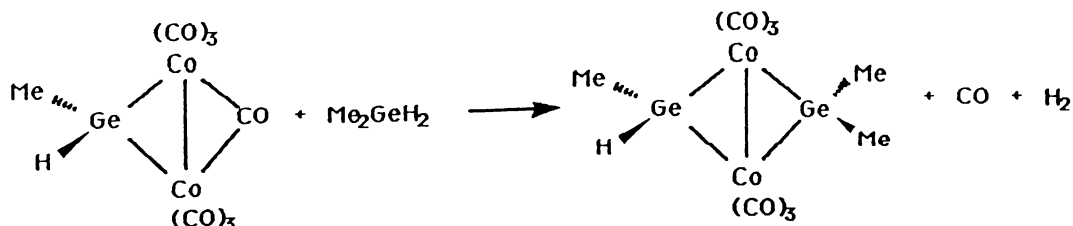
The production of $\text{Me}_2\text{GeHCo}(\text{CO})_4$ must result by some breakdown of $\text{MeGeCo}_3(\text{CO})_{11}$ - possibly by an abstraction of a terminal $\text{Co}(\text{CO})_4$ unit from the cluster as shown in scheme 4.2.



Scheme 4.2.

$[\text{MeGeH}]\text{Co}_2(\text{CO})_7$ would show similar carbonyl vibrations to $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and this compound may be present in the mixture rather than $\text{Me}_2\text{GeCo}_2(\text{CO})_7$, although the presence of both products is quite possible.

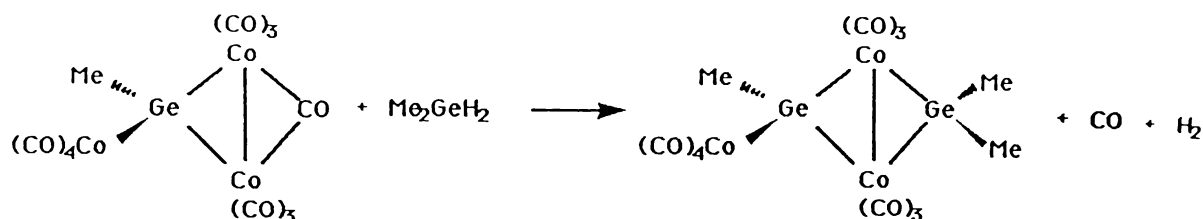
Similarly, $[\text{Me}(\text{H})\text{Ge}]\text{Co}_2(\text{CO})_7$ could react with Me_2GeH_2 as shown in scheme 4.3.



Scheme 4.3.

This product would be expected to give rise to similar carbonyl vibrations to $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$, thus it could be this compound that is present in the mixture rather than $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$.

It is also possible that Me_2GeH_2 reacts directly with $\text{MeGeCo}_3(\text{CO})_{11}$ replacing the bridging carbonyl as shown in scheme 4.4.



Scheme 4.4.

The presence of this species in the product mixture would account for the 2097 cm^{-1} band as this would arise through vibrations of the terminal $\text{Co}(\text{CO})_4$ unit carbonyls. This species would also provide a good source of terminal $\text{Co}(\text{CO})_4$ units for abstraction by Me_2GeH_2 and this may be a major route for formation of $\text{Me}_2\text{GeHCo}(\text{CO})_4$.

It would have been useful to record the ^1H NMR spectrum of this product mixture which might have suggested the number of different species present. Unfortunately, before this could be carried out the product mixture had decomposed.

4.6.1.3. General discussion of the reaction between Me_2GeH_2 and $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$.

The overall mass balance of this reaction shows one major discrepancy. 0.45 mmols of Me_2GeH_2 were used initially while at the reaction end 0.28 mmols were recovered, leaving 0.17 mmols of reacted Me_2GeH_2 . However, from the incondensable gas measurements, 0.32 mmols of H_2 were evolved. This is, of course, impossible if only 0.17 mmols of Me_2GeH_2 were reacting thus at least one of these values must be inaccurate. It has been found that the incondensable gas measurements are usually reliable to within 10% which is not a large enough error to compensate for this difference. The measurement of recovered Me_2GeH_2 , however, could easily have been overestimated by the presence of some solvent in this fraction. Thus, for this discussion, the hydrogen measurement will be regarded as accurate, while the amount of recovered Me_2GeH_2 will be ignored.

The amount of produced H_2 suggested approximately 2 moles of hydride reacting for each mole of cluster consumed. The 0.04 mmols of

$\text{Me}_2\text{GeHCo}(\text{CO})_4$ corresponds to approximately $\frac{1}{4}$ of the available terminal $\text{Co}(\text{CO})_4$ units. Thus approximately 0.04 mmols of $[\text{MeGeH}]\text{Co}_2(\text{CO})_7$ could be produced. This process would not account for any incondensable gas.

Reaction of the remaining amount of $\text{MeGeCo}_3(\text{CO})_{11}$ (0.068 g; 0.119 mmols) with Me_2GeH_2 to provide $[\text{MeGeCo}(\text{CO})_4]\text{Co}_2(\text{CO})_6[\text{GeMe}_2]$ would yield 0.24 mmols of incondensable gas. Even if complete reaction of the $[\text{MeGeH}]\text{Co}_2(\text{CO})_7$ with Me_2GeH_2 then took place only 0.08 mmols of incondensable gas would be produced which gives a total of only 0.32 mmols (1:1 CO to H_2). This value corresponds quite well to the 0.17 mmols of evolved CO, however some other process must be involved to account for the further 0.17 mmols of evolved H_2 . No explanation for this feature has been found.

4.6.2. Reaction of MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$.

4.6.2.1. Experimental details and results.

MeGeH_3 (2.43 mmols by volume) and $\text{MeGeCo}_3(\text{CO})_{11}$ (0.346 g; 0.60 mmols) (4:1 ratio) were allowed to react in hexane (5 mls) for 1 year at room temperature. Incondensable gases (1.13 mmols) were measured of composition 40% CO, 60% H_2 . Unreacted MeGeH_3 (1.7 mmols) was recovered on fractionation of the volatiles while a small amount (ca. 0.1 mmols) remained with the solvent fraction.

In the absence of solvent the involatile products appeared as an oil. These were soluble in hexane giving a bright orange solution. A carbonyl region infrared spectrum of these products in hexane was recorded. This showed the presence of a small amount of unreacted $\text{MeGeCo}_3(\text{CO})_{11}$ as well as some other species. These could not be separated by either extraction or fractional crystallisation. The observed bands are listed in table 4.15. together with those reported for $\text{MeGeCo}_3(\text{CO})_{11}$ [35, 36] and $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ [31].

Table 4.15. Carbonyl region infrared data for the products of reaction between MeGeH_3 and $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, together with that reported for $\text{MeGeCo}_3(\text{CO})_{11}$, and $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$. (cm^{-1}).

Product Mix (a)	$\text{MeGeCo}_3(\text{CO})_{11}$ [35, 36]	(b)	$[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ [31]	(a)
2102 m		2104 w		
2094 s				2097 w
2083 vs				2087 s
2079 w, sh		2080 s		
2073 s				
2070 w, sh				
2065 s				2067 m
2053 w, sh		2055 s		
		2044 w		2042 w
2038 vs, br		2036 s		2039 m
		2025 m		
2017 vs, br		2014 m		2017 s
		1998 w		2002 w
				1989 w
1966 w, sh				1970 w
1954 w, sh				
1847 w		1847 m		
1834 vw, sh		1834 w, sh		

(a) Recorded from hexane solution

(b) Recorded from cyclohexane solution

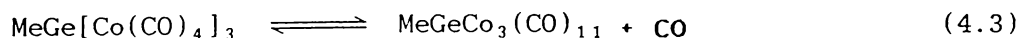
A portion of the product mixture from the reaction of MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_{11}$ (0.131 g) was allowed to react with $\text{Co}_2(\text{CO})_8$ (0.04 g; 0.12 mmols) in hexane (5 mls) for 20 weeks at room temperature. Incondensable gases could not be measured because of a leak in the Toepler pump apparatus. The volatiles were not examined.

The reaction vessel contained an orange-brown solution which was decanted away from a large number of red brown crystals. The solution was found to contain a small amount of unreacted $\text{Co}_2(\text{CO})_8$ and $\text{MeGeCo}_3(\text{CO})_{11}$, and a reasonable quantity of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ characterised by infrared spectroscopy [35, 36, 87]. The carbonyl stretches in the infrared spectrum of the crystals in CH_2Cl_2 /hexane solution showed them to be $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.058 g; 0.08 mmols). This was confirmed by mass spectroscopy [20, 87].

4.6.2.2. Discussion of the product mixture obtained from the reaction of MeGeH_3 and $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$.

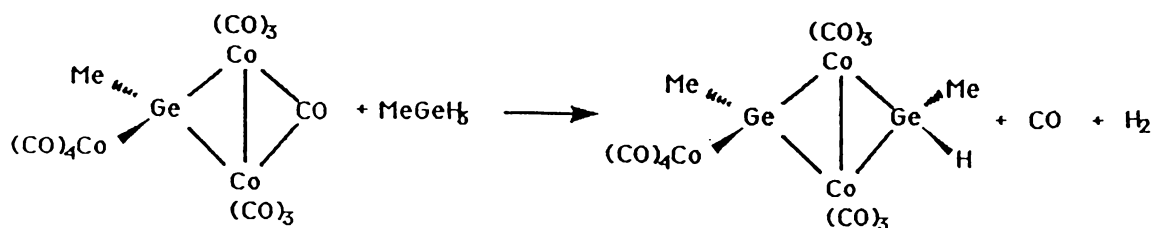
From table 4.15 it appears that the reaction of $\text{MeGeCo}_3(\text{CO})_{11}$ with MeGeH_3 gives rise to a mixture of products. It is possible that some unreacted $\text{MeGeCo}_3(\text{CO})_{11}$ still remains even after a year of reaction. This feature is surprising, particularly in light of the ^1H NMR experiment conducted to follow the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ in a 4:1 ratio (see section 2.5.2.3.) where it was observed that after 3 days of reaction all of the produced $\text{MeGeCo}_3(\text{CO})_{11}$ had reacted further with the excess MeGeH_3 . It is possible that this reaction involves breakdown of the cluster to some degree and over this long reaction time the fragments are reforming $\text{MeGeCo}_3(\text{CO})_{11}$. It is equally possible that the system under study here was of lower concentration and under lower pressure thus the rate of reaction may just have been very much slower.

$\text{MeGe}[\text{Co}(\text{CO})_4]_3$ may also be present in the product mixture. This species shows strong carbonyl bands in the infrared spectrum at 2084, 2020 and 2012 cm^{-1} [20]. The phenyl equivalent of $\text{MeGeCo}_3(\text{CO})_{11}$ is known to open out to $\text{PhGe}[\text{Co}(\text{CO})_4]_3$ under CO pressure [37]. Similarly, reactions of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ - which under normal conditions provides $\text{MeGeCo}_3(\text{CO})_{11}$ - conducted under CO pressure yielded $\text{MeGe}[\text{Co}(\text{CO})_4]_3$ [20]. It is possible that, here, $\text{MeGeCo}_3(\text{CO})_{11}$ reacted with evolved CO to form $\text{MeGe}[\text{Co}(\text{CO})_4]_3$. This suggestion is supported by the recording of the carbonyl stretches of the product mixture some months after work-up which showed a reduction in intensity of the bands corresponding to $\text{MeGe}[\text{Co}(\text{CO})_4]_3$ and an increase in the intensity of those assigned to $\text{MeGeCo}_3(\text{CO})_{11}$. This is consistent with the decarbonylation of $\text{MeGe}[\text{Co}(\text{CO})_4]_3$ as shown in equation 4.3.



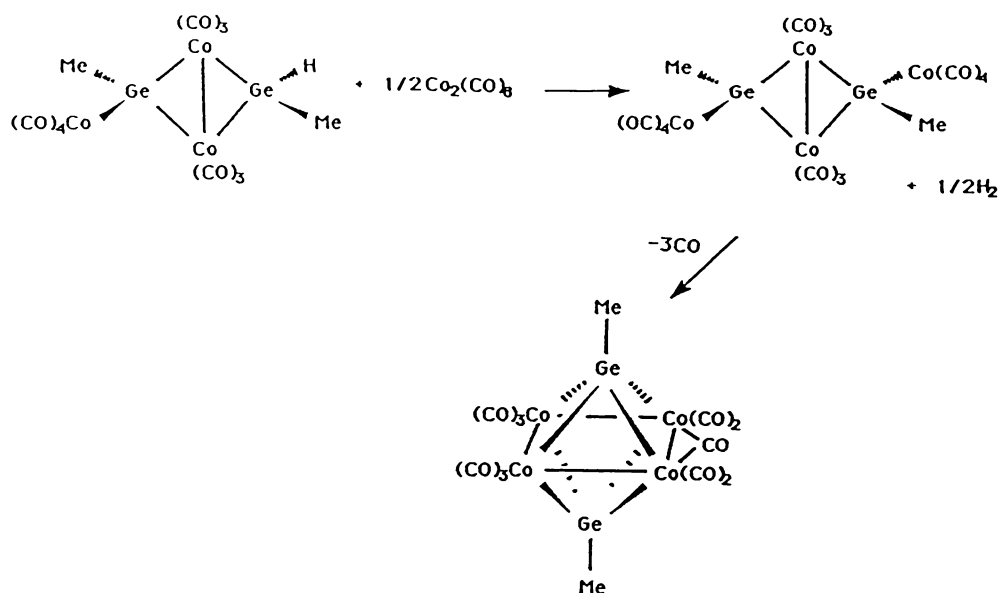
It is, however, equally possible that it is some other species which is breaking down or rearranging to form $\text{MeGeCo}_3(\text{CO})_{11}$.

Several of the carbonyl bands observed in the infrared spectrum of the product mixture have not been assigned to known species. From table 4.15. it can be seen that at least some of these bands correspond reasonably with those reported for $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ [31]. It is thus proposed that the major process occurring in the reaction of $\text{MeGeCo}_3(\text{CO})_{11}$ with MeGeH_3 is replacement of the bridging carbonyl to form $[\text{MeGeH}]\text{Co}_2(\text{CO})_6[\text{MeGeCo}(\text{CO})_4]$ as shown in scheme 4.5.



Scheme 4.5.

This suggestion is supported by the further reaction of the product mixture with $\text{Co}_2(\text{CO})_8$. This system mainly provided $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ which could be envisaged to arise via the process shown in scheme 4.6.



Scheme 4.6.

The production of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ by condensation of $[\text{MeGeCo}(\text{CO})_4]\text{Co}_2(\text{CO})_6$ is known [31].

4.6.2.3. General discussion of the reaction of MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$.

Approximately 0.63 mmols of MeGeH_3 were found to have reacted with a maximum of 0.6 mmols of $\text{MeGeCo}_3(\text{CO})_{11}$. From the carbonyl region infrared spectrum it may be estimated that approximately 10% of the starting cluster remained in solution as either unreacted $\text{MeGeCo}_3(\text{CO})_{11}$ or $\text{MeGe}[\text{Co}(\text{CO})_4]_3$. This would then suggest that 0.54 mmols of $\text{MeGeCo}_3(\text{CO})_{11}$ reacted with ca. 0.63 mmols of MeGeH_3 giving a reacting ratio of 1:1.2.

The incondensable gas measurements showed that 0.68 mmoles of H_2 and 0.45 mmoles of CO were evolved during the reaction. If it is considered that a small amount of the evolved CO was involved in the carbonylation of $MeGeCo_3(CO)_{11}$ to give $MeGe[Co(CO)_4]_3$ then these results agree within reasonable experimental error.

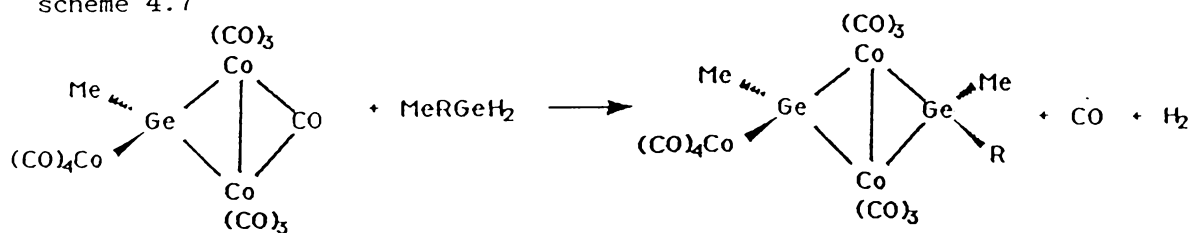
In the further reaction of the product mixture with $Co_2(CO)_8$ the incondensable gases were not measured thus the mass balance of this system cannot be analysed.

4.6.3. Comparison of the Reactions of Me_2GeH_2 or $MeGeH_3$ with $MeGeCo_3(CO)_{11}(A)$.

The reaction of $MeGeCo_3(CO)_{11}$ with Me_2GeH_2 resulted in a considerable degree of breakdown of the cluster to form small products such as $Me_2GeHCo(CO)_4$ and $(MeGeR)Co_2(CO)_7$. The analogous reaction with $MeGeH_3$ did not show any evidence for cluster breakdown, however, it should be noted that if a species such as $MeGeH_2Co(CO)_4$ were produced then this could react with $MeGeCo_3(CO)_{11}$ itself to provide $(MeGe)_2Co_4(CO)_{11}(J)$ as observed in section 3.8. If this were the case then the presence of this product might not have been noticed in the infrared spectrum, especially if present as a small proportion of the mixture, as the major carbonyl bands of this species - 2034 and 2016 cm^{-1} [87] - lie under the complex region of this spectrum. It does not appear, however, that breakdown of the cluster was occurring to the same extent in the $MeGeH_3$ system as for Me_2GeH_2 .

A second difference between the two reactions is the fact that while all $MeGeCo_3(CO)_{11}$ had reacted with Me_2GeH_2 after 22 weeks, in the $MeGeH_3$ system a small amount of $MeGeCo_3(CO)_{11}$ still remained after 1 year. This reaction was more concentrated than that involving Me_2GeH_2 thus the rate of this process must be much slower.

In both cases it was suggested that one product of the reaction of $MeGeCo_3(CO)_{11}$ with the hydride was of the form $[MeGeCo(CO)_4]Co_2(CO)_6[MeGeR]$ ($R = Me, H$). This would occur through the typical substitution reaction of a bridging carbonyl by an R_2Ge group. This is shown for these systems in scheme 4.7



Scheme 4.7. ($R = Me, H$)

4.7. Reactions of Me_2GeH_2 and MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_9(\text{H})$.

4.7.1. Experimental Details and Results.

Run 1: Me_2GeH_2 (0.90 mmoles by volume) and $\text{MeGeCo}_3(\text{CO})_9$ (0.05 g; 0.095 mmoles) (9.5:1 ratio) were allowed to react in hexane (5 mls) for four weeks at room temperature. After approximately 10 days no trace of the original purple colour of the solution remained. This was now red-brown in colour. Incondensable gases (0.124 mmoles) were measured, of composition 12% CO , 88% H_2 . Unreacted Me_2GeH_2 (0.77 mmoles) was recovered on fractionation of the volatiles while a small amount (ca. 0.01 mmoles) remained with the solvent.

The involatile products were separated into two fractions. The first (0.044 g) was soluble in hexane giving an orange-brown solution. A carbonyl region infrared spectrum of this solution was recorded and is shown in figure 4.9. The second fraction (0.015 g) was insoluble in hexane but fairly soluble in CH_2Cl_2 giving an orange solution. A carbonyl region infrared spectrum of this product in CH_2Cl_2 /hexane was very broad and ill-resolved. The bands of this are listed in table 4.16.

Table 4.16. Carbonyl region infrared data for the CH_2Cl_2 soluble product from the reaction of Me_2GeH_2 and $\text{MeGeCo}_3(\text{CO})_9(\text{H})$. (cm^{-1}).

2062 sh, m
2055 vs, br
2041-1963 m, v.br

Run 2: MeGeH_3 (0.81 mmoles by volume) and $\text{MeGeCo}_3(\text{CO})_9$ (0.10 g; 0.19 mmoles) (4:1 ratio) were allowed to react in hexane (5 mls) for 7 weeks at room temperature. After approximately 3 weeks the solution was clearly changing from the original purple to brown. On work-up, incondensable gases (0.425 mmoles) were measured, of composition 24% CO , 76% H_2 . Unreacted MeGeH_3 (0.59 mmoles) was recovered on fractionation of the volatiles with a small amount (ca. 0.02 mmoles) remaining with the solvent fraction.

The involatile products were separated into three fractions. The first (0.109 g) was soluble in hexane giving an orange-brown solution. A carbonyl region infrared spectrum of this solution was recorded and is shown in figure 4.10. The second fraction (0.033 g) was insoluble in hexane but

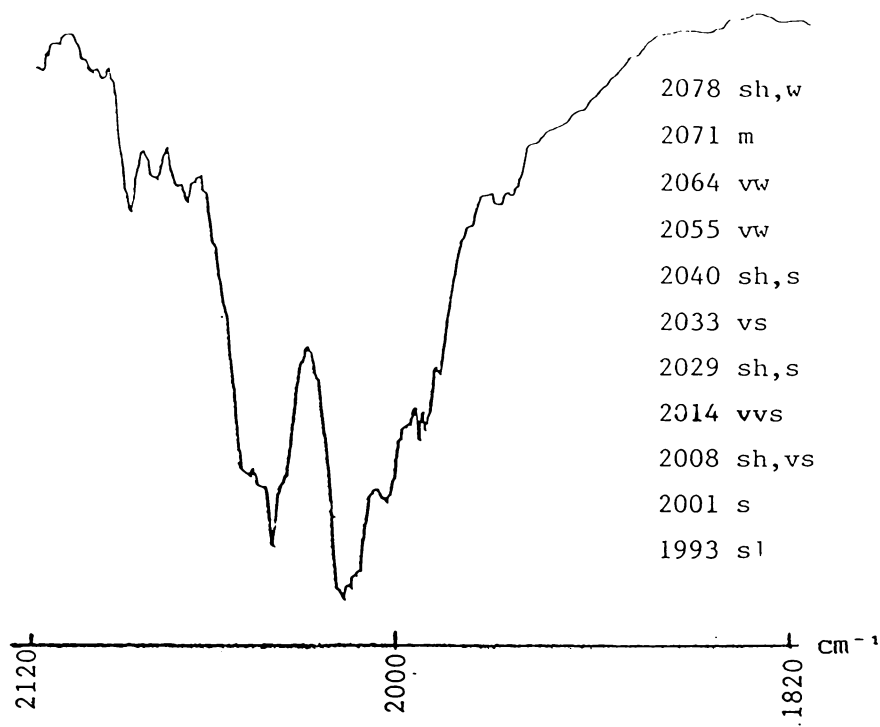


Figure 4.9. Carbonyl region infrared spectrum of the hexane soluble product from the reaction of Me_2GeH_2 with $\text{MeGeCo}_3(\text{CO})_9$. (In hexane).

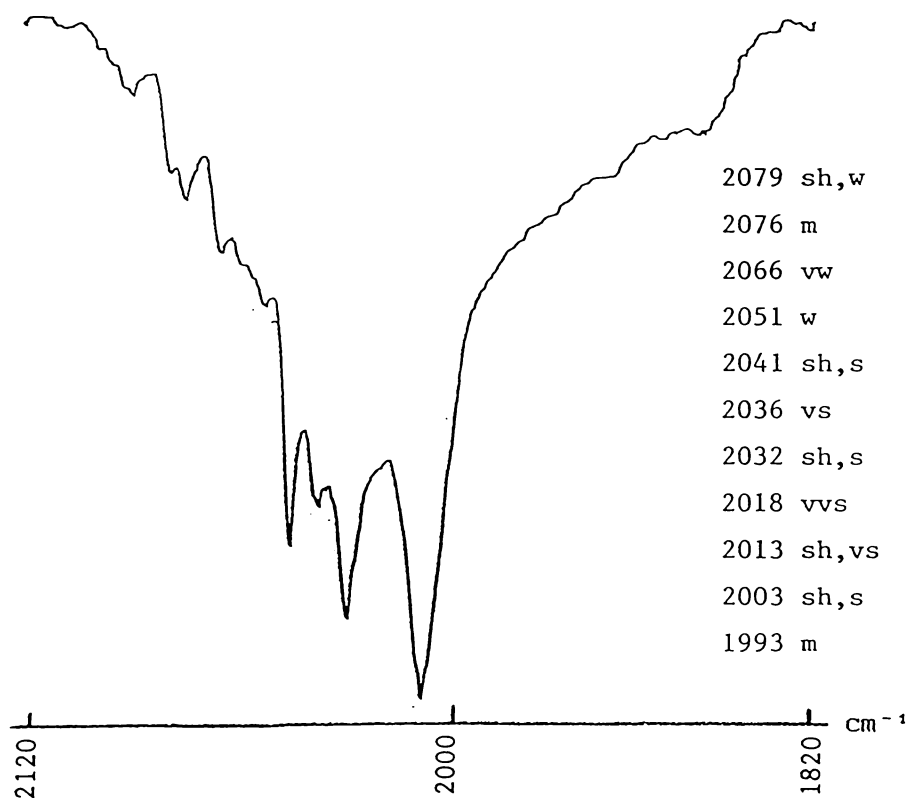


Figure 4.10. Carbonyl region infrared spectrum of the hexane soluble product from the reaction of MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_9$. (In hexane).

fairly soluble in CH_2Cl_2 giving an orange solution. A carbonyl region infrared spectrum of this species in CH_2Cl_2 /hexane was recorded and showed an ill-resolved spectrum. The bands from this are listed in table 4.17. The final fraction (0.012 g) was an insoluble dark coloured material which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a decomposition product and was discarded.

Table 4.17. Carbonyl region infrared data for the CH_2Cl_2 soluble product from the reaction of MeGeH_3 and $\text{MeGeCo}_3(\text{CO})_9(\text{H})$. (cm^{-1}).

2052 m-s, br
2020 s, v.br

Run 3: MeGeH_3 (0.65 mmol) and $\text{MeGeCo}_3(\text{CO})_9$ (0.041 g; 0.08 mmol) (13:1 ratio) were allowed to react in hexane (5 ml) for 4 weeks at room temperature. Incondensable gas evolution was measured at intervals and the results of this are shown in table 4.18. The total amount of incondensable gas measured was 0.131 mmol of approximate composition 17% CO, 83% H_2 . Unreacted MeGeH_3 (0.56 mmol) was recovered on fractionation of the volatile components, the remainder of which was solvent.

The involatile species were separated into two fractions: a hexane soluble species (0.028 g) showing the same carbonyl region infrared spectrum as this fraction from run 2; and a CH_2Cl_2 soluble product (0.018 g) again showing the same infrared spectrum as this fraction obtained in run 2.

Table 4.18. Incondensable gas evolution over time from run 3.

Time interval (days)	Gas evolved (mmol)	%CO	% H_2	Total time (days)	Total gas (mmol)
8	0.068	16	84	8	0.080
11	0.023	19	81	19	0.121
13	0.010	*	*	32	0.131

* Not measured

Run 4: The hexane soluble products from run 2 (0.109 g) were allowed to react with $\text{Co}_2(\text{CO})_8$ (0.038 g; 0.11 mmol) in hexane (5 ml) for 10 months. Incondensable gases (0.61 mmol) were measured of composition 85% CO, 15% H_2 . Fractionation of the volatiles yielded only solvent.

The involatile products were separated into two fractions. A carbonyl region infrared spectrum of the head fraction in hexane solution showed a mixture of unreacted $\text{Co}_2(\text{CO})_8$ [130], and $\text{Co}_4(\text{CO})_{12}$ [139] (0.013 g). The tail fraction was also dissolved in hexane solution. This species was characterised by carbonyl region infrared spectroscopy and by mass spectroscopy as $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ [20, 87] (0.11 g; 0.15 mmoles).

4.7.2. Discussion of the Reactions of Me_2GeH_2 or MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_9(\text{H})$.

Both Me_2GeH_2 and MeGeH_3 appeared to react very similarly with $\text{MeGeCo}_3(\text{CO})_9$, thus these reactions are discussed together.

As described in Chapter 3 (section 3.6.3.), the cluster $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ reacted with MeGeH_3 to provide $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}(\text{C})$, the same product obtained from the reaction of the open analogue of this cluster, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, with MeGeH_3 . It was thus of interest to find if $\text{MeGeCo}_3(\text{CO})_9(\text{H})$ would react with Me_2GeH_2 or MeGeH_3 to yield the same products as its open-skeleton relation, $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$. From the results of this study it appears that, to some extent, this is the case.

The carbonyl stretches in the infrared spectra of the hexane soluble products from runs 1 and 2 are shown in figures 4.9 and 4.10 respectively. The bands are also listed in table 4.19. together with the bands assigned to the new species from the reactions of $\text{MeGeCo}_3(\text{CO})_{11}$ with Me_2GeH_2 or MeGeH_3 .

Table 4.19. Carbonyl region infrared data for the hexane soluble products of the reactions of Me_2GeH_2 or MeGeH_3 and for the new products from the reactions of $\text{MeGeCo}_3(\text{CO})_{11}$ with Me_2GeH_2 or MeGeH_3 . (cm^{-1}).

$\text{Me}_2\text{GeH}_2 +$ $\text{MeGeCo}_3(\text{CO})_{11}$	$\text{Me}_2\text{GeH}_2 +$ $\text{MeGeCo}_3(\text{CO})_9$	$\text{MeGeH}_3 +$ $\text{MeGeCo}_3(\text{CO})_9$	$\text{MeGeH}_3 +$ $\text{MeGeCo}_3(\text{CO})_{11}$
2080 w	2078 w, sh	2079 w, sh	2079 w
2071 m	2071 m	2076 m	2073 s
			2070 sh, w
2064 w	2064 vw	2066 vw	2065 m
2056 w	2055 vw	2051 w	2053 sh, w
2036 sh, vs	2040 sh, s	2041 sh, s	2040 sh, s
2034 vvs, br	2033 vs	2036 vs	2038 vs, br
	2029 sh, s	2032 sh, s	2031 sh, s
2013 vvs, br	2014 vvs	2018 vvs	2017 vs, br
2009 vvs, br	2008 sh, vs	2013 sh, vs	2013 sh, vs
	2001 s	2003 sh, s	2003 sh, vs
1993 vs	1993 s	1993 m	1993 sh, s

From table 4.19 it can be seen that the hexane soluble products of reaction of Me_2GeH_2 or MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_9(\text{H})$ appear to be the same compound as the new species obtained from the reaction of the respective hydride with $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$.

For the $\text{MeGeCo}_3(\text{CO})_{11}$ systems it was proposed that these new products arise from replacement of the bridging carbonyl on $\text{MeGeCo}_3(\text{CO})_{11}$ by the MeGeR group ($\text{R} = \text{Me}, \text{H}$) with loss of H_2 and CO . This would give the product shown in figure 4.11.

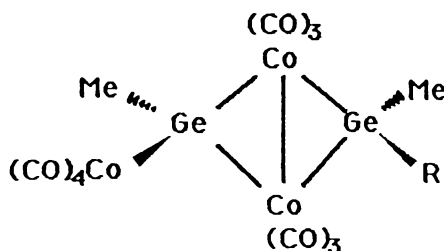
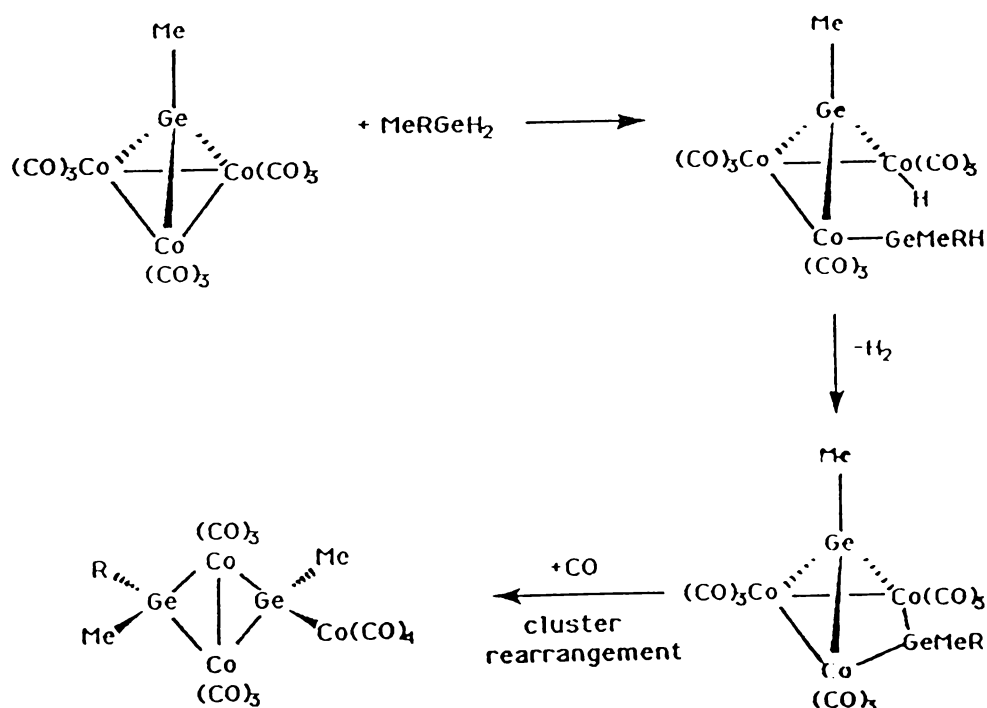


Figure 4.11.

A mass spectrum was recorded of the hexane soluble product from the reaction of MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_9$. The spectrum obtained showed the characteristic intensity pattern of a Ge_2 containing compound throughout. Although the higher mass peaks were difficult to assign, several lower mass peaks corresponded well to fragments of the form $\text{Me}_2\text{GeCo}_3 - n\text{Me}^+$ and $\text{Me}_2\text{Ge}_2\text{Co}_2 - n\text{Me}^+$ ($n = 0, 1, 2$) which supports the formulation of this product as $[\text{MeGeCo}_4]\text{Co}_2(\text{CO})_6[\text{MeGeH}]$.

This formulation for the hexane soluble product of reaction of $\text{MeGeCo}_3(\text{CO})_9$ with the hydrides is also supported by the results of run 4 where the hexane soluble fraction from the reaction of MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_9$ was reacted with $\text{Co}_2(\text{CO})_8$. This provided as major product the *clos*o-hexanuclear cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ which is known to arise through the condensation of $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ [31] as has been shown in scheme 4.6.

The production of the species $[\text{MeGeR}]\text{Co}_2(\text{CO})_6[\text{MeGeCo}(\text{CO})_4]$ through the reaction of $\text{MeGeCo}_3(\text{CO})_9(\text{H})$ with these hydrides is harder to rationalise than the analogous reactions of $\text{MeGeCo}_3(\text{CO})_{11}$ since $\text{MeGeCo}_3(\text{CO})_9$ must gain a carbonyl ligand from some source before it can open out. It may be assumed that the production of the dichloromethane soluble product arises through the necessary process to provide the extra CO, although the nature of this product cannot be determined at this stage. Assuming the occurrence of some sort of CO abstraction then the following pathway for the reaction of Me_2GeH_2 or MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_9$ may be proposed.



R = Me, H

Scheme 4.8.

This type of pathway was previously suggested for the reaction of $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ with MeGeH_3 to form $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$, although in this case the abstraction of CO was not necessary (see section 3.6.4.). This type of opening of the GeCo_3 tetrahedron has been used to rationalise ligand substitution reactions by reagents such as phosphines on $\text{L}_n\text{EM}_3(\text{CO})_x$ clusters [77]. Cluster opening is also observed as the first step to metal exchange in the reactions of organometalarsenides with $\text{RGeCo}_3(\text{CO})_9$ clusters [44] as shown in figure 3.18.

The incondensable gas evolution results obtained from these reactions appear to be reasonably consistent with the observed products. In the reaction of Me_2GeH_2 0.044 g of the hexane soluble product was found which would correspond to 0.068 mmols of $[\text{Me}_2\text{Ge}]\text{Co}_2(\text{CO})_6[\text{MeGeCo}(\text{CO})_4]$. The production of this would be expected to give rise to 0.068 mmols of H_2 . The remaining evolved H_2 (0.041 mmols) and CO (0.015 mmols) may be accounted for by the production of the unidentified CH_2Cl_2 soluble product. Similarly, approximately 0.12 mmols of Me_2GeH_2 were found to have reacted. 0.068 mmols of this is accounted for by the production of $[\text{Me}_2\text{Ge}]\text{Co}_2(\text{CO})_6[\text{MeGeCo}(\text{CO})_4]$ while the remainder (0.052 mmols) must be involved in the formation of the CH_2Cl_2 soluble species.

In the reaction of MeGeH_3 with $\text{MeGeCo}_3(\text{CO})_9$, described as run 3 the three measurements of incondensable gas evolution taken during the course of reaction show the typical pattern of fast gas production at the beginning of the reaction, with slower gas release towards the reaction end. In this run 0.028 g of the hexane soluble product was obtained which would correspond to 0.044 mmols of reacted MeGeH_3 , 0.044 mmols of H_2 and 0.044 mmols of reacted $\text{MeGeCo}_3(\text{CO})_9$. The remaining evolved H_2 (0.065 mmols) and CO (0.022 mmols) and the additional reacted MeGeH_3 (0.46 mmols) must be accounted for in the production of the CH_2Cl_2 soluble product.

The lower proportion of CO compared to H_2 in the remaining incondensable gas on these runs indicates the requirement of CO addition to the hexane soluble product for it to be able to form an open-skeleton species.

In run 2 a slightly higher proportion of CO was present in the incondensable gases as compared to the other runs. This may be attributed to the presence of the decomposition product which would, presumably have evolved CO during its production.

Unfortunately there is no correlation between the ratio of reacted hydride to unaccounted cluster which makes it impossible to propose a formulation for the CH_2Cl_2 soluble species.

In run 4 the mass balance between reactants and products also seems reasonable. 0.109 g of the hexane soluble species reacted which corresponds to 0.17 mmols of $[\text{MeGeH}]\text{Co}_2(\text{CO})_6[\text{MeGeCo}(\text{CO})_4]$. This provided 0.15 mmols of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with evolution of 0.61 mmols of incondensable gas. 0.09 mmols of this was H_2 which would be given off by the replacement of the single hydrogen by a $\text{Co}(\text{CO})_4$ unit. The remainder of the incondensable gas, carbon monoxide, is accounted for by the decarbonylation of $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and, to a lesser extent, by condensation of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$.

In conclusion, $\text{MeGeCo}_3(\text{CO})_9$ appears to react with Me_2GeH_2 or MeGeH_3 to open out yielding the same products as observed in the reactions of $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ with these hydrides assumed to be $[\text{MeGeR}]\text{Co}_2(\text{CO})_6[\text{MeGeCo}(\text{CO})_4]$ ($\text{R} = \text{Me}, \text{H}$). Also found from the reactions is an unidentified CH_2Cl_2 soluble species which is probably produced as a result of the requirement of CO for the formation of the hexane soluble products.

4.8. Reactions of *clos*o-hexanuclear germanium-cobalt carbonyl clusters with mono- or dimethylgermane.

4.8.1. Reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with Me_2GeH_2 or MeGeH_3 .

4.8.1.1. Experimental details and results.

Run 1: Me_2GeH_2 (0.46 mmol by volume) and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ (0.033 g; 0.046 mmol) (10:1 ratio) were allowed to react in hexane (5 ml) for 16 weeks at room temperature. Incondensable gases (0.097 mmol) were measured, of composition 40% CO, 60% H_2 . Unreacted Me_2GeH_2 (0.39 mmol) was recovered on fractionation of the volatiles with a small amount (*ca.* 0.02 mmol) remaining with the solvent fraction.

All involatile products (0.034 g) were soluble in hexane giving a dark orange solution. A carbonyl region infrared spectrum of this solution was recorded and is shown in figure 4.13.

Run 2: MeGeH_3 (1.09 mmol by volume) and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ (0.039 g; 0.054 mmol) (20:1 ratio) were allowed to react in hexane (5 ml) for 28 weeks at room temperature. Incondensable gases could not be measured due to a leak in the Toepler pump apparatus. Unreacted MeGeH_3 (1.01 mmol) was recovered on fractionation of the volatiles while a trace (*ca.* 0.02 mmol) remained with the solvent fraction.

The involatile products were separated by extraction with hexane. The first fraction (0.025 g) was soluble in hexane giving an orange solution and showed the carbonyl region infrared spectrum depicted in figure 4.14. Also present (0.015 g) was a product insoluble in hexane but fairly soluble in

CH_2Cl_2 giving an orange-brown solution. A carbonyl region infrared spectrum recorded of this species in CH_2Cl_2 /hexane showed a broad ill-resolved band. This spectrum is reported in table 4.20. but this product has not yet been identified.

Table 4.20. Carbonyl region infrared spectrum of the CH_2Cl_2 soluble product from run 2. (cm^{-1}).

2050 s
1975 s, v.br

Recorded in CH_2Cl_2 /hexane.

4.8.1.2. Characterisation of the major products of the reactions of Me_2GeH_2 or MeGeH_3 with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$.

(i) Handling

These hexane soluble products have very similar handling characteristics to other new species observed in the work of this chapter. They are both bright orange solids which will decompose if left in air at room temperature for more than short periods of time.

It would again appear that the addition of hydrocarbon groups increases the solubility of these species in non-polar solvents such as hexane relative to the parent cluster.

Both of these products crystallised readily from hexane solution cooled to -30°C . However, unfortunately, none of the crystals obtained were of sufficient quality to allow X-ray crystal structure determination.

(ii) Analytical data and possible formulation of the hexane soluble products.

(a) Evidence from the reaction.

In the reaction of Me_2GeH_2 with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ it was found that the reacting ratio of hydride to cluster was approximately 1.1:1. Similarly, in the MeGeH_3 system the reacting ratio of hydride to cluster was found to be approximately 1.1:1.

The incondensable gas measurements from the reaction of Me_2GeH_2 with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ showed that approximately 1.3 moles of H_2 are evolved per mole of reacted cluster. Unfortunately in the MeGeH_3 system the incondensable gases were not measured.

The above results suggest that one mole of hydride reacts with each mole of cluster.

(b) Electron probe analysis.

Electron probe analysis was carried out on the hexane soluble products from the reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with Me_2GeH_2 or MeGeH_3 . The results of this are shown in table 4.21.

Table 4.21. Atomic percentage values obtained for the hexane soluble products from the reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with Me_2GeH_2 or MeGeH_3 .

	Element	Shell	Atomic Percentage
Me_2GeH_2	Ge	K	41.7
	Co	K	58.3
MeGeH_3	Ge	K	39.4
	Co	K	60.6

(c) Conclusions from the above evidence.

From the results described in the previous sections of this chapter it could be anticipated that the most straightforward reaction of these hydrides with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ would be to replace the bridging carbonyl of the cluster to form a species of the form $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{MeGeR}]$.

The evidence obtained from these reactions clearly suggests that both Me_2GeH_2 and MeGeH_3 react with the cluster in a 1:1 ratio which is consistent with this formulation.

The electron probe analysis of the two products, although not conclusive, could suggest the presence of approximately 3 germanium atoms to four cobalt atoms, although a Ge:Co ratio of 4:6 would match this data equally well. It should be noted that this analysis was carried out on the hexane soluble fractions on which no purification had been carried out thus it is possible that these results have been affected by the presence of minor components in the product mixture.

Further evidence on the nature of these products is presented in the following sections.

(iii) Mass Balance of these reactions.

If the formulation of these products as $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{MeGeR}]$ species is accepted for the moment then analysis of the mass balance of these reactions may be carried out.

In run 1 0.046 mmoles of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.033 g) reacted with approximately 0.05 mmoles of Me_2GeH_2 to provide 0.034 g of the hexane soluble product, assumed to be $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{GeMe}_2]$. This would correspond to 0.043 mmoles of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{GeMe}_2]$ giving a 93% yield based on consumed $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. The slight loss of product may be attributed to handling.

In this reaction 0.097 mmoles of incondensable gas was evolved, of composition 40% CO, 60% H_2 . From the reaction of 0.46 mmoles of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with 0.046 mmoles of Me_2GeH_2 0.092 mmoles of incondensable gas would be produced, containing equal proportions of CO and H_2 . These values correspond within experimental error with those obtained by measurement.

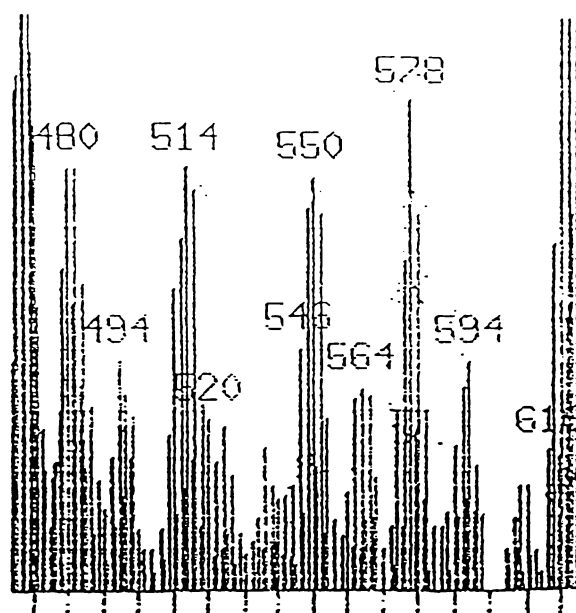
In run 2 0.054 mmoles of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.039 g) reacted with approximately 0.06 mmoles of MeGeH_3 to provide 0.025 g of the product assumed to be $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{MeGeH}]$. This weight corresponds to 0.032 mmoles giving a yield of 59% based on initial $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. Also obtained from this reaction was 0.015 g of an unidentified CH_2Cl_2 soluble fraction. The amount of this species together with the hexane soluble reaction, assumed to be $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{MeGeH}]$, corresponds well with the amounts of the initial reactants. Unfortunately, the incondensable gases from this reaction could not be measured thus further analysis is not possible.

For run 1, the mass balance works out extremely well using the formulation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{GeMe}_2]$ for the major product. If this formulation is incorrect then it may still be stated that the product must have a very similar molecular weight. This evidence certainly supports the proposal that the major products of the reactions are of the form $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{MeGeR}]$ ($\text{R} = \text{Me}, \text{H}$).

- (iv) Mass spectrum of the hexane soluble product from the reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with MeGeH_3 .

The mass spectrum of the product of this reaction is listed in table 4.22. As a result of the uncertainty of m/e values obtained from the machine used, particularly at high mass, it was not possible to distinguish between the loss of one carbonyl ligand or the loss of two methyl groups. Similarly, the effect of the single proton could not be discerned from this spectrum. Various possible assignments are thus given in table 4.22 for each observed peak. Since the methyl groups of this species are present on separate germanium atoms it is felt that the loss of two of these simultaneously is unlikely. However the formation of methane by

fragmentation from the MeGeH group is quite probable. Throughout the spectrum the characteristic intensity pattern of a Ge_3 containing species was observed. Figure 4.12. shows the central portion of this mass spectrum where the overlap of envelopes resulting from fragmentations of similar mass can be clearly seen.



Section of the mass spectrum recorded for the hexane soluble product from reaction of $\text{MeGeCo}_3(\text{CO})_{11}$ with MeGeH_3 .

Figure 4.12.

No peak corresponding to the anticipated parent ion, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{Ge}(\text{H})\text{Me}]^+$, was found. However, a peak at $m/e = 754-770$, which corresponds to the parent ion after loss of one methyl group, was observed. From this a stepwise loss of ten carbonyl groups was clear. A similar situation was found in the mass spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(D)$ (see section 3.4.2.4.) where the parent ion was not observed but M-Me-nCO^+ provided the major series of peaks.

Other series of peaks corresponding to the stepwise loss of ten carbonyl groups were found - from $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_n$ and from $\text{Ge}_3\text{Co}_4(\text{CO})_n$. The loss of seven carbonyl groups from the parent ion after three carbonyl ligands had already been released was also observed. All of these peaks accounted for 75% of the total ion current.

Peaks corresponding to loss of the additional germanium were observed at reasonable intensity and carbonyl and methyl loss from the Ge_2Co_4 core was found to occur after this germanium had been released. The Ge_2Co_4 unit, however, remained intact until all of the carbonyl groups had been released. Low intensity peaks corresponding to the loss of one and two

cobalt atoms were observed.

It was, unfortunately, not possible to obtain a mass spectrum of the dimethylgermyl equivalent of this species as the solution had decomposed.

Table 4.22. Mass spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{Ge}(\text{H})\text{Me}]$.
($\text{P}^+ = \text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_{10}$).

m/e	Rel. Int.	Possible Assignments				
CO loss		$(\text{P}-n\text{CO})^+$	$(\text{P}-\text{Me}-n\text{CO})^+$	$(\text{P}-2\text{Me}-n\text{CO})^+$	$(\text{P}-3\text{Me}-n\text{CO})^+$	$(\text{P}-\text{MeGe}-n\text{CO})^+$
754-770	19	n =	n = 10	n =	n =	n =
728-743	61		9		10	
700-715	27		8		9	
686-700	7	7		8		10
674-688	37		7		8	
658-670	13	6		7		9
645-658	100		6		7	
628-640	16	5		6		8
616-629	97		5		6	
604-616	10	4		5		7
588-599	22		4		5	
570-584	47	3		4		6
559-568	19		3		4	
542-555	37	2		3		5
532-545	14		2		3	
519-531	16	1		2		4
504-516	41		1		2	
490-504	15	0		1		3
474-487	41		0		1	
460-473	74			0		2
447-460	85				0	
435-446	14					1
404-417	39					0

Other fragmentations.

417-426	8	$\text{Me}_2\text{Ge}_3\text{Co}_3^+$
404-417	39	$\text{MeGe}_3\text{Co}_3^+$
388-400	63	Ge_3Co_3^+ or $\text{MeGe}_2\text{Co}_4^+$
375-388	34	Ge_2Co_4^+
345-356	3	$\text{Me}_2\text{Ge}_2\text{Co}_3^+$
331-342	22	$\text{MeGe}_2\text{Co}_3^+$
317-328	24	Ge_2Co_3^+
273-282	7	$\text{MeGe}_2\text{Co}_2^+$
260-266	15	Ge_2Co_2^+

(v) Carbonyl stretches in the infrared spectrum:

The carbonyl region infrared spectra of the hexane soluble products obtained in the reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with each of MeGeH_3 and Me_2GeH_2 are shown in figures 4.13. and 4.14. The bands are also listed in table 4.23. together with those reported for the crystallographically characterised compound, $(\text{MeSi})_2\text{Co}_4(\text{CO})_{10}[\text{GeMe}_2]$ [82].

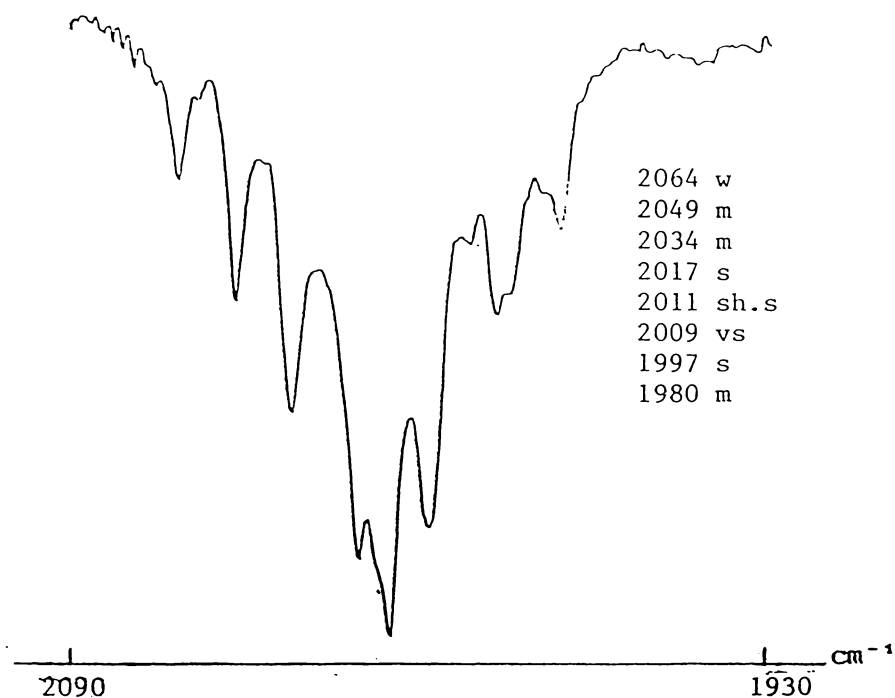


Figure 4.13. Infrared active carbonyl stretches of the hexane soluble product obtained from the reaction of Me_2GeH_2 with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. Recorded in hexane.

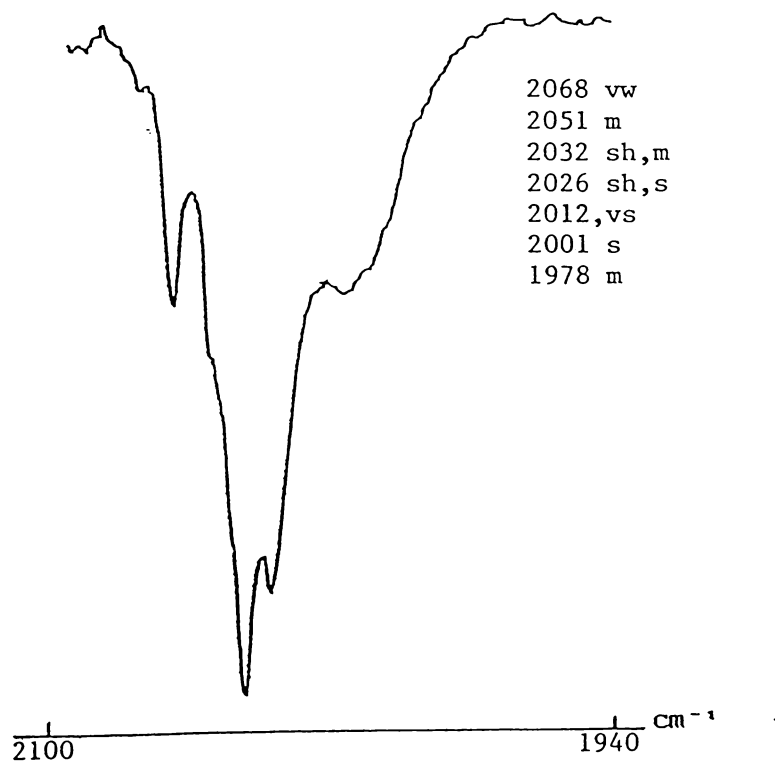


Figure 4.14. Infrared active carbonyl stretches of the hexane soluble product obtained from the reaction of MeGeH_3 with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. Recorded in hexane.

Table 4.23. Carbonyl stretches of the hexane soluble products from the reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with Me_2GeH_2 or MeGeH_3 , together with the terminal carbonyl stretches of the parent compound, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [87], and those of the known compound $(\text{MeSi})_2\text{Co}_4(\text{CO})_{10}[\text{GeMe}_2]$ [82]. (cm^{-1}).

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	From Me_2GeH_2 reaction	From MeGeH_3 reaction	$(\text{MeSi})_2\text{Co}_4(\text{CO})_{10}[\text{GeMe}_2]$
	2064 w	2068 vw	
	2049 m	2051 m	2071 m
	2034 m	2032 sh, m	2051 vw
	2017 s		
	2011 sh, s	2026 sh, s	2026 sh, s
2034 vs	2009 vs	2012 vs	2022 vs
2016 m	1997 s	2001 s	2009 m
2004 sh	1980 m	1978 m	1986 s

All recorded in hexane.

No bands corresponding to bridging carbonyl stretches were observed for either of the new species.

The carbonyl region infrared spectra of the products of these reactions correspond closely with the pattern of that observed for the known compound $(\text{MeSi})_2\text{Co}_4(\text{CO})_{10}[\text{GeMe}_2]$. The bands, however, have been shifted to lower wavenumber consistent with replacement of silicon by germanium. For example, on moving from $[(\text{CO})_4\text{CoSi}]_2\text{Co}_4(\text{CO})_{11}$ [81, 86] to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ [19, 20] the carbonyl infrared bands are observed to shift to lower frequency by an average 4 cm^{-1} . The shift to this new product from the silicon analogue is of an average 12 cm^{-1} which is unexpectedly large. An explanation of this feature has not been found as yet.

The carbonyl region infrared spectra of these products are more complicated than that of the parent cluster, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, presumably reflecting a loss of symmetry resulting from the replacement of the bridging carbonyl by a MeGeR group.

From the evidence presented above it seems reasonable to suggest that the major product of reaction between $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ and Me_2GeH_2 or MeGeH_3 is $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{MeGeR}]$ ($\text{R} = \text{Me}, \text{H}$ respectively).

4.8.1.3. Discussion of the reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with Me_2GeH_2 or MeGeH_3 .

The reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with either Me_2GeH_2 or MeGeH_3 were investigated to determine if the edge-bridging carbonyl ligand could be

replaced by a R_2Ge group as has been observed for the germanium-cobalt carbonyl cluster $GeCo_4(CO)_{14}(B)$ and probably for $Ge_2Co_6(CO)_{20}(E)$ and $MeGeCo_3(CO)_{11}(A)$. Recently, it has also been observed that the silicon analogue of this cluster, $(MeSi)_2Co_4(CO)_{11}$, will react with Me_2GeH_2 to provide the crystallographically characterised species, $(MeSi)_2Co_4(CO)_{11}[GeMe_2]$ [82].

This study shows a 1:1 reaction ratio between the cluster and the hydride and good spectroscopic evidence for a product containing one added R_2Ge group has been obtained. It is thus proposed that the most likely structure of the hexane soluble product found in the reactions of $(MeGe)_2Co_4(CO)_{11}$ with Me_2GeH_2 or $MeGeH_3$ is that shown in figure 4.15.

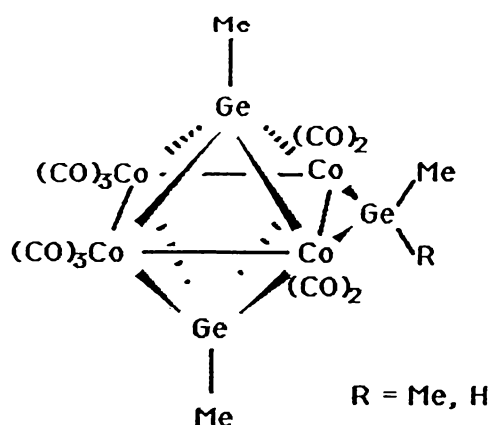


Figure 4.15.

It would appear that both Me_2GeH_2 and $MeGeH_3$ react quite similarly with $(MeGe)_2Co_4(CO)_{11}$. However in the $MeGeH_3$ system there was a second product obtained which was only soluble in CH_2Cl_2 . This presumably arises as a result of the third functional hydrogen on the germanium group which could react further either intra- or intermolecularly. The carbonyl stretches in the infrared spectrum of this species (at 2050 and 1975 cm^{-1}) could suggest some sort of polymeric species as could its low solubility. However any definite suggestions on the nature of this product are not possible at this stage.

4.8.2. Reactions of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ with Me_2GeH_2 or MeGeH_3 .

4.8.2.1. Experimental details and results.

Run 1: Me_2GeH_2 (0.50 mmol) and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ (0.049 g; 0.048 mmol) (10:1 ratio) were allowed to react in CH_2Cl_2 (9 ml) for 10 weeks at room temperature. Incondensable gases (0.209 mmol) were measured of composition 43% CO , 57% H_2 . Unreacted Me_2GeH_2 (0.45 mmol) was recovered on fractionation of the volatiles, the remainder of which was solvent.

The involatile products were separated into two fractions. The hexane soluble products (0.034 g) gave a burgundy coloured solution in hexane. A carbonyl region infrared spectrum of this solution was recorded and is shown in figure 4.16. Also present was a CH_2Cl_2 soluble product (0.020 g) which gave a dark brown solution in CH_2Cl_2 /hexane. A carbonyl region infrared spectrum of this solution showed a broad ill-resolved series of bands which are listed in table 4.24. This product has not been identified.

Table 4.24. Carbonyl region infrared spectrum of the CH_2Cl_2 soluble product from run 1. (cm^{-1}).

2043 sh, m
2016 s
1984 sh, s
1960 vs, vbr

1844 w

Recorded in CH_2Cl_2 /hexane.

Run 2: MeGeH_3 (0.82 mmol) and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ (0.105 g; 0.10 mmol) (8:1 ratio) were allowed to react in CH_2Cl_2 (10 ml) for 21 weeks at room temperature. Incondensable gases (0.669 mmol) were measured, of composition 28% CO , 72% H_2 . Unreacted MeGeH_3 (0.67 mmol) was recovered on fractionation of the volatiles with a small amount (ca. 0.01 mmol) remaining with the solvent.

The involatile products were separated into two fractions. The first (0.08 g) was soluble in hexane giving a wine-red coloured solution. A carbonyl region infrared spectrum of this solution was recorded and is shown in figure 4.17. Also present was a species (0.022 g) insoluble in hexane but fairly soluble in CH_2Cl_2 . This gave a dark brown solution in CH_2Cl_2 /hexane. A carbonyl region infrared spectrum of this solution showed

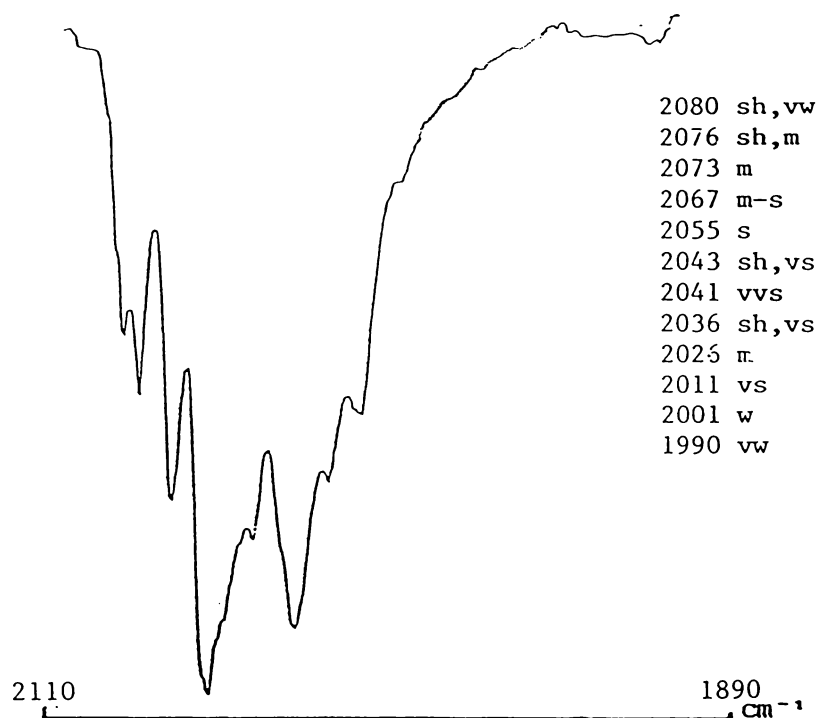


Figure 4.16. Infrared active carbonyl stretches of the hexane soluble product obtained from reaction of Me_2GeH_2 with $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$. Recorded in hexane.

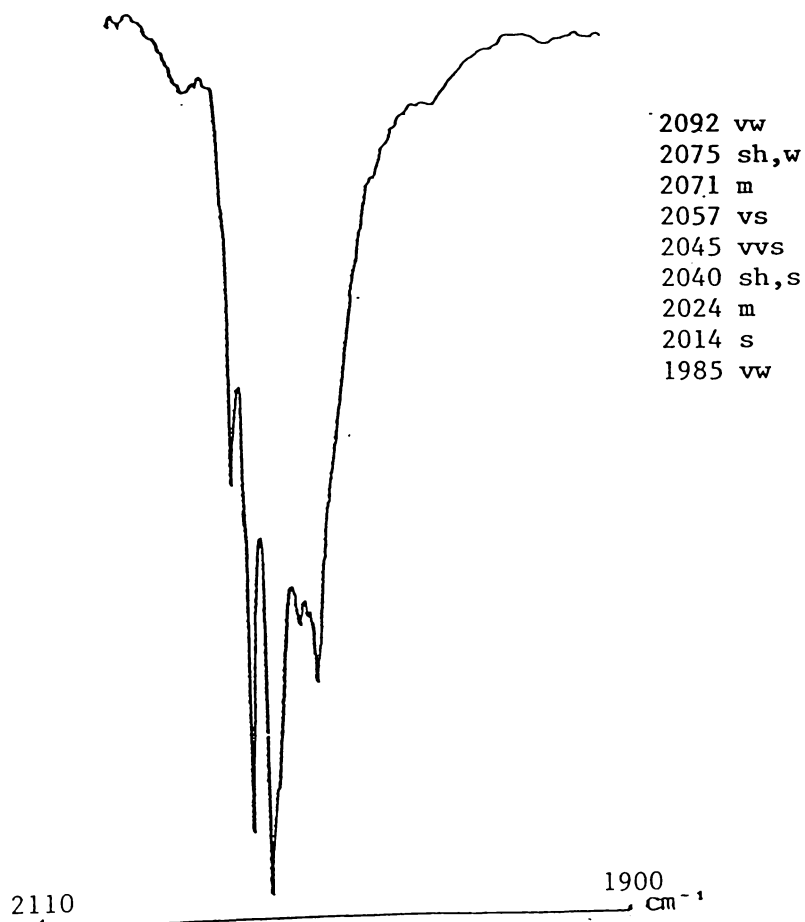


Figure 4.17. Infrared active carbonyl stretches of the hexane soluble product obtained from the reaction of MeGeH_3 with $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$. Recorded in hexane.

a broad, ill-resolved series of bands which are listed in table 4.25. This species has not been characterised.

Table 4.25. Carbonyl region infrared spectrum of the CH_2Cl_2 soluble product from run 2. (cm^{-1}).

2065 sh, m
2048 sh, s
2033 vs
2002 vs
1992 vs
1960 m, br

Recorded in CH_2Cl_2 /hexane.

4.8.2.2. Discussion of the reactions of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ with Me_2GeH_2 or MeGeH_3 .

As in the reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with Me_2GeH_2 or MeGeH_3 , these investigations were carried out to determine if the bridging carbonyl group of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ could be replaced by a GeR_2 group.

Although this process may be occurring, the results obtained in this study suggest that other pathways may also be involved.

In run 1 0.05 mmol of Me_2GeH_2 reacted with 0.048 mmol of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ apparently producing 0.12 mmol of H_2 . Clearly this is not possible and some error must have been made in the measurements either of the amount of remaining Me_2GeH_2 or of the evolved gases. In run 2 it was found that 0.14 mmol of MeGeH_3 reacted with 0.10 mmol of the cluster producing 0.48 mmol of H_2 . Again it would appear that these values are unreliable and no conclusions on the reaction ratio can be made from these results.

In both runs the mass of the products correspond reasonably well with the consumed reactants.

The carbonyl region infrared data recorded for the hexane soluble products obtained from runs 1 and 2 are collected in table 4.26.

Table 4.26. Carbonyl stretches of the hexane soluble products obtained from the reactions of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ with Me_2GeH_2 or MeGeH_3 together with the terminal carbonyl stretches of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ [19]. (cm^{-1}).

with Me_2GeH_2 (a)	with MeGeH_3 (a)	$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (b)
2080 sh, vw	2092 vw	2100 s
2076 sh, m		
2073 m	2075 sh, w	2065 w, sh
2067 m-s	2071 m	
2055 s	2057 vs	2050 s
2043 sh, vs		
2041 vvs	2045 vvs	2037 vs
2036 sh, s	2040 sh, s	
2026 m	2024 m	2014 m
2011 vs	2014 s	
2001 w		
1990 vw	1985 vw	2003 w, sh 1990 vw, sh

(a) Recorded in hexane solution. (b) Recorded in CH_2Cl_2 /hexane.

The absence of any bridging carbonyl modes in these spectra could suggest that replacement of the bridging carbonyl on the cluster by a GeMeR group has taken place. However the major bands have been shifted to higher frequency compared to the parent cluster while for substitution of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ a downward shift was observed.

There is a reasonably consistent shift to higher frequency between the product of the Me_2GeH_2 system and that of MeGeH_3 . This effect is commonly observed on replacing a methyl group by a hydrogen. (For example, see section 3.4.2.2.). The spectra are much more complex than that of the parent cluster $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ which shows only 3 main bands in this region. This feature may be attributed to a lowering of symmetry resulting from the replacement of the bridging carbonyl by a MeGeR group, however this could also suggest that the products have opened out in some manner. The spectra do not match those reported for $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$ [20, and this work, section 4.4.2.2.] but some other open form could conceivably have been produced. It is also possible that these are in fact product mixtures.

It should be noted that these reactions were carried out in CH_2Cl_2 . It is conceivable that the hydrides reacted with the solvent and this may also account for the complicated infrared spectrum. Unfortunately these products were too involatile to allow characterisation by mass spectroscopy, and electron probe analysis was not available at the time of work-up, thus

it was not possible to establish the presence of chlorine in these products and their identity remains uncertain,

Also found as a fairly major product in each of these reactions was a species soluble only in dichloromethane. The lack of resolution of the infrared spectra of these products limits the information that may be obtained from these. The very broad nature of the bands could suggest some sort of polymeric species which is also supported by the low solubility of these products. Any further proposals on the nature of these compounds is not practical at this stage.

The unreliable values for the amount of hydride consumed in each reaction and for the incondensable gas measurements make it extremely desirable that these reactions are repeated and, of course, full characterisation of the products would be of great interest.

4.9. Conclusion.

Table 4.27. summarises the results of the reactions described in this chapter.

Table 4.27. Summarised results for the reactions described in this chapter.

Cluster	Hydride	Apparent reaction ratio	Duration	Products (approx. yield based on initial cluster)
$\text{Ge}_2\text{Co}_6(\text{CO})_{20} (E)$	Me_2GeH_2	2:1	ca. 6 wks	Probably $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (F) (80%) + unidentified CH_2Cl_2 soluble fraction
$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$	MeGeH_3	2:1	ca. 8 wks	Probably $[\text{MeGeH}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (F) (80%) + unidentified CH_2Cl_2 soluble fraction
$\text{Ge}_3\text{Co}_8(\text{CO})_{26} (G)$	MeGeH_3	4:1	45 wks	Probably $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ (38%) + unidentified CH_2Cl_2 soluble fraction + insoluble species
$\text{MeGeCo}_3(\text{CO})_{11} (A)$	Me_2GeH_2	2:1	22 wks	Mixture of $\text{Me}_2\text{GeHCo}(\text{CO})_4$ (25%) and possibly $(\text{Me}_2\text{Ge})_2\text{-}$ $\text{Co}_2(\text{CO})_6$, $\text{Me}_2\text{GeCo}_2(\text{CO})_7$, $\text{Me}(\text{H})\text{GeCo}_2(\text{CO})_7$ and $(\text{Me}_2\text{Ge})\text{Co}_2(\text{CO})_6[\text{Ge}(\text{Me})\text{Co}(\text{CO})_4]$

Table 4.27. Continued

$\text{MeGeCo}_3(\text{CO})_{11}$	MeGeH_3	1:1	1 year	Probably $[\text{Me}(\text{H})\text{Ge}]\text{Co}_2(\text{CO})_6 - [\text{Ge}(\text{Me})\text{Co}(\text{CO})_4]$
$\text{MeGeCo}_3(\text{CO})_9$ (H)	Me_2GeH_2	1.3:1	4 wks	Probably $(\text{Me}_2\text{Ge})\text{Co}_2(\text{CO})_6 [\text{Ge}(\text{Me})\text{Co}(\text{CO})_4]$ (76%) + unidentified CH_2Cl_2 soluble fraction
$\text{MeGeCo}_3(\text{CO})_9$	MeGeH_3	1:1	ca. 6 wks	Probably $[\text{Me}(\text{H})\text{Ge}]\text{Co}_2(\text{CO})_6 - [\text{Ge}(\text{Me})\text{Co}(\text{CO})_4]$ (73%) + unidentified CH_2Cl_2 soluble fraction
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (J)	Me_2GeH_2	1:1	16 wks	Probably $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}(\text{GeMe}_2)$ (93%)
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	MeGeH_3	1:1	28 wks	Probably $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11} - [\text{Ge}(\text{H})\text{Me}]$ (59%) + unidentified CH_2Cl_2 soluble fraction
$[(\text{CO})_4\text{CoGe}]_2 - \text{Co}_4(\text{CO})_{11}$ (K)	Me_2GeH_2	-	19 wks	Possibly $[(\text{CO})_4\text{CoGe}]_2 - \text{Co}_4(\text{CO})_{10}[\text{GeMe}_2]$ + unidentified CH_2Cl_2 soluble fraction
$[(\text{CO})_4\text{CoGe}]_2 - \text{Co}_4(\text{CO})_{11}$	MeGeH_3	-	21 wks	Possibly $[(\text{CO})_4\text{CoGe}]_2 - \text{Co}_4(\text{CO})_{10}[\text{Ge}(\text{H})\text{Me}]$ + unidentified CH_2Cl_2 soluble fraction

Most of these systems deserve further study. In particular, attempts at obtaining fast atom bombardment mass spectra for some of the higher mass products should be useful. Also, as has been suggested earlier, it is possible that reaction of the starting clusters with other germanium hydrides might yield products which would crystallise more readily, allowing X-ray crystallography to be employed in their characterisation.

CHAPTER 5: Preliminary Studies of the Chemistry of $(RGe)_2Co_4(CO)_{11}$ Clusters ($R = Me, Co(CO)_4$).

5.1. Background and aim

As yet, very little work has been carried out to determine the reactivity of the two E_2M_4 type clusters synthesised at the University of Waikato, $(MeGe)_2Co_4(CO)_{11}$ and $[(CO)_4CoGe]_2Co_4(CO)_{11}$ (figure 5.1). Other than the reactions of those species with germanium hydrides described in the previous chapter, the studies have been limited to the thermal stability of $[(CO)_4CoGe]_2Co_4(CO)_{11}$. This was found to decompose at $70^\circ C$ leaving a mixed metal residue [21].

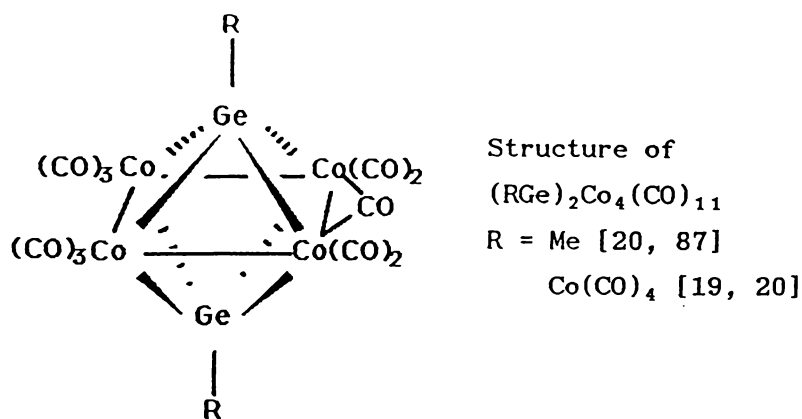
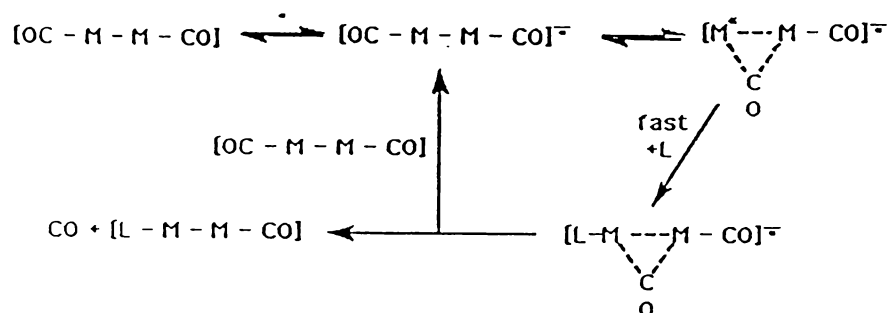


Figure 5.1

Section 1.3.2.3 in Chapter 1 described the numerous products obtained from reactions of E_2M_4 clusters of this type (in particular for $E = P$). Straightforward ligand substitutions have been carried out on several of the available clusters employing both thermal means and electron transfer catalysis for initiation. The latter technique uses a one electron reducing agent such as the benzophenone ketyl radical anion (bpk) which transfers one electron to the substrate producing a complex activated towards substitution [162]. For electron transfer chain catalysis (ETC) to be viable it is necessary for the polynuclear metal carbonyl to be easily reduced, to form a relatively long lived radical anion and for electron transfer to be rapid. Generally these parameters are fulfilled and, in particular, many metal carbonyl cluster radical anions are persistent and, in some cases, may be isolated and their structures determined [163, 164].

A mechanism for carbonyl substitution on metal carbonyl complexes using this process has been proposed [165] and is depicted in scheme 5.1.



Scheme 5.1 [165]

Here it is suggested that bond stretching in the activated complex will produce a coordinatively unsaturated 17-electron metal atom (M^*) which will be susceptible to nucleophilic attack [165]. However, the precise ordering of events and relative rates for CO dissociation and nucleophilic addition is not clear as yet. Another group [166] question this bond stretching mechanism and suggest a pathway involving dissociative loss of CO. Nevertheless, the rate of nucleophilic attack on the radical anion is increased by a factor of $>10^6$ compared to the neutral substrate [165].

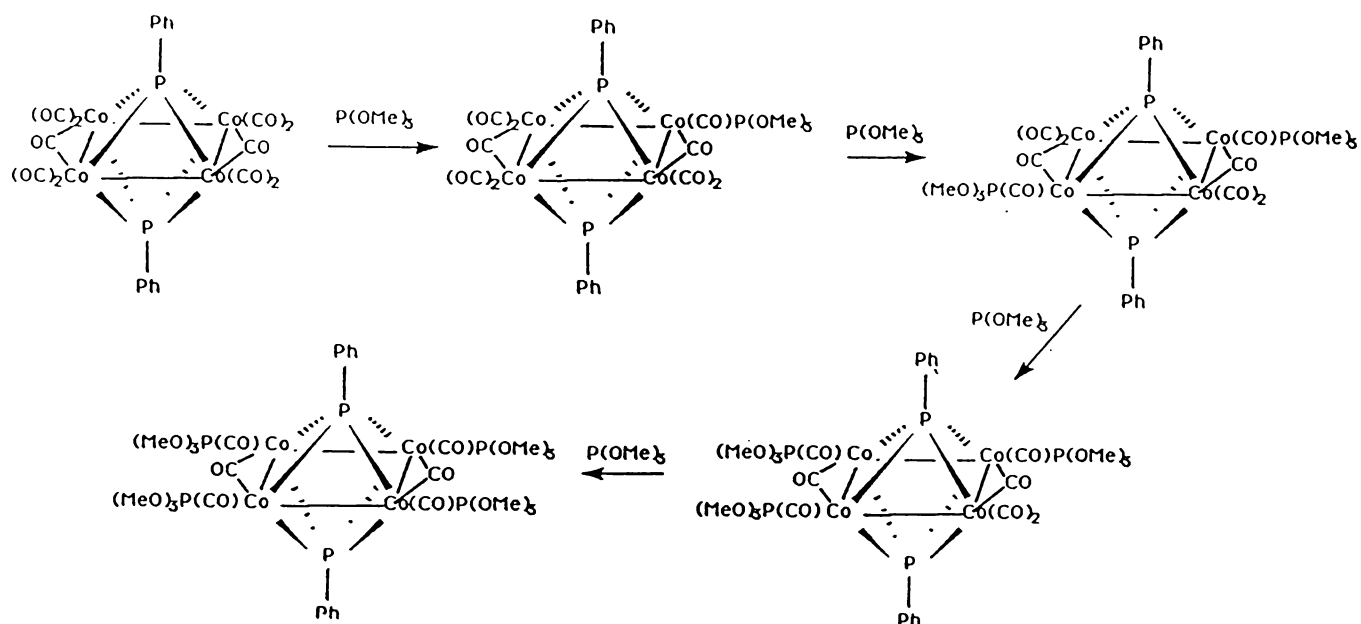
In any event, electron transfer catalysis provides an efficient route for ligand substitution on clusters. While thermal means generally produce a mixture of products, ETC often gives much greater selectivity. Also, as these reactions are conducted at room temperature, large scale decomposition of the cluster is usually avoided.

For the E_2M_4 clusters this technique is of particular interest because of the unusual electronic properties of these species. For example, the groups of clusters $(RP)_2Fe_4(CO)_{11}$ and $(RP)_2Fe_4(CO)_{12}$ interchange readily via CO addition and elimination [109, 110]. The $(RP)_2Fe_4(CO)_{12}$ clusters have the correct electron count by the 18 electron rule for a quadrilateral Fe_4 unit, while, according to Wade's rules [174], these clusters have the correct electron count for a closo Fe_4P_2 unit. Halet [96] has carried out a study of the electronic structure of these E_2M_4 clusters and has found that either seven or eight skeletal electron pairs (SEP) will provide similar stability.

The two clusters investigated here, $(MeGe)_2Co_4(CO)_{11}(J)$ and $[(CO)_4CoGe]_2Co_4(CO)_{11}(K)$, both have eight SEP thus nucleophilic addition reactions are not expected to be favourable.

Perhaps the most closely related E_2M_4 cluster to those under study here is $(PhP)_2Co_4(CO)_{10}$ which has been investigated in detail by Kochi who has

published several reports on the ligand substitution reactions of this species [104-108, 168]. For example, the ligand substitution of the tetracobalt cluster by trimethyl phosphite was carried out thermally by sequentially replacing a single carbonyl ligand in each species as shown in scheme 5.2 [104].



Scheme 5.2. [104]

The preparations of the phosphite-substituted clusters were also achieved simply by adding a stoichiometric measure of $\text{P}(\text{OMe})_3$ to the parent cluster all at once, and then controlling the reaction temperature [104]. Optimum conditions for conversion to the desired derivative were ascertained by thin layer chromatography or by monitoring the appearance of each product by its characteristic carbonyl region infrared spectrum (figure 5.2) [104].

For $(\text{PhP})_2\text{Co}_4(\text{CO})_{10-n}[\text{P}(\text{OMe})_3]_n$

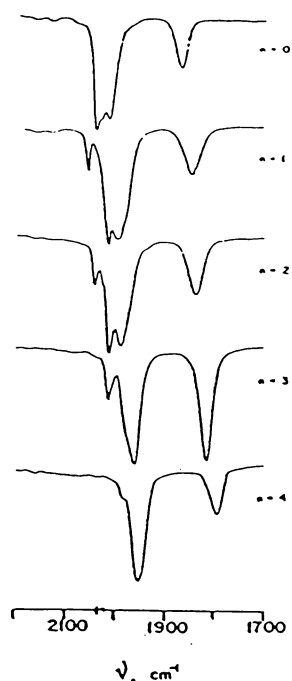
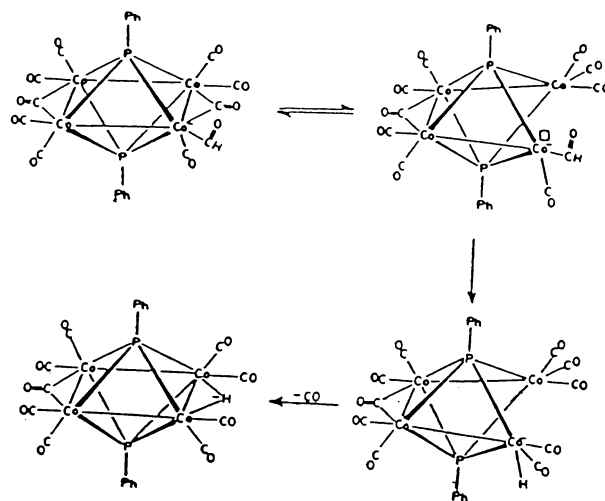


Figure 5.2.

From figure 5.2 it may be seen that the stretching bands associated with both the terminal and bridging carbonyl ligands are systematically shifted to lower energies by successive phosphite substitution. This observation is consistent with a greater degree of π back-bonding in the cobalt-carbon linkages with increasing substitution by the phosphite, which is a stronger σ -donor but weaker π -acceptor ligand than the displaced CO [169].

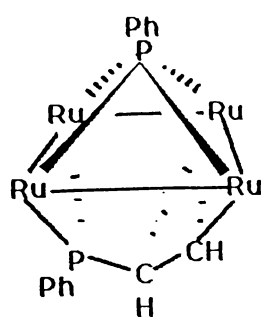
The reaction of $(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ with Et_3BH provides the bridged hydride $[(\text{PhP})_2\text{Co}_4(\text{CO})_9(\mu\text{-H})]^-$ which is formed through an intermediate formyl derivative $[(\text{PhP})_2\text{Co}_4(\text{CO})_9\text{CHO}]^-$ as shown in scheme 5.3 [200].



Scheme 5.3 [200]

Also of interest here are the ligand substitution reactions of the diphosphido tetrairon carbonyl cluster, $(\text{PhP})_2\text{Fe}_4(\text{CO})_{11}$. This contains only one bridging carbonyl group thus the incoming ligand may occupy either an axial or an equatorial position. It is reported [110] that the axial site is preferred which may be explained by the reduced steric interactions found for this orientation.

More complicated processes are observed on reaction of E_2M_4 clusters with less predictable species, such as acetylenes. For example, the reaction of $(\text{PhP})_2\text{Ru}_4(\text{CO})_{11}$ with C_2H_2 under ambient conditions leads to insertion of the acetylene into the skeletal framework resulting in the formation of $\text{Ru}_4(\mu_4\text{-PPh})(\mu_4\text{-}\eta^3\text{-P(Ph)CHCH(CO)}_{11})$ (figure 5.3) [126].



Carbonyls omitted
for clarity

Figure 5.3 [126]

This chapter is concerned with preliminary studies of the chemistry of the clusters $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (*J*) and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*). First described are carbonylation reactions of these species and then basic ligand substitution reactions with Ph_3P and $\text{P}(\text{OEt})_3$. Also covered are some brief experiments using $^t\text{BuNC}$ and XyNC .

5.2. Preparation of starting materials.

Ph_3P , $\text{P}(\text{OEt})_3$, $^t\text{BuNC}$, XyNC ($m\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NC}$) and CO were available in the laboratory.

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was prepared by the reaction of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$ as described in section 4.2.

$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was prepared by the reaction of Ge_2H_6 and $\text{Co}_2(\text{CO})_8$ as described in section 4.2.

$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ was produced by the decarbonylation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ as described in section 4.2.

Benzophenone ketyl radical anion, $[\text{bpk}]^{\cdot-}$, was prepared by refluxing a solution of benzophenone (0.091 g; 0.5 mmol) in THF with finely cut sodium metal under nitrogen. After approximately 2 hours a deep purple colour indicated the $[\text{bpk}]^{\cdot-}$ was present in a concentration of $\text{Ca.}0.025\text{M}$ [170].

5.3. General experimental techniques.

Three main types of reaction conditions were employed. The first series of experiments were concerned with carbonylation reactions. Here the cluster, dissolved in CH_2Cl_2 , was placed in a high pressure bomb under about 40 atmospheres of CO pressure and left overnight. The bomb was cooled in ice-water before releasing the pressure. On opening, a carbonyl region infrared spectrum of the solution was recorded immediately and then each experiment was treated differently. This will be described for each system in section 5.4.1.

The thermal ligand substitution reactions, and the reactions of the clusters with $^t\text{BuNC}$ and XyNC were all carried out in a similar manner. The cluster was dissolved in hexane and a stoichiometric quantity of reagent added. The temperature of the reacting mixture was raised until monitoring by infrared spectroscopy showed the production of new species. The reaction was allowed to continue until no further change was observed. Solvent was removed and the residue extracted with hexane and then dichloromethane.

The final set of reaction conditions applies to the ETC ligand substitution experiments. Here, the cluster was dissolved in THF solution and a stoichiometric amount of reagent was added. $[\text{bpk}]^-$ anion in THF was added dropwise until a change was observed in the infrared spectrum of the mixture. The reaction was generally complete after approximately five minutes once sufficient initiator had been added. Solvent was then removed and hexane added to extract the products.

5.4. Carbonylation reactions of $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ ($\text{R} = \text{Me}, \text{Co}(\text{CO})_4$), and of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$.

5.4.1 Experimental Details and Results.

5.4.1.1 Carbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.011 g; 0.015 mmol) in CH_2Cl_2 (5 mls) was placed in a high pressure bomb under CO pressure of 40 atm for 16 hours. On opening, no change in colour of the solution was observed. A carbonyl region infrared spectrum of the solution was recorded and is listed in table 5.1. The solution was left at -15°C for 1 week but no change was observed in the carbonyl region infrared spectrum. The solution was then left at room temperature for 12 hours and, again, no change was observed in either the solution or its infrared spectrum. Solvent was then removed and the products were pumped under vacuum for 1 hour. CH_2Cl_2 was added to the solid and it was found that some dark-coloured powder would not redissolve. An infrared spectrum of this species, recorded as a nujol mull, showed no carbonyl vibrations and this was assumed to be a decomposition product. A carbonyl region infrared spectrum was taken of the redissolved products which showed complete reversion to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.007 g; 0.01 mmol; 67% recovery).

Table 5.1: Carbonyl region infrared data for the mixture resulting from carbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ together with that reported for $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [87] (cm^{-1}).

Mixture	$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$
2082 w	
2071 w	
2062 w	
2055 m	
2039 sh, w	2034 vs
2022 vbr, s	2016 m
1933 br, vs	2004 sh
	1853 w, br.

Both recorded in CH_2Cl_2 .

5.4.1.2 Carbonylation of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$

$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (0.009 g; 0.009 mmoles) in CH_2Cl_2 (5 mls) was placed in a high pressure bomb under 40 atm of CO pressure for 16 hours. On opening, no change in the colour of the solution was observed. A carbonyl region infrared spectrum of the solution was recorded and is listed in table 5.2. The solution was left at -15°C for 1 week but no change was observed in the carbonyl region infrared spectrum. The solution was then left at room temperature for 12 hours at which point it was found that decomposition had occurred as the products were now a very dark brown and were insoluble in CH_2Cl_2 .

Table 5.2. Carbonyl region infrared data for the mixture resulting from carbonylation of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ together with that reported for $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ [19] (cm^{-1}).

Mixture	$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$
2084 vw	2100 s
2065 vw	2065 w, sh
2050 sh, w	2050 s
2034 sh, m	2037 vs
2020 br, s	2014 m
	2003 w, sh
1992 br, vs	1990 w, sh
	1844 w, br

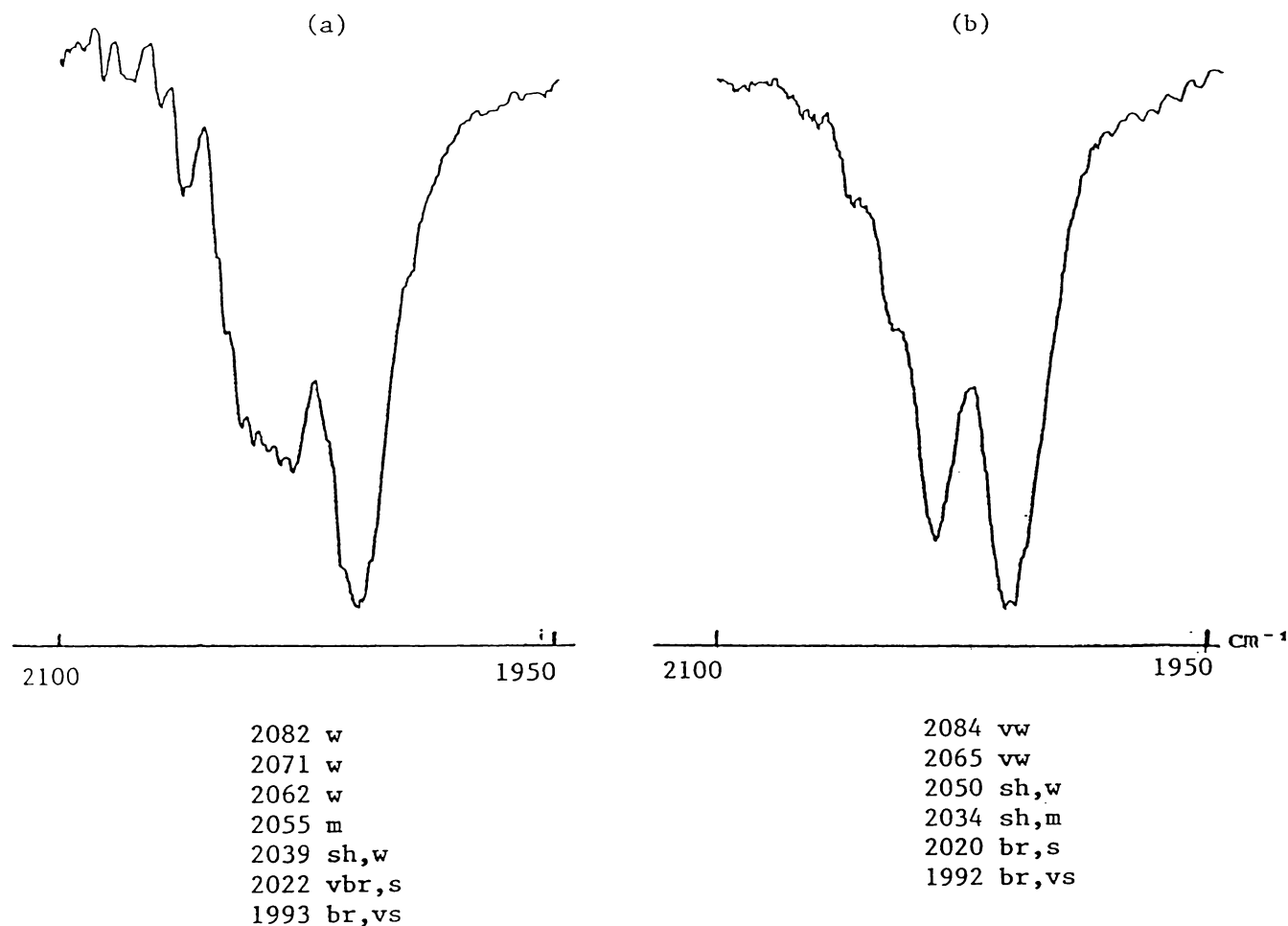
Both recorded in CH_2Cl_2 .

5.4.1.3 Carbonylation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$

$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.012 g; 0.011 mmoles) in CH_2Cl_2 (5 mls) was placed in a high pressure bomb under 40 atm of CO pressure for 16 hours. On opening no change in the colour of the solution was observed. A carbonyl region infrared spectrum of the solution was recorded which showed bands at 2087(s), 2068(vs), 2054(s) 2027(m) and 1844(w) cm^{-1} corresponding to unreacted $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ [19] but also bands at 2020 (m-s) and 1992 cm^{-1} (m-s) corresponding to a small amount of the same product as obtained from the carbonylation of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$. The solution was then placed in a vessel fitted with a Kontes greaseless tap and was heated at 50°C for 2 days. A carbonyl region infrared spectrum of the solution was again recorded. This showed that the $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was decarbonylating to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (see section 1.3.2.1) but the new product was unaffected by heat and its carbonyl bands were of the same intensity as before heating.

5.4.2 Discussion of the Carbonylation Reactions of $(RGe)_2Co_4(CO)_{11}$ ($R = Me, Co(CO)_4$) and of $Ge_2Co_6(CO)_{20}$.

Both $(MeGe)_2Co_4(CO)_{11}(J)$ and $[(CO)_4CoGe]_2Co_4(CO)_{11}(K)$ quantitatively formed products with very similar carbonyl region infrared spectra when placed under high CO pressure for 16 hours. The infrared active carbonyl stretches of the products obtained from the two species are shown in figure 5.4.



Infrared active carbonyl stretches of the carbonylation products of
(a) $(MeGe)_2Co_4(CO)_{11}$ and (b) $[(CO)_4CoGe]_2Co_4(CO)_{11}$.

Both recorded in CH_2Cl_2 .

Figure 5.4.

As no quantitative data was obtained from these experiments it is only possible to speculate on the nature of the products. If one mole of CO was taken up by each mole of cluster then the addition of one electron pair should result in the cleavage of one M-M bond. This could provide an open-edged octahedron as shown in figure 5.5.

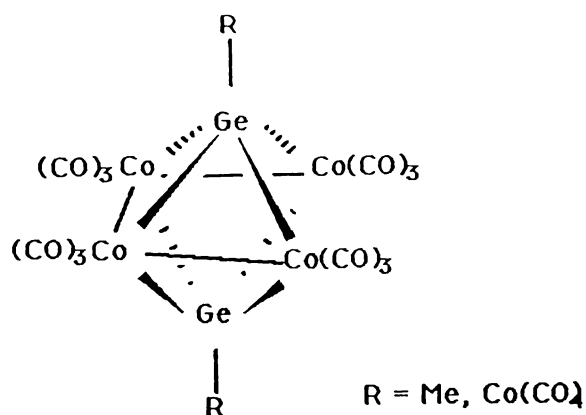


Figure 5.5

It has recently been reported [201] that $(\mu_4\text{-Te})_2\text{Co}_4(\text{CO})_{10}$ will take up a further CO ligand under pressure to form $(\mu_4\text{-Te})_2\text{Co}_4(\text{CO})_{11}$. This species has been crystallographically characterised and is found to contain an octahedral Te_2Co_4 unit where one Co-Co bond has cleaved.

It is also possible that one or both of the germanium atoms becomes μ_3 . For example, the carbonylation of $(\text{PhP})_2\text{Ru}_4(\text{CO})_{11}$ affords the tridecacarbonyl derivative depicted in figure 5.6.

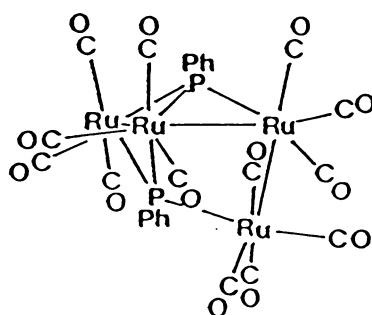
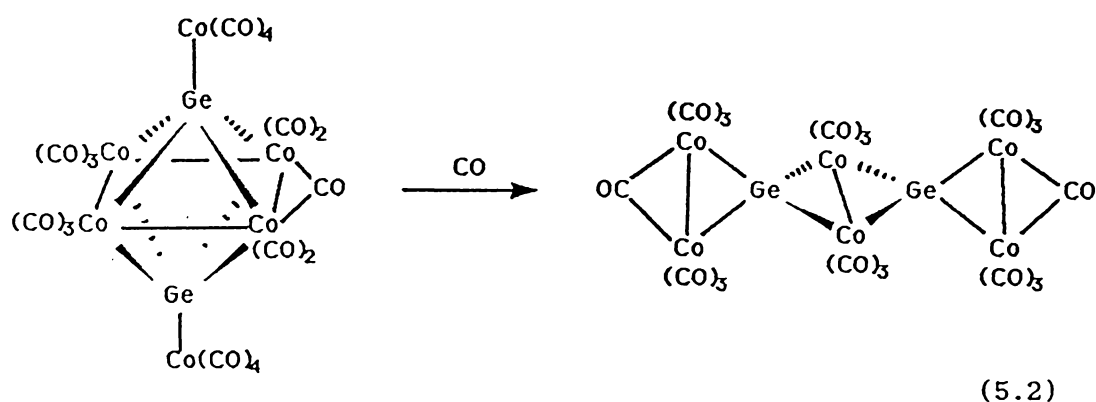
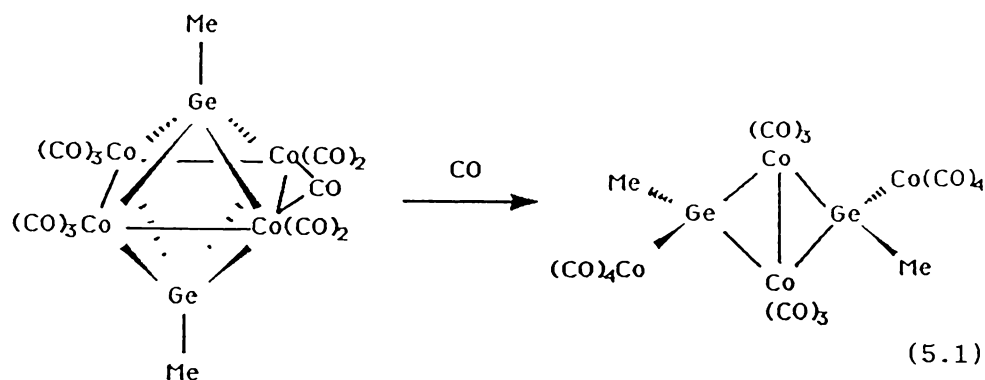


Figure 5.6

Although this species derives from the addition of two carbonyl ligands, similar possibilities may be envisaged for the carbonylation products obtained here.

Finally, it could be anticipated that the addition of CO could cause these species to revert to their open-skeleton precursors, as shown in equations 5.1 and 5.2.



The carbonyl region infrared spectra of the products, however, being entirely different from the two known species $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ [31] and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ [19,20], shows that this is not the case.

If two or more carbonyl ligands were taken up similar discussions are possible, and it is also conceivable that no CO addition has taken place and the products have simply resulted from some rearrangement caused by the high pressure employed.

It is desirable that these preliminary studies are repeated and quantitative data obtained to clarify these processes. In particular, the results found here on the reversibility of the reactions appear somewhat contradictory.

The carbonylation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) produced mainly unaffected starting material and a small amount of the same product as obtained from the carbonylation of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*). This may be explained by the presence of a small amount of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ - which is produced by condensation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ [19] - in solution. It is also possible, however, that the CO pressure causes a rearrangement of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ to the

new product, but this process would have to be extremely slow to account for the very minor production of this species.

5.5. Thermal ligand substitution reactions of $(RGe)_2Co_4(CO)_{11}$ ($R = Me, Co(CO)_4$).

5.5.1. Experimental Details and Results.

5.5.1.1. Reaction of $(MeGe)_2Co_4(CO)_{11}(J)$ with PPh_3

PPh_3 (0.005 g; 0.02 mmol) was added to a stirred solution of $(MeGe)_2Co_4(CO)_{11}$ (0.015 g; 0.021 mmol) (1:1 ratio) in hexane (10 ml). The temperature was raised to 40°C where the carbonyl region infrared spectrum of the mixture was seen to change. The mixture was left to react at this temperature for 2 hours at which time the solution had changed from orange to light brown with a dark coloured solid at the bottom of the flask. The solution was decanted away from the solid. The carbonyl region infrared spectrum of the solution after it had been concentrated showed a medium intensity peak at 2017 cm^{-1} , which is consistent with monosubstitution of a carbonyl ligand by a phosphine on a E_2M_4 cluster [104]. The solid material was separated into two fractions. The first was slightly soluble in CH_2Cl_2 and benzene and showed a very strong band at 1951 cm^{-1} in the carbonyl region infrared spectrum recorded as a nujol mull. This has been characterised by infrared spectroscopy and electron probe analysis as $[(Ph_3P)Co(CO)_3]_2$ [172]. The second fraction was insoluble in CH_2Cl_2 and showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a decomposition product and its characterisation was not pursued.

5.5.1.2. Reaction of $[(CO)_4CoGe]_2Co_4(CO)_{11}(K)$ with PPh_3

PPh_3 (0.013 g; 0.05 mmol) was added to a stirred solution of $[(CO)_4CoGe]_2Co_4(CO)_{11}$ (0.051 g; 0.05 mmol) (1:1 ratio) in hexane (20 ml). The temperature was raised to 40°C at which point the infrared spectrum of the solution began to change. The mixture was left to react at this temperature for 3 hours when the solution was virtually colourless and a large amount of a dark coloured deposit was observed at the bottom of the flask. After the solid was separated, the solution was concentrated and a carbonyl region infrared spectrum was recorded. This showed no carbonyl bands and was discarded. The solid material was separated into two fractions. The first was slightly soluble in CH_2Cl_2 and benzene and showed a strong band at 1951 cm^{-1} in the carbonyl region infrared spectrum recorded

as a nujol mull. This has been characterised by infrared spectroscopy and electron probe analysis as $[(\text{Ph}_3\text{P})_2\text{Co}(\text{CO})_3]_2$ [172], the same product as obtained from the reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with PPh_3 . The remainder of the solid was insoluble in CH_2Cl_2 and showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a decomposition product and its characterisation was not pursued.

5.5.1.3 Reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with $\text{P}(\text{OEt})_3$

$\text{P}(\text{OEt})_3$ (0.005 g; 0.03 mmoles) in hexane (5 mls) was added to a stirred solution of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.021 g; 0.03 mmoles) (1:1 ratio) in hexane (10 mls) and the temperature raised to 50°C where the infrared spectrum of the mixture began to change. This was left to react for $3\frac{1}{2}$ hours at which point the solution was a dark orange colour and a large amount of brown solid material was observed at the bottom of the flask. The solution was decanted from the solid material and a carbonyl region infrared spectrum of the solution was recorded. This mainly showed bands corresponding to unreacted $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (2034 (s), 2016 (m) 2004 (sh) and 1853 (w) cm^{-1} [20]) but also some new peaks at 2019 cm^{-1} (m), 2006 cm^{-1} (w) and 1990 cm^{-1} (w). TLC of the solution showed five fractions, however preparative separation of the various compounds by this technique proved impossible. The solid material was separated into two fractions. The first was soluble in CH_2Cl_2 and showed a strong band at 1976 cm^{-1} in the infrared spectrum. This has been characterised by infrared and mass spectroscopy and by electron probe analysis as $\{[(\text{EtO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$. The remaining solid material, which was dark brown in colour, was insoluble in CH_2Cl_2 and showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a decomposition product and its characterisation was not pursued.

5.5.1.4 Reaction of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ and $\text{P}(\text{OEt})_3$

$\text{P}(\text{OEt})_3$ (0.007 g; 0.044 mmoles) (1:1 ratio) in hexane (5 mls) was added to a stirred solution of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (0.046 g; 0.045 mmoles) in hexane (20 mls). The temperature of the mixture was raised to 50°C where the infrared spectrum began to change. This was left to react for 4 hours at which point the solution was orange in colour and a dark coloured deposit was observed at the base of the flask. After separation a carbonyl region infrared spectrum of the solution was recorded. This showed mainly unreacted $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (2100 (s), 2065 (w,sh), 2050 (s) 2037 (vs) 2014 (m), 2003 (w) 1990 (w,sh) and 1844 cm^{-1} (w) [19]) but also some new

peaks at 2023 (m), 2010 (w) and 1997 cm^{-1} (w). TLC of the mixture showed the presence of up to four fractions but no attempt was made to separate these. The solid material was divided into two fractions. The first, which was light brown in colour, was soluble in CH_2Cl_2 and showed a strong band at 1976 cm^{-1} in the carbonyl region infrared spectrum. This has been characterised by infrared and mass spectroscopy and by electron probe analysis as $\{[(\text{EtO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$, the same product as obtained in the reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $\text{P}(\text{OEt})_3$. The remainder of the solid was dark brown, insoluble in CH_2Cl_2 and showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a decomposition product and its characterisation was not pursued.

5.5.2 Characterisation of $[(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3]_2$ and $\{[(\text{EtO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$.

5.5.2.1 Carbonyl region infrared spectroscopy.

The carbonyl region infrared spectra of the two major products obtained in this work are depicted in figures 5.7(a) and (b). The bands are listed in table 5.3. together with those previously reported for $[(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3]_2$, $\{[(\text{MeO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$ and $\{[(\text{PhO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$. [172]

Table 5.3. Carbonyl region infrared data for some derivatives of $\text{Co}_2(\text{CO})_8$ (cm^{-1}).

From PPh_3 reactions (a)	$[(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3]_2$ [172] (b)	From $\text{P}(\text{OEt})_3$ reactions (c)	$\{[(\text{MeO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$ [172] (d)	$\{[(\text{PhO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$ [172] (b)
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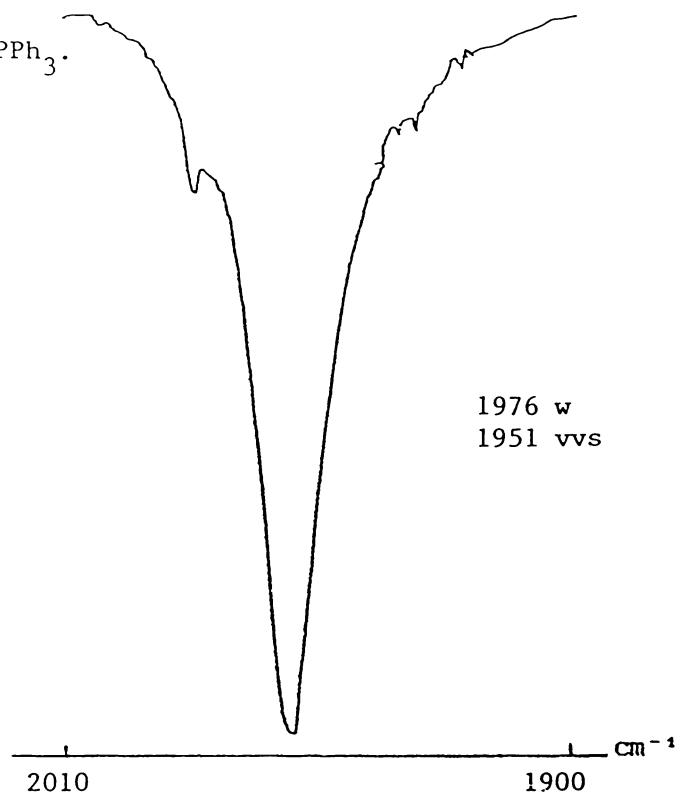
		2015 w		
1976 w	1977 sh, w	1999 sh, w	1991 w	1998 sh, w
1951 vvs	1957 vvs	1976 vvs	1975 vvs	1979 vvs

- (a) Recorded as a nujol mull. (b) Recorded from CHCl_3 solution.
(c) Recorded from benzene solution. (d) Recorded from C_7H_{16} solution.

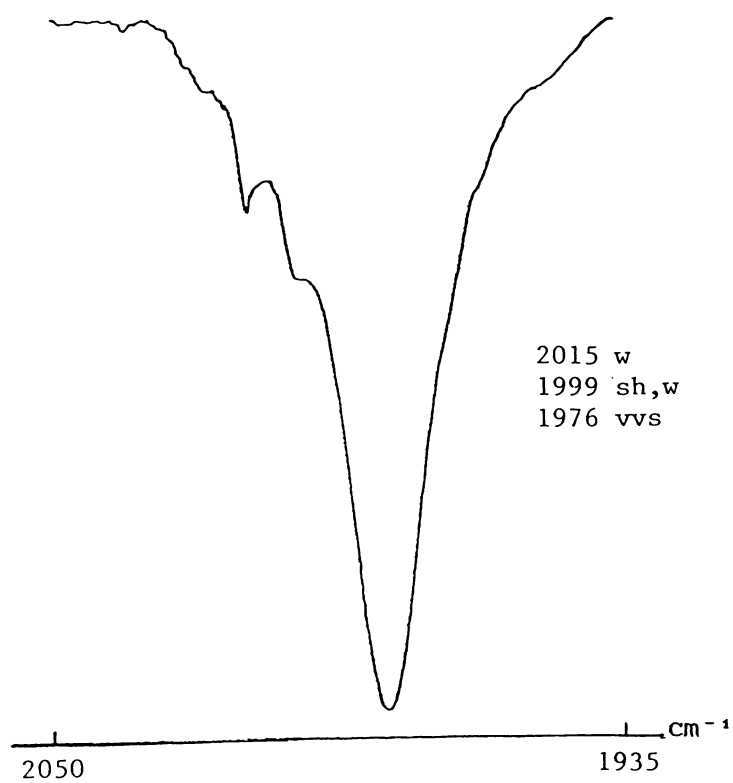
From table 5.3 it can be seen that, allowing for the different solvents used, the spectra of the compounds obtained in this work match extremely closely to those expected for $[(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3]_2$ or $\{[(\text{EtO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$.

Figure 5.7. Infrared active carbonyl stretches of the major products from reaction of $(RGe)_2Co_4(CO)_{11}$ ($R = Me, Co(CO)_4$) with PPh_3 or $P(OEt)_3$.

(a) With PPh_3 .



(b) With $P(OEt)_3$.



5.5.2.2. Mass spectroscopy.

The mass spectrum recorded for the major product obtained from the reactions using $\text{P}(\text{OEt})_3$ is listed in table 5.4. No peak corresponding to the expected parent ion $\{(\text{EtO})_3\text{P}\text{Co}(\text{CO})_3\}_2^+$ was observed and the highest mass peak found was at $m/e = 565$, attributed to $\{[(\text{EtO})_3\text{P}]_2\text{Co}_2(\text{CO})_4\}^+$. It is apparent that all carbonyl ligands are lost before the triethyl phosphite groups start to fragment. 95% of the ion current was carried by fragments containing no carbonyl groups.

Table 5.4. Mass spectrum of $[(\text{EtO})_3\text{P}]_2\text{Co}_2(\text{CO})_6$.

	m/e	Relative intensity	Assignment
loss of CO:			
	565	4	$[(\text{EtO})_3\text{P}]_2\text{Co}_2(\text{CO})_4^+$
	508	4	$[(\text{EtO})_3\text{P}]_2\text{Co}_2(\text{CO})_2^+$
	474	2	$[(\text{EtO})_3\text{P}]_2\text{Co}_2(\text{CO})^+$
	448	19	$[(\text{EtO})_3\text{P}]_2\text{Co}_2^+$
loss of OEt:			
	405	64	$(\text{EtO})_5\text{P}_2\text{Co}_2^+$
	365	68	$(\text{EtO})_4\text{P}_2\text{Co}_2^+$
	318	40	$(\text{EtO})_3\text{P}_2\text{Co}_2^+$
	270	62	$(\text{EtO})_2\text{P}_2\text{Co}_2^+$
	224	11	$(\text{EtO})\text{P}_2\text{Co}_2^+$
	181	21	P_2Co_2^+
Other fragmentations:			
	282	83	$(\text{EtO})_3\text{PCo}_2^+$
	253	86	$(\text{EtO})_2(\text{O})\text{PCo}_2^+$
	237	13	$(\text{EtO})_2\text{PCo}_2^+$
	226	53	$(\text{EtO})_3\text{PCo}^+$
	196	34	$(\text{EtO})_2(\text{O})\text{PCo}^+$
	181	21	$(\text{EtO})_2\text{PCo}^+$
	152	17	$(\text{EtO})(\text{O})\text{PCo}^+$
	137	15	$(\text{EtO})\text{PCo}^+$
	106	7	$(\text{O})\text{PCo}^+$
	166	72	$(\text{EtO})_3\text{P}^+$
	139	100	$(\text{EtO})_2(\text{O})\text{P}^+$
	121	78	$(\text{EtO})_2\text{P}^+$

Unfortunately the major product of the reactions with Ph_3P was too involatile to give a useful mass spectrum.

5.5.2.3. Electron probe analysis.

The electron probe analysis of the two major products obtained in this work gave the atomic percentages shown in table 5.5.

Table 5.5. Electron probe analysis data for the major products of reactions of $(RGe)_2Co_4(CO)_{11}$ ($R = Me, Co(CO)_4$) with PPh_3 or $P(OEt)_3$.

	Element	Shell	Atomic percentage
PPh ₃ product	P	K	51.9
	Co	K	48.1
P(OEt) ₃ product	P	K	49.8
	Co	K	50.2

In both cases the atomic ratios obtained give a P:Co ratio of 1:1, consistent with the formulation of the products as $[(Ph_3P)Co(CO)_3]_2$ and $\{[(EtO)_3P]Co(CO)_3\}_2$.

Through these techniques the major products of reaction of $(RGe)_2Co_4(CO)_{11}$ ($R = Me, Co(CO)_4$) with PPh_3 or $P(OEt)_3$ have been characterised as $[(Ph_3P)Co(CO)_3]_2$ and $\{[(EtO)_3P]Co(CO)_3\}_2$ respectively.

5.5.3 Discussion of the Thermal Reactions of $(RGe)_2Co_4(CO)_{11}$ ($R = Me, Co(CO)_4$) with PPh_3 or $P(OEt)_3$.

These preliminary studies of thermal ligand substitutions of $(RGe)_2Co_4(CO)_{11}$ clusters ($R = Me, Co(CO)_4$) by phosphines or phosphites have shown the major product in each case to be a disubstituted derivative of dicobalt octacarbonyl. Also found in each experiment was an insoluble residue containing no carbonyl groups which suggests that large scale decomposition of the cluster occurs during the reaction. Although these reactions were not studied quantitatively it was apparent that the majority of the cobalt from the starting clusters was found in the disubstituted dicobalt carbonyl products. The majority of the germanium appeared to be present in the insoluble residue.

It appears that the two clusters under study here, $(MeGe)_2Co_4(CO)_{11}$ (*J*) and $[(CO)_4CoGe]_2Co_4(CO)_{11}$ (*K*), are not as stable to thermal ligand substitution as the related phosphorus cluster, $(PhP)_2Co_4(CO)_{10}$ [104]. This undergoes sequential replacement of carbonyl groups by $P(OMe)_3$, and the particular substitution products can be obtained in moderate to near-quantitative yields by controlling the reaction temperature. At no time was fragmentation of the cluster framework observed [104]. Degradation of clusters in this type of reaction is not uncommon, however, and is promoted by the fact that bonding of a metal atom to a ligand nearly always liberates more energy than bonding of a metal atom to another metal atom [175].

Although the major products of these systems resulted from breakdown of the cluster there was also some indication of ligand substitution on the cluster itself. In the reaction of PPh_3 with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (run 5.5.1.1) a carbonyl region infrared spectrum of the solution after concentration showed a major band at 2017 cm^{-1} which is a shift of 17 cm^{-1} to lower frequency from that of the parent cluster [20]. This is consistent with monosubstitution by a phosphine ligand on E_2M_4 clusters [104]. Similarly, the reactions of $\text{P}(\text{OEt})_3$ with both $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$, apart from providing $\{[\text{P}(\text{OEt})_3]\text{Co}(\text{CO})_3\}_2$, also showed evidence through carbonyl region infrared spectroscopy and thin layer chromatography of possibly mono-, di-, and trisubstitution on the cluster. These products, unfortunately, could not be separated and were present in such small amounts that formal characterisation was not possible. The stability of these substitution products appears to be lower than that of the parent cluster since an attempt at separation of the mixture by TLC gave either decomposition of the fractions or reconversion to the starting material.

There appears to be little difference in the reactivity of the two clusters $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (*J*) and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*). Both required similar temperatures before any reaction began and similar products were obtained from each. Thus the terminal group, Me or $\text{Co}(\text{CO})_4$, can have little effect on the reactivity of the E_2M_4 core.

The reactions using PPh_3 were conducted at 40°C and provided only a very small amount of the species suggested to retain the E_2M_4 core. The $\text{P}(\text{OEt})_3$ experiments required a temperature of 50°C before any reaction was observed and a larger proportion of the products appeared to retain the E_2M_4 framework. These observations are consistent with PPh_3 being a stronger σ -donor than $\text{P}(\text{OEt})_3$ [202].

In conclusion to this section of work it may be stated that thermally initiated reactions are not a promising route to phosphine or phosphite substituted derivatives of $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ clusters ($\text{R} = \text{Me}, \text{Co}(\text{CO})_4$).

5.6 Electron transfer catalysed ligand substitution reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (*J*)

5.6.1. Experimental Details and Results.

Run 1: PPh_3 (0.006 g; 0.023 mmol) in THF (3 ml) was added to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.017 g; 0.023 mmol) (1:1 ratio) in THF (5 ml).

Benzophenone ketyl radical anion ($[bpk]^-$) in THF (ca. 0.025 M) was added dropwise (usually 3 - 5 drops were necessary) until reaction was observed by monitoring with infrared spectroscopy. Once the reaction had commenced it was virtually instantaneous, leaving a pale orange solution and a small amount of a dark coloured deposit. THF was removed and the residue extracted with hexane and CH_2Cl_2 .

The hexane soluble fraction (ca. 40%) showed carbonyl region infrared bands corresponding to a small amount of unreacted $(MeGe)_2Co_4(CO)_{11}$ and a strong band at 2017 cm^{-1} consistent with a monosubstituted product, $(MeGe)_2Co_4(CO)_{10}PPh_3$. TLC confirmed the presence of two species but these were not separated. The CH_2Cl_2 soluble fraction (ca. 40%) showed carbonyl region infrared bands corresponding to $[(Ph_3P)Co(CO)_3]_2$ [172]. The final fraction (ca. 20%) was a dark insoluble solid which showed no carbonyl bands in the infrared spectrum recorded as a nujol mull and was thus assumed to be a decomposition product.

Run 2: Ph_3P (0.014 g; 0.055 mmol) in THF (7 ml) was added to $(MeGe)_2Co_4(CO)_{11}$ (0.008 g; 0.011 mmol) (5:1 ratio) in THF (5 ml). $[bpk]^-$ (ca. 0.025 M) in THF was added dropwise until a reaction began. After five minutes the reaction was complete and a pale orange solution remained with a dark solid deposit. THF was removed and the residue extracted with hexane and CH_2Cl_2 .

The hexane soluble fraction (ca. 20%) gave a carbonyl region infrared spectrum showing a band at 2017 cm^{-1} , suggesting the formation of the monosubstituted phosphine derivative of $(MeGe)_2Co_4(CO)_{11}$. TLC showed the presence of two fractions but these were not separated. The CH_2Cl_2 soluble fraction (ca. 60%) showed bands in an infrared spectrum corresponding to $[(Ph_3P)Co(CO)_3]_2$. The final fraction (ca. 20%) was an insoluble dark solid which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull and was thus assumed to be a decomposition product.

Run 3: $P(OEt)_3$ (0.004 g; 0.026 mmol) in THF (3 ml) was added to $(MeGe)_2Co_4(CO)_{11}$ (0.019 g; 0.026 mmol) (1:1 ratio) in THF (5 ml). $[bpk]^-$ (ca. 0.025 M) in THF was added dropwise until a reaction began. After five minutes the reaction was complete and an orange solution remained. THF was removed and the residue re-dissolved in hexane. A carbonyl region infrared spectrum was recorded of the solution which showed bands corresponding to only one carbonyl containing species which has been tentatively characterised as $(MeGe)_2Co_4(CO)_{10}P(OEt)_3$ by carbonyl region infrared

spectroscopy and by electron probe analysis. This characterisation is discussed in section 5.6.2

Run 4: $\text{P}(\text{OEt})_3$ (0.021 g; 0.130 mmol) in THF (3 ml) was added to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.019 g; 0.026 mmol) (5:1 ratio) in THF (5 ml). $[\text{bpc}]^-$ (ca. 0.025 M) in THF was added dropwise until a reaction began. After five minutes a dark brown solution remained. THF was removed and the residue extracted with hexane and CH_2Cl_2 .

Two fractions were obtained. The first (ca. 80%) was soluble in hexane giving a dark brown solution and a carbonyl region infrared spectrum of this solution showed weak bands at 2020 cm^{-1} , 2008 cm^{-1} and 1995 cm^{-1} and a very strong band at 1975 cm^{-1} , suggesting a mixture of small amounts of the mono-, di- and trisubstituted derivatives of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and a large proportion of $\{[(\text{EtO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$. The second fraction was an insoluble dark solid which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull.

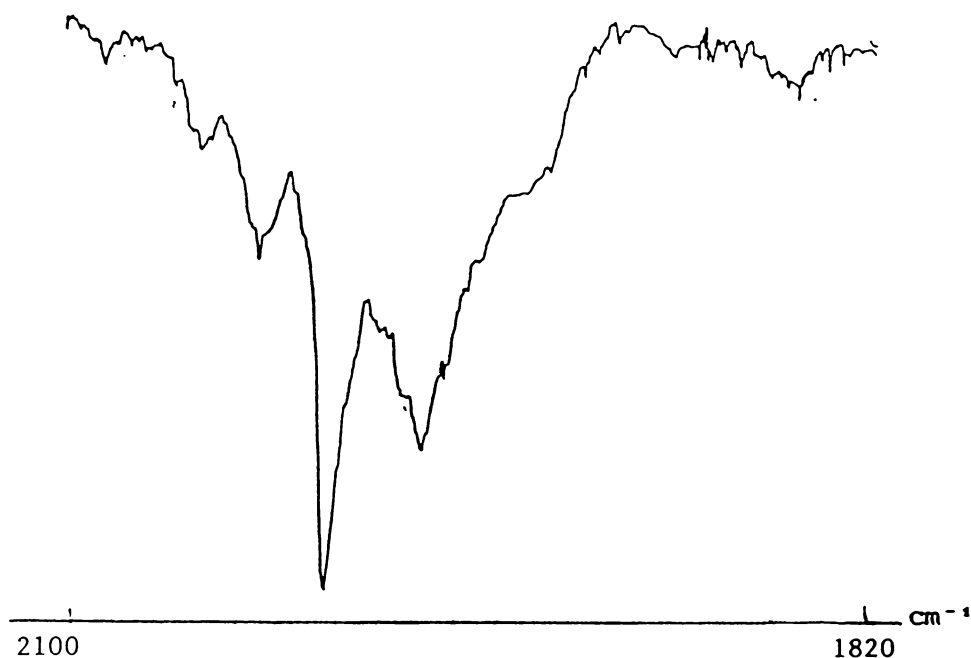
5.6.2. Tentative Characterisation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{P}(\text{OEt})_3$.

5.6.2.1. Handling.

The product of the reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with $\text{P}(\text{OEt})_3$ in a 1:1 ratio is a red-brown solid that appears reasonably stable at room temperature in the absence of air. This species is quite soluble in hexane and very soluble in dichloromethane. It was, unfortunately, too involatile to give a useful mass spectrum.

5.6.2.2. Carbonyl stretches in the infrared spectrum.

The carbonyl region infrared spectrum recorded of the product of reaction between $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{P}(\text{OEt})_3$ in a 1:1 ratio is shown in figure 5.8. The bands are listed in table 5.6. together with those of the parent cluster, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, and those reported for $(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ and $(\text{PhP})_2\text{Co}_4(\text{CO})_9\text{P}(\text{OMe})_3$.



Infrared active carbonyl stretches of the product obtained from reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $\text{P}(\text{OEt})_3$ in a 1:1 ratio (recorded in hexane).
Figure 5.8.

Table 5.6. Carbonyl region infrared data for the product of run 3, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, $(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ and $(\text{PhP})_2\text{Co}_4(\text{CO})_9\text{P}(\text{OMe})_3$ (cm^{-1}).

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [20, 87] (a)	Product of run 3 (a)	$(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ [104] (b)	$(\text{PhP})_2\text{Co}_4(\text{CO})_9\text{P}(\text{OMe})_3$ [104] (b)
	2071 w		
	2056 m		2058 m
	2037 w, sh		
2034 vs	2020 vs	2041 vs	2023 vs
2016 m	1994 m, br	2029 s	2008 s
2004 sh		2015 s	
1853 w, br.	1845 w, br	1871 m	1850 m

(a) Recorded from $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution

(b) Recorded from CH_2Cl_2 solution.

From table 5.6 it can be seen that substitution of one carbonyl ligand of $(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ by $\text{P}(\text{OMe})_3$ results in the following changes to the carbonyl region infrared spectrum: The appearance of a medium intensity band at 2052 cm^{-1} , a shift to lower frequency of the main bands by an average 20 cm^{-1} and the disappearance of one strong band from the spectrum. The product of reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $\text{P}(\text{OEt})_3$ in a 1:1 ratio shows the following

differences from the parent cluster in the carbonyl region infrared spectrum: The appearance of a new weak band at 2056 cm^{-1} and a shift to lower frequency of the main bands by an average 15 cm^{-1} . It thus seems reasonable to suggest that the product of this reaction is the monosubstituted species, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{P}(\text{OEt})_3$.

5.6.2.3. Electron probe analysis.

The electron probe analysis of a sample of the product of the reaction between $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{P}(\text{OEt})_3$ in a 1:1 ratio gave the atomic percentage values listed in table 5.7.

Table 5.7. Electron probe analysis data for the product of run 3.

Element	Shell	Atomic Percentage
Ge	K	28.5
Co	K	57.4
P	K	14.1

These give a P:Ge:Co ratio of 1:2:4, which is consistent with the formulation of the product as $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{P}(\text{OEt})_3$.

Through the two techniques employed the product of reaction between $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{P}(\text{OEt})_3$ in a 1:1 ratio has thus been tentatively characterised as $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{P}(\text{OEt})_3$.

5.6.3 Discussion of the Electron Transfer Catalysed Ligand Substitution Reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$.

The electron transfer catalysed (ETC) ligand substitution reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with PPh_3 or $\text{P}(\text{OEt})_3$ seem to provide a number of different products depending on the reaction conditions.

The reaction between $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{P}(\text{OEt})_3$ in a 1:1 ratio appeared to quantitatively produce the monosubstituted derivative, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{P}(\text{OEt})_3$. Using a five fold excess of $\text{P}(\text{OEt})_3$, however, gave $\{[(\text{EtO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$ as the major product. This is the same species as obtained from the thermally induced substitution reactions. In this system there were also indications from the carbonyl region infrared spectrum of the presence of small amounts of mono-, di- and trisubstituted derivatives of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

From these observations it could be suggested that the fourth substitution of a carbonyl ligand on $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ by $\text{P}(\text{OEt})_3$ results in the breakdown of the cluster to $\{[(\text{EtO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$ and the dark insoluble residue which was also observed from this reaction. This suggestion could be confirmed by preparation of the tris - $\text{P}(\text{OEt})_3$ derivative and reaction of this with a further stoichiometric quantity of $\text{P}(\text{OEt})_3$.

It is also possible that the orientation of the additional phosphite ligands on the cluster contributes to the breakdown to the disubstituted dicobalt species. That is, once one carbonyl ligand has been replaced by $\text{P}(\text{OEt})_3$ then the second replacement can occur either on an adjacent cobalt or on the cobalt atom diagonally opposite. If the substitution occurs on the adjacent cobalt atom this could promote breakdown to $\{[(\text{EtO})_3\text{P}]\text{Co}(\text{CO})_3\}_2$ since this portion of the cluster would be conveniently arranged for this process to occur. Similarly, once three carbonyl ligands have been replaced then breakdown of the cluster would be very favourable.

The reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with PPh_3 in a 1:1 ratio appeared to provide some of the monosubstituted species, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{PPh}_3$, but also yielded $\{(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3\}_2$. Reaction with a five-fold excess of PPh_3 again provided mainly $\{(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3\}_2$ and only a trace amount of what is proposed to be the monosubstituted derivative. These results would suggest that for PPh_3 only two substitutions of a carbonyl ligand on $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ are required for breakdown of the cluster to occur yielding $\{(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3\}_2$ and the insoluble residue.

The results found using the two different ligands - where PPh_3 caused a greater degree of cluster degradation than $\text{P}(\text{OEt})_3$ - is again consistent with PPh_3 being a stronger σ -donor than $\text{P}(\text{OEt})_3$ [202].

From these preliminary investigations of the ETC ligand substitution reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ it may be concluded that:

(i) $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{P}(\text{OEt})_3$ is quantitatively produced by reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $\text{P}(\text{OEt})_3$ in a 1:1 ratio.

(ii) $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{PPh}_3$ may be produced in moderate yields by reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with PPh_3 but breakdown of the cluster is difficult to avoid.

(iii) For $\text{P}(\text{OEt})_3$ it appears that the fourth substitution of a carbonyl ligand on $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ results in breakdown of the cluster, while for PPh_3 only two substitutions appear to be required for breakdown to occur.

5.6.4. Comparison of the Thermal and ETC Ligand Substitution Reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with PPh_3 and $\text{P}(\text{OEt})_3$

All of these ligand substitution reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ may be considered together as the same system carried out under different conditions. While the thermally initiated reactions resulted in large scale degradation of the cluster, the ETC reactions provided at least some proportion of the desired products. Clearly, the more rigorous conditions of the thermal reactions increase the likelihood of cluster breakdown.

In the previous section it was suggested that the number of substituting R_3P ligands contributed to the amount of observed breakdown. For the thermal reactions, however, even where there was a 1:1 ratio of cluster to ligand, very little of the monosubstituted product was observed. Thus the high temperature of these systems must be a factor in the cluster degradation.

It is thus felt that thermal substitution is not a promising route to derivatives of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

5.7 Reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with $^t\text{BuNC}$ and XyNC

5.7.1 Experimental Details and Results

5.7.1.1 $^t\text{BuNC}$ (0.002 g; 0.022 mmoles) in hexane (2 mls) was added to a stirred solution of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (0.015 g; 0.021 mmoles) (1:1 ratio) in hexane (5 mls). The reaction was followed by infrared spectroscopy. After *ca.* 30 minutes the solution could be seen to be definitely getting paler in colour and a solid deposit was being produced. The carbonyl bands in the infrared spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (prominent band at 2037 cm^{-1} [20]) diminished and a new band was observed at 2020 cm^{-1} . After 1 hour solvent was removed and the residue extracted with hexane and CH_2Cl_2 .

Three fractions were obtained. The first (*ca.* 40%) gave a dark orange solution in hexane. A carbonyl region infrared spectrum of the solution was recorded and showed bands corresponding to a small amount of unreacted $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and a new product. This spectrum is listed in table 5.8. The second fraction (*ca.* 50%) was soluble in CH_2Cl_2 giving a pale yellow solution. This showed bands in the infrared spectrum corresponding to $^t\text{BuNC}$ (at 2150 cm^{-1}), $[\text{Co}(\text{CO})_4]^-$ (at 1885 cm^{-1}) and a broad ill-resolved band centred on 1970 cm^{-1} . The final fraction (*ca.* 10%) was an insoluble residue which was assumed to be a decomposition product.

Table 5.8. Carbonyl region infrared data for the hexane soluble product of run 5.7.1.1. (cm^{-1}).

2143 w	C≡N stretch
2055 w	
2042 sh	
2034 w	(MeGe) ₂ Co ₄ (CO) ₁₁
2021 vs	
2012 sh	
1992 m	
1844 w,br	

5.7.1.2 ^tBuNC (0.003 g; 0.036 mmol) in THF (3 ml) was added to a stirred solution of (MeGe)₂Co₄(CO)₁₁ (0.025 g; 0.035 mmol) (1:1 ratio) in THF (5 ml). The reaction was followed by infrared spectroscopy. Immediately after the addition of ^tBuNC the infrared spectrum showed the production of [Co(CO)₄]⁻ and the virtual disappearance of the carbonyl bands of (MeGe)₂Co₄(CO)₁₁. The mixture was left stirring for 15 minutes and then worked up.

Again, three fractions were obtained. The first (ca. 40%) was soluble in hexane giving a dark orange solution. A carbonyl region infrared spectrum was recorded of the hexane solution and showed only one carbonyl containing species which appeared to be the same hexane soluble product as obtained in run 5.7.1.1. This spectrum is depicted in figure 5.9. The CH₂Cl₂ soluble fraction (ca. 50%) showed bands in the carbonyl region corresponding to ^tBuNC, [Co(CO)₄]⁻ and a broad ill-resolved band centred on 1970 cm^{-1} . The final fraction (ca. 10%) was an insoluble residue which was assumed to be a decomposition product.

5.7.1.3. XyNC (0.008 g; 0.061 mmol) in THF (3 ml) was added to a stirred solution of (MeGe)₂Co₄(CO)₁₁ (0.043 g; 0.06 mmol) (1:1 ratio) in THF (5 ml). On addition of XyNC the solution was observed to effervesce, presumably showing CO evolution, and the colour changed from orange to a pale yellow. Solvent was removed and the residue was extracted with hexane and CH₂Cl₂.

No products were soluble in hexane. A carbonyl region infrared spectrum of the CH₂Cl₂ soluble fraction (ca. 80%) showed a strong band at 2103 cm^{-1} , which probably corresponds to C≡N stretch, and a medium intensity band at 1885 cm^{-1} which corresponds to [Co(CO)₄]⁻. The remaining material (ca. 20%) was insoluble in CH₂Cl₂ and showed no carbonyl bands in an infrared spectrum recorded as nujol mull.

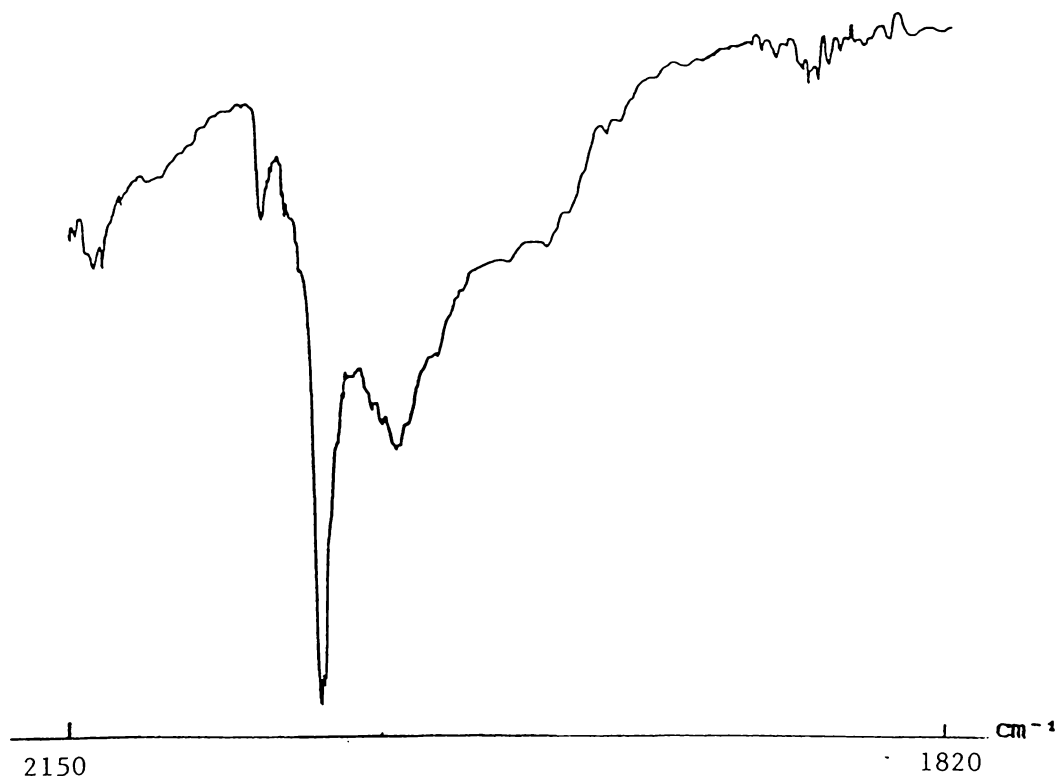
5.7.2 Properties and Tentative Characterisation of the Hexane Soluble Product Obtained From the Reactions of $t\text{BuNC}$ with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$

5.7.2.1. Handling.

The hexane soluble product obtained from these reactions is an orange-brown solid which has very similar handling characteristics to the parent cluster, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. That is, it is reasonably stable to oxidation over short periods, but will decompose if exposed to air for too long, and it is fairly soluble in non-polar solvents such as hexane.

5.7.2.2. Carbonyl stretches in the infrared spectrum.

The carbonyl region of the infrared spectrum of a hexane solution of this product is shown in figure 5.9. The bands are listed in table 5.9 together with those of the parent compound, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.



Infrared active carbonyl stretches of the hexane soluble product obtained from reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $t\text{BuNC}$. Recorded in hexane.

Figure 5.9

Table 5.9 Carbonyl region infrared data for the hexane soluble product obtained from the reaction of ${}^t\text{BuNC}$ with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and for $(\text{MeGe})_2(\text{CO})_{11}$ (cm^{-1}).

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [20, 87]	Product of reaction with ${}^t\text{BuNC}$
	2143 w
	2055 w
	2042 sh, vw
2034 vs	2021 vs
	2012 sh
2016 m	1992 m, br
2004 sh	
1853 w, br	1844 w, br

As discussed earlier (section 5.6.2.2) a large shift to lower wavenumber is consistent with monosubstitution of a CO ligand on an E_2M_4 cluster by a stronger σ -donor [104]. From table 5.11 it could thus be suggested that this product is $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{NC}^t\text{Bu}$.

5.7.2.3. Mass spectrum.

The mass spectrum of this product is shown in table 5.10. The highest mass peak observed was at $m/e = 745$ which corresponds to $[(\text{MeGe})_2\text{Co}_4(\text{CO})_9\text{NC}^t\text{Bu}]^+$. A peak at $m/e = 717$ corresponding to $(\text{MeGe})_2\text{Co}_4(\text{CO})_8\text{NC}^t\text{Bu}]^+$ was not observed but then a stepwise series of peaks corresponding to the loss of the seven remaining carbonyl groups was found. This series carries 47% of the total ion current. After the loss of all carbonyls the five methyl groups were released and three peaks corresponding to this series were observed. The orientation of the methyl groups on the attached ${}^t\text{BuNC}$ allows the possibility of ethane loss thus it is not surprising that not all of the peaks corresponding to individual methyl loss were observed. The Ge_2Co_4 skeleton was retained until all other groups were lost and 81% of the total ion current results from fragments containing this unit. Throughout the more intense peaks of the spectrum the isotope pattern consistent with a Ge_2 containing species was found.

Table 5.10 Mass spectrum of the hexane soluble product obtained from reaction of ${}^t\text{BuNC}$ with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$

m/e	Relative intensity	Assignment $(\text{MeGe})_2\text{Co}_4(\text{CO})_n\text{CN}^t\text{Bu}$
745	3	$n = 9$

690-693	5	7
662	5	6
630-637	19	5
600-607	100	4
575-580	13	3
546-550	11	2
518-523	21	1
490-496	16	0
Ge ₂ Co ₄ CNMe _n		
463	8	n = 3
432-439	12	1
415-422	30	0
389-395	73	Ge ₂ Co ₄ C
378-384	15	Ge ₂ Co ₄
318-324	26	Ge ₂ Co ₃
302-309	52	GeCo ₄

5.7.2.4. Conclusions.

The characterisation techniques employed in this study clearly suggest that the Ge₂Co₄ skeleton is retained in the hexane soluble product obtained from the reaction of ^tBuNC with (MeGe)₂Co₄(CO)₁₁.

The carbonyl vibrations in the infrared spectrum of this species are entirely consistent with this product being the monosubstituted species (MeGe)₂Co₄(CO)₁₀CN^tBu. The mass spectrum however suggests the molecular weight of this compound to be 745 m.u. containing only 9 carbonyl groups. While this might suggest that the ^tBuNC unit is bridging this would not be consistent with the observed carbonyl vibrations. It is more likely that the parent ion, having m/e = 773, is of too low an intensity to be observed. This is supported by the fact that the highest mass peaks in the spectrum are of extremely low intensity.

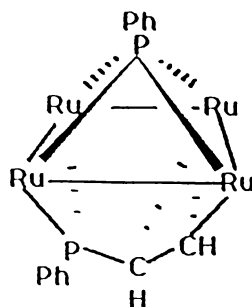
With the data available it is thus concluded that the most reasonable characterisation of this product is as the monosubstituted species, (MeGe)₂Co₄(CO)₁₀CN^tBu.

5.7.3. Discussion of the Reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with $^t\text{BuNC}$ and XyNC .

These preliminary studies of the reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $^t\text{BuNC}$ and XyNC show an interesting difference in the reactivity of these ligands with this cluster compared to the phosphines and phosphites described earlier (see section 5.5). These reactions proceeded at room temperature without the need of thermal or electrocatalytic initiation.

The reactions of $^t\text{BuNC}$ with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ in either hexane or THF appeared to provide identical products, the only difference being in the rate of reaction. In THF the production of $[\text{Co}(\text{CO})_4]^-$ was noted immediately after the addition of $^t\text{BuNC}$ while in hexane no change was observed until approximately 30 minutes after the start of the reaction. Similarly, no unreacted $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was found among the products of the reaction conducted in THF, while a small amount still remained in the system carried out in hexane. This is consistent with a polar solvent helping to labilise the carbonyl ligands of the cluster, thus facilitating reaction with the new ligand.

It was not possible to definitively characterise any of the new products found in this brief study, however, some tentative suggestions may be made. As discussed in the previous section, the hexane soluble product obtained from reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $^t\text{BuNC}$ has been tentatively characterised as $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{CN}^t\text{Bu}$. It could be thought surprising that $^t\text{BuNC}$ will react at relatively mild conditions compared to either PPh_3 or $\text{P}(\text{OEt})_3$ to provide the monosubstituted product, however, this feature may be rationalised by consideration of steric factors. $^t\text{BuNC}$ will possess a much smaller cone angle than either PPh_3 or $\text{P}(\text{OEt})_3$ and would thus be able to approach the cluster comparatively easily. This difference could also result in the lesser breakdown of the cluster when using this reagent. Similarly, XyNC will have a larger cone angle than $^t\text{BuNC}$ (although smaller than PPh_3 and $\text{P}(\text{OEt})_3$) thus this could explain the greater degradation of the cluster for this reagent. It should be noted, however, that the different reactivity of $^t\text{BuNC}$ and XyNC compared to PPh_3 and $\text{P}(\text{OEt})_3$ may be equally well explained by a different reaction pathway. For example, isocyanides are known to undergo insertion reactions [203]. In the chemistry of E_2M_4 clusters a process of this type has been reported between $(\text{PhP})_2\text{Ru}_4(\text{CO})_{11}$ and $\text{HC}\equiv\text{CH}$ [126]. This reaction occurred under ambient conditions and yielded $[\mu_4-\eta^3-\text{P}(\text{Ph})\text{CHCH}]\text{Ru}_4(\text{CO})_{11}(\mu_4-\text{PPh})$ shown in figure 5.10.

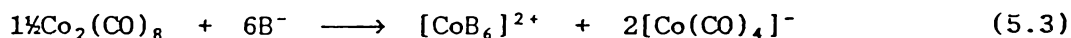


Carbonyls omitted
for clarity

Figure 5.10[126]

Unfortunately the report of this species did not list the infrared spectrum thus it cannot be compared with that of the product obtained here. However, with the data available at present it is felt that the most reasonable characterisation of this species is as $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{CN}^t\text{Bu}$.

The CH_2Cl_2 soluble products and the insoluble residue obtained from the reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $^t\text{BuNC}$ or XyNC seem to result from a general disintegration of the cluster. It is known that $\text{Co}_2(\text{CO})_8$ will react with a base as shown in equation 5.3.



Thus the production of $[\text{Co}(\text{CO})_4]^-$ from these systems could result from the action of the isocyanide as a base. Similarly, phosphines and phosphites may react with $\text{Co}_2(\text{CO})_8$ to form products of the type $[(\text{R}_3\text{P})_2\text{Co}(\text{CO})_3]^+[\text{Co}(\text{CO})_4]^-$ [176], which under heating convert to $[(\text{R}_3\text{P})\text{Co}(\text{CO})_3]_2$, thus it is also possible that $^t\text{BuNC}$ and XyNC are behaving in this manner.

Clearly, further study of these systems is required. In particular, more quantitative evidence should be obtained and, of course, a crystal structure of the hexane soluble product would be definitive.

5.8. Conclusion.

These preliminary studies of the reactions of $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ clusters ($\text{R} = \text{Me}, \text{Co}(\text{CO})_4$) have given indications of several interesting products.

The effect of high pressure of carbon monoxide on these species appears to be more complicated than might be anticipated. The decarbonylation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*) and of $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$ to

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ have been found to be irreversible. The carbonylation products of these clusters have not been characterised but are suggested to result from the cleavage of one or more Co-Co bonds, although the metal framework appears to be retained.

The thermal reactions of $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ ($\text{R} = \text{Me}, \text{Co}(\text{CO})_4$) with PPh_3 and $\text{P}(\text{OEt})_3$ results mainly in breakdown of the cluster to yield disubstituted derivatives of dicobalt octacarbonyl.

The electrocatalytic reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with PPh_3 again result mainly in breakdown of the cluster, however, with $\text{P}(\text{OEt})_3$ the monosubstituted species $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{P}(\text{OEt})_3$ is obtained in moderate yield.

The reactions of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ with $^t\text{BuNC}$ proceed readily at room temperature. It is suggested that the hexane soluble product is the monosubstituted derivative, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{CN}^t\text{Bu}$.

CHAPTER 6: Reactions of Germanium - Cobalt Carbonyl Clusters with Transition Metal Carbonyl Anions and Related Studies

6.1 Background and aim.

In the reactions of germanium - cobalt carbonyl clusters with transition metal carbonyl anions so far reported, two alternative routes may occur.

Where the transition metal carbonyl anion employed was either $[\text{Co}(\text{CO})_4]^-$ [28,29] or $[\text{Fe}_2(\text{CO})_8]^{2-}$ [85] an addition reaction was observed. For example, figure 6.1 shows the product of the reaction of $[\text{Co}(\text{CO})_4]^-$ with $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ [29].

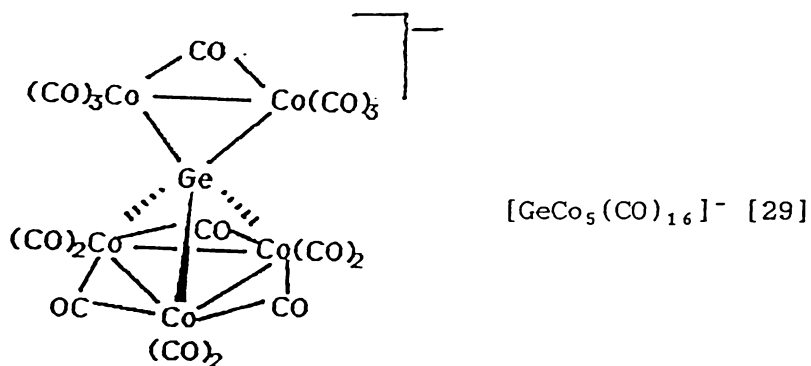


Figure 6.1

This product was also obtained from the reaction of $[\text{Co}(\text{CO})_4]^-$, with $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, the open-skeleton derivative of $\text{GeCo}_4(\text{CO})_{13}$. However, in this case heat was required before any reaction occurred, and it appeared that the condensed species formed before the addition of $[\text{Co}(\text{CO})_4]^-$ took place [28].

Also obtained from these systems was the anion $[\text{GeCo}_7(\text{CO})_{20}]^-$ (figure 6.2) which seemed to form through some side reaction of $[\text{GeCo}_5(\text{CO})_{16}]^-$ with excess $[\text{Co}(\text{CO})_4]^-$ in solution [83].

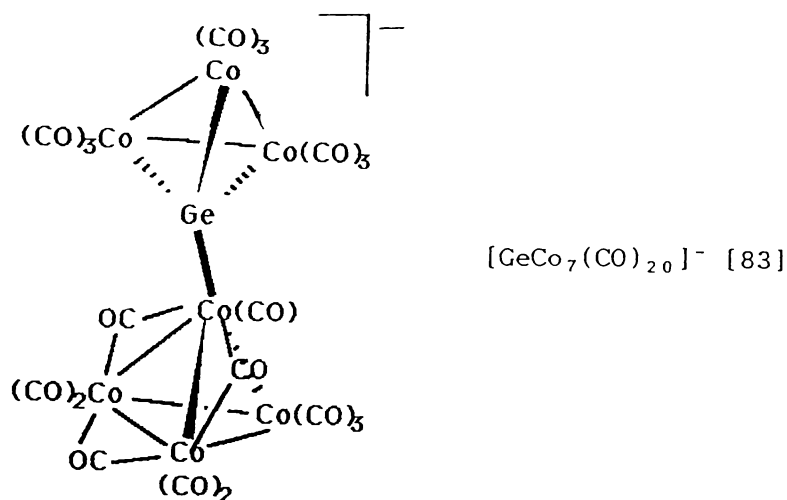


Figure 6.2

The major product of these reactions, $[\text{GeCo}_5(\text{CO})_{16}]^-(L)$ was reacted with $\text{Co}_2(\text{CO})_8$ under forcing conditions and, a further cluster expansion was observed in the formation of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ (figure 6.3) [83]

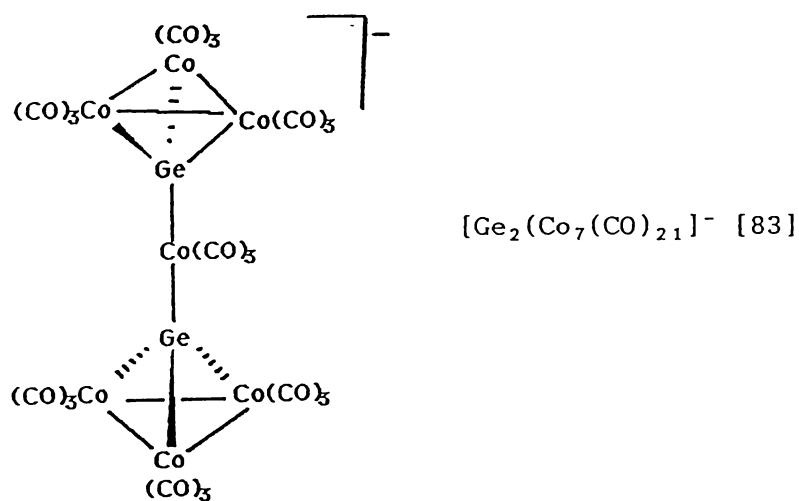


Figure 6.3

The room temperature reaction of $[\text{Fe}_2(\text{CO})_8]^{2-}$ with $\text{GeCo}_4(\text{CO})_{14}(B)$ provided an analogous cluster to $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ where a $\text{Co}_2(\text{CO})_6$ unit of one GeCo_3 trigonal pyramid had been replaced by a $\text{Fe}_2(\text{CO})_7$ moiety as shown in figure 6.4 [85]

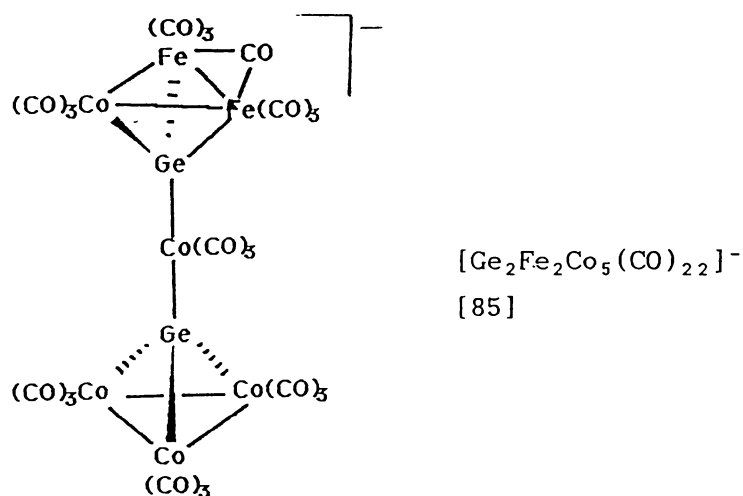


Figure 6.4

These reactions provide a useful route to higher nuclearity germanium-cobalt carbonyl clusters.

The second available pathway in the reactions of transition metal carbonyl anions with germanium-cobalt carbonyl clusters is that of substitution.

The reaction of [Mn(CO)₅]⁻ with GeCo₄(CO)₁₃(*I*) resulted in the formation of the manganese pentacarbonyl substituted GeCo₃ trigonal pyramid shown in figure 6.5. [28].

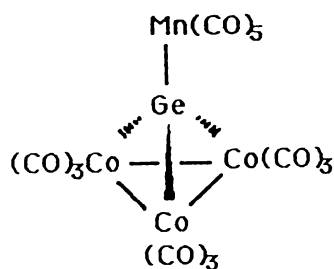
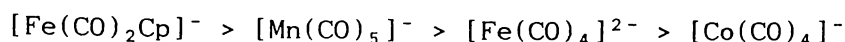


Figure 6.5 [28]

This product was also obtained from the reaction of GeCo₄(CO)₁₄(*B*) with [Mn(CO)₅]⁻ but, again, heat was required to begin the condensation to GeCo₄(CO)₁₃ before any reaction with the anion took place. [28].

A similar process was observed between GeCo₄(CO)₁₃ and [Fe(CO)₂Cp]⁻, although the product was only tentatively characterised as [Cp(CO)₂Fe]GeCo₃(CO)₉ through carbonyl region infrared spectroscopy [28].

The work of Gerlach [26] and several Russian authors [27] suggested the following displacement series on Ge, and also on Si or Sn.



This also corresponds to the order of relative nucleophilicities of these anions.

The above displacement series suggests that where a terminal $\text{Co}(\text{CO})_4$ unit exists in a molecule, reaction with any of $[\text{Fe}(\text{CO})_2\text{Cp}]^-$, $[\text{Mn}(\text{CO})_5]^-$ or $[\text{Fe}(\text{CO})_4]^{2-}$ should result in its displacement to yield a compound containing the new terminal group.

This chapter describes a survey of the reactions of various germanium-cobalt carbonyl clusters with transition metal carbonyl anions.

Since the cluster $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ has become available it was of interest to study its reactions with transition metal carbonyl anions to determine if similar pathways to those observed for the smaller clusters will occur. Reactions with $[\text{Co}(\text{CO})_4]^-$ have been examined in the hope of increasing the nuclearity of this cluster while reactions of this species with $[\text{Mn}(\text{CO})_5]^-$ have been carried out to find if the analogous substitution process will take place.

Similar reactions have also been attempted with the open-skeleton relation of this cluster, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$, to determine if a parallel situation to the smaller clusters exists - that is, whether $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ will react with the transition metal carbonyl anion in its own right, or if condensation to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ is necessary for reaction to occur. A preliminary study of the reaction of $[\text{Co}(\text{CO})_4]^-$ with the next homologue of the series, $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$, is also described here.

Brief examinations of the reactions of $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, $\text{MeGeCo}_3(\text{CO})_9(\text{H})$, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$, $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$, and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ with $[\text{Co}(\text{CO})_4]^-$ have been carried out to find if the presence of the alkyl groups affects the reaction of the metal core.

Reactions of $[\text{Fe}(\text{CO})_4]^{2-}$ with $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ have been attempted in the hope of replacing the terminal $\text{Co}(\text{CO})_4$ units with the dianion to form a species such as that shown in figure 6.6, which might be obtained from the reaction of $[\text{Fe}(\text{CO})_4]^{2-}$ with $\text{GeCo}_4(\text{CO})_{13}$.

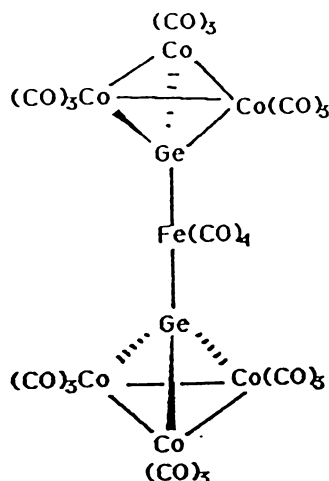


Figure 6.6

Also included in this chapter is a description of the reactions of $[\text{GeCo}_5(\text{CO})_{16}]^-(L)$ or $[\text{GeCo}_7(\text{CO})_{20}]^-(N)$ with GeCl_4 . It has been reported [158] that GeCl_4 will react with $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ to provide either $[\text{GeNi}_{12}(\text{CO})_{22}]^{2-}$ or $[\text{GeNi}_{10}(\text{CO})_{20}]^{2-}$ depending on the reaction ratio employed. It was hoped that the germanium-cobalt carbonyl system would also yield interesting high nuclearity products.

6.2. Preparation of starting materials.

$\text{K}[\text{Co}(\text{CO})_4]$ and $\text{K}[\text{Mn}(\text{CO})_5]$ were prepared by reduction of the appropriate metal carbonyl over Na/K alloy in diethyl ether [12]. As a result of the air sensitive nature of these anions this preparation was carried out under a nitrogen atmosphere. The resulting metal carbonyl anion solution was removed from the alloy mixture by syringe to a clean vessel where solvent was removed and the anion weighed. A stoichiometric quantity of either Et_4NCl or PPNCl could then be added in CH_2Cl_2 to provide the desired salt [12].

$(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{CO})_8]$ was prepared by the addition of $\text{Fe}_2(\text{CO})_9$ to methanolic KOH and the mixture stirred until the solution was deep red in colour. This was filtered and a solution of Et_4NCl in aqueous KOH was added dropwise to produce a deep red precipitate, which was washed with water and dried under vacuum before use [144].

$\text{Na}_2[\text{Fe}(\text{CO})_4]$ was prepared by reduction of $\text{Fe}(\text{CO})_5$ by sodium in an ammonia solution held at -63.5°C [206]. A deficit of $\text{Fe}(\text{CO})_5$ was used to avoid the formation of higher iron carbonyl anions. The product was then pumped under vacuum overnight to remove any traces of ammonia before use.

The $[\text{Fe}(\text{CO})_4]^{2-}$ was only used in experiments if it was white or a pale buff colour, as darker colours indicated the presence of impurities [173].

$\text{Et}_4\text{N}[\text{GeCo}_5(\text{CO})_{16}]$ was prepared by the reaction of excess $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ with $\text{GeCo}_4(\text{CO})_{13}$ in CH_2Cl_2 solution as described by Duffy [28, 29]. The resulting $[\text{GeCo}_5(\text{CO})_{16}]^-$ was extracted from the mixture in Et_2O .

$\text{Et}_4\text{N}[\text{GeCo}_7(\text{CO})_{20}]$ was formed from a solution of $\text{Et}_4\text{N}[\text{GeCo}_5(\text{CO})_{16}]$ and $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ left at -15°C for 2 weeks [83].

GeCl_4 was used as supplied by the Laramie Chemical Co.

6.3. General experimental techniques.

As all the anionic starting materials and reaction products worked with were very air sensitive all manipulations were carried out under nitrogen using Schlenk apparatus.

In a typical reaction of a germanium-cobalt carbonyl cluster with a transition metal carbonyl anion, the desired amount of anion in CH_2Cl_2 solution was added to a stirred CH_2Cl_2 solution of the cluster. The reaction was followed by carbonyl region infrared spectroscopy performed by removing aliquots of the reacting mixture at intervals which, after the spectrum was recorded, were discarded. If no reaction was observed after approximately one hour gentle heating was employed. At completion of the reaction, judged to be when no further change was observed in the infrared spectrum, solvent was removed and the products were separated by sequential extractions with hexane, Et_2O and CH_2Cl_2 . Characterisation of the products was difficult as the majority were anionic which prevented mass spectroscopy from being used. Generally characterisation was carried out by the use of infrared spectroscopy and, on occasion, electron probe analysis.

The reactions of $[\text{GeCo}_5(\text{CO})_{16}]^-$ or $[\text{GeCo}_7(\text{CO})_{20}]^-$ with GeCl_4 were performed by addition of the desired quantity of the anion in CH_2Cl_2 to a stirred CH_2Cl_2 solution of GeCl_4 which had been weighed under vacuum. The reactions were followed by infrared spectroscopy and worked up as above.

As a full characterisation of an anionic product is really dependent on an X-ray crystal structure determination it was hoped that at least some of the products of the above systems would crystallize. Various conditions were attempted using different solvents and temperatures less than -10°C .

6.4. Reactions of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ with transition metal carbonyl anions.

6.4.1. Reaction of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ with $[\text{Co}(\text{CO})_4]^-$.

6.4.1.1. Experimental details and results.

Run 1: $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (0.443 g; 0.43 mmol) and $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.400 g; 1.33 mmol) (1:3 ratio) were allowed to react in CH_2Cl_2 (20 ml) at room temperature. The reaction was followed by infrared spectroscopy. After ca. 30 minutes of reaction it became clear that the major peak of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (at 2042 cm^{-1} [19, 20]) was diminishing in intensity while a new peak, at 2025 cm^{-1} , was appearing. After 3 hours no bands resulting from $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ were observed in the carbonyl region infrared spectrum of the mixture and it was worked up as described in section 6.3.

The reaction mixture provided two main fractions. The first (0.310 g) was soluble in diethyl ether and has been characterised by carbonyl region infrared spectroscopy and electron probe analysis as $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}](\text{M})$ (0.243 mmol 57% yield based on initial $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$). The second fraction (0.30 g) was soluble in CH_2Cl_2 and proved to be unreacted $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.33 mmol). Also present was a small amount of a dark purple-coloured insoluble powder which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a $\text{Co}(\text{II})$ species and its characterisation was not pursued.

Run 2: This was essentially a repeat of run 1. $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (0.319 g; 0.31 mmol) and $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.181 g; 0.60 mmol) (1:2 ratio) were allowed to react in CH_2Cl_2 (20 ml) at room temperature. The reaction followed an identical course to that described above. After 3½ hours work up was carried out. $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ (0.204 g; 0.16 mmol; 53% yield based on initial $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$), unreacted $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.066 g; 0.22 mmol) and the dark coloured insoluble $\text{Co}(\text{II})$ species (0.11 g) were again obtained.

6.4.1.2. Characterisation of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}](\text{M})$.

(i) Handling of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}](\text{M})$.

$\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ is a dark-coloured material which is briefly stable to air in the solid form but is very sensitive to oxidation when in solution. On other runs to those described above difficulty was found with flasks that were not adequately dry or solvents, in particular diethyl ether, which were not sufficiently free of oxygen or water. This resulted in the anion rapidly decomposing to $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ and the dark purple $\text{Co}(\text{II})$ species. However, in thoroughly dried vessels and well purified solvents the anion will exist in solution indefinitely at -30°C .

In this work, although numerous attempts were made to grow crystals of this species none were ever obtained under any of the conditions employed (i.e. from CH_2Cl_2 solution, Et_2O solution, $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution, by slow diffusion of Et_2O into CH_2Cl_2 or by solution of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ in warm CH_2Cl_2 and cooling slowly to room temperature). An X-ray crystal structure determination of this anion has been previously carried out [83] but a personal communication reported that only two crystals were ever obtained.

(ii) Infrared active carbonyl stretches of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}](\text{M})$.

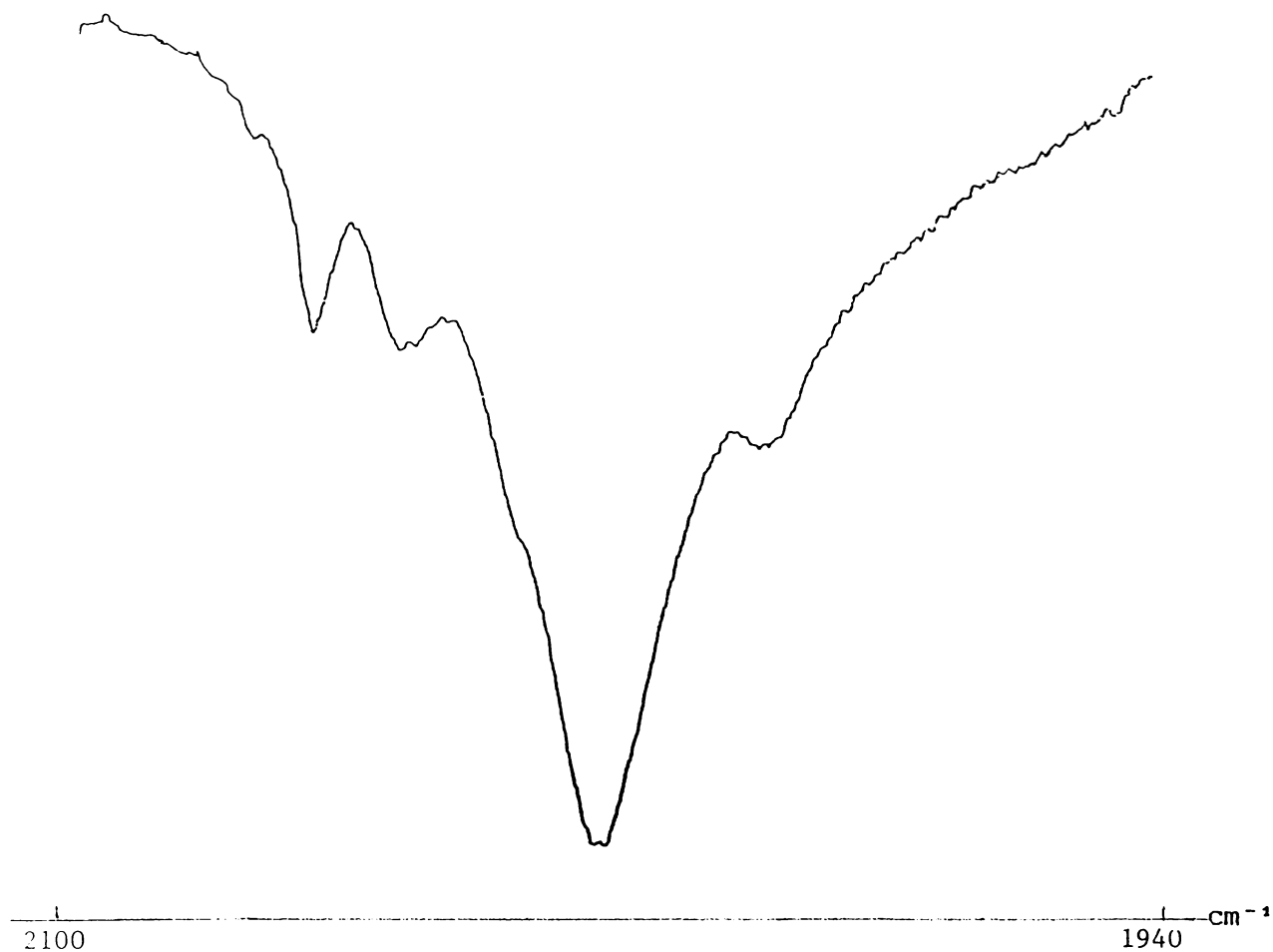
The infrared spectrum in the carbonyl region of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ obtained from this work is depicted in figure 6.7 while table 6.2 lists the observed bands, together with those previously reported [28, 83].

Table 6.2. Carbonyl region infrared data recorded for $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-(\text{M})$ (cm^{-1}).

This work	[28, 83]
2065 w-m	2064 w-m
2052 w	2052 w
2025 vs	2027 vs
2003 w	2004 w

The identical pattern of these spectra, together with the very close positioning of the bands strongly suggested that the product of this reaction was $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$. In the crystal state this anion has C_{3v} symmetry, however in solution it would be expected that rotation of the

Figure 6.7. Infrared active carbonyl stretches of $(\text{Ge}_2\text{Co}_7(\text{CO})_{21})^-$.
Recorded in dichloromethane.



2065 w-m
2052 w
2025 vs
2003 w

$\text{GeCo}_3(\text{CO})_9$ units about the central $\text{Co}(\text{CO})_3$ group would allow the higher D_{3h} symmetry. For this, six infrared active CO modes are predicted ($2A_2'' + 4E'$) although only four are observed. The very intense band at 2025 cm^{-1} is probably an overlap of the remaining bands. When the symmetry is reduced to C_{3v} then a maximum of twelve infrared active modes are predicted ($5A_1 + 7E$).

(iii) Electron probe analysis of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}](M)$

Electron probe analysis was performed on two samples of the ether soluble product of these reactions. Table 6.3. shows the Ge:Co atomic percentages obtained in each case.

Table 6.3. Atomic percentage ratios of germanium to cobalt obtained from samples of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$

	Element	Shell	Atomic percentage
Sample 1	Co	K	78.1
	Ge	K	21.9
Sample 2	Co	K	76.8
	Ge	K	23.2

These figures suggest a germanium to cobalt ratio of 2:6.9 (± 0.2) which is consistent with the product being $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$.

6.4.1.3. Discussion of the reaction of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(K)$ with $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$.

The reaction between $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ and $\text{Et}_4\text{NCo}(\text{CO})_4$ proceeds readily at room temperature to provide $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ (figure 6.8) as the major product.

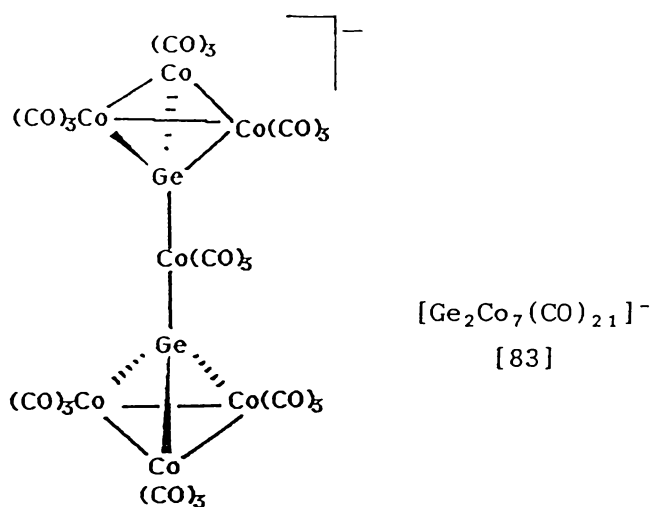
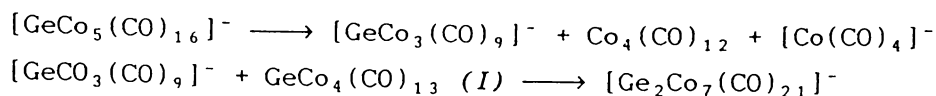


Figure 6.8.

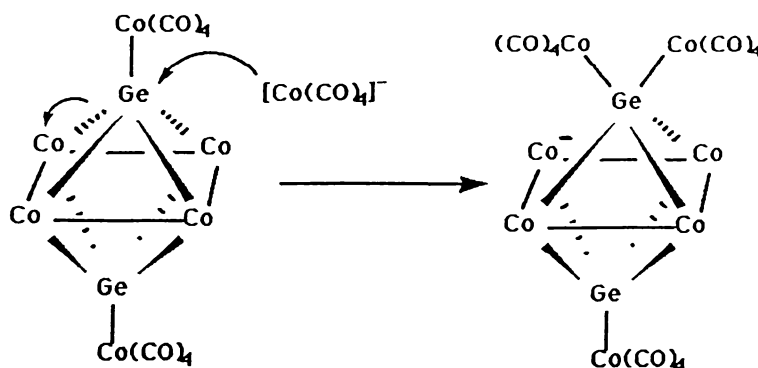
In the two runs described in this chapter $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ was obtained in 57% and 53% yields based on initial $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$. Also found were unreacted $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ and a dark purple solid assumed to be a Co(II) species. The quantities of each component appear to give an overall mass balance which is reasonable. For example, in run 2 0.31 mmols of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ were reacted with 0.60 mmols of $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$. 0.16 mmols of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ were obtained which corresponds to 0.16 mmols of each of the starting materials. Also, 0.22 mmols of unreacted $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ were obtained accounting for 0.38 mmols of this reagent. If it is assumed that $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ is quantitatively converted to $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ and it is this latter species which is decomposing to the dark purple coloured powder, then 0.15 mmols of this species, together with 0.07 mmols of unreacted $[\text{Co}(\text{CO})_4]^-$ must be accounted for by the insoluble powder. Once the loss of CO is considered this leaves 0.116 g of Et_4N^+ , Ge and the Co(II) species. Although the exact nature of the latter is unknown it is probably of the form CoO or $\text{Co}(\text{OH})_2$. The deficit in the weight recorded for the insoluble powder (0.11 g) may be accounted for by the removal of aliquots of the reacting mixture for infrared analysis. These results are then within experimental error.

$\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ was originally produced in low yield from the reaction of $\text{Et}_4\text{N}[\text{GeCo}_5(\text{CO})_{16}]$ with $\text{Co}_2(\text{CO})_8$ under forcing conditions [28, 83]. The pathway suggested for its formation was as shown in scheme 6.1 [83].



Scheme 6.1 [83]

It is unlikely that this type of process is involved in its formation from the reaction of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ with $[\text{Co}(\text{CO})_4]^-$. In fact a much more straightforward route for the initial attack by $[\text{Co}(\text{CO})_4]^-$ may be envisaged for this reaction, as depicted in scheme 6.2.



Scheme 6.2.

Carbonyls of $\text{Co}_4(\text{CO})_{11}$ plane
omitted for clarity

Further bond cleavage, rearrangement and decarbonylation of the cluster presumably follows this initial step to result in the formation of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$.

The high yield of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ from this route, compared to that obtained from $\text{Et}_4\text{N}[\text{GeCo}_5(\text{CO})_{16}]$ reacted with $\text{Co}_2(\text{CO})_8$ [28, 83], and the fact that $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(K)$ is more readily accessible than $\text{Et}_4\text{N}[\text{GeCo}_5(\text{CO})_{16}]$, makes this reaction a much more practical route to the cluster $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}](M)$.

6.4.2. Reactions of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ with $[\text{Mn}(\text{CO})_5]^-$

6.4.2.1. Experimental details and results.

Run 1: $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (0.091 g; 0.088 mmol) and $\text{K}[\text{Mn}(\text{CO})_5]$ (0.188 g; 0.80 mmol) (1:9 ratio) were reacted in CH_2Cl_2 (10 ml) at room temperature. Infrared spectra recorded of the reacting mixture showed

$\text{Mn}_2(\text{CO})_{10}$ to be readily produced while no displaced $[\text{Co}(\text{CO})_4]^-$ was observed. Work up of the solution after two hours yielded only $\text{Mn}_2(\text{CO})_{10}$ and unreacted $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$. Presumably the extremely air sensitive nature of $[\text{Mn}(\text{CO})_5]^-$ led to its oxidation as a result of small amounts of oxygen in the solvent before any reaction with $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ could take place.

Run 2: $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (0.428 g; 0.415 mmol) and $\text{PPN}[\text{Mn}(\text{CO})_5]^-$ (0.885 g; 1.6 mmol) (1:4 ratio) were reacted in CH_2Cl_2 (20 ml) at room temperature. The reaction was monitored by infrared spectroscopy and the production of $[\text{Co}(\text{CO})_4]^-$ was noted almost immediately on mixing. After 3 hours, when no further change could be observed, work up was carried out.

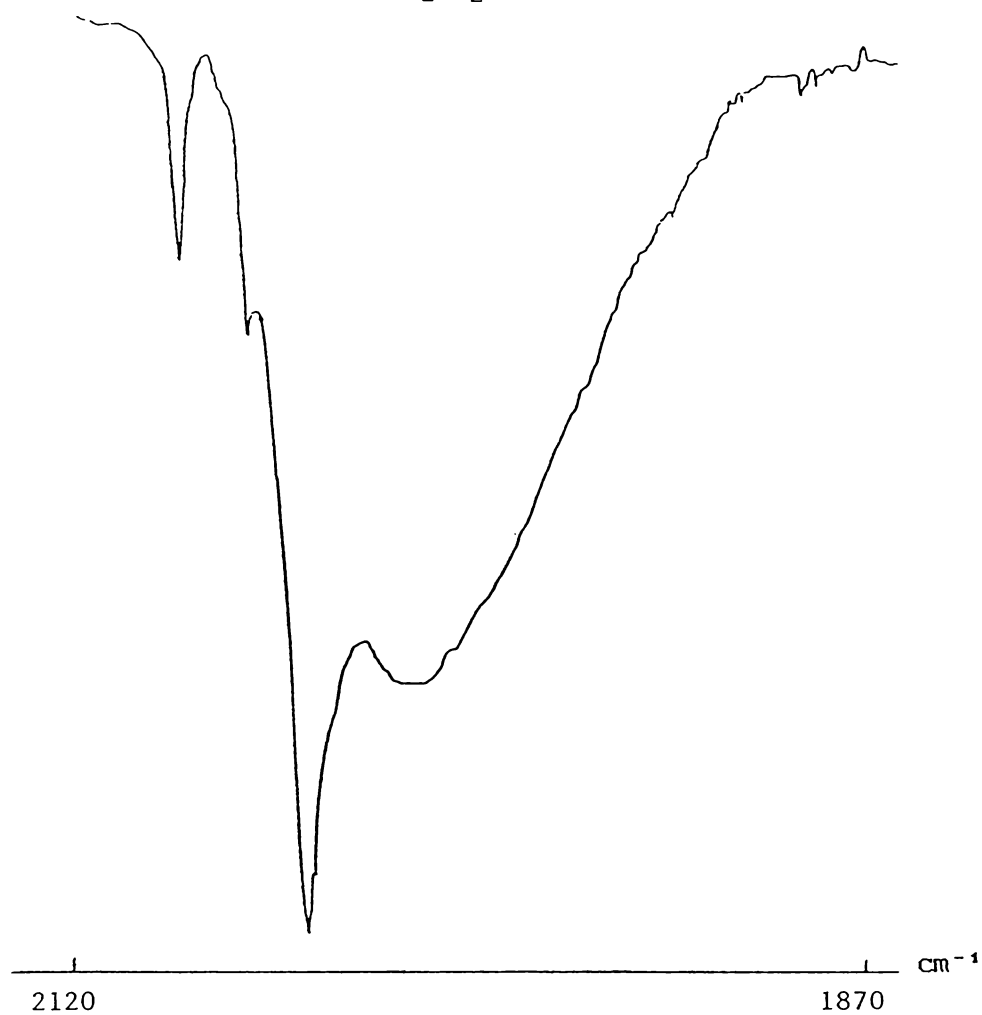
The hexane extracts comprised a small amount of $\text{Mn}_2(\text{CO})_{10}$ but the weight of this was not measured. The ether soluble fraction (0.400 g) gave a dark brown solution in CH_2Cl_2 . The carbonyl region infrared spectrum of this product is shown in figure 6.9. Electron probe analysis of this species was carried out which suggested a Mn:Ge:Co ratio of 1:2:6. The final fraction (0.670 g) was soluble only in CH_2Cl_2 and showed a mixture of unreacted $\text{PPN}[\text{Mn}(\text{CO})_5]^-$ and produced $\text{PPN}[\text{Co}(\text{CO})_4]^-$.

6.4.2.2. Discussion of the reactions of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ with $[\text{Mn}(\text{CO})_5]^-$.

The reaction of $[\text{Mn}(\text{CO})_5]^-$ with $\text{GeCo}_4(\text{CO})_{13}$ (I) produced the cluster $[(\text{CO})_5\text{Mn}]\text{GeCo}_3(\text{CO})_9$, where the $[\text{Mn}(\text{CO})_5]^-$ had displaced the terminal $\text{Co}(\text{CO})_4$ group. It was therefore anticipated that a similar reaction would occur with $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (K) giving a species such as $[(\text{CO})_5\text{MnGe}]_2\text{Co}_4(\text{CO})_{11}$ as the major product. The production of $[\text{Co}(\text{CO})_4]^-$ during run 2 suggests that, at least initially, a displacement reaction is occurring, however both the carbonyl region infrared spectrum and the electron probe analysis of the ether soluble product seem to conflict with the suggestion that the product is $[(\text{CO})_5\text{MnGe}]_2\text{Co}_4(\text{CO})_{11}$.

The carbonyl region infrared spectrum of the ether soluble species in CH_2Cl_2 solution is shown in figure 6.9. The bands are also recorded in table 6.4. together with those of the starting material, $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$, and the known compound $[(\text{CO})_5\text{MnGe}]\text{Co}_4(\text{CO})_{11}[\text{GeCo}(\text{CO})_4]^-$ [43].

Figure 6.9. Infrared active carbonyl stretches of the ether soluble product obtained from the reaction of PPNMn(CO)_5 with $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$.
Recorded in CH_2Cl_2 .



2100 m
2076 w
2047 sh
2037 w-m
2022 vs
1984 m,br

Table 6.4. Carbonyl region infrared data for the ether soluble product of run 2, $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ and $[(\text{CO})_5\text{MnGe}]\text{Co}_4(\text{CO})_{11}[\text{GeCo}(\text{CO})_4]$ (cm^{-1}).

Ether soluble product $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ $[(\text{CO})_5\text{MnGe}]\text{Co}_4(\text{CO})_{11}[\text{GeCo}(\text{CO})_4]$
from run 2

(a)	(b)	(c)
		2120 sh, w
		2117 m
		2104 sh, w
2100 m	2100 s	2099 w-m
		2087 sh, w
2076 w	2065 sh, w	2076 m
2047 sh		2061 sh, w
2037 w-m	2050 s	2053 m
2022 vs	2037 vs	2038 vs
1984 m, br	2003 sh, w	2024 sh, w
	1990 sh, w	
	1844 br, w	1851 br, w

(a) In CH_2Cl_2 solution

(b) In $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution [20]

(c) In $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ solution [39]

Although the pattern of the bands of the product could suggest the formulation of this species as $[(\text{CO})_5\text{MnGe}]_2\text{Co}_4(\text{CO})_{11}$, the position of the major band, at 2022 cm^{-1} , appears extremely low compared to the other two clusters. In fact, this position is low enough to suggest an anionic species.

A solid state infrared spectrum was recorded of this species as a nujol mull. This showed the presence of the cation PPN^+ (prominent bands at 1280 , 1100 , 720 , 695 , 520 and 500 cm^{-1}) which strongly supports the suggestion that this product is an anionic species. Also observed in the solid infrared spectrum was a strong band at 1885 cm^{-1} which corresponds to $[\text{Co}(\text{CO})_4]^-$. This was not present in the solution spectrum thus it appears that the preparation of the sample as a nujol mull caused the product to break down.

Mass spectroscopy was attempted to aid in the characterisation of this product but no useful spectra were obtained. Even peaks that might correspond to fragments were not observed which, again, supports the proposal that the species is anionic.

Finally, the electron probe analysis of the sample gave the atomic percentage values listed in table 6.5.

Table 6.5. Electron probe analysis results for the ether soluble product of run 2.

Element	Shell	Atomic percentage
Mn	K	11.4
Ge	K	21.7
Co	K	66.9

This clearly suggests a Mn:Ge:Co ratio of 1:2:6 (± 0.3) while the ratio expected for $[(\text{CO})_5\text{MnGe}]_2\text{Co}_4(\text{CO})_{11}$ would be 1:1:2.

As a result of the evidence given above it may be concluded that the product of this reaction is an anionic species, perhaps of the form shown in figure 6.10.

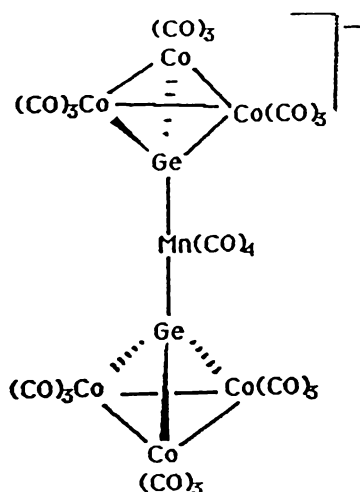


Figure 6.10

This is consistent with the Mn:Ge:Co ratio of 1:2:6 obtained from the electron probe analysis, and also with the carbonyl region infrared spectrum. The bands of this product are repeated in table 6.6., together with those of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-(M)$ which has the structure shown above except a $\text{Co}(\text{CO})_3$ moiety replaces the $\text{Mn}(\text{CO})_4$ group [83].

Table 6.6. Carbonyl region infrared data for the ether soluble product of run 2 and for $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-(\text{cm}^{-1})$.

Ether soluble Product of run 2	$[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ [28, 83]
2100 m	
2076 w	2064 w-m
2047 sh	2052 w-m
2037 w-m	
2022 vs	2027 vs
1984 m, br	2004 w

The pattern of the bands in the lower regions of these spectra is close enough to suggest that they could be of a similar nature.

The formation of an anionic species from this reaction is conceivable since some of the displaced $[\text{Co}(\text{CO})_4]^-$, observed from the infrared spectrum of the reaction mixture, could react with the neutral product, as found in the reaction of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ with $[\text{Co}(\text{CO})_4]^-$ described in the previous section. It is also possible that the $[\text{Mn}(\text{CO})_5]^-$ undergoes an addition reaction as well as displacement of $\text{Co}(\text{CO})_4$, however this would result in an anionic species containing two manganese atoms which is not consistent with the electron probe analysis.

There is one anomaly in the proposal that this product is an anionic species. Although it was not possible to dissolve the solid in hexane, the addition of small amounts of hexane to a dichloromethane solution of this species did not immediately bring it out of solution. However, at this stage the most reasonable formulation for the product of reaction between $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ with $[\text{Mn}(\text{CO})_5]^-$ is $[\text{Ge}_2\text{Co}_6\text{Mn}(\text{CO})_{22}]^-$ which would lead to a 74% yield of this species based on initial $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ obtained from run 2.

The overall mass balance of run 2 appears to be reasonable. 1.31 g of reactants were used initially while 1.07 g of material was obtained at the reaction end, together with a small amount (ca. 0.1 g, 8%) which may be accounted for by the removal of samples during the reaction for infrared analysis.

Clearly it is very desirable to obtain a crystal structure of the product of this reaction to determine its exact nature. During the course of this work several attempts were made to obtain crystals under varying conditions (ie from CH_2Cl_2 solution, Et_2O solution, $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution, $\text{CH}_2\text{Cl}_2/\text{hexane}$ solution, and by slow diffusion of Et_2O into a CH_2Cl_2 solution), but were unsuccessful.

Further experiments may also help in the identification of this product. For example, the use of a 1:1 ratio of $[\text{Mn}(\text{CO})_5]^-$ to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ should confirm the number of manganese carbonyl groups involved in this product, and reaction of $[(\text{CO})_5\text{MnGe}]\text{Co}_4(\text{CO})_{11}[\text{GeCo}(\text{CO})_4]$ with $[\text{Co}(\text{CO})_4]^-$ may provide another route to this species.

6.4.3. Reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) with $[\text{Co}(\text{CO})_4]^-$.

6.4.3.1. Experimental details and results.

Run 1: $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.056 g; 0.053 mmol) and $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.060 g; 0.20 mmol) (1:4 ratio) were allowed to react in CH_2Cl_2 (20 ml). After 1 hour at room temperature no reaction had occurred (as observed from the infrared spectrum of the reactant mixture) and the solution was heated at 40°C . Infrared spectra of the solution recorded at intervals showed the condensation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*) [19, 20], and then the appearance of a new band at approximately 2025 cm^{-1} . After 10 hours the reaction appeared complete and work up was carried out.

The hexane soluble fraction (0.017 g) showed carbonyl vibrations in the infrared spectrum corresponding to those of $\text{Co}_4(\text{CO})_{12}$ [139]. The ether soluble fraction (0.027 g) contained the major anionic product which has been characterised by infrared spectroscopy as $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ (*M*) (0.021 mmol; 40% yield based on initial $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$). The CH_2Cl_2 soluble fraction (0.020 g) contained only unreacted $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$. Also present was a dark purple insoluble solid (0.020 g) which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be a Co(II) species and was discarded.

Run 2: $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.085 g; 0.08 mmol) and $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.482 g; 1.60 mmol) (1:20 ratio) were allowed to react in CH_2Cl_2 (10 ml) for 24 hours at room temperature. Infrared spectra recorded of the solution at intervals again showed the condensation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*) before the appearance of the new band at 2025 cm^{-1} .

On work up, two soluble fractions were obtained. The first, soluble in Et_2O , was identified as $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ (0.051 g; 0.04 mmol; 47% yield based on initial $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$). The second (0.240 g), soluble in CH_2Cl_2 , contained only unreacted $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$. Also present was the dark purple insoluble Co(II) species (0.109 g).

Run 3: $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.180 g; 0.17 mmol) and $\text{K}[\text{Co}(\text{CO})_4]$ (0.11 g; 0.5 mmol) (1:3 ratio) and CH_2Cl_2 (10 ml) were sealed in a high pressure ampoule and allowed to react at 50°C for 24 hours. Evolved CO (0.495 mmol) was measured and then PPNCl (0.287 g; 0.5 mmol) was added to the reaction mixture. Produced KCl and the Co(II) species were removed by filtering and then the mixture was worked up as usual.

The products were separated into two fractions. The first was soluble in Et_2O and was identified as $\text{PPN}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ (0.123 g; 0.073 mmol; 43% yield based on initial $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$). The second (0.160 g), soluble in CH_2Cl_2 , consisted of $\text{PPN}[\text{Co}(\text{CO})_4]$ and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$. No unreacted $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was observed.

6.4.3.2. Discussion of the reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) with $[\text{Co}(\text{CO})_4]^-$

From the results described above it appears that $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) will react with $[\text{Co}(\text{CO})_4]^-$ under comparatively stringent conditions to provide $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ (*M*). This is the same product as obtained in the reactions of $[\text{Co}(\text{CO})_4]^-$ with $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*), the condensation product of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$.

In those reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with $[\text{Co}(\text{CO})_4]^-$ followed by infrared spectroscopy, before any anionic product was observed it could be seen that the $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was converting to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ and it seems likely that it is this species which is the precursor in the reaction with $[\text{Co}(\text{CO})_4]^-$.

A similar observation was reported for the reaction of $\text{GeCo}_4(\text{CO})_{14}$ (*B*) with $[\text{Co}(\text{CO})_4]^-$ [28, 29]. Here, no reaction was observed at room temperature and it was necessary to heat the reactant mixture at 40°C . At this stage the condensation product of $\text{GeCo}_4(\text{CO})_{14}$, $\text{GeCo}_4(\text{CO})_{13}$ (*I*), was observed in solution and it was only then that formation of the anionic product, $[\text{GeCo}_5(\text{CO})_{16}]^-$ (*L*), began.

From these facts it seems reasonable to suggest that the *clos*o structure is necessary for reaction with $[\text{Co}(\text{CO})_4]^-$ to occur. This could possibly result from steric restrictions about the germanium atom at which the $[\text{Co}(\text{CO})_4]^-$ attack occurs, where the condensation species perhaps allows a less hindered approach. It is equally likely that the condensation occurs for electronic reasons. For example, if an intermediate in this process was of a radical anionic nature these are known to be particularly stable as closed clusters [164].

From the study described here it is apparent that the presence of $[\text{Co}(\text{CO})_4]^-$ will actually promote the condensation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$. For example, a typical decarbonylation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ takes up to one week of heating at 50°C while complete conversion in these reactions was observed after approximately 8 hours at 40°C , or 24 hours at room temperature in the presence of a large excess of $[\text{Co}(\text{CO})_4]^-$. The ordinary condensation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ to

$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ is usually carried out in hexane while these reactions were conducted in dichloromethane. Although $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ is much more soluble in CH_2Cl_2 than in hexane, and it is thus possible that lattice energies could help to drive the condensation, it is still felt that the solvent alone would not effect the reaction duration to this extent. This impression is supported by the fact that at room temperature, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ is perfectly stable in any solvent, yet as stated above, the addition of a twenty fold excess of $[\text{Co}(\text{CO})_4]^-$ resulted in its conversion to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ in 24 hours.

In these reactions a larger proportion of the purple Co(II) species was observed compared to those where $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ was used as the starting cluster. This is presumably a result of heating the reaction mixtures. In run 2, where the reaction was left at room temperature, a lesser proportion of this decomposition product was observed.

In run 3, the evolved CO was measured as 0.495 mmols. This corresponds reasonably well with the observed products. The formation of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ should result in 3 moles of CO for each mole of reacting $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, while decarbonylation of the remaining $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ will afford 1 mole of CO for each mole of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ produced. A 43% yield of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ was obtained which would lead to 0.22 mmols of CO. Decarbonylation of the remaining $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ would provide 0.10 mmols of CO giving a total of 0.32 mmols. The remaining 0.175 mmols may be accounted for by the presence of the decomposition product. A lower proportion of this species was observed in this run, as compared to run 1 conducted at the same temperature. This is presumably a result of the closed vessel which would allow the build up of evolved gas inhibiting the further evolution of CO. This would also account for the incomplete reaction of this run, where unreacted $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ was found after 24 hours of reaction at 50°C .

In run 1, a small amount of $\text{Co}_4(\text{CO})_{12}$ was found among the products. This species was not observed in any of the other runs and it seems likely that this was present in the starting material rather than being formed during the reaction. $\text{Co}_4(\text{CO})_{12}$ is commonly found as a minor product in the preparation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ from the reaction of Ge_2H_6 with $\text{Co}_2(\text{CO})_8$ [19, 20, 21] and this may not have been thoroughly separated before use.

In run 3 PPN^+ was employed as the cation rather than Et_4N^+ . This did not appear to affect either the handling of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-(M)$ or its ease of crystallisation. At the end of the work up the sample was divided in two portions so that different conditions could be attempted for crystallisation.

The overall mass balance of these experiments appears reasonable. In run 1 0.017 g of $\text{Co}_4(\text{CO})_{12}$ was obtained and if it is assumed that this was present in the original starting material then 0.037 mmol of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ were available to react with $[\text{Co}(\text{CO})_4]^-$. Assuming quantitative reaction then 0.047 g of $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ would be produced and 0.049 g of $\text{Et}_4\text{NCo}(\text{CO})_4$ would remain unreacted. 0.027 g of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]$ was obtained and 0.020 g of $[\text{Co}(\text{CO})_4]^-$ was recovered which leaves 0.049 g of material unaccounted for. After CO loss is taken into consideration this leaves a weight of 0.029 g to which must be added an unknown weight of oxygen or hydroxide to account for the oxidation which has occurred. 0.020 g of the purple insoluble powder was obtained giving a deficit of approximately 10%. Similar calculations may be carried out for run 2 which again gives a deficit of approximately 10% in the mass of products obtained at the reaction end. These are rationalised by the removal of samples from solution for infrared analysis.

These experiments provided yields of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ between 37% and 47% lower than those obtained using $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ as the starting cluster. Thus the direct reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with $[\text{Co}(\text{CO})_4]^-$ to provide $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ takes longer and is less efficient than that of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$. It should be noted, however, that the usual route to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ is by the quantitative decarbonylation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, thus condensation of this species prior to the addition of $[\text{Co}(\text{CO})_4]^-$ would greatly improve the efficiency of the preparation of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ by this route.

6.4.4. Reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) with $[\text{Mn}(\text{CO})_5]^-$

6.4.4.1. Experimental details and results.

$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.063 g; 0.06 mmol) and $\text{PPN}[\text{Mn}(\text{CO})_5]$ (0.083 g; 0.15 mmol) (1:2.5 ratio) were allowed to react in CH_2Cl_2 (10 ml). After 1 hour at room temperature no reaction had been observed thus the temperature was raised to 50°C. Infrared spectra of the reaction mixture recorded at intervals showed the conversion of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*). It was also observed that $\text{Mn}_2(\text{CO})_{10}$ was slowly forming, together with $[\text{Co}(\text{CO})_4]^-$. After 5 hours the reaction appeared complete.

On work-up the produced $\text{Mn}_2(\text{CO})_{10}$ was extracted in hexane. The ether soluble fraction gave a dark brown solution in CH_2Cl_2 and was found by infrared spectroscopy to be the same product as obtained from the reaction of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ with $[\text{Mn}(\text{CO})_5]^-$. The carbonyl region infrared bands

of this species are listed in table 6.7. The CH_2Cl_2 soluble material was $\text{PPN}[\text{Co}(\text{CO})_4]$ and also present was a small amount of dark coloured insoluble material which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull.

Table 6.7. Carbonyl region infrared data for the ether soluble product from the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with $[\text{Mn}(\text{CO})_5]^-$ (cm^{-1}).

2101 m
2075 w
2048 sh, w
2038 w-m
2021 vs
1982 m, br

6.4.4.2. Discussion of the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ with $[\text{Mn}(\text{CO})_5]^-$.

From the results obtained in the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with $\text{PPN}[\text{Mn}(\text{CO})_5]$ it appears that this cluster provides the same product as obtained from reaction of the condensed analogue $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$, with $[\text{Mn}(\text{CO})_5]^-$. Unfortunately this has still not been identified.

It is apparent that, as in the reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with $[\text{Co}(\text{CO})_4]^-$, it is necessary for condensation to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ to take place before any reaction will occur. This effect was also noted in the reaction of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ with $[\text{Mn}(\text{CO})_5]^-$ [28, 43], where no change was observed until heat was applied. At this point the $\text{GeCo}_4(\text{CO})_{14}$ began to convert to $[(\text{CO})_4\text{Co}]\text{GeCo}_3(\text{CO})_9(\text{I})$, and only then did any reaction with $[\text{Mn}(\text{CO})_5]^-$ take place to provide the substitution product $[(\text{CO})_5\text{Mn}]\text{GeCo}_3(\text{CO})_9$ [28, 43]. Clearly this is due to the requirement of a terminal $\text{Co}(\text{CO})_4$ unit to be present for displacement by $[\text{Mn}(\text{CO})_5]^-$ to occur.

Again, as observed in the $\text{Ge}_2\text{Co}_6(\text{CO})_{20}/[\text{Co}(\text{CO})_4]^-$ systems, the presence of the anion seems to promote condensation to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$. As $[\text{Co}(\text{CO})_4]^-$ is produced quite early in this reaction it cannot be stated definitely if this increased rate of condensation results from the presence of $[\text{Mn}(\text{CO})_5]^-$ or $[\text{Co}(\text{CO})_4]^-$. However, it could be anticipated that $[\text{Mn}(\text{CO})_5]^-$ will only displace a terminal $\text{Co}(\text{CO})_4$ unit thus it is proposed that, initially at least, it is predominantly $[\text{Mn}(\text{CO})_5]^-$ which promotes the condensation. It appears that reaction of the anion with the closed cluster to provide the new species is favourable, thus the scheme shown in figure 6.11. is pushed to the right hand side.

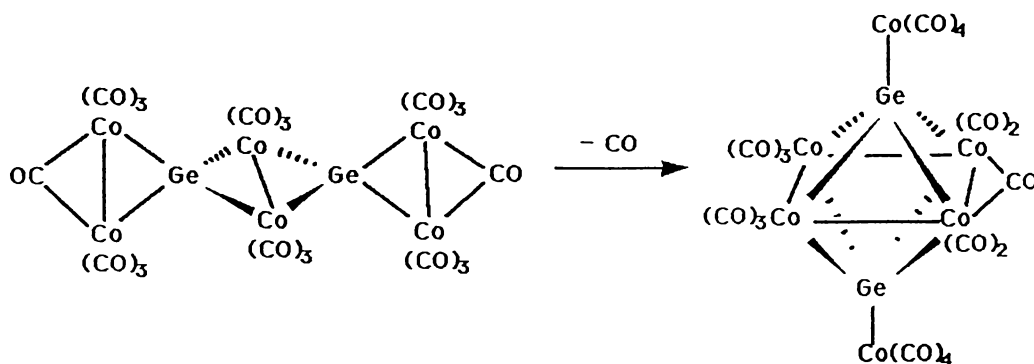


Figure 6.11.

A review by Colville *et al.* [161] discusses the catalysis of metal carbonyl substitution reactions. Transition metal catalysts of various types are known to aid in straightforward ligand substitution reactions and this is assumed to occur by a labilisation of a CO ligand by a change in oxidation state of the metal carbonyl substrate, or by metal carbonyl radical formation [161]. In the work described above, where the presence of the anions $[\text{Co}(\text{CO})_4]^-$ or $[\text{Mn}(\text{CO})_5]^-$ seems to promote the condensation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$, it is reasonable to suggest that the anions are acting as catalysts to labilise a carbonyl ligand of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ thus causing its closure to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$.

In any event, the results obtained from the two reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with transition metal carbonyl anions show that before any new products are obtained, condensation to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ must occur.

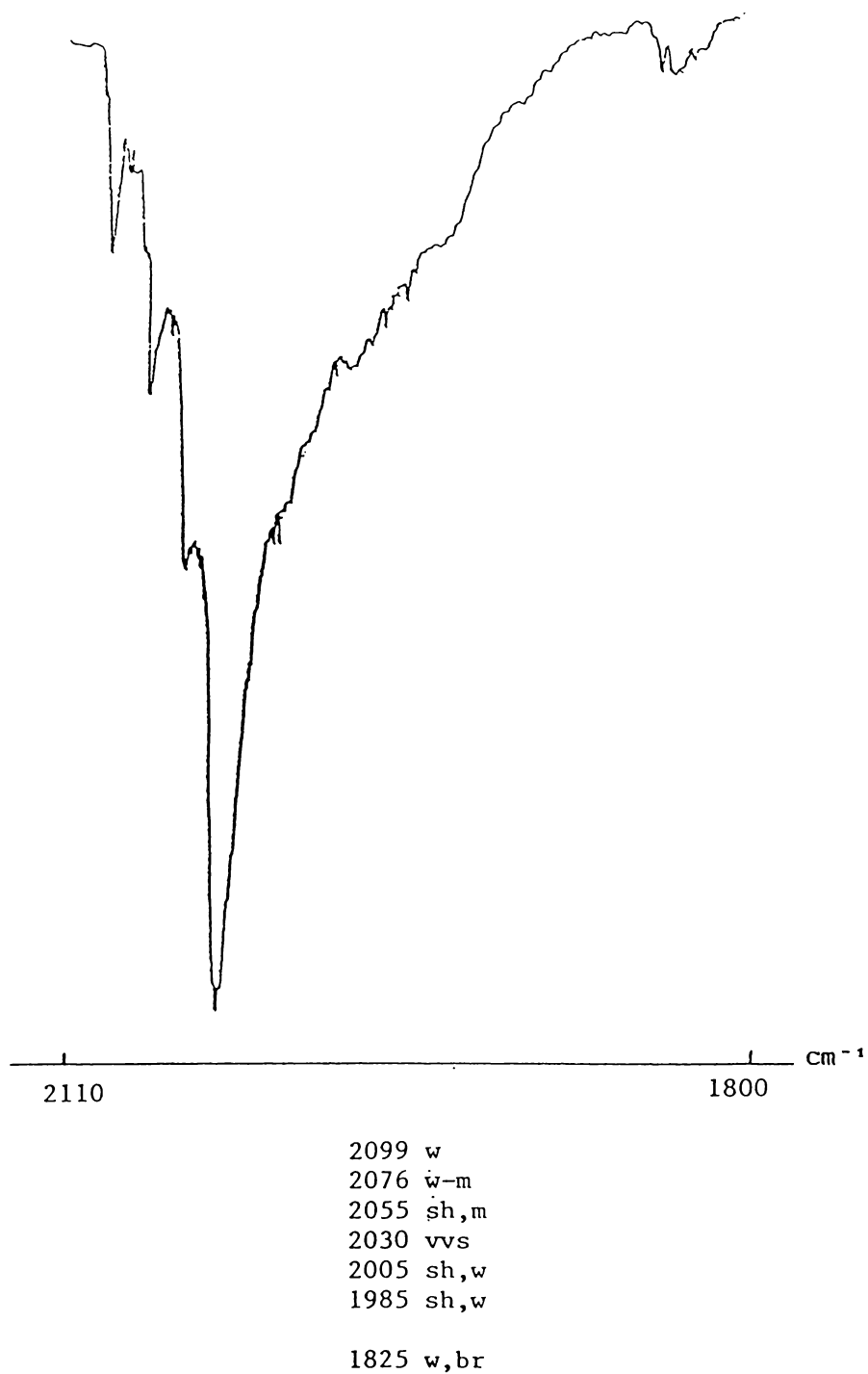
As the masses of the products obtained were not recorded it is not possible to carry out a detailed analysis of the mass balance of this experiment. However, it may be stated that qualitatively the products corresponded well with the starting materials used.

6.4.5. Reaction of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ with $[\text{Co}(\text{CO})_4]^-$

6.4.5.1. Experimental details and results.

$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (0.139 g, 0.098 mmol) and $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.046 g; 0.15 mmol) (1:1.5 ratio) were allowed to react in CH_2Cl_2 (20 ml) at room temperature. The reaction was followed by infrared spectroscopy and after 2 hours no further change was observed. Solvent was removed and the products were worked up as described in section 6.3.

Figure 6.12. Infrared active carbonyl stretches of the ether soluble product from the reaction of $\text{Et}_4\text{NCo}(\text{CO})_4$ with $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$. Recorded in CH_2Cl_2 .



The products were separated into two fractions. The first (ca. 40%) was soluble in Et₂O and gave a dark brown solution in CH₂Cl₂. An infrared spectrum recorded of this fraction in CH₂Cl₂ showed carbonyl bands corresponding to a new species. This spectrum is shown in figure 6.12. Electron probe analysis was also carried out which gave a Ge:Co ratio of approximately 1:3. No further characterisation of this compound was possible. The second fraction (ca. 60%), soluble only in CH₂Cl₂, contained a mixture of unreacted Et₄NCo(CO)₄, possibly some unreacted Ge₃Co₈(CO)₂₆ and a product giving a very broad ill-resolved band centred at 2040 cm⁻¹ in a carbonyl region infrared spectrum recorded in CH₂Cl₂. These species could not be separated.

6.4.5.2. Discussion of the reaction of Ge₃Co₈(CO)₂₆ (G) with [Co(CO)₄]⁻.

It has, unfortunately, not been possible to identify the products of this preliminary study. The ether soluble species was characterised by carbonyl region infrared spectroscopy (figure 6.13 and table 6.8) and electron probe analysis. The former does not help greatly with the identification of this species while the latter, although limiting the range of possibilities to those where there is a Ge to Co ratio of 1:3, and thus suggesting the addition of one [Co(CO)₄]⁻ to Ge₃Co₈(CO)₂₆ to give a Ge₃Co₉ species, does not allow any more definite proposals on the nature of this product. The dichloromethane soluble fraction, containing several species which could not be separated, could only be characterised by carbonyl region infrared spectroscopy (table 6.8.).

Table 6.8. Carbonyl region infrared data for the products of reaction between Ge₃Co₈(CO)₂₆ and [Co(CO)₄]⁻ (cm⁻¹).

Ether soluble fraction	CH ₂ Cl ₂ soluble fraction
2099 w	2112 sh, w
2076 w-m	2093 sh, w (Ge ₃ Co ₈ (CO) ₂₆)
2055 sh, m	2088 sh, w
2030 vvs	2070 sh, w (Ge ₃ Co ₈ (CO) ₂₆)
2005 sh, w	2060 vs
1985 sh, w	2038 vs
	2020 sh, s
1825 w, br	1993 sh, w
	1885 vs ([Et ₄ NCo(CO) ₄])

The most useful identification technique for these types of product is X-ray crystallography, however neither of these species crystallised under the conditions attempted (i.e. from CH_2Cl_2 solution, $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution, CH_2Cl_2 /hexane solution or by slow diffusion of Et_2O into a CH_2Cl_2 solution all held at -30°C) so this could not be employed.

Obviously further study of this system is desirable. Obtaining crystals of the products would be extremely helpful, however other experiments could also prove useful. Measurement of evolved CO might give some idea of the processes involved, and fast atom bombardment mass spectroscopy, particularly of the apparently pure ether fraction, could give at least some idea of the nature of the products. A sample of the ether soluble fraction was sent to the University of Adelaide for FAB MS but this product unfortunately did not survive transport.

The only important information obtained from this study is that $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ does not react with $[\text{Co}(\text{CO})_4]^-$ by the same path as the smaller homologues, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ [28, 29] and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$. These both require conversion to their respective condensation products before reaction with $[\text{Co}(\text{CO})_4]^-$ will take place. This is either accomplished by applying heat to the reaction mixture, or by using a large enough excess of $[\text{Co}(\text{CO})_4]^-$ to promote the decarbonylation at room temperature.

$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ does not readily decarbonylate to form a *closo* analogue. It is stable under heating to 70°C and, at higher temperatures, complete decomposition to the metal residue was observed [23]. During its reaction with $[\text{Co}(\text{CO})_4]^-$ the infrared spectra recorded at intervals showed only the presence of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ and the products formed at completion of the reaction. At no stage did it appear that $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ was transforming to a second species before reaction with $[\text{Co}(\text{CO})_4]^-$ occurred.

It thus seems likely that the mechanism of attack of $[\text{Co}(\text{CO})_4]^-$ at a $\text{Ge-Co}(\text{CO})_4$ moiety, postulated to occur in the reactions of $\text{GeCo}_4(\text{CO})_{14}$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, is not applicable to the analogous reaction of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$.

6.5. Preliminary studies of the reactions of some methylgermyl substituted cobalt carbonyl clusters with $[\text{Co}(\text{CO})_4]^-$.

6.5.1. Experimental Details and Results.

Unfortunately, none of the products obtained from the preliminary studies of these reactions crystallised under the conditions attempted, and it was not possible to characterise the new species. The reaction conditions employed and the results obtained are, therefore, merely reported briefly in table 6.9. It is hoped that these data may prove useful when the systems are investigated more thoroughly.

Table 6.9. Reaction conditions and results of reactions of some methylgermyl substituted germanium-cobalt carbonyl clusters with $[\text{Co}(\text{CO})_4]^-$.

Cluster (mmoles)	$\text{Co}(\text{CO})_4^-$ (mmoles)	Duration (hours)	Temp. (°C)	Approximate yield and νCO of products obtained.
$\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ (0.16)	$\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.60)	27	40	Hexane soluble fraction: Unreacted $\text{MeGeCo}_3(\text{CO})_{11}$ (10%) Et ₂ O soluble fraction (40%) 2052 w (CH_2Cl_2) 2004 s 1994 sh, m CH ₂ Cl ₂ soluble fraction (40%) 2052 w (CH_2Cl_2) 2005 sh, m 1985 vs 1885 vvs ($\text{Co}(\text{CO})_4^-$) Insoluble decomposition product (10%)
(No reaction at room temperature)				
$\text{MeGeCo}_3(\text{CO})_9(\text{H})$ (0.04)	$\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.4)	2	R.T.	Et ₂ O soluble fraction (60%) 2080 w 2052 w (CH_2Cl_2) 2005 s 1990 sh, w CH ₂ Cl ₂ soluble fraction: (35%) 2052 w (CH_2Cl_2) 1885 vs $[\text{Co}(\text{CO})_4]^-$ Insoluble decomposition product (5%)

Table 6.9 continued

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11} (J)$ (0.03)	$\text{PPN}[\text{Co}(\text{CO})_4]$ (0.14)	6	50	Et ₂ O soluble fraction: (90%) 2052 w (CH ₂ Cl ₂) 2014 sh, w 1998 s 1885 vs (Co(CO) ₄) ⁻ Insoluble decomposition product (10%)
(No reaction at room temperature)				
$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13} (C)$ (0.06)	$\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.60)	5	R.T.	Et ₂ O soluble fraction (80%) 2052 w (CH ₂ Cl ₂) 2040 sh, w 2010 vs 1997 sh, m CH ₂ Cl ₂ soluble fraction (20%) 2052 (w) (CH ₂ Cl ₂) 1885 (vs) (Co(CO) ₄) ⁻
$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12} (D)$ (0.13)	$\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (0.45)	1 2 2	R.T. 35 50	} No reaction. } Complete recovery } of starting } material

* All spectra recorded from CH₂Cl₂ solution.

6.5.2. Discussion of the Reactions of Methylgermyl Substituted Germanium-Cobalt Carbonyl Clusters with $[\text{Co}(\text{CO})_4]^-$.

The carbonyl region infrared spectra of the ether soluble fractions obtained from each of these experiments showed bands which could not be assigned to any known germanium-cobalt carbonyl anions and are thus assumed to arise from new species. As it was not possible to characterise the products of these reactions it is only practical to give a limited discussion of these systems.

It is interesting that the reactions of $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ or $\text{MeGeCo}_3(\text{CO})_9(\text{H})$ with $[\text{Co}(\text{CO})_4]^-$ provide a similar product in the ether soluble fractions. The two starting clusters are related by a decarbonylation reaction as depicted in figure 6.13 [38].

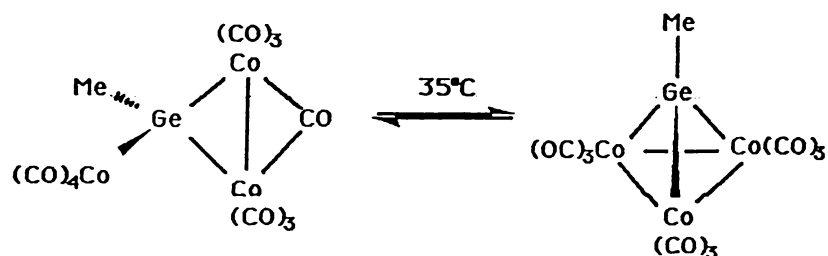


Figure 6.13 [38]

The reaction of $\text{MeGeCo}_3(\text{CO})_{11}$ with $[\text{Co}(\text{CO})_4]^-$ required heat before any changes in the system were observed and it may be suggested that condensation to $\text{MeGeCo}_3(\text{CO})_9$ was necessary for reaction to take place. A second product was observed in this system, soluble only in dichloromethane solution. It is possible that this formed as a result of the effect of heat on the ether soluble product, since this was not observed in the $\text{MeGeCo}_3(\text{CO})_9$ reaction, conducted at room temperature.

The reaction of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ with $[\text{Co}(\text{CO})_4]^-$ required very strong heating before any change was observed in the infrared spectrum of the system. This may be a result of the cation used in this case as $\text{PPN}[\text{Co}(\text{CO})_4]$ could be less reactive than $\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$ (it was observed in this work that $\text{PPN}[\text{Mn}(\text{CO})_5]$ is less air sensitive than $\text{Et}_4\text{N}[\text{Mn}(\text{CO})_5]$). It is also possible that the high temperature was necessary for some degradation of the cluster to occur before $[\text{Co}(\text{CO})_4]^-$ attack could take place.

A comparison of the reactions of the species $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ with $[\text{Co}(\text{CO})_4]^-$ is interesting since the former reacted at room temperature while the latter showed no sign of reaction even

after heating at 50°C. This difference in reactivity is presumably due to steric factors as the presence of the extra dimethylgermyl group could prevent attack by the $[\text{Co}(\text{CO})_4]^-$.

These reactions appear to have provided some interesting new species and it is desirable that some further study is applied to these systems in the hope of identifying the new products.

6.6. Reactions of some germanium-cobalt carbonyl clusters with iron carbonyl anions.

6.6.1. Reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ with $[\text{Fe}_2(\text{CO})_8]^{2-}$.

6.6.1.1. Experimental details and results.

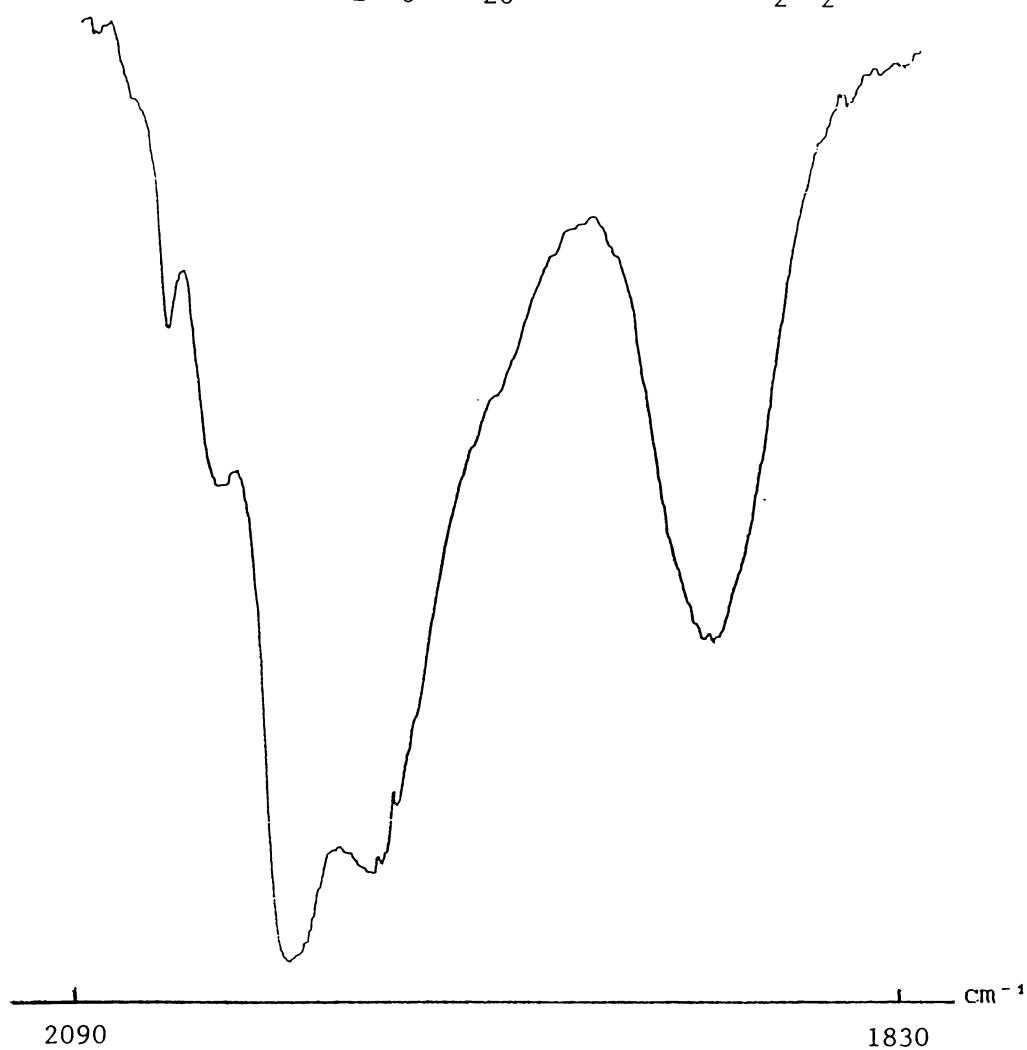
$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (0.069 g; 0.068 mmols) and $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{CO})_8]$ (0.035 g; 0.059 mmols) were allowed to react in CH_2Cl_2 (15 mls) at room temperature. The reaction was followed by infrared spectroscopy and within 5 minutes bands corresponding to the carbonyl vibrations of $[\text{Co}(\text{CO})_4]^-$ could be observed. The carbonyl bands of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ gradually diminished in intensity while new bands at 2026 cm^{-1} and 1995 cm^{-1} appeared. After 24 hours the solvent was removed and the involatile products were worked up as described in section 6.3.

These products were divided into two fractions. The first, (ca. 10%) was soluble in Et_2O and showed carbonyl vibrations corresponding to unreacted $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$. The remainder (ca. 90%) was soluble in CH_2Cl_2 and showed a large amount of displaced $[\text{Co}(\text{CO})_4]^-$ and a new species.

6.6.1.2. Discussion of the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ with $[\text{Fe}_2(\text{CO})_8]^{2-}$.

The reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ with $[\text{Fe}_2(\text{CO})_8]^{2-}$ appears to occur readily at room temperature. The carbonyl region infrared spectrum of the product mixture obtained is shown in figure 6.14. The bands are repeated in table 6.10. together with those reported for $[\text{Ge}_2\text{Co}_5\text{Fe}_2(\text{CO})_{22}]^-$ [85].

Figure 6.14. Infrared active carbonyl stretches of the products of reaction of $(\text{Et}_4\text{N})_2\text{Fe}_2(\text{CO})_8$ with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$. Recorded in CH_2Cl_2 .



2075 sh,w
 2063 m
 2047 sh,w
 2023 vvs
 1994 vs

1885 s $\text{Co}(\text{CO})_4^-$

Table 6.10. Carbonyl region infrared data for the product of the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and $[\text{Fe}_2(\text{CO})_8]^{2-}$ and that of $[\text{Ge}_2\text{Co}_5\text{Fe}_2(\text{CO})_{22}]^-$. (cm^{-1}).

Products from $\text{Ge}_2\text{Co}_6(\text{CO})_{20} + [\text{Fe}_2(\text{CO})_8]^{2-}$	$[\text{Ge}_2\text{Co}_5\text{Fe}_2(\text{CO})_{22}]^-$ [85]
2075 sh, w	2071 w
2063 m	
2047 sh, w	
2023 vvs	2016 vs
1994 vs	1949 w
	1913 m
1885 s $[\text{Co}(\text{CO})_4]^-$	1810 w, br

The smaller homologue of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, reacts with $[\text{Fe}_2(\text{CO})_8]^{2-}$ at room temperature to provide the cluster $[\text{Ge}_2\text{Co}_5\text{Fe}_2(\text{CO})_{22}]^-$ [85] shown in figure 6.15.

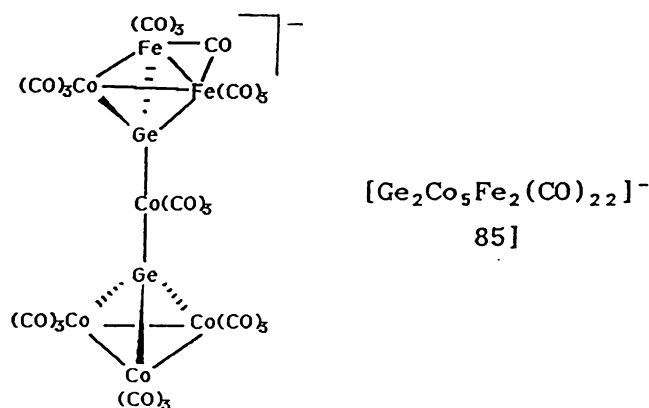


Figure 6.15.

It could be anticipated that reaction of $[\text{Fe}_2(\text{CO})_8]^{2-}$ with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (E) would proceed by a similar route to provide a higher nuclearity cluster. From this experiment it appears that a similar pathway is followed since the reaction occurred readily at room temperature and $[\text{Co}(\text{CO})_4]^-$ displacement was evident. The higher nuclearity of the final product is supported by its only being soluble in CH_2Cl_2 while $[\text{Ge}_2\text{Co}_5\text{Fe}_2(\text{CO})_{22}]^-$ is quite soluble in Et_2O solution.

Unfortunately, this new species did not crystallise under any of the conditions attempted (ie from CH_2Cl_2 solution, $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution or by slow diffusion of Et_2O into CH_2Cl_2 solution, all held at -30°C) thus its identification was not possible. In fact, using $[\text{Et}_4\text{N}]^+$ as the cation made its separation from produced $[\text{Co}(\text{CO})_4]^-$ difficult, preventing the use of other characterisation techniques. Further study of this system could prove useful, particularly if other cations were employed, partly to simplify the removal of $[\text{Co}(\text{CO})_4]^-$, and also as this could aid the crystallisation of the product.

6.6.2. Reactions of some Germanium-Cobalt Carbonyl Clusters with $[\text{Fe}(\text{CO})_4]^{2-}$.

6.6.2.1. Experimental details and results.

All of these reactions were treated similarly using CH_2Cl_2 as solvent. None of the systems showed any reaction at room temperature thus heat was applied. Table 6.11 shows the conditions employed in each case. The experiments were followed by infrared spectroscopy and no displaced $[\text{Co}(\text{CO})_4]^-$ was observed in any of the reactions.

Table 6.11. Conditions and results of the reactions between some germanium-cobalt carbonyl clusters and $\text{Na}_2[\text{Fe}(\text{CO})_4]$.

Cluster (mmoles)	Ratio of $[\text{Fe}(\text{CO})_4]^{2-}$	Temp. (°C)	Duration (hours)	Species obtained on work-up (mmoles)
$\text{GeCo}_4(\text{CO})_{13}(\text{I})$ (0.056)	0.7:1	40	24	$\text{GeCo}_4(\text{CO})_{13}$ (0.044) $\text{Na}_2[\text{Fe}(\text{CO})_4]$ (0.038)
$\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ (0.195)	1.1:1	50	24	$\text{MeGeCo}_3(\text{CO})_{11}$ + $\text{MeGeCo}_3(\text{CO})_9$ $\text{Na}_2[\text{Fe}(\text{CO})_4]$ (0.20)
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ (0.009)	10:1	50	24	$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (0.008) $\text{Na}_2[\text{Fe}(\text{CO})_4]$ (0.087)

From table 6.11 it can be seen that, apart from the experiment using $\text{MeGeCo}_3(\text{CO})_{11}$ where the application of heat resulted in its partial conversion to $\text{MeGeCo}_3(\text{CO})_9$, [38], the reactants were almost quantitatively recovered.

6.6.2.2. Discussion of the reactions of some germanium-cobalt carbonyl clusters with $[\text{Fe}(\text{CO})_4]^{2-}$.

It was hoped that $[\text{Fe}(\text{CO})_4]^{2-}$ would displace the terminal $\text{Co}(\text{CO})_4$ unit present in each of the molecules to form a neutral species consisting of two clusters bridged by a $\text{Fe}(\text{CO})_4$ unit. This clearly does not occur as no reaction was observed with any of these species and the starting materials were recovered almost quantitatively.

Exchange of metal carbonyl moieties on germanium groups has been observed for species such as $\text{H}_3\text{GeM}(\text{CO})_n$, $\text{MeH}_2\text{GeM}(\text{CO})_n$ and $\text{Me}_2\text{HGeM}(\text{CO})_n$ where $[\text{Mn}(\text{CO})_5]^-$ will displace either $[\text{Fe}(\text{CO})_4]^{2-}$ or $[\text{Co}(\text{CO})_4]^-$ and $[\text{Fe}(\text{CO})_4]^{2-}$

will displace $[\text{Co}(\text{CO})_4]^-$ [26]. The displacement of $[\text{Co}(\text{CO})_4]^-$ by $[\text{Mn}(\text{CO})_5]^-$ may be extended to relatively large germanium cobalt carbonyl clusters as has been observed in the reactions of $\text{GeCo}_4(\text{CO})_{13}$ [28, 29] or $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (section 7.4.2.) with $[\text{Mn}(\text{CO})_5]^-$. However, it appears from the results obtained here that this is not the case for $[\text{Fe}(\text{CO})_4]^{2-}$. Although the displacement of $[\text{Co}(\text{CO})_4]^-$ by $[\text{Fe}(\text{CO})_4]^{2-}$ will take place for the small molecules, new considerations must take effect in the case of the clusters, preventing this displacement reaction.

It is possible that some steric restrictions are involved, although this cannot be the only factor involved since $[\text{Mn}(\text{CO})_5]^-$ is a larger group than $\text{Fe}(\text{CO})_4^{2-}$ and its reactions appear to occur with ease. It is probable that the resulting $\text{Fe}(\text{CO})_4$ substituted clusters are not favourable enough to promote the displacement of the $\text{Co}(\text{CO})_4$ unit.

An alternative explanation for the lack of reaction between these clusters and $[\text{Fe}(\text{CO})_4]^{2-}$ is the use of CH_2Cl_2 as solvent. The studies of the exchange of metal carbonyl moieties on germanes carried out by Mackay *et al.* [26] used ether as solvent and it is reported that no reaction was observed in hydrocarbon solvents [26]. It is possible that the ether allows a dissociation to occur so that the $[\text{Fe}(\text{CO})_4]^{2-}$ may move in to bond the germanium group, rather than the $[\text{Fe}(\text{CO})_4]^{2-}$ actively displacing the $\text{Co}(\text{CO})_4$ unit. It is unfortunate that this feature was noticed only when there was no time available to repeat these reactions. It would certainly be worthwhile to attempt these in an ether solvent at some stage although it should be noted that in the original study of these displacements [26] no reaction was observed using $[\text{Mn}(\text{CO})_5]^-$ as the reagent in hydrocarbon solvents, while this species has been observed to react readily in CH_2Cl_2 solution during this work.

In any event, it is possible that the desired clusters may be prepared by other routes. For example, the anticipated product of the reaction of $\text{GeCo}_4(\text{CO})_{13}$ (I) with $[\text{Fe}(\text{CO})_4]^{2-}$ was $[(\text{CO})_9\text{Co}_3\text{Ge}]_2\text{Fe}(\text{CO})_4$. This could perhaps be prepared by the reaction of $\text{XGe}[\text{Co}_3(\text{CO})_9]$ or $\text{XGe}[\text{Co}(\text{CO})_4]_3$ (X = halogen) with $[\text{Fe}(\text{CO})_4]^{2-}$. Similar routes may be envisaged for the desired products of $\text{MeGeCo}_3(\text{CO})_{11}$ (A) and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (K).

6.7. Reactions of $[\text{GeCo}_7(\text{CO})_{20}]^-$ (N) and $[\text{GeCo}_5(\text{CO})_{16}]^-$ (L) with GeCl_4 .

6.7.1. Experimental Details and Results.

Run 1: $\text{Et}_4\text{N}[\text{GeCo}_7(\text{CO})_{20}]$ (0.05 g; 0.042 mmol) and GeCl_4 (0.003 g; 0.013 mmol) (3:1 ratio) were allowed to react in CH_2Cl_2 (10 ml) at room temperature. An immediate reaction was observed from changes in the infrared spectrum. After 1 hour the solvent was removed and the products worked up as described in section 6.3.

These were separated into three fractions. The first (ca. 60%) was soluble in hexane and a carbonyl region infrared spectrum of this solution showed bands corresponding mainly to $\text{Cl}_3\text{GeCo}(\text{CO})_4$ [160] and a small amount of $\text{Co}_4(\text{CO})_{12}$ [139]. The second (ca. 20%) was soluble in CH_2Cl_2 giving a bright orange solution which showed a broad ill-resolved band in its carbonyl region infrared spectrum. This is shown in figure 6.16. The third fraction (ca. 20%) was an insoluble blue powder which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was characterised by electron probe analysis as CoCl_2 .

Run 2: $\text{Et}_4\text{N}[\text{GeCo}_5(\text{CO})_{16}]$ (0.038 g; 0.04 mmol) and GeCl_4 (0.004 g; 0.02 mmol) (2:1 ratio) were reacted in CH_2Cl_2 (10 ml) at room temperature. After 3 hours little change had been observed and the reaction mixture was left stirring for 56 hours. It was then worked up as described in section 6.3.

This was again separated into three fractions. The first (0.013 g) was soluble in Et_2O giving a light purple solution. The carbonyl region infrared spectrum of this species is shown in figure 6.17. The second fraction (0.005 g) was soluble in CH_2Cl_2 solution giving a bright orange solution. The carbonyl region infrared spectrum of this species, though not very detailed, suggested it to be the same product as obtained in the reaction of $[\text{GeCo}_7(\text{CO})_{20}]^-$ with GeCl_4 . The final fraction (0.019 g) was an insoluble blue powder which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be CoCl_2 .

Figure 6.16. Infrared active carbonyl stretches of the CH_2Cl_2 soluble product obtained from reaction of GeCl_4 with $(\text{GeCo}_7(\text{CO})_{20})^-$. Recorded in CH_2Cl_2 .

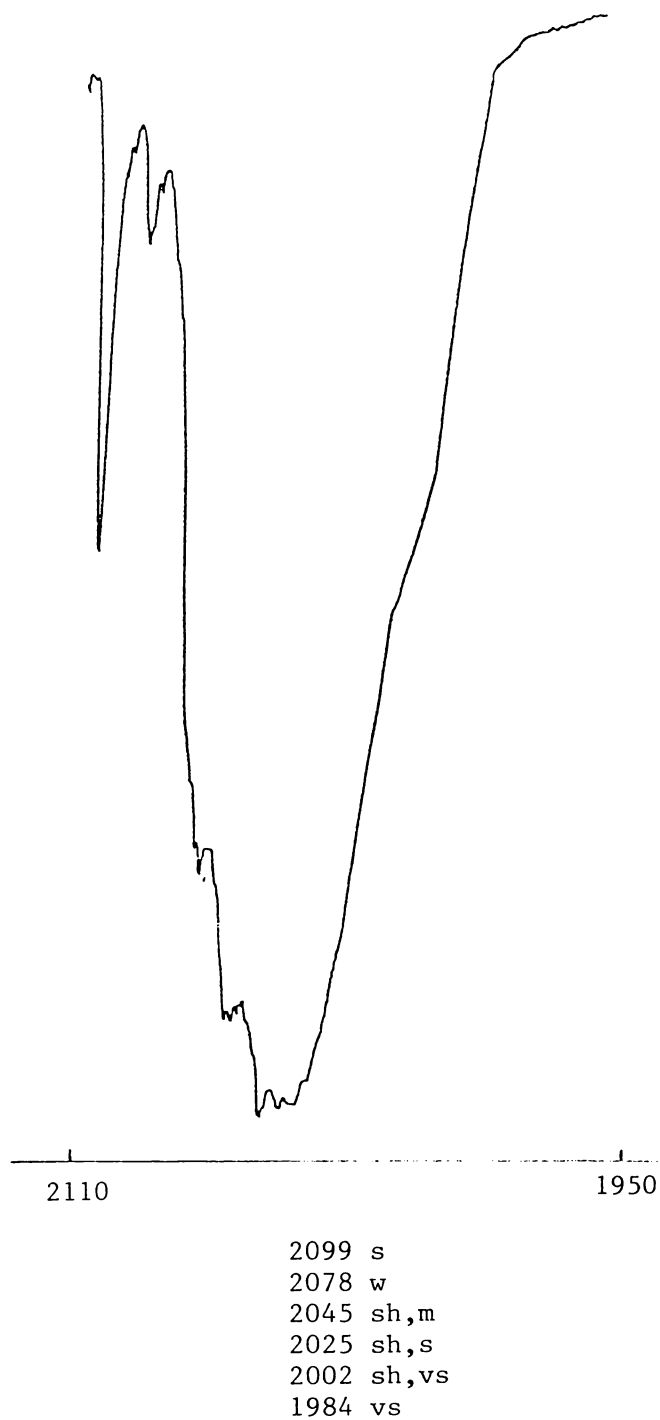
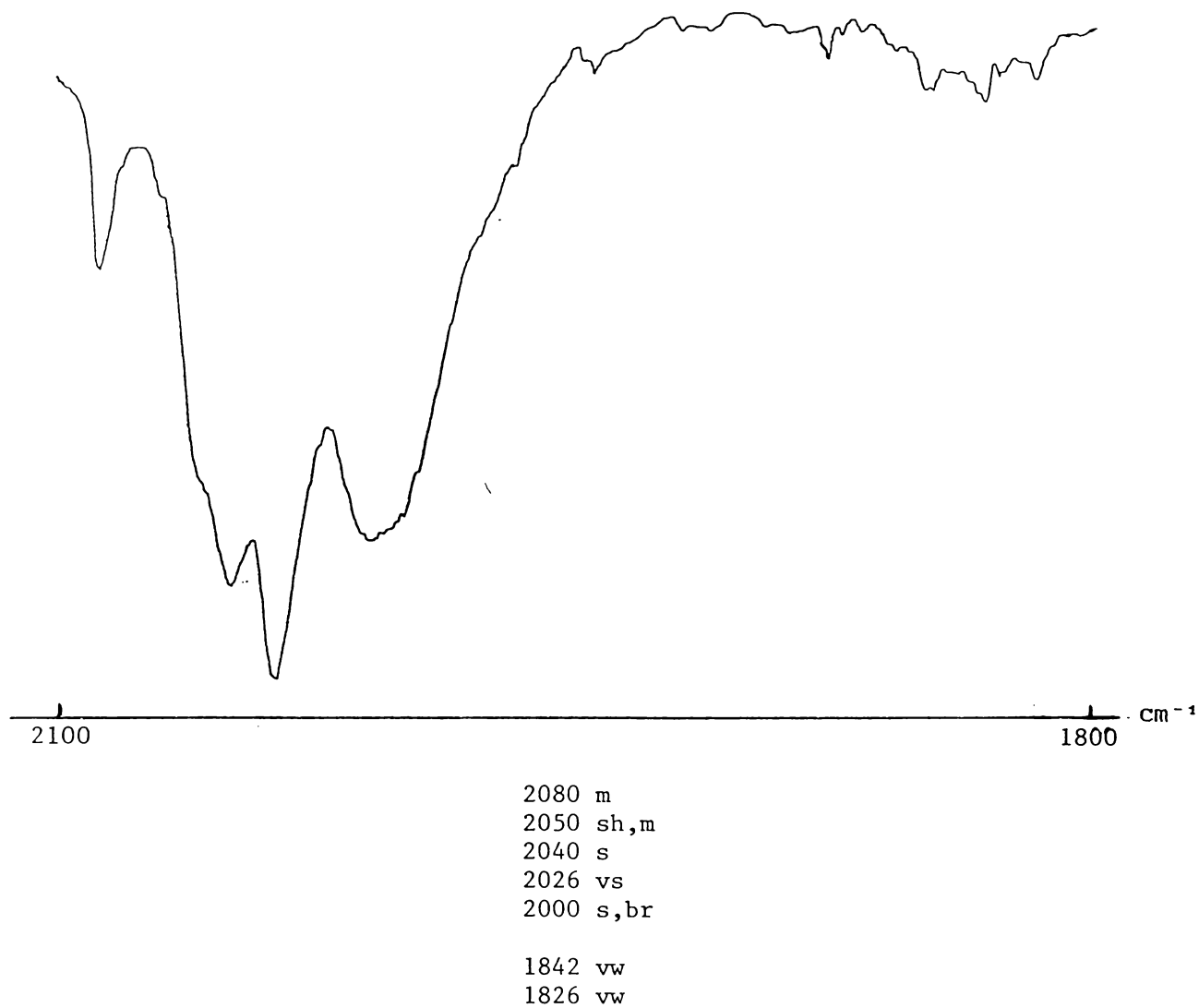


Figure 6.17. Infrared active carbonyl stretches of the ether soluble products obtained from the reaction of GeCl_4 with $(\text{GeCo}_5(\text{CO})_{16})^-$.
Recorded in CH_2Cl_2 .



As the reaction of $[\text{GeCo}_7(\text{CO})_{20}]^-$ with GeCl_4 seemed to cause large scale degradation of the cluster, it would be interesting to examine the reaction of this species with GeCl_2 which could result in a higher yield of the new anionic product, although it is possible that a completely different process would take place.

The reaction of $[\text{GeCo}_5(\text{CO})_{16}]^-$ with GeCl_4 proceeded quite differently from that of $[\text{GeCo}_7(\text{CO})_{20}]^-$. The process took a much longer time to reach completion and, in fact, it appears from the carbonyl region infrared spectrum of the ether soluble fraction (figure 6.17) that some unreacted $[\text{GeCo}_5(\text{CO})_{16}]^-$ remained after 56 hours. No hexane soluble products were obtained from this system although CoCl_2 was formed as a major product. All the other species obtained were anionic in nature and possibly as many as three different compounds were present in the ether fraction which could not be separated. The presence of these anionic products and the lack of neutral species suggests that this cluster is not broken down by the GeCl_4 , but rather reacts as a whole unit. The CH_2Cl_2 soluble material appears from its carbonyl region infrared spectrum to be the same species as obtained from the reaction of $[\text{GeCo}_7(\text{CO})_{20}]^-$ with GeCl_4 but in both cases this was a minor product, and it seems clear that the two anions react with GeCl_4 by very different paths.

The CH_2Cl_2 soluble fraction in each case, which seem to be the same product, appears to be an interesting species. The carbonyl region infrared spectrum of this compound is shown in figure 6.16 and the bands are repeated in table 6.13.

Table 6.13. Carbonyl region infrared data for the CH_2Cl_2 soluble species. (cm^{-1}).

2099 s
2078 w
2045 sh, m
2025 sh, s
2002 sh, vs
1984 vs

The strong band at 2099 cm^{-1} suggests that a terminal $\text{Co}(\text{CO})_4$ unit may be present in this molecule, as this band might correspond to an a' mode of this group (see section 1.4.1.1.). The relatively low frequency of the very strong band, at 1984 cm^{-1} , indicated that this may be a dianion as the increasing negative charge on the cluster lowers the frequency of the carbonyl stretching modes [169].

A further attempt at characterisation of this species was made by obtaining the preliminary crystal parameters shown in table 6.12. These suggest that this is a very large molecule where, depending on whether z is 4 or 8, the molecular weight is approximately 3471 or 1735 respectively. This study also allowed an estimate of the number of non-hydrogen atoms within the molecule and, again depending on whether z is 4 or 8, there are around 168 or 84 non hydrogen atoms. These values limit the possibilities for the structure of this species and reasonable suggestions may be made. For example, figure 6.18. shows one possibility for $z = 8$ where $M_r = 1826$ and the number of atoms is 87 (including $2[Et_4N]^+$).

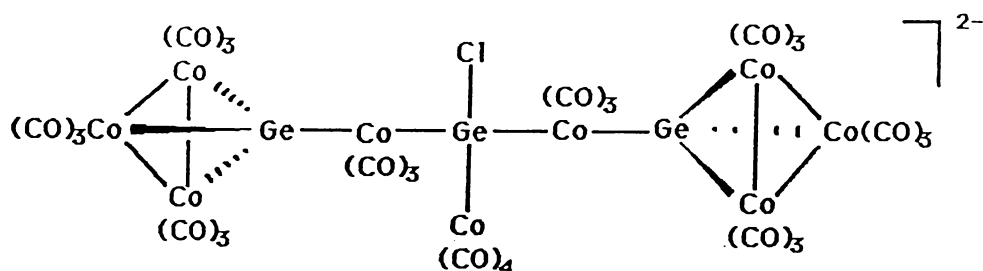


Figure 6.18.

This structure is consistent with the carbonyl region infrared spectrum as the presence of the $Co(CO)_4$ unit would account for the strong band at 2009 cm^{-1} , while the almost polymeric nature of the cluster would account for the broadness of the main band at 1984 cm^{-1} . However, there are several other possibilities and it is hoped that the structure of this product is determined at some stage.

6.8. General summary of the work of this chapter.

The aim of the work described in this chapter was to survey the reactions of various germanium-cobalt carbonyl clusters with a variety of transition metal carbonyl anions. Table 6.14. summarises the systems that have been studied and suggests whether or not they are worthy of further investigation.

Table 6.14. Summary of experiments described in this chapter.

System	Anionic Products obtained	Ease of Handling	Value of further study
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ + $[\text{Co}(\text{CO})_4]^-$	$[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-(\text{M})$	Reasonable	Not necessary
$\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ + $[\text{Co}(\text{CO})_4]^-$	$[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-(\text{M})$	Reasonable	Not necessary
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ + $[\text{Mn}(\text{CO})_5]^-$	Possibly $[\text{Ge}_2\text{Co}_6\text{Mn}(\text{CO})_{22}]^-(\text{X}_1)$	Reasonable	Extremely desirable
$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ + $[\text{Mn}(\text{CO})_5]^-$	Possibly $[\text{Ge}_2\text{Co}_6\text{Mn}(\text{CO})_{22}]^-(\text{X}^1)$	Reasonable	Not worthwhile
$\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$ + $[\text{Co}(\text{CO})_4]^-$	Possibly a $[\text{Ge}_3\text{Co}_9(\text{CO})_n]^-$ cluster (X_2) + other unidentified anions	Reasonable	Extremely desirable
$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ + $[\text{Fe}_2(\text{CO})_8]^{2-}$	Unknown	Reasonable	Desirable
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ + $[\text{Fe}(\text{CO})_4]^{2-}$	No reaction	Reasonable	Possibly try Et_2O as solvent
$\text{GeCo}_4(\text{CO})_{13}(\text{I})$ + $[\text{Fe}(\text{CO})_4]^{2-}$	No reaction	Reasonable	Possibly try Et_2O as solvent
$\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$ + $[\text{Fe}(\text{CO})_4]^{2-}$	No reaction	Reasonable	Possibly try Et_2O as solvent
$\text{MeGeCo}_3(\text{CO})_{11}$ + $[\text{Co}(\text{CO})_4]^-$	Unknown	Difficult	Desirable

Table 6.14. continued

$\text{MeGeCo}_3(\text{CO})_9(\text{H})$ + $[\text{Co}(\text{CO})_4]^-$	Unknown	Difficult	Desirable
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ + $[\text{Co}(\text{CO})_4]^-$	Unknown	Difficult	Desirable
$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}(\text{C})$ + $[\text{Co}(\text{CO})_4]^-$	Unknown	Difficult	Desirable
$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ + $[\text{Co}(\text{CO})_4]^-$	No reaction	-	Not worthwhile
$[\text{GeCo}_7(\text{CO})_{20}]^-(\text{N})$ + GeCl_4	$\text{Cl}_3\text{GeCo}(\text{CO})_4 +$ $\text{Co}_4(\text{CO})_{12} + \text{CoCl}_2$ + large unidentified cluster (X_3)	Reasonable	Extremely desirable
$[\text{GeCo}_5(\text{CO})_{16}]^-(\text{L})$ + GeCl_4	Large unidentified cluster (X_3) + other anionic products + CoCl_2	Reasonable	Extremely desirable

It should be useful to carry out these experiments using different cations, particularly larger ones such as PPN^+ or crown ethers reacted with alkali metal cations. This should hopefully aid in the crystallisation of the new anionic products. It may also be helpful to form neutral products from these anions using, for example, H^+ or Ph_3PAu^+ . These may then crystallise more readily than the anionic species and handling of these species should be easier. Neutralisation of $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-(\text{M})$ using H_3PO_4 or Ph_3PAuCl was attempted but neither of these species gave any reaction with this anion. However, they may be more effective with the products of the other experiments.

In the reactions of the alkyl substituted clusters with $[\text{Co}(\text{CO})_4]^-$ a great deal of difficulty was found in handling the products obtained. Often these would just decompose as they formed, commonly giving a green solution. Care must therefore be taken to ensure that vessels and solvents are completely free of oxygen and water.

6.9. Conclusion

This preliminary survey of the reactions of some germanium-cobalt carbonyl clusters with a variety of transition metal carbonyl anions has produced clear evidence for three new products (X_1 , X_2 and X_3 in table 6.14.) and indications of several others. It has also shown that the $[\text{Mn}(\text{CO})_5]^- > [\text{Fe}(\text{CO})_4]^{2-} > [\text{Co}(\text{CO})_4]^-$ displacement series holds only in part and it has been found that the reactivities of $\text{GeCo}_4(\text{CO})_{14}$ (*B*) and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) are similar under these conditions while the higher homologue, $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$, behaves quite differently.

The room temperature reaction of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*) with $[\text{Co}(\text{CO})_4]^-$ provided the known anionic cluster $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$ (*M*) in approximately 55% yields. The analogous reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) produced the same product but in lower yields and accompanied by a larger proportion of decomposition. This latter reaction required initial condensation to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ which then reacted to form the anionic product. The presence of $[\text{Co}(\text{CO})_4]^-$ promoted this condensation of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$.

The room temperature reaction of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ (*K*) with $[\text{Mn}(\text{CO})_5]^-$ provided a new anionic product tentatively characterised as $[\text{Ge}_2\text{Co}_6\text{Mn}(\text{CO})_{22}]^-$ (X_1). $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) also reacted with $[\text{Mn}(\text{CO})_5]^-$ to produce this species, but again required initial condensation to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ before any reaction with the anion occurred. It is, therefore, not really worthwhile to continue the examination of the reactions of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ in this area as those of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ provide a more straightforward and efficient route to the same products.

In contrast to its reactions with $[\text{Co}(\text{CO})_4]^-$ and $[\text{Mn}(\text{CO})_5]^-$, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) reacted directly with $[\text{Fe}_2(\text{CO})_8]^{2-}$ to provide a new mixed germanium-iron/cobalt carbonyl anionic cluster. The reaction proceeded analogously to that reported between the smaller homologue of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, $\text{GeCo}_4(\text{CO})_{14}$ (*B*), and $[\text{Fe}_2(\text{CO})_8]^{2-}$.

$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (*G*) reacted with $[\text{Co}(\text{CO})_4]^-$ in a different manner to the smaller members of this series, $\text{GeCo}_4(\text{CO})_{14}$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, as it reacted directly with the anion, rather than initially condensing to a *closso*-structure. This system produced several new products, one of which is indicated to be of the form $[\text{Ge}_3\text{Co}_9(\text{CO})_n]^-$ (X_2).

$[\text{Fe}(\text{CO})_4]^{2-}$ did not react with any of the clusters $\text{MeGeCo}_3(\text{CO})_{11}(\text{A})$, $\text{GeCo}_4(\text{CO})_{13}(\text{I})$ or $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ in CH_2Cl_2 solution. This may have resulted from the use of CH_2Cl_2 as the solvent or from the unfavourable nature of the possible products.

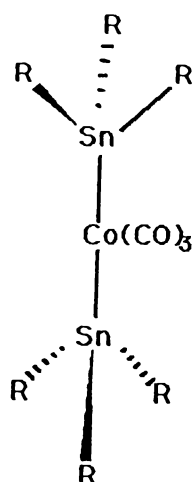
The anionic species $\text{Et}_4\text{N}[\text{GeCo}_7(\text{CO})_{20}](\text{N})$ reacted with GeCl_4 to provide $\text{Cl}_3\text{GeCo}(\text{CO})_4$, $\text{Co}_4(\text{CO})_{12}$ and CoCl_2 through a general degradation of the cluster. Also obtained in low yield from this reaction was a new high molecular weight anionic cluster (X_3).

The only sure technique to determine the nature of an anionic species is by X-ray crystal structure determination. All of the methods attempted during this work did not provide any single crystals of sufficient quality to be used for this, and until good crystals are obtained, all of the characterisations of new products in this chapter must remain extremely tentative.

CHAPTER 7: Further Studies of Some Tin-Cobalt Carbonyl Anions.

7.1. Background and aim.

Recent work at the University of Waikato has provided a series of tin-cobalt carbonyl anions of general formula $[(R_3Sn)_2Co(CO)_3]^-$ ($R_3 = Cl_3$, $Cl_2[Co(CO)_4]$, $Cl[Co(CO)_4]_2$, $[Co(CO)_4]_3$) [94, 95]. These are related to the anion $\{[(CO)_9Co_3Ge]_2Co(CO)_3\}^- (M)$ described in the previous chapter, however the comparatively large size of the tin atoms prevents the formation of bonds between the cobalts of the R_3Sn unit. A generalised structure of these anions is shown in figure 7.1.

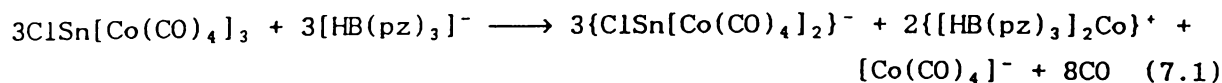


Generalised structure
of the anions
 $[(R_3Sn)_2Co(CO)_3]^-$
($R_3 = Cl_3$, $Cl_2[Co(CO)_4]$,
 $Cl[Co(CO)_4]_2$, $[Co(CO)_4]_3$)
[94, 95]

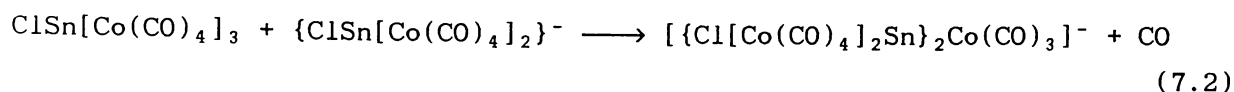
Figure 7.1

These anions have been prepared by several routes. The first to be synthesised was $\{[Cl[(CO)_4Co]_2Sn]_2Co(CO)_3\}^-$ which was found as the major product in the reaction of $ClSn[Co(CO)_4]_3$ with tris(pyrazolyl-1)borate ($[HB(pz)_3]^-$ where pz - pyrazolyl, $C_3H_3N_2$) [95]. The corresponding cation here was $\{[HB(pz)_3]_2Co\}^+$. Similarly, $\{[Cl_2[(CO)_4Co]Sn]_2Co(CO)_3\}^-$ was the major product isolated from the reaction of $[HB(pz)_3]SnCl_3$ with $Na[Co(CO)_4]$. Again, $\{[HB(pz)_3]_2Co\}^+$ was found as the cation [94]. Reaction of $Sn[Co(CO)_4]_4$ with either $[HB(pz)_3]^-$ or $[H_2B(pz)_2]^-$ provided the third anion of this series which has been tentatively characterised as $\{[(CO)_4Co]_3Sn\}_2Co(CO)_3\}^-$ [94].

A rationalisation of these systems has been made for the reaction of $ClSn[Co(CO)_4]_3$ with $[HB(pz)_3]^-$ [94]. This is outlined in equation 7.1.



The tin anion, $\{\text{ClSn}[\text{Co}(\text{CO})_4]_2\}^-$, in which tin has a formal oxidation state of II, can then replace a *trans* carbonyl ligand on $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ to give the observed anionic product (equation 7.2) [94]. Replacement of the *trans* carbonyl ligand is most likely on steric grounds.



Further investigations showed more straightforward routes to these anions. For example, $[\{\text{Cl}[\text{Co}(\text{CO})_4]_2\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ was produced directly from the reaction of $[\text{HB}(\text{pz})_3]^-$ with $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. Also, $[\text{SnCl}_3]^-$ was employed to produce the anions $\{\text{Cl}_3\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ and $\{\text{Cl}_3\text{Sn}\}\text{Co}(\text{CO})_3[\text{Sn}[\text{Co}(\text{CO})_4]\text{Cl}_2]^-$ from $\text{Cl}_3\text{SnCo}(\text{CO})_4$ or $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ respectively [94]. In these reactions the $[\text{SnCl}_3]^-$ acts directly to replace a *trans* carbonyl ligand of a $\text{Co}(\text{CO})_4$ unit in an analogous manner to phosphine substitution [169].

X-ray crystal structure determinations have been carried out for three of these anions - $[\{\text{Cl}[\text{Co}(\text{CO})_4]_2\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$, $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ and $\{\text{Cl}_3\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ - and it is found that, as an axial carbonyl is replaced by an $[\text{R}_3\text{Sn}]^-$ group, the length of the bond between Sn and the Co of the central $\text{Co}(\text{CO})_3$ unit decreases while all of the external bond lengths to Sn increase [94]. Also noted was the fact that all bond lengths to Sn decrease as $\text{Co}(\text{CO})_4$ groups are replaced by Cl atoms [94].

Two main theories were used to rationalise these observations. The first, $(\text{d-d})_\pi$ bonding, suggests that replacement of CO by a weaker π acceptor, $[\text{R}_3\text{Sn}]^-$, allows greater backbonding from Co to Sn. Pure $(\text{d-d})_\pi$ bonding would not predict a marked lengthening. Replacement of electropositive $\text{Co}(\text{CO})_4$ groups by electronegative Cl atoms withdraws electron density from Sn making it a better π acceptor by lowering the energy of its empty d orbitals, thus increasing the amount of backbonding [94]. Alternatively, $\text{d}_\pi \rightarrow \sigma^*$ backbonding to Sn would predict an increase in the R-Sn bond lengths [94].

The second theory which was used to explain the observed changes in bond length is based on Bent's rules for atom isovalent rehybridisation due to substituent changes [181]. This is a σ -bonding theory and states that "in the absence of marked steric effects, replacement in the structure X-A-Y of X by an atom more electronegative than X causes the adjacent A-Y bond to become shorter". This results since "atomic s character concentrates in orbitals directed towards electropositive substituents". Conversely,

"atomic p character concentrates in orbitals directed towards electronegative substituents" [181].

In the case of the tin-cobalt carbonyl anions this theory suggests that replacement of CO by a stronger σ donor and weaker π acceptor, $[\text{R}_3\text{Sn}]^-$, increases the electron density on Co and effectively increases its electropositivity. This increases the s character in the Sn-Co bond, giving the observed contraction. The s character in the R-Sn bonds will correspondingly decrease, thus lengthening them. Replacement of the electropositive $\text{Co}(\text{CO})_4$ groups by electronegative Cl atoms increases the s character in the other bonds, thus they are all observed to contract [94]. This, of course, is in addition to the general contraction of all orbitals found on replacement of substituents by more electronegative species.

A study by M. Severensin of EHM0 calculations was recently carried out for a series of compounds of general formula *trans*- $\text{LCo}(\text{CO})_3\text{SiCl}_3$ ($\text{L} = \text{NH}_3$, CO, CN^- , H^- , PCl_3 , SiCl_3 , SiF_3 , SiH_3), both with and without d orbitals on the Si [179]. The results of this suggested a small amount of $(\text{d-d})_\pi$ bonding, but not enough to account for bond length changes. However, the hybridisation at Co was found to be very dependent on the σ -donating orbitals of the incoming ligand, L, thus it was strongly indicated that changes in the Si-Co bond lengths are predominantly due to σ -bonding effects [179].

It was anticipated that the preparation and structure determination of an unsymmetrical tin-cobalt carbonyl anion of the form $[\text{R}_3\text{SnCo}(\text{CO})_3\text{SnR}_3]^-$ would give valuable information on the bonding of these species. Also, ^{119}Sn NMR spectroscopy of an unsymmetrical anion of this type should give insight into the s and p character of the individual tin atoms through analysis of the 2J ^{119}Sn - ^{119}Sn coupling constants.

This chapter describes the attempts to prepare an unsymmetrical tin-cobalt carbonyl anion of the form $\{[\text{R}_3\text{Sn}]\text{Co}(\text{CO})_3[\text{SnCl}_3]\}^-$ where R = alkyl or aryl group. Also described here are the attempted preparations of a mixed group 14-cobalt carbonyl anion containing both tin and either germanium or silicon.

7.2. Preparation of starting materials.

SnCl_4 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, GeCl_4 , HSiCl_3 , SnBr_4 , Ph_3SnCl , Me_3SnCl , $n\text{Bu}_3\text{SnCl}$, Ph_3GeBr , $\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}$, were all used as supplied.

SnCl_2 was prepared by the addition of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to acetic anhydride and refluxing the mixture for 2 hours. SnCl_2 was precipitated on cooling. This was then filtered off and washed with Et_2O [177]. (30% yield of SnCl_2

with m.p. 242–247°C. cf. Lit. [178] 246°C).

$\text{Et}_4\text{NSnCl}_3$ was prepared by the addition of SnCl_2 in ethanol to a stirred ethanol solution of $\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}$. The product was separated by cooling to -30°C overnight when it came down from solution as white needles [94] (71% yield of $\text{Et}_4\text{NSnCl}_3$ obtained with Mp. 77–80°C. cf. Lit [94] 79–81°C).

$\text{K}[\text{Co}(\text{CO})_4]$ was produced by the reduction of $\text{Co}_2(\text{CO})_8$ over Na/K alloy in diethyl ether [12].

$\text{Me}_3\text{SnCo}(\text{CO})_4$, $\text{Ph}_3\text{SnCo}(\text{CO})_4$ and $^n\text{Bu}_3\text{SnCo}(\text{CO})_4$ were all produced by the addition of an excess of $\text{K}[\text{Co}(\text{CO})_4]$ to the appropriate trialkyl tin chloride in CH_2Cl_2 solution. The product was then extracted from the mixture in hexane (Average yield 65%).

$\text{Ph}_3\text{GeCo}(\text{CO})_4$ was prepared in a similar manner to the alkyl tin species, by the addition of excess $\text{KCo}(\text{CO})_4$ to a stirred solution of Ph_3GeBr in CH_2Cl_2 . The product was then extracted in hexane (yield 60%).

$\text{Cl}_3\text{SnCo}(\text{CO})_4$ was prepared by the dropwise addition of $\text{Co}_2(\text{CO})_8$ in benzene to a stirred benzene solution of SnCl_4 [150]. $\text{Cl}_3\text{SnCo}(\text{CO})_4$ was extracted from the resulting mixture in hexane and purified by sublimation under vacuum at 50°C (yield 5%).

$\text{Br}_3\text{SnCo}(\text{CO})_4$ was prepared in a similar manner to the trichloro derivative, by the dropwise addition of $\text{Co}_2(\text{CO})_8$ in benzene to a stirred benzene solution of SnBr_4 [150]. The product was extracted in hexane and recrystallised by cooling the hexane solution to -15°C (yield 10%).

$\text{Cl}_3\text{GeCo}(\text{CO})_4$ was prepared by the addition of $\text{KCo}(\text{CO})_4$ to a stirred solution of GeCl_4 in Et_2O [160]. The product was extracted in hexane and recrystallised by cooling the hexane solution to -30°C (yield 48%).

$\text{Cl}_3\text{SiCo}(\text{CO})_4$ was synthesised by the reaction of HSiCl_3 and $\text{Co}_2(\text{CO})_8$ at room temperature for 10 minutes. H_2 and excess HSiCl_3 were removed by pumping briefly, then the residue was sublimed onto a cold finger [180] (yield 74%).

$\text{Et}_4\text{N}^+ \{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ was prepared by the addition of $\text{Et}_4\text{NSnCl}_3$ to a stirred solution of $\text{Cl}_3\text{SnCo}(\text{CO})_4$ in CH_2Cl_2 . When the infrared spectra of aliquots taken from the reacting mixture at intervals showed the reaction to be complete solvent was removed under vacuum. Any unreacted $\text{Cl}_3\text{SnCo}(\text{CO})_4$ was removed by extraction in hexane and the product was extracted in CH_2Cl_2 . Cooling this solution to -30°C gave orange needles of $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ [94] (yield 46%).

Purity of all of these carbonyl containing compounds was checked by comparison of their infrared active carbonyl vibrations with the literature: $\text{Me}_3\text{SnCo}(\text{CO})_4$, $\text{Ph}_3\text{SnCo}(\text{CO})_4$, $\text{Ph}_3\text{GeCo}(\text{CO})_4$, $\text{Cl}_3\text{GeCo}(\text{CO})_4$ [160]; $\text{Cl}_3\text{SnCo}(\text{CO})_4$, $\text{Br}_3\text{SnCo}(\text{CO})_4$ [150]; $\text{Cl}_3\text{SiCo}(\text{CO})_4$ [180], $\text{Et}_4\text{N}[(\text{Cl}_3\text{Sn})_2\text{Co}(\text{CO})_3]$ [94].

Ph_3SnLi was prepared from reaction of phenyl-lithium with tin(II) chloride in Et_2O [182]. The PhLi was prepared in situ by the addition of finely cut lithium metal to Et_2O stirred under N_2 , then bromobenzene was added dropwise [204]. The approximate concentration of the triphenyltinlithium solution was determined by adding water and then titrating against standardised hydrochloric acid.

7.3. General experimental techniques.

All of the following experiments were carried out in a similar manner. The reactions usually proceeded quite quickly at room temperature and were monitored by carbonyl region infrared spectroscopy. When no further change was apparent in the infrared spectrum the reaction mixture was worked up.

For example, the reaction of $\text{Ph}_3\text{SnCo}(\text{CO})_4$ with $\text{Et}_4\text{NSnCl}_3$ illustrates these experiments: An equimolar amount of $\text{Et}_4\text{NSnCl}_3$ in CH_2Cl_2 was added to a stirred solution of $\text{Ph}_3\text{SnCo}(\text{CO})_4$ in CH_2Cl_2 . This was allowed to react for approximately 2 hours when no further change was observed in the infrared spectrum of the reaction mixture. The solvent was removed and hexane added to extract any unreacted starting material. The residue was then extracted with Et_2O to dissolve the desired anionic products away from any produced $[\text{Co}(\text{CO})_4]^-$ ($\text{Et}_4\text{NCo}(\text{CO})_4$ is only slightly soluble in Et_2O [28]).

7.4. Reactions of $\text{Et}_4\text{NSnCl}_3$ with $\text{R}_3\text{M}'\text{Co}(\text{CO})_4$, where R_3 = alkyl or aryl groups and $\text{M}' = \text{Sn}, \text{Ge}$.

7.4.1. Experimental Details and Results.

These reactions were all carried out as described in section 7.3. Table 7.1 lists the conditions used and the products obtained in each case.

Table 7.1 Conditions and results of the reactions between $\text{Et}_4\text{NSnCl}_3$ and $\text{R}_3\text{M}'\text{Co}(\text{CO})_4$.

$\text{R}_3\text{M}'\text{Co}(\text{CO})_4$ (mmoles)	$\text{Et}_4\text{NSnCl}_3$ (mmoles)	Duration (hours)	$\text{R}_3\text{M}'\text{Co}(\text{CO})_4$ recovered (mmoles)	Product (mmoles)
$\text{Me}_3\text{SnCo}(\text{CO})_4$ (1.01)	1.00	1	0.061	$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ (0.25)
$\text{Ph}_3\text{SnCo}(\text{CO})_4$ (0.89)	0.85	3	trace	$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ (0.25)
$^n\text{Bu}_3\text{SnCo}(\text{CO})_4$ (1.95)	1.95	2½	0.05	$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ (0.54)
$\text{Ph}_3\text{GeCo}(\text{CO})_4$ (0.26)	0.25	2	trace	$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ (0.06)

From table 7.1 it can be seen that all of these reactions produced the same species, $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$, as the major product. This has been characterised by carbonyl region infrared spectroscopy, FAB mass spectroscopy, electron probe analysis and by an X-ray crystal structure determination. This will be discussed in the following section.

The above experiments were monitored by carbonyl region infrared spectroscopy and in each case the production of $[\text{Co}(\text{CO})_4]^-$ (strong band at 1885 cm^{-1}) was observed during the reaction. Often the intensity of this peak was reduced to zero by the reaction end, as had that of the bands arising from the carbonyl containing starting materials.

7.4.2. Characterisation of $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

7.4.2.1. Carbonyl region infrared spectroscopy.

The carbonyl region infrared spectra of the products obtained from reaction of $\text{Et}_4\text{NSnCl}_3$ with each of $\text{Me}_3\text{SnCo}(\text{CO})_4$, $^n\text{Bu}_3\text{SnCo}(\text{CO})_4$, $\text{Ph}_3\text{SnCo}(\text{CO})_4$ and $\text{Ph}_3\text{GeCo}(\text{CO})_4$ are listed in table 7.2 while figure 7.2 depicts this spectrum obtained from the $\text{Me}_3\text{SnCo}(\text{CO})_4$ system. The very similar pattern and position of the bands in each case strongly suggests that these are all the same compound. Also included in table 7.2 is the carbonyl region infrared spectrum previously reported for the anion $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ [94].

Figure 7.2. Infrared active carbonyl stretches of the product of reaction between $\text{Et}_4\text{NSnCl}_3$ and $\text{Me}_3\text{SnCo(CO)}_4$.
Recorded in CH_2Cl_2 .



Table 7.2 Carbonyl region infrared data for the products of reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Me}_3\text{SnCo}(\text{CO})_4$, $\text{Ph}_3\text{SnCo}(\text{CO})_4$, ${}^n\text{Bu}_3\text{SnCo}(\text{CO})_4$, or $\text{Ph}_3\text{GeCo}(\text{CO})_4$ and $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ (cm^{-1}).

Product of $\text{Et}_4\text{NSnCl}_3$ with $\text{R}_3\text{M}'\text{Co}(\text{CO})_4$				$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ [94]
$\text{Me}_3\text{SnCo}(\text{CO})_4$	$\text{Ph}_3\text{SnCo}(\text{CO})_4$	${}^n\text{Bu}_3\text{SnCo}(\text{CO})_4$	$\text{Ph}_3\text{GeCo}(\text{CO})_4$	$\text{Co}(\text{CO})_3$
	2097 m	2097 m	2094 m	2094 m
2086 s	2090 s	2088 m-s	2086 m-s	2087 s
				2069 w
2050 w	2053 w	2052 w	2050 w	2052 m
2035 m	2035 m	2032 m	2035 m	2034 m
2010 vs, br	2010 vs, br	2009 vs, br	2010 vs, br	2010 s, br
1984 m, br	1969 m, br	1965 m, br	1984 sh, m	1967 m, br

All recorded in CH_2Cl_2 solution

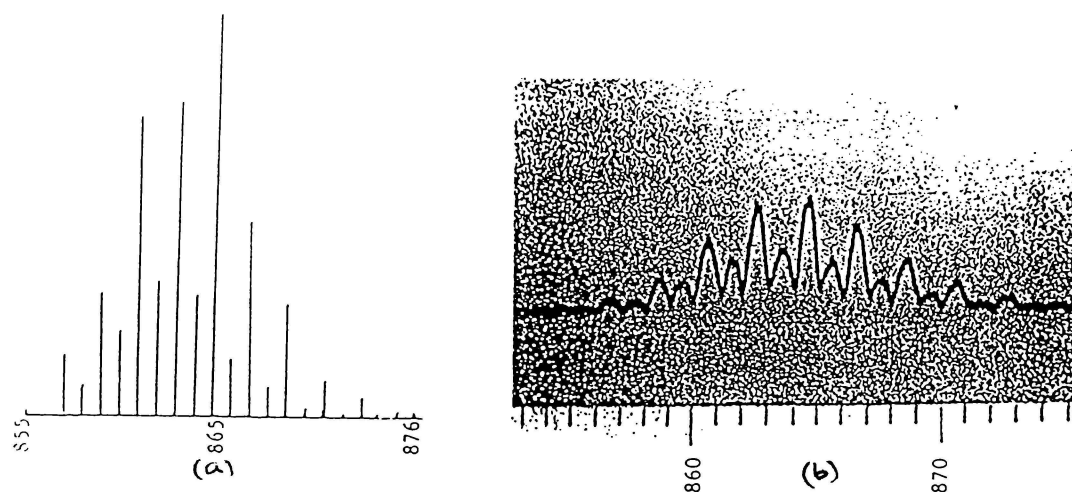
The infrared spectra recorded for the product of each reaction correlate extremely closely with the data reported for the anion $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ [94]. The only band present in the spectrum of the latter, which was not observed in this study, is the weak peak at 2069 cm^{-1} . It may be assumed that this resulted from an impurity in the original solution of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ ideally has C_{2v} symmetry leading to ten infrared active carbonyl vibrations ($5\text{A}_1 + 3\text{B}_1 + 2\text{B}_2$). Not all of these modes are distinguished from the solution spectrum, however the very strong band at 2010 cm^{-1} is quite broad and could result from an overlap of some of these vibrations.

7.4.2.2. Fast atom bombardment mass spectrum (FAB-MS).

The FAB mass spectrum of $\text{Et}_4\text{N}[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]$ was recorded at the University of Adelaide from a sample of the anion obtained from the reaction of $\text{Ph}_3\text{SnCo}(\text{CO})_4$ with $\text{Et}_4\text{NSnCl}_3$. The spectrum is listed in table 7.3.

Throughout the spectrum an isotope pattern consistent with the presence of two tin and four chlorine atoms was observed. Figure 7.3. shows both the calculated isotope pattern of a Sn_2Cl_4 containing species and the isotope pattern observed for the parent ion, $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$, at $m/e = 855\text{--}874$.



- (a) Calculated isotope pattern for a Sn_2Cl_4 containing fragment.
 (b) Observed isotope pattern for $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

Figure 7.3.

From the parent ion a clear series of 11 peaks, separated by 28 m.u., was observed corresponding to the loss of eleven carbonyl units. This series carried 95% of the total ion current. No Cl, Co or Sn loss was found until all the carbonyls were released. The remaining fragmentations appear to be somewhat random with not all possible species of sufficient intensity to be observed.

Table 7.3 FAB mass spectrum of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

m/e	Relative Intensity	Assignment $[\text{Cl}_4\text{Sn}_2\text{Co}_3(\text{CO})_n]^-$
855-874	100	n = 11
830-845	8	10
803-817	20	9
770-788	25	8
744-760	15	7
717-734	50	6
688-704	10	5
660-677	12	4
628-642	18	3
608-620	5	2
582-597	25	1
555-568	10	0
515-529	5	$[\text{Cl}_3\text{Sn}_2\text{Co}_3]^-$
445-460	5	$[\text{ClSn}_2\text{Co}_3]^-$
422-435	12	$[\text{Cl}_2\text{Sn}_2\text{Co}_2]^-$
387-400	10	$[\text{ClSn}_2\text{Co}_2]^-$
353-368	15	$[\text{Sn}_2\text{Co}_2]^-$
327-344	20	$[\text{ClSn}_2\text{Co}]^-$
300-312	5	$[\text{Cl}_2\text{SnCo}_2]^-$

7.4.2.3. X-ray crystallographic structure determination.

Single crystals of $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ suitable for study were grown from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution obtained from the reaction of $\text{Me}_3\text{SnCo}(\text{CO})_4$ with $\text{Et}_4\text{NSnCl}_3$. A red plate was mounted in Araldite on a glass fibre. Preliminary precession photography indicated monoclinic symmetry with systematic absences appropriate for $\text{P}2_1/\text{m}$. Intensity data was collected at the University of Canterbury on a Nicolet P3 Diffractometer. Table 7.4 records the crystal data for $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

Table 7.4 Crystal data for $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

Formula: $\text{C}_{19}\text{H}_{20}\text{Cl}_4\text{Co}_3\text{NO}_{11}\text{Sn}_2$.
Mr: 993.97
Space group: Monoclinic, $\text{P}2_1/\text{m}$.

$a = 7.617 (2)$ $b = 20.778 (7)$ $c = 10.341 (3) \text{ \AA}$
 $\beta = 94.96^\circ (2)$

$U = 1630.4 (8) \text{ \AA}^3$
 $D_{\text{calc}} = 2.03 \text{ g/cm}^3$ $D_{\text{obs}} = 2.11 \text{ g/cm}^3$
 $z = 2$
 $F(000) 956$ $\mu(\text{Mo-K}\alpha) = 57 \text{ cm}^{-1}$
 $T -140^\circ\text{C}$ $\lambda(\text{Mo-K}\alpha) = 0.7107$

Crystal dimensions: $0.12 \text{ mm} \times 0.26 \text{ mm} \times 0.46 \text{ mm}$.

A total of 2193 unique reflections in the range $4^\circ < 2\theta < 45^\circ$ were collected, with $-8 < h < 8$, $0 < k < 22$, $0 < l < 11$. Of these, the 1884 with $I > 2\sigma(I)$ were used in all calculations. The intensity data were corrected for Lorentz, polarisation and absorption effects, the latter by an empirical correction method. Transmission factors were $\text{max} = 0.807$ and $\text{min} = 0.556$.

Solution of the structure was achieved using direct methods. Once the heavy metal atoms of the unique molecule were found, the remaining atoms were located in subsequent refinements and difference maps. The hydrogen atoms of the tetraethylammonium cation were not included in the refinements because of the disorder of these ions. Full matrix least squares refinement to convergence gave $R = 0.041$, $R_w = 0.046$ with $w = (\sigma^2 F + 0.002797 F^2)^{-1}$. At this point the largest parameter shift was 0.435 while the final

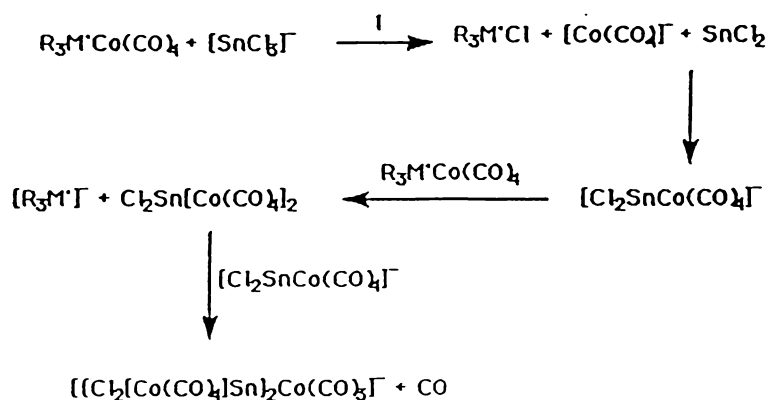
difference map showed the highest peak to have 0.908 e/A³. This peak was adjacent to one of the tin atoms.

The final positional and thermal parameters and a full list of bond lengths and angles of Et₄N⁺[(Cl₂[Co(CO)₄]Sn)₂Co(CO)₃]⁻ are shown in Appendix 3. Structure factors have been archived at the University of Waikato.

7.4.3. Discussion

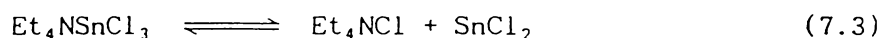
7.4.3.1. Discussion of the reactions of Et₄NSnCl₃ with R₃M'Co(CO)₄.

All of the reactions of Et₄NSnCl₃ with R₃M'Co(CO)₄ species described produced Et₄N⁺[(Cl₂[Co(CO)₄]Sn)₂Co(CO)₃]⁻ as the major product. Monitoring by infrared spectroscopy during the reactions showed the presence of [Co(CO)₄]⁻ at an early stage thus a possible pathway for the formation of this anion may be suggested. This is shown as scheme 7.1.



Scheme 7.1

Step 1 is supported by the suggestion that Et₄NSnCl₃ actually exists in equilibrium with Et₄NCl + SnCl₂ as shown in equation 7.3.



The presence of R₃M'Cl and [R₃M']⁻ species was not definitely observed, although the characteristic odour of R₃M'Cl species was commonly noted during work-up.

It appears that the R₃M'-Co bond is not strong enough to prevent dissociation when Et₄NSnCl₃ is also in solution. It is also apparent that the anion [(Cl₂[Co(CO)₄]Sn)₂Co(CO)₃]⁻ is a preferred product while formation of unsymmetrical anions from these systems is not favoured.

7.4.3.2. Discussion of the structure of $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ and a comparison with that of $\{[\text{HB}(\text{pz})_3]_2\text{Co}\}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

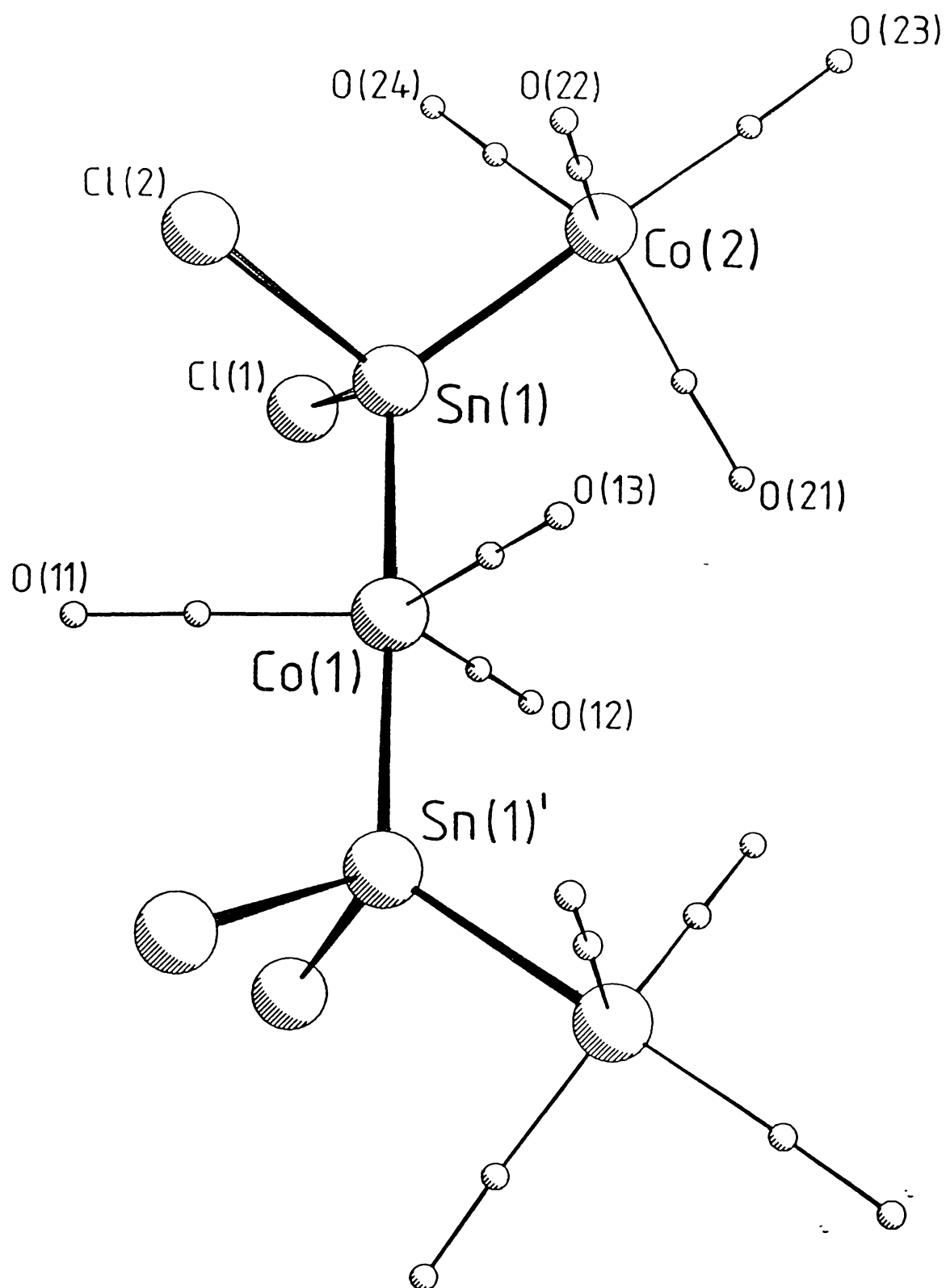
The unique component of the unit cell of $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ consists of half cation/half anion situated on a mirror plane. A view of the anion showing the labelling system used is shown in figure 7.4 and a stereo view is shown in figure 7.5.

The structure is that of two $\text{Cl}_2\text{SnCo}(\text{CO})_4$ units bonded *trans* to each other through a central $\text{Co}(\text{CO})_3$ group. The structure is identical to that found for the anion when $\{[\text{HB}(\text{pz})_3]_2\text{Co}\}^+$ is the corresponding cation [94]. Table 7.5 lists selected bond lengths and angles for the anion found in this work together with the corresponding values for that previously reported.

Table 7.5 Selected bond lengths and angles for $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ and $\{[\text{HB}(\text{pz})_3]_2\text{Co}\}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ [94].

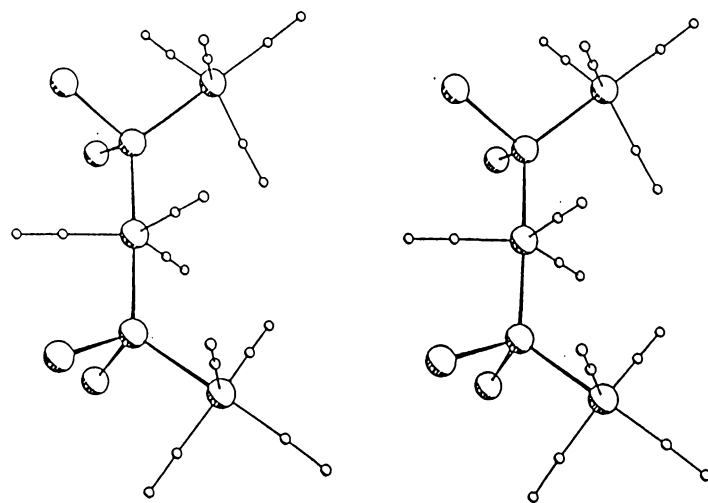
$\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$		$\{[\text{HB}(\text{pz})_3]_2\text{Co}\}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ [94]
Bond	Bond length (in Å)	
Sn_1-Co_1	2.474 (1)	2.468 (1)
Sn_1-Co_2	2.561 (1)	2.562 (1)
Sn_1-Cl_1	2.394 (2)	2.394 (2)
Sn_1-Cl_2	2.396 (2)	2.401 (2)
Bond angle	Bond Angles (in degrees)	
$\text{Co}_1-\text{Sn}_1-\text{Co}_2$	125.2 (1)	127.5 (1)
$\text{Co}_1-\text{Sn}_1-\text{Cl}_1$	107.7 (1)	109.5 (1)
$\text{Co}_2-\text{Sn}_1-\text{Cl}_1$	105.8 (1)	104.4 (1)
$\text{Sn}_1-\text{Co}_1-\text{C}_{11}$	89.1 (1)	91.8 (1)

The bond lengths and angles of the anions in different environments, although crystallographically different, are very close chemically and it is clear that the cation has very little effect on the structure of the anion. The slight differences observed are more likely to be a result of the intensity data for $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ being collected at -140°C while that for $\{[\text{HB}(\text{pz})_3]_2\text{Co}\}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ was collected at room temperature [94].



Perspective view of $[\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}_2\text{Co}(\text{CO})_3]^-$.

Figure 7.4.



Stereo view of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$

Figure 7.5.

The two tetraethylammonium cations in the crystal lattice are disordered giving C-N bond lengths ranging from 1.51(1)Å to 1.54(1)Å and C-C bond lengths ranging from 1.65(3)Å to 1.83(3)Å. The C-N-C bond angles are around 111° while the N-C-C bond angles are around 108°.

7.4.3.3. Crystal structure of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and a comparison with $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

As described in section 7.1, the original study of these anions used two main theories to rationalise the observed bond length trends within the series. While (d-d)_π bonding theory explained some of the features, the best rationalisation of all the observations was obtained by using isovalent rehybridisation theory. This suggested that σ-bonding effects predominated. It was hoped that determination of the X-ray crystal structure of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ would aid in the analysis of the bonding of these tin-cobalt carbonyl anions.

Crystals of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ suitable for study were grown from a hexane solution cooled to -15°C. A red rod-shaped crystal was mounted in Araldite on a glass fibre. Preliminary precession photography indicated monoclinic symmetry with systematic absences appropriate for $P2_1/c$. The crystal was then sent to the University of Canterbury where it was mounted on a Nicolet P3 Diffractometer for data collection. Table 7.6 gives the crystal data for $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.

Table 7.6 Crystal data for $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.

Formula: $\text{C}_8\text{Cl}_2\text{Co}_2\text{O}_8\text{Sn}$
Mr: 481.45
Space group: Monoclinic, $P2_1/c$

$a = 11.716 (4)$ $b = 11.486 (4)$ $c = 12.765 (8)\text{Å}$
 $\beta = 108.42^\circ (3)$

$U = 1630 (1) \text{Å}^3$
 $D_{\text{calc}} = 2.08 \text{ g/cm}^3$
 $Z = 4$

$F(000) = 1000$
 $T = 293 \text{ K}$

$D_{\text{obs}} = \text{Not measured}$

$\mu(\text{Mo-K}\alpha) = 36.82 \text{ cm}^{-1}$
 $\lambda(\text{Mo-K}\alpha) = 0.7107\text{Å}$

Crystal Dimensions = 0.6 mm x 0.5 mm x 0.5 mm

A total of 3858 unique reflections in the range $4^\circ < 2\theta < 55^\circ$ were collected with $0 < h < 16$, $0 < k < 15$, $-17 < l < 17$. Of these, the 2558 with $I > 2\sigma(I)$ were used in all calculations. The intensity data were corrected for Lorentz, polarisation and absorption effects. The transmission factors were $\max = 0.855$ and $\min = 0.771$.

Solution of the structure was achieved by direct methods. The heavy atoms of the unique molecule were found with ease while subsequent refinements and difference maps gave the positions of all of the carbonyl groups. Full matrix least squares refinement was carried out after omitting the twelve reflections with deviations greater than 4σ . These were assumed to result from a seed crystal on the surface of the crystal under study. At convergence $R = 0.045$, $R_w = 0.0373$ with $w = (\sigma^2 F + 0.0001 F^2)^{-1}$. At this point the largest parameter shift was 0.001. The highest peak of the final difference map, having $0.95 \text{ e}/\text{\AA}^3$, was adjacent to the tin atom.

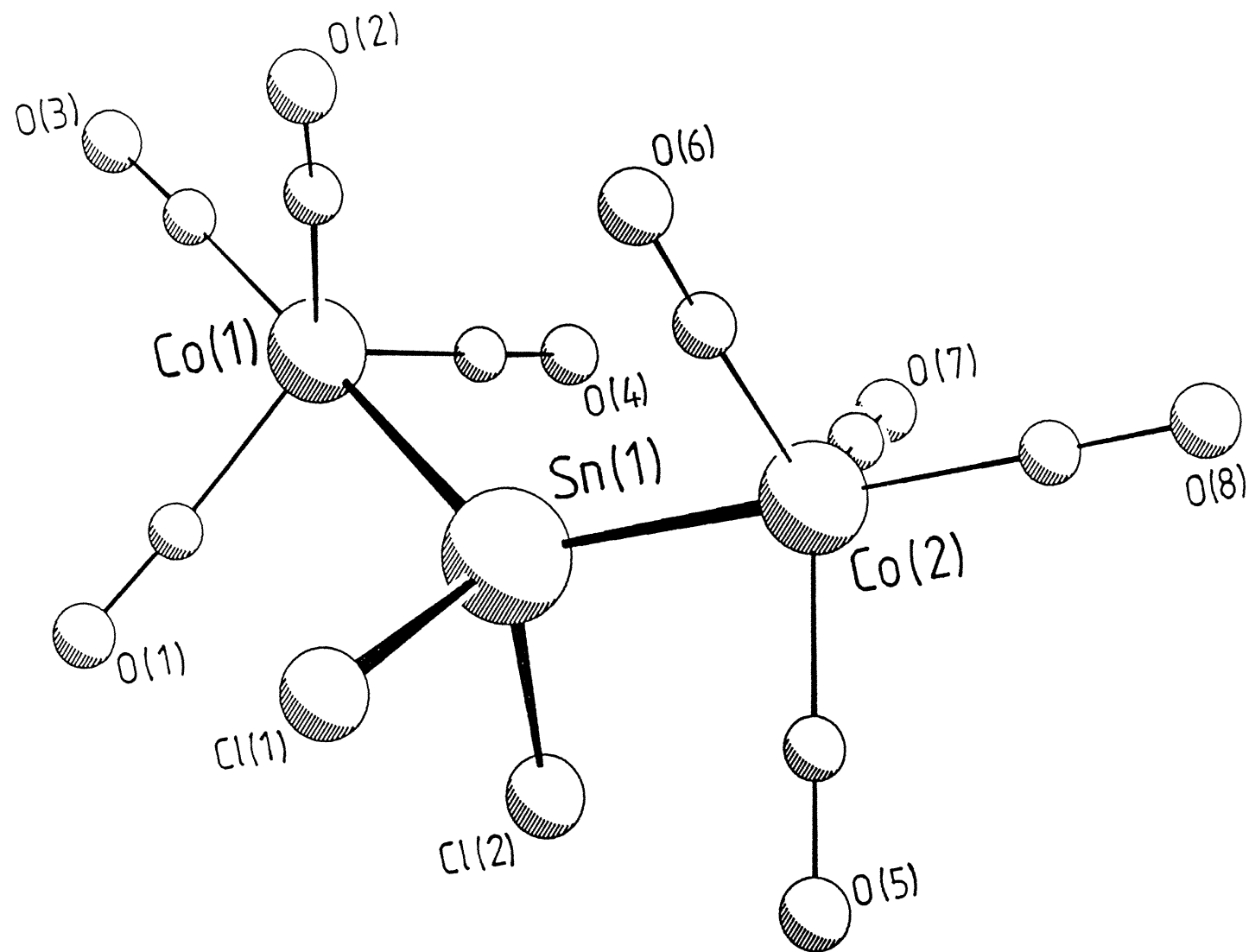
The final positional and thermal parameters and a full list of bond lengths and angles of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ are shown in Appendix 3. Structure factors have been archived by the University of Waikato.

A view of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ is shown in figure 7.6 which gives the labelling system used, while figure 7.7 shows a stereo view of the molecule.

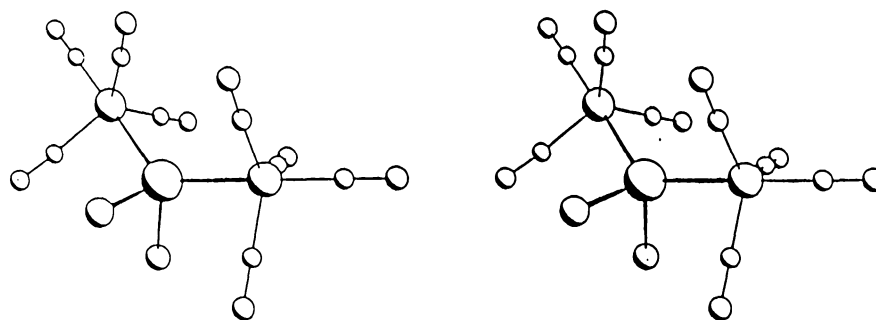
As expected, the tin is coordinated in a distorted tetrahedral arrangement to the two $\text{Co}(\text{CO})_4$ groups and the two chlorine atoms. The Co-Sn-Co bond angle ($129.3^\circ(1)$) is increased with respect to the ideal, while both the Co-Sn-Cl (average 106°) and Cl-Sn-Cl ($101.3^\circ(1)$) bond angles are decreased. These effects could simply be due to steric factors, however it is reasonable to suggest that isovalent rehybridisation may also be involved. As stated in section 7.1, this theory predicts a decrease in bond length when substituents are replaced by more electronegative groups [181]. It also predicts a decrease in the valence angle as the electronegativity and hence the p character in the bond increases [181]. This would then explain the comparatively small Cl-Sn-Cl bond angle of 101.3° since the p character in the orbitals involved would be concentrated towards the electronegative chlorine atoms.

In the molecule $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ the bond angles are again distorted from the ideal value but the effect is not as marked as for $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. For $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ the Co-Sn-Co bond angles are of an average 114° while the Cl-Sn-Co bond angle is 104° [183]. This would support the suggestion that

the differing electronegativities of the substituents are a factor in the distortion from the idealised tetrahedral situation, since only one electronegative chlorine atom results in a lesser distortion. It could be



Perspective view of $\text{Cl}_2\text{Sn}(\text{Co}(\text{CO})_4)_2 \cdot$
Figure 7.6.



Stereo view of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$
Figure 7.7.

envisaged that the third molecule of this series - $\text{Cl}_3\text{SnCo}(\text{CO})_4$ - would have Cl-Sn-Cl bond angles of less than 100° while the Cl-Sn-Co bond angles would be larger than 114° .

The two $\text{Co}(\text{CO})_4$ units of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ have the expected trigonal bipyramidal structure with the equatorial carbonyls bent towards the weaker π -acceptor (average Sn-Co- C_{eq} angle of 85.2°).

Table 7.7 shows selected bond lengths and angles of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ together with the corresponding values for $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

Table 7.7 Selected bond lengths and angles of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

Bond	$\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$
	Bond length (in Å)	
$\text{Sn}_1\text{-Co}_1^*$	2.533 (1)	2.474 (1)
$\text{Sn}_1\text{-Co}_2^*$	2.535 (1)	2.561 (1)
$\text{Sn}_1\text{-Cl}_1$	2.373 (2)	2.394 (2)
$\text{Sn}_1\text{-Cl}_2$	2.363 (2)	2.396 (2)
Bond angle	Bond angle (in degrees)	
$\text{Co}_1\text{-Sn}_1\text{-Co}_2$	129.30 (1)	125.2 (1)
$\text{Co}_1\text{-Sn}_1\text{-Cl}_1$	106.0 (1)	107.7 (1)
$\text{Co}_1\text{-Sn}_1\text{-Cl}_2$	106.0 (1)	105.8 (1)
$\text{Cl}_1\text{-Sn}_1\text{-Cl}_2$	101.3 (1)	97.1 (1)
$\text{Co}_2\text{-Sn}_1\text{-Cl}_1$	105.0 (1)	104.4 (1)
$\text{Co}_2\text{-Sn}_1\text{-Cl}_2$	106.0 (1)	102.3 (1)
$\text{Sn}_1\text{-Co}_1\text{-C}_{\text{eq}}$	85.2 (ave)	89.9 (ave)

* For $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$, Co_1 is the internal cobalt of the $\text{Co}(\text{CO})_3$ unit while Co_2 is the external cobalt.

Figure 7.8 depicts the two molecules and shows the relevant bond lengths and angles to aid in the following discussion.

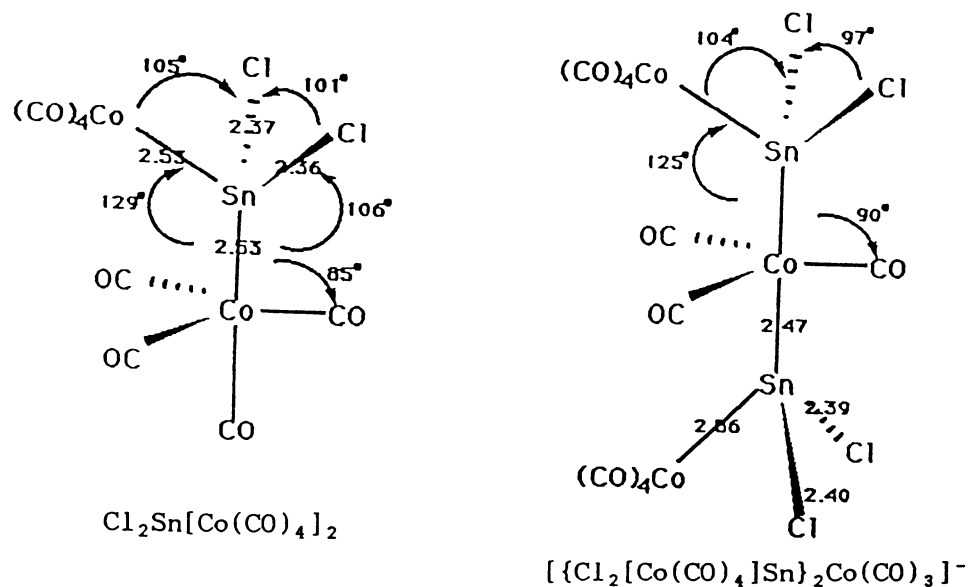


Figure 7.8

Replacement of the axial carbonyl group by $[\text{Cl}_2\text{SnCo}(\text{CO})_4]^-$ results in a marked contraction of $\text{Co}_1\text{-Sn}_1$ by 0.059 (1)Å and a lengthening of the external Sn-Co_2 bond by 0.026 (1)Å. A corresponding lengthening of the two Sn-Cl bonds (ave. 0.027 (2)Å) is also observed.

Similarly, changes in the bond angles are found. The $\text{Co}_1\text{-Sn}_1\text{-R}$ angles increase by an average 1.9° (1) while the $\text{R}_1\text{-Sn-R}_2$ bond angles decrease by an average 2.8° (1).

These observations correlate well with those noted when an axial carbonyl of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ is replaced by a $\{\text{ClSn}[\text{Co}(\text{CO})_4]_2\}^-$ unit giving $[\{\text{Cl}[\text{Co}(\text{CO})_4]_2\text{Sn})_2\text{Co}(\text{CO})_3\}]^-$ [94]. These effects have been alternatively rationalised [94] using (d-d) π bonding theory or Bent's rules for atom isovalent rehybridisation caused by substituent changes [181]. As stated earlier this latter theory is concerned with σ -bonding effects and basically suggests that increasing the electronegativity of attached groups alters the amount of s and p character within the various bonds causing bond length and valence angle changes. Thus the main argument in the case of these anions is whether the observed bond length and angle changes results from π - or σ -bonding effects.

As discussed in the introduction, it was found that (d-d) π bonding theory only partially explained the observed effects, while isovalent rehybridisation gave a much more complete rationalisation. It was thus

concluded that the changes resulting from replacement of an axial carbonyl by an $[R_3Sn]^-$ group arose predominantly through σ -bonding effects [94]. The findings of this study confirm this proposal since (d-d) π bonding, again, does not predict such a marked lengthening of the internal Sn-Co bond, nor does it explain the bond angle changes. In contrast, isovalent rehybridisation theory suggests that replacement of CO by a stronger σ donor and weaker π acceptor, $[R_3Sn]^-$, increases the electron density on Co and effectively increases its electropositivity. This increases the s character in the Sn-Co bond, thus shortening it. The s character in the R-Sn bonds will correspondingly decrease, thus they are lengthened. Isovalent rehybridisation also predicts a decrease in the valence angle as the p character in the bond increases [181]. This would then explain the observed decrease in the R-Sn-R bond angles as CO is replaced by $[R_3Sn]^-$.

As stated in section 7.1, EMO calculations have recently been carried out for a series of compounds of general formula *trans* - $LCo(CO)_3SiCl_3$ (L = NH_3 , CO, CN^- , H^- , PCl_3 , $SiCl_3$, SiF_3 , SiH_3) both with and without d orbitals on Si [179]. A small amount of (d-d) π bonding was suggested, but not enough to account for bond length changes. The hybridisation at Co, however, was found to be very dependent on the energy of the σ -donating orbitals of the incoming ligand, L. This would strongly indicate that changes in bond lengths of this type of compound are predominantly due to σ -bonding effects [179].

These findings thus support the suggestion that the bond length and angle changes observed on replacement of an axial carbonyl in $Cl_xSn[Co(CO)_4]_{4-x}$ by $\{Cl_ySn[Co(CO)_4]_{3-y}\}^-$ ($x, y = 0-3$) to yield an anion of the form $[\{Cl_x[Co(CO)_4]_{3-x}Sn\}Co(CO)_3\{Sn[Co(CO)_4]_{3-y}Cl_y\}]^-$ result mainly through σ -bonding factors. It is probable that π bonding is involved in this anion since the appropriate orbitals are likely to be orientated in the correct direction, however, with the information available at present, it seems that the major cause of bond length changes are σ -bonding effects.

7.4.3.4. Preliminary study of the crystal parameters of $Cl_3SnCo(CO)_4$.

It was originally hoped to determine the X-ray crystal structure of both $Cl_2Sn[Co(CO)_4]_2$ and $Cl_3SnCo(CO)_4$. The crystal structure of $ClSn[Co(CO)_4]_3$ has previously been reported [183] and determination of the remaining two chlorotin-cobalt carbonyl compounds of this series would be expected to give useful information to aid analysis of the bonding in the series of chlorotin-cobalt carbonyl anions. Unfortunately, it proved impossible to grow a crystal of $Cl_3SnCo(CO)_4$ of sufficient quality to allow

data collection. However, preliminary precession photography was carried out on a slightly twinned needle crystal grown by sublimation under vacuum at room temperature. The crystal parameters are listed in table 7.8.

Table 7.8 Preliminary crystal data for $\text{Cl}_3\text{SnCo}(\text{CO})_4$.

Formula: $\text{C}_4\text{Cl}_3\text{CoO}_4\text{Sn}$
 Mr: 395.97
 Space group: Rhombohedral, $R\bar{3}$.
 $a = 9.93$ $c = 9.30 \text{ \AA}$
 $U = 794 \text{ \AA}^3$
 $D_{\text{calc}} = 2.48 \text{ g/cm}^3$ $D_{\text{obs}} = \text{Not measured}$
 $Z = 3$

7.5. Spectroscopic data for some tin-cobalt carbonyl species.

7.5.1. Raman Spectra of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

7.5.1.1. Raman spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.

The Raman spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ was recorded from a sample of the powdered solid. For convenience, the discussion of the spectrum is divided in two where the carbonyl region is discussed first and then the lower frequency section is compared with that reported for $\text{Cl}_3\text{SnCo}(\text{CO})_4$ [185].

The carbonyl region vibrational bands of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ are listed in Table 7.9.

Table 7.9 Carbonyl region vibrational data for $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. (cm^{-1}) .

Infrared (a) [160]	Raman (b)
2114 w	2120 m
2097 vs	2066 vs
2056 s	2056 s
2052 m	
2040 vs	2043 m
2023 m-s	2028 w
2016 m	2010 m

(a) Recorded from cyclohexane solution (b) Recorded from solid.

For $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ having C_{2v} symmetry the carbonyl stretches span the representation $3\text{A}_1 + \text{A}_2 + 3\text{B}_1 + \text{B}_2$ where all eight modes are Raman active and all but A_2 are infrared active.

The carbonyl region infrared spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ was previously recorded and analysed by Graham [160]. The seven predicted infrared active modes were observed but only the bands at 2114 cm^{-1} and 2097 cm^{-1} were definitely assigned - as an A_1 and a B_1 mode respectively - where the individual vibrations are as shown in figure 7.9.

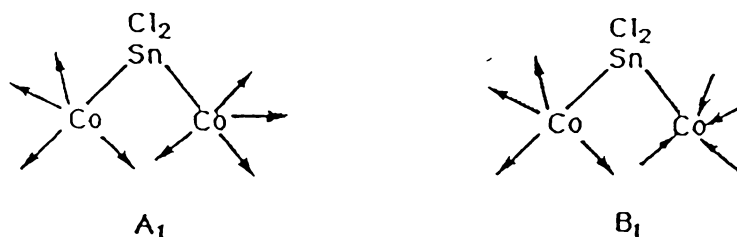


Figure 7.9 [160]

The remainder of the bands were assigned collectively to $2\text{A}_1 + 2\text{B}_1 + \text{B}_2$ modes.

With the additional Raman data, a total of eight different frequencies are observed although two bands appear to be of too low intensity to be seen in the Raman spectrum.

As stated above, the two high wavenumber bands in the infrared spectrum were assigned to an A_1 and a B_1 mode. The weak 2114 cm^{-1} vibration is also observed as a medium intensity band at 2120 cm^{-1} in the Raman spectrum. The very strong infrared band at 2097 cm^{-1} , however, does not have a counterpart in the Raman, thus this B_1 mode must be of too low an intensity to be observed here.

The band found at 2066 cm^{-1} in the Raman spectrum is presumably the infrared inactive A_2 mode. However, it is unusual for this type of vibration to give rise to such an intense band. No explanation for this observation has been found as yet.

The remaining bands have been tentatively assigned on the basis of their intensities, where those of higher intensity in the Raman spectrum are anticipated to be symmetric vibrations.

Table 7.10 repeats the carbonyl vibrational spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ showing the assignments which have been made during this discussion.

Table 7.10 Carbonyl vibrational spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ with tentative assignments.

Wavenumber (cm^{-1})	Activity	Assignment
2114	IR, R	A_1
2097	IR	B_1
2066	R	A_2
2056	IR, R	A_1
2052	IR	B_1
2040	IR, R	B_1
2023	IR, R	B_2
2010	IR, R	A_1

Table 7.11 lists the observed bands in the lower frequency region of the Raman spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, together with the corresponding vibrational bands reported for $\text{Cl}_3\text{SnCo}(\text{CO})_4$.

Table 7.11 Lower frequency vibrational data for $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $\text{Cl}_3\text{SnCo}(\text{CO})_4$ with possible assignments. (cm^{-1}).

$\text{Cl}_3\text{SnCo}(\text{CO})_4$ [185] (a)	Assignment	$\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ (b)
545	$\delta\text{Co-C-O}$ (ax)	545 w
490	$\nu\text{Co-C} + \delta\text{Co-C-O}$	
463	$\nu\text{Co-C}$ (ax)	458 w
449 ^(c)	$\delta\text{Co-C-O}$	442 w
405	$\nu\text{Co-C}$ (eq)	412 m-s
365		365 w
360	$\nu\text{Sn-Cl}$	335 w-m 322 w
204	$\nu\text{Co-Sn}$	215 m 185 vvs
125	$\delta\text{SnCl}_x + \delta\text{CO-Co-CO}$	
107	$\delta\text{SnCl}_x + \delta\text{CO-Co-CO}$	
92 ^(c)	$\delta\text{CO-Co-CO}$	90 s

(a) Only the bands at 365 and 204 cm^{-1} were observed in the Raman spectrum, the remainder are infrared vibrations [185]; recorded either from benzene solution or as a nujol mull.

(b) Recorded from the solid power. (c) Calculated position.

The assignments for $\text{Cl}_3\text{SnCo}(\text{CO})_4$ were supported [185] by force constant calculations.

In the region above 400 cm^{-1} the vibrations of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ are reasonably described by comparison with $\text{Cl}_3\text{SnCo}(\text{CO})_4$.

For Sn-Cl stretching, the frequencies observed for $\text{Cl}_3\text{SnCo}(\text{CO})_4$ are very close and give a mean value of approximately 360 cm^{-1} (taking the 360 cm^{-1} band to result from the E mode). Three bands are observed in this region for $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, only two of which can result from $\nu\text{Sn-Cl}$ of this molecule. If the weak low energy one (at 322 cm^{-1}) is neglected, the average frequency becomes 350 cm^{-1} indicating somewhat weaker Sn-Cl bonds compared to $\text{Cl}_3\text{SnCo}(\text{CO})_4$. This is consistent with the replacement of an electronegative Cl substituent by a $\text{Co}(\text{CO})_4$ group. The band at 322 cm^{-1} is either adventitious or, perhaps, results from a rather large solid state splitting.

In contrast, the $\nu\text{Co-Sn}$ modes of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ average to 200 cm^{-1} , only very slightly lower than the 204 cm^{-1} value found for $\text{Cl}_3\text{SnCo}(\text{CO})_4$.

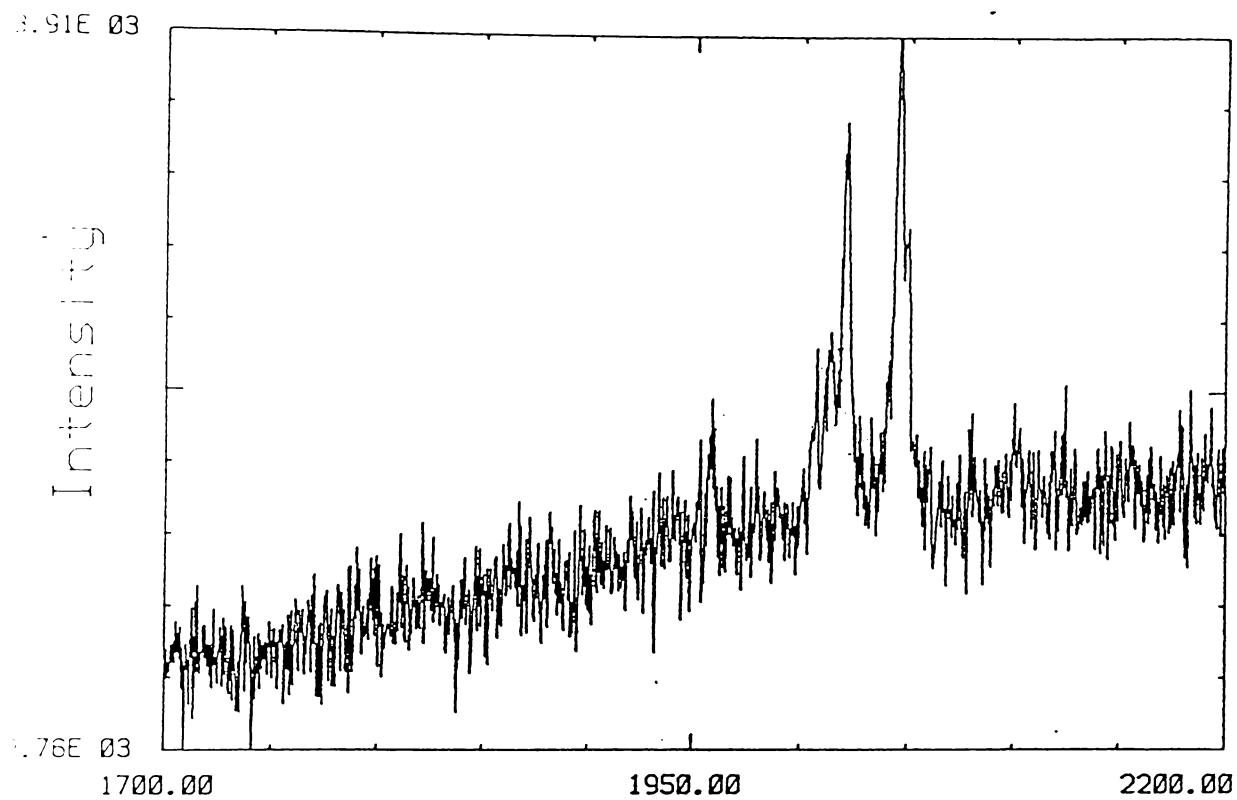
It would be expected that the symmetric Co-Sn stretch would be the higher frequency of the two modes, however it would also be expected that the symmetric mode would be of the highest intensity in the Raman, and yet it is the band at 185 cm^{-1} which is very strong while the 215 cm^{-1} band is of only medium intensity. Cases where the symmetric stretch is found at lower energy than the antisymmetric stretch are known. For example, the symmetric stretch of methyl groups is observed at $2870 \pm 10\text{ cm}^{-1}$ while the asymmetric stretch arises near $2960 \pm 10\text{ cm}^{-1}$ [171].

It is interesting that the Sn-Co stretch of $\text{Cl}_3\text{SnCo}(\text{CO})_4$, and apparently of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, shows no mixing with other modes since the $\text{M}'\text{-Co}$ stretch of both $\text{Cl}_3\text{GeCo}(\text{CO})_4$ and $\text{Cl}_3\text{SiCo}(\text{CO})_4$ shows mixing with both $\nu\text{M}'\text{-Cl}$ and $\delta\text{M}'\text{Cl}_3$ [185].

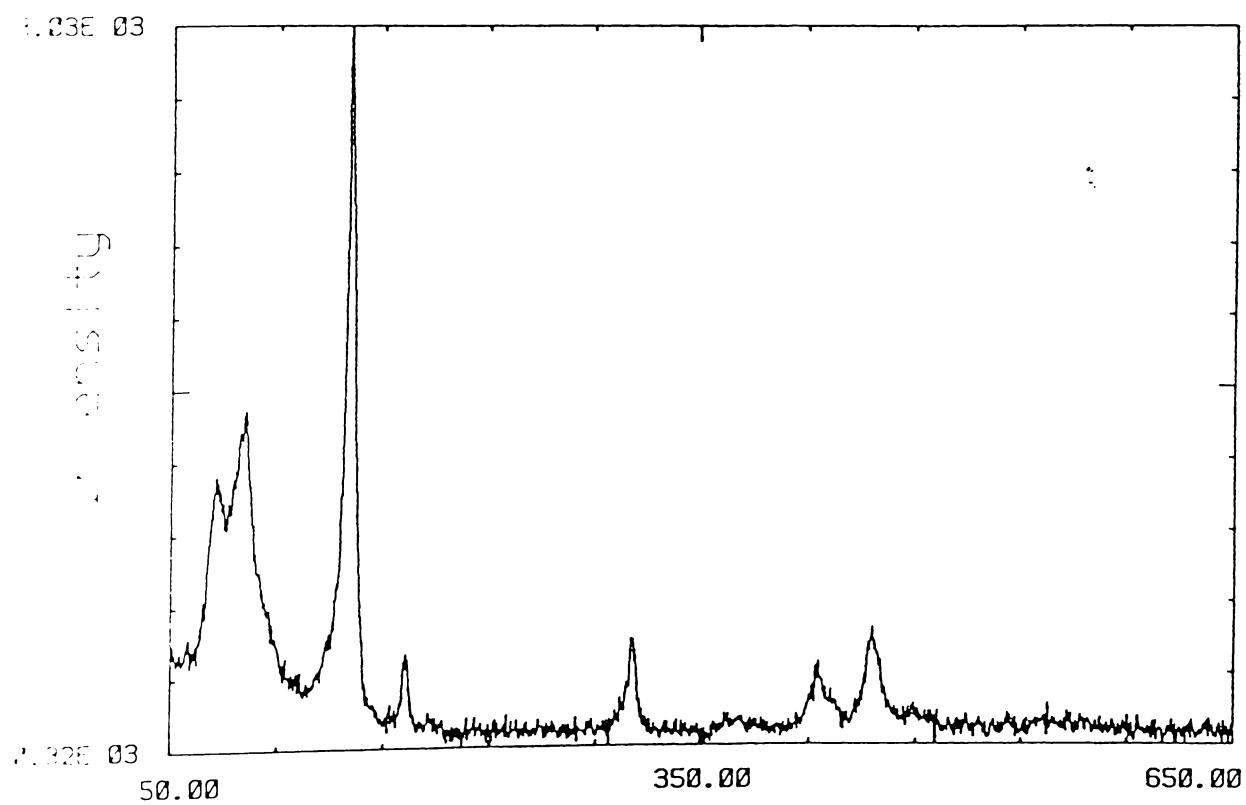
7.5.1.2. Raman spectrum of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$.

The Raman spectra of $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ shown in figure 7.10 (a) and (b) were recorded from a crystalline sample. For convenience, the following discussion is again separated into the carbonyl region and the lower frequency modes.

Table 7.12 lists the carbonyl region Raman spectrum of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$. The carbonyl region infrared data of a solid sample of the anion was also recorded at this time and is included in the table.



(a) Between 1700 and 2200 cm^{-1}



(b) Between 50 and 650 cm^{-1}

Table 7.12 Carbonyl region vibrational spectrum of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ (cm^{-1}).

Infrared (a)	Raman (b)
2109 m-s	
2099 s	
2049 sh	2050 m
	2045 vs
2032 s	
2021 sh	2021 s
2011 vs	2014 w-m
	2007 w-m
1997 sh	
1953 s	1959 w
1933 s	

(a) Recorded as a nujol mull.

(b) Recorded from crystals.

As stated in the discussion of the carbonyl region infrared spectrum of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ recorded from solution (section 7.4.2.1), this anion ideally has C_{2v} symmetry leading to ten infrared active carbonyl vibrations ($5A_1 + 3B_1 + 2B_2$). In the solution spectrum only six of these modes were observed, however from the solid state infrared spectrum three more bands are resolved. Eleven Raman active modes ($5A_1 + A_2 + 3B_1 + 2B_2$) are predicted for this anion with only six being observed, however, together with the infrared data, the expected total of eleven carbonyl vibrations are found.

The two high wavenumber bands observed in the infrared spectrum at 2109 and 2099 cm^{-1} are assigned to an A_1 and a B_1 mode respectively. These are commonly observed for molecules containing terminal $\text{Co}(\text{CO})_4$ units (see section 1.4.1.1). These bands have no counterparts in the Raman spectrum which is surprising since A_1 modes are usually observed here. No explanation has been found for this feature.

Two bands (at 2045 and 2007 cm^{-1}) are found in the Raman which have no counterparts in the infrared spectrum. One of these presumably results from the infrared inactive A_2 mode. This is tentatively assigned to the band at 2045 cm^{-1} since this mode is commonly of moderate to high energy, however the very strong intensity of this band is surprising since an A_2 mode usually gives rise to low intensity bands. The second of these two bands, at 2007 cm^{-1} , is assigned to an A_1 mode which are often weaker in the infrared than in the Raman spectrum.

The remainder of the bands have been tentatively assigned on the basis of their intensity since symmetric modes are expected to be of higher intensity in the Raman than in the infrared spectrum. Although the expected number of frequencies is found, the listed bands are not necessarily all fundamentals - for example, the shoulder at 1997 cm^{-1} infrared spectrum may be a ^{13}CO mode. For this large species, any assignment can only be tentative.

Table 7.13 Carbonyl region vibrational data for $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ with tentative assignments.

Wavenumber (cm^{-1})	Activity	Assignment
2109	IR	A_1
2099	IR	B_1
2049	IR, R	A_1
2045	R	A_2
2032	IR	B_2
2021	IR, R	A_1
2011	IR, R	B_1
2007	R	A_1
1997	IR	B_1
1953	IR, R	A_1
1933	IR	B_2

The lower frequency region of the Raman spectrum of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ is listed in table 7.14 together with assignments made on the basis of a comparison with $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.

Table 7.14 Lower frequency Raman spectra of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ and $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ with tentative assignments. (cm^{-1}).

$\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	Assignment	$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$
442 w	$\delta\text{Co-C-O}$	446 w-m
412 m	$\nu\text{Co-C}$	415 w-m
365 w	$\nu\text{Sn-Cl}$	365 w
335 w-m		
322 w*		311 w-m
215 w	$\nu\text{Sn-Co}$	182 w
185 vvs		151 vvs
90 s	$\delta\text{CO-Co-CO}$	91 m-s
	$\delta\text{Co-Sn-Cl}$	75 m

* Possibly from an impurity.
Both recorded as solids.

The cobalt carbonyl stretching and bending modes correspond very well for these two molecules and are thus assigned unambiguously.

The Sn-Cl stretching vibrations assigned to bands at 365 and 335 cm^{-1} for $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and to bands at 365 and 311 cm^{-1} for the anion are interesting since the bands at 365 cm^{-1} correspond exactly while the second one has shifted to lower frequency by 24 cm^{-1} on going from $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ to $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$. It was deduced through a comparison of the crystal structures of these molecules (section 7.4.3.3) that replacement of an axial carbonyl on $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ by $\{\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]\}^-$ results in lengthening of all external bonds to tin. The weaker Sn-Cl bonds would give a lower average stretching frequency, as observed. This discussion assumes that the two SnCl_2 groups in the anion do not couple.

Since there are four Sn-Co bonds in the anion, four Sn-Co stretching modes could be expected. Only two, however, are observed. The very high intensity mode at 151 cm^{-1} may result from symmetric stretching of the entire molecule through the Sn-Co-Sn backbone. The second mode, giving rise to the weak band at 182 cm^{-1} , is likely to result from stretches of the terminal Sn-Co bonds. It is interesting that these bands are at a considerably lower frequency than $\nu\text{Sn-Co}$ of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and it is possible that some mixing of modes has occurred for the anion.

7.5.2. ^{119}Sn NMR Spectroscopy of Some Tin-Cobalt Carbonyl Species.

When this work was first undertaken it was hoped that an unsymmetrical tin-cobalt carbonyl anion of the form $\{[\text{Cl}_3\text{Sn}]\text{Co}(\text{CO})_3[\text{SnR}_3]\}^-$ could be obtained. ^{119}Sn NMR spectroscopy could then usefully be employed to gain insight into the hybridisation of the two tin atoms through the coupling constants. This has not been possible since an unsymmetrical anion was not obtained.

It was felt, however, that ^{119}Sn NMR spectroscopy would still be a useful characterisation technique for the product of the previous reactions, $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$, and it was of interest to determine how far the tin resonance of this species was shifted from that of the parent compound, $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. As the ^{119}Sn NMR spectra of the latter species has never been reported this was also recorded, together with that of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ and $\text{Cl}_3\text{SnCo}(\text{CO})_4$. The spectra obtained are reported in table 7.15.

Table 7.15 ^{119}Sn NMR signals recorded for some tin-cobalt carbonyl species. (See section A1.4.4).

Compound	$\delta^{119}\text{Sn}$ (ppm)	$\Delta\nu_{1/2}$ (ppm)	No. of scans	Approximate concentration
$\text{ClSn}[\text{Co}(\text{CO})_4]_3$	-5.86	1	64430	0.02 M
$\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	212.7	1	8722	0.1 M
$\text{Cl}_3\text{SnCo}(\text{CO})_4$	-30.8	1	50000	0.02 M
$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$	-53.1	1	10028	0.1 M

All recorded from CH_2Cl_2 solution.

The first noticeable feature of these results is the lack of a regular trend in the positions of the peaks resulting from the neutral species $\text{ClSn}[\text{Co}(\text{CO})_4]_3$, $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $\text{Cl}_3\text{SnCo}(\text{CO})_4$. It is, of course, possible that errors were made in recording the spectra however the samples were definitely pure and all the conditions have been checked to ensure these were correct. It should be noted, however, that the spectrum of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ showed the ^{119}Sn signal to be only 2% times the intensity of the background noise after over 60,000 scans. Unfortunately, time limitations did not permit a repeat of these experiments but it is to be hoped that these results are confirmed at a later date.

If, for the moment, these spectra are taken at face value then some features other than straightforward inductive effects caused by substituent changes must be involved.

Table 7.16 lists the ^{119}Sn NMR data recorded for the products of sequential replacement of Me on Me_4Sn by $\text{Co}(\text{CO})_4$ units or by Cl atoms.

Table 7.16 ^{119}Sn NMR data for some species related by substituent changes.

Compound	^{119}Sn (ppm)	Solvent	Reference
Me_4Sn	0	-	-
$\text{Me}_3\text{SnCo}(\text{CO})_4$	+ 151	C_6H_6	186
$\text{Me}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	+ 293	C_6H_6	186.
$\text{MeSn}[\text{Co}(\text{CO})_4]_3$	+ 483	C_6H_6	186
Me_3SnCl	+ 164	3-20% C_6H_6	187
Me_2SnCl_2	+ 137	30% CH_2Cl_2	188
MeSnCl_3	+ 21	3-20% C_6H_6	187
SnCl_4	- 150	CS_2 at -30°C	189

The ^{119}Sn signals for the series of compounds $\text{Me}_n\text{Sn}[\text{Co}(\text{CO})_4]_{4-n}$ ($n = 1-4$) show a consistent shift to higher δ on replacement of a methyl by a more electropositive $\text{Co}(\text{CO})_4$ unit. However, it is noticeable that this shift is by no means regular, ranging from 142-190 ppm.

In the case of the series $\text{Me}_n\text{SnCl}_{4-n}$ ($n = 0-4$) the shifts also show a change of direction. Here the first replacement of Me by Cl gives a shift of 164 ppm to higher frequency while all further replacements give much smaller shifts to lower frequency.

A recent review of ^{119}Sn NMR spectroscopy discusses the problems of substituent effects [190]. This states that the shielding of the ^{119}Sn nucleus is significantly affected by the number of the various substituents present, and by their electronic and steric properties. The qualitative application of the theory of nuclear screening predicts major changes when the tetrahedral geometry is distorted and the symmetry is lowered [191] (see figure 7.11). It is also found that there is no obvious general relationship between δ ^{119}Sn and other empirical parameters. Instead it appears that a number of possibly counteracting influences should be considered, that is (i) electronegativity, (ii) excitation energies, and (iii) neighbour contributions. In particular, it seems that the evaluation of neighbour contributions constitutes a serious problem for the interpretation of tin chemical shifts [190]. Figure 7.11 shows the dependence of nuclear screening of ^{119}Sn on the number (n) of group X and

7.6. Reactions of $\text{Et}_4\text{NSnCl}_3$ with trihalogenocobalt tetracarbonyl substituted group 14 compounds.

Since the results of the reactions of $[\text{SnCl}_3]^-$ with $\text{R}_3\text{M}'\text{Co}(\text{CO})_4$ species showed that this was not a suitable method for the synthesis of unsymmetrical $\{\text{R}_3\text{M}'\text{Co}(\text{CO})_3\text{M}'\text{R}_3\}^-$ anions, it was hoped that the use of halogenated starting materials would prove more satisfactory. The following experiments were thus carried out.

7.6.1. Experimental Details and Results.

7.6.1.1. Reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Br}_3\text{SnCo}(\text{CO})_4$.

$\text{Et}_4\text{NSnCl}_3$ (0.213 g; 0.6 mmol) in CH_2Cl_2 (10 ml) was added to a stirred solution of $\text{Br}_3\text{SnCo}(\text{CO})_4$ (0.319 g; 0.6 mmol) in CH_2Cl_2 (10 ml). On mixing, the solution changed from a light orange to a deep orange-brown colour. Change in the carbonyl region infrared spectrum was immediately apparent with complete disappearance of the bands arising from $\text{Br}_3\text{SnCo}(\text{CO})_4$ (2116 (m-s), 2063 (m), 2043 (vs) [150]) in 30 minutes. No $[\text{Co}(\text{CO})_4]^-$ was observed. Solvent was removed and the mixture extracted with hexane which yielded a trace of unreacted $\text{Br}_3\text{SnCo}(\text{CO})_4$. All of the products were soluble in Et_2O . Characterisation of these species will be discussed in section 7.6.2.

7.6.1.2. Reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Cl}_3\text{GeCo}(\text{CO})_4$.

$\text{Et}_4\text{NSnCl}_3$ (0.081 g; 0.25 mmol) in CH_2Cl_2 (10 ml) was added to a stirred solution of $\text{Cl}_3\text{GeCo}(\text{CO})_4$ (0.089 g; 0.25 mmol) in CH_2Cl_2 (10 ml). On mixing, the colour of the solution changed from yellow to lime-green. Over the course of the reaction this changed back to a yellow colour again. Little change in the carbonyl region infrared spectrum was apparent at first, however, after about one hour of reaction a peak became noticeable at approximately 2000 cm^{-1} . This gradually became stronger in intensity. No $[\text{Co}(\text{CO})_4]^-$ was observed. After 3 hours the reaction was worked up although it appeared that the starting material had not completely reacted. This was confirmed when $\text{Cl}_3\text{GeCo}(\text{CO})_4$ (0.056 g; 0.16 mmol) was recovered from the hexane extracts. All soluble products were dissolved in Et_2O giving a bright yellow solution. A carbonyl region infrared spectrum in CH_2Cl_2 was recorded and is listed in table 7.17. Also present was a white insoluble

powder which showed no carbonyl bands in an infrared spectrum recorded as a nujol mull. This species has not been identified.

Table 7.17 Carbonyl region infrared data for the soluble products of reaction between $\text{Et}_4\text{NSnCl}_3$ and $\text{Cl}_3\text{GeCo(CO)}_4$ (cm^{-1}).

2120 m
2050 s
1996 vs, br

Recorded in CH_2Cl_2 .

7.6.1.3. Reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Cl}_3\text{SiCo(CO)}_4$.

$\text{Et}_4\text{NSnCl}_3$ (0.511 g; 1.43 mmol) in CH_2Cl_2 (10 ml) was added to a stirred solution of $\text{Cl}_3\text{SiCo(CO)}_4$ (0.439 g; 1.44 mmol) in CH_2Cl_2 (10 ml). On mixing the solution changed from a pale yellow colour to a darker orange. A light coloured solid was precipitated at this stage. Monitoring by carbonyl region infrared spectroscopy showed immediate production of $[\text{Co(CO)}_4]^-$ on addition of $\text{Et}_4\text{NSnCl}_3$, however, after 20 minutes this band had completely disappeared. At this stage, although the bands resulting from $\text{Cl}_3\text{SiCo(CO)}_4$ (2120 vs, 2065 vs, 2038 vvs, 2000 m [180]) did not appear to have changed in intensity, two new peaks could be seen at 2015 cm^{-1} and 1970 cm^{-1} . After ca. 16 hours the reaction mixture was worked up. No species were soluble in hexane. All soluble products were dissolved in Et_2O and a carbonyl region infrared spectrum of these species in CH_2Cl_2 was recorded. This is listed in table 7.18 and showed a mixture of the anion $[\{\text{Cl}_2[\text{Co(CO)}_4]\text{Sn}\}_2\text{Co(CO)}_3]^-$ and a second species. Also present was an insoluble white powder which showed no carbonyl bands in an infrared spectrum recorded as a nujol mull. This species has not been identified.

Table 7.18 Carbonyl region infrared data for the soluble products of reaction between $\text{Et}_4\text{NSnCl}_3$ and $\text{Cl}_3\text{SiCo(CO)}_4$ (cm^{-1}).

2116 w	
2009 s	
2088 s	$[\{\text{Cl}_2[\text{Co(CO)}_4]\text{Sn}\}_2\text{Co(CO)}_3]^-$
2062 w, sh	
2035 s	$[\{\text{Cl}_2[\text{Co(CO)}_4]\text{Sn}\}_2\text{Co(CO)}_3]^-$
2013 vs, sh	
2010 vs, br	$[\{\text{Cl}_2[\text{Co(CO)}_4]\text{Sn}\}_2\text{Co(CO)}_3]^-$
1991 w, sh	
1970 m, br	$[\{\text{Cl}_2[\text{Co(CO)}_4]\text{Sn}\}_2\text{Co(CO)}_3]^-$

Recorded in CH_2Cl_2 .

Approximately two months after work-up dark-orange crystals were observed in the solution stored at -30°C . A preliminary study of the crystal structure of one of these was carried out which gave identical cell parameters to those obtained for $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$. A carbonyl region infrared spectrum of the solution was then recorded which showed only the presence of this anion.

7.6.2. Properties and Characterisation of the Products Obtained From Reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Br}_3\text{SnCo}(\text{CO})_4$

7.6.2.1. Handling.

The products of this reaction have very similar handling characteristics to the anion $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$. The bright orange solid is moderately air stable, however, in solution the presence of even small quantities of oxygen results in immediate decomposition leaving a green material.

7.6.2.2. Carbonyl stretches in the infrared spectrum.

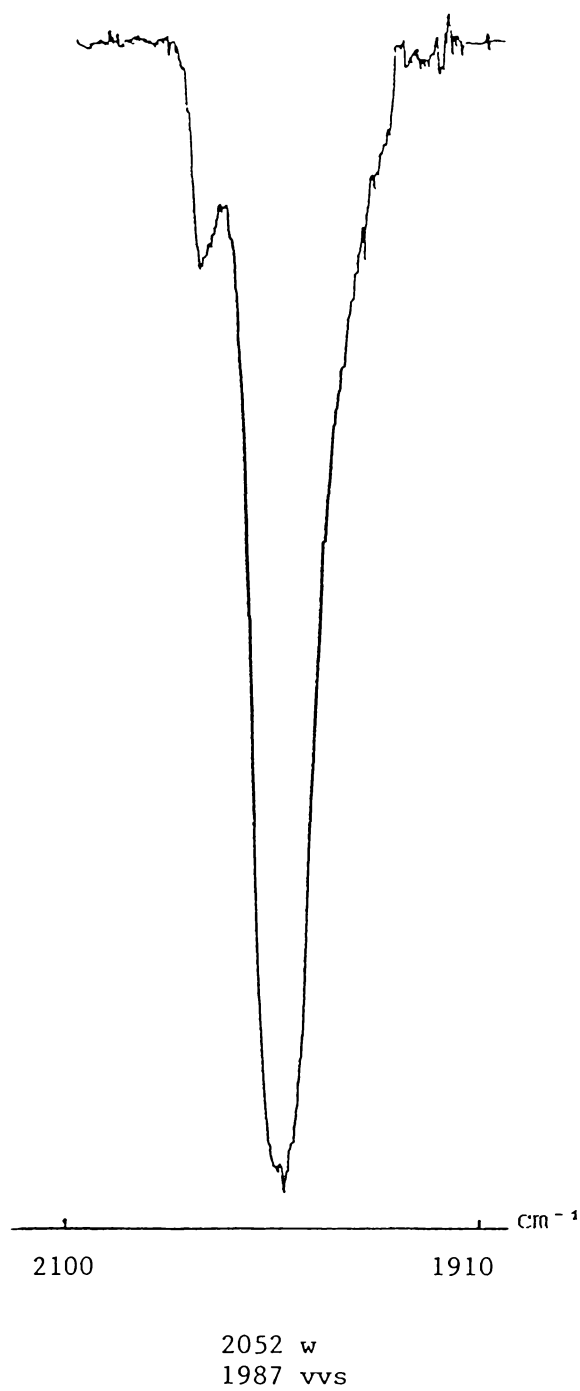
The infrared active carbonyl bands of these products are shown in figure 7.12 and are also listed in table 7.19 together with those reported for $\text{Et}_4\text{N}^+[(\text{Cl}_3\text{Sn})_2\text{Co}(\text{CO})_3]^-$ [94].

Table 7.19 Carbonyl region infrared data for the products of reaction between $[\text{SnCl}_3]^-$ and $\text{Br}_3\text{SnCo}(\text{CO})_4$ together with that reported for $[\{\text{Cl}_3\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ [94] (cm^{-1}).

From $[\text{SnCl}_3]^- + \text{Br}_3\text{SnCo}(\text{CO})_4$	$\{\text{Cl}_3\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$
2052 w	
1987 vvs	1991 vs

Both recorded in CH_2Cl_2 .

These spectra are very similar and the shift to lower frequency by 4 cm^{-1} observed for the product spectrum is consistent with replacement of chlorine atoms by bromine.



7.6.2.3. Electron probe analysis.

The atomic percentage values shown in table 7.20 were obtained by electron probe analysis. This was performed on a sample of crystals obtained from an Et_2O solution of the product mixture.

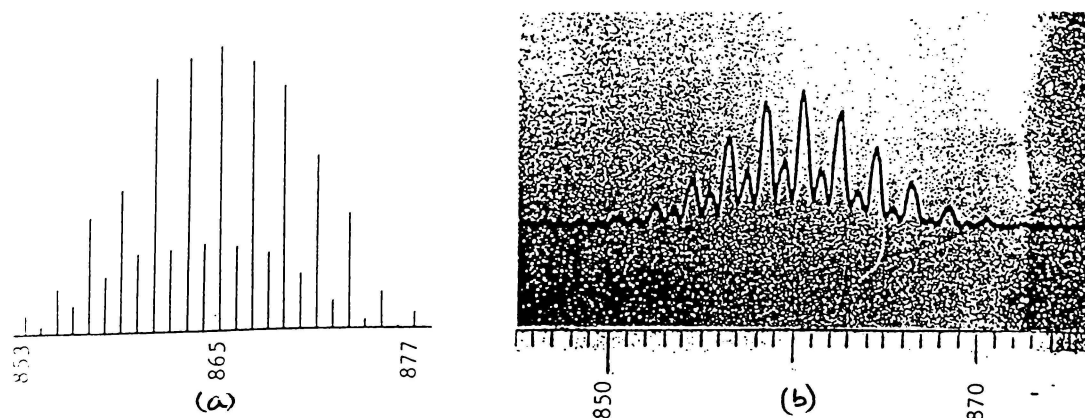
Table 7.20 Atomic percentage values for the products obtained from reaction of $[\text{SnCl}_3]^-$ with $\text{Br}_3\text{SnCo}(\text{CO})_4$.

Element	Shell	Atomic percentage
Co	K	12.1
Sn	L	23.6
Cl	K	21.2
Br	L	43.1

These atomic percentage values give an approximate empirical Co:Sn:Cl:Br ratio of 1:2:2:4. This would be consistent with formulation of the product as $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$, although it is possible that a mixture of different species is present giving an averaged figure.

7.6.2.4. Fast atom bombardment mass spectroscopy.

The FAB mass spectrum listed in table 7.21 was recorded from a sample of the product mixture at the University of Adelaide. Throughout the high mass part of the spectrum an isotope pattern consistent with an Sn_2X_6 containing ion was observed, as shown for the highest mass fragment in figure 7.13.



(a) Calculated isotope pattern for an Sn_2Br_6 containing species.

(b) Observed isotope pattern for envelope assigned to $\{(\text{Br}_3\text{Sn})_2\text{Co}(\text{CO})_3\}^-$

Figure 7.13

Table 7.21 FAB-MS of product mixture obtained from reaction of $\text{Et}_4\text{NSnCl}_3$ and $\text{Br}_3\text{SnCo}(\text{CO})_4$.

m/e	Rel. int.	Assignment
852-870	34	$[\text{Br}_6\text{Sn}_2\text{Co}(\text{CO})_3]^-$
808-825	63	$[\text{Br}_5\text{ClSn}_2\text{Co}(\text{CO})_3]^-$
796-808	13	$[\text{Br}_6\text{Sn}_2\text{Co}(\text{CO})]^-$
765-783	63	$[\text{Br}_4\text{Cl}_2\text{Sn}_2\text{Co}(\text{CO})_3]^-$
752-767	25	$[\text{Br}_5\text{ClSn}_2\text{Co}(\text{CO})]^-$
718-742	40	$[\text{Br}_3\text{Cl}_3\text{Sn}_2\text{Co}(\text{CO})_3]^-$
706-722	25	$[\text{Br}_4\text{Cl}_2\text{Sn}_2\text{Co}(\text{CO})]^-$
673-690	12	$[\text{Br}_2\text{Cl}_4\text{Sn}_2\text{Co}(\text{CO})_3]^-$
660-679	10	$[\text{Br}_3\text{Cl}_3\text{Sn}_2\text{Co}(\text{CO})]^-$
630-648	5	$[\text{BrCl}_5\text{Sn}_2\text{Co}(\text{CO})_3]^-$
618-635	4	$[\text{Br}_2\text{Cl}_4\text{Sn}_2\text{Co}(\text{CO})]^-$
582-602	5	$[\text{Cl}_6\text{Sn}_2\text{Co}(\text{CO})_3]^-$
569-583	2	$[\text{Br}_3\text{ClSn}_2\text{Co}]^-$
541-557	2	$[\text{Br}_2\text{ClSn}_2\text{Co}(\text{CO})_2]^-$
526-540	2	$[\text{BrCl}_2\text{Sn}_2\text{Co}(\text{CO})_3]^-$
516-535	11	$[\text{Cl}_4\text{Sn}_2\text{Co}(\text{CO})_3]^-$
506-519	2	$[\text{Cl}_6\text{Sn}_2\text{Co}]^-$
490-508	12	$[\text{BrClSn}_2\text{Co}(\text{CO})_3]^-$
473-488	15	$[\text{BrCl}_3\text{Sn}_2\text{Co}]^-$
467-478	5	$[\text{Cl}_5\text{Sn}_2\text{Co}]^-$
446-462	13	$[\text{Cl}_2\text{Sn}_2\text{Co}(\text{CO})_3]^-$
438-450	8	$[\text{Br}_3\text{SnCo}(\text{CO})]^-$
423-441	7	$[\text{Cl}_3\text{Sn}_2\text{Co}(\text{CO})]^-$
393-408	6	$[\text{Br}_2\text{ClSnCo}(\text{CO})]^-$
380-397	6	$[\text{BrCl}_2\text{SnCo}(\text{CO})_2]^-$
359-382	4	$[\text{Cl}_2\text{Sn}_2\text{Co}]^-$
350-367	50	$[\text{Br}_3\text{Sn}]^-$
307-323	43	$[\text{Br}_2\text{ClSn}]^-$
292-304	30	$[\text{Sn}_2\text{Co}]^-$
273-287	4	$[\text{Br}_2\text{Sn}]^-$
262-278	15	$[\text{BrCl}_2\text{Sn}]^-$
228-240	9	$[\text{BrClSn}]^-$
220-232	4	$[\text{Cl}_3\text{Sn}]^-$
196-206	12	$[\text{BrSn}]^-$
184-195	4	$[\text{Cl}_2\text{Sn}]^-$
148-158	100	$[\text{ClSn}]$

From table 7.21 it is clear that there was a mixture of anions present - that is $[\text{Br}_6\text{Sn}_2\text{Co}(\text{CO})_3]^-$, $[\text{Br}_5\text{ClSn}_2\text{Co}(\text{CO})_3]^-$, $[\text{Br}_4\text{Cl}_2\text{Sn}_2\text{Co}(\text{CO})_3]^-$, $[\text{Br}_3\text{Cl}_3\text{Sn}_2\text{Co}(\text{CO})_3]^-$, $[\text{Br}_2\text{Cl}_4\text{Sn}_2\text{Co}(\text{CO})_3]^-$, $[\text{BrCl}_5\text{Sn}_2\text{Co}(\text{CO})_3]^-$ and $[\text{Cl}_6\text{Sn}_2\text{Co}(\text{CO})_3]^-$. Because of this mixture the mass spectrum was very complicated and only the most obvious peaks have been assigned. It is quite possible that other fragments were present but were obscured by the confused patterns of overlapping peaks.

It was apparent that loss of two carbonyl ligands from the parent ions was a favoured process while the loss of only one or of all three was not

commonly observed. Other fragmentations appeared to be fairly random and the most intense peaks, apart from the parent ions, resulted for halo-tin species.

7.6.2.5. ^{119}Sn NMR spectroscopy.

The ^{119}Sn NMR spectrum shown in figure 7.14 was recorded from a CH_2Cl_2 solution of the product mixture and resulted from 6039 scans. The peak shifts are also listed in table 7.22.

Table 7.22 ^{119}Sn NMR spectrum of the product mixture obtained from reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Br}_3\text{SnCo}(\text{CO})_4$.

Peak shift (ppm)	Relative intensity
-33.4	56
-41.0	61
-50.7	44
-85.1	71
-92.6	100
-101.1	64
-138.0	36
-145.3	57
-153.0	52

It is clear from the spectrum that the peaks form a pattern of three groups of three. Each group is separated from the next by an average 52.1 ppm while within each group peaks are separated by an average 8 ppm.

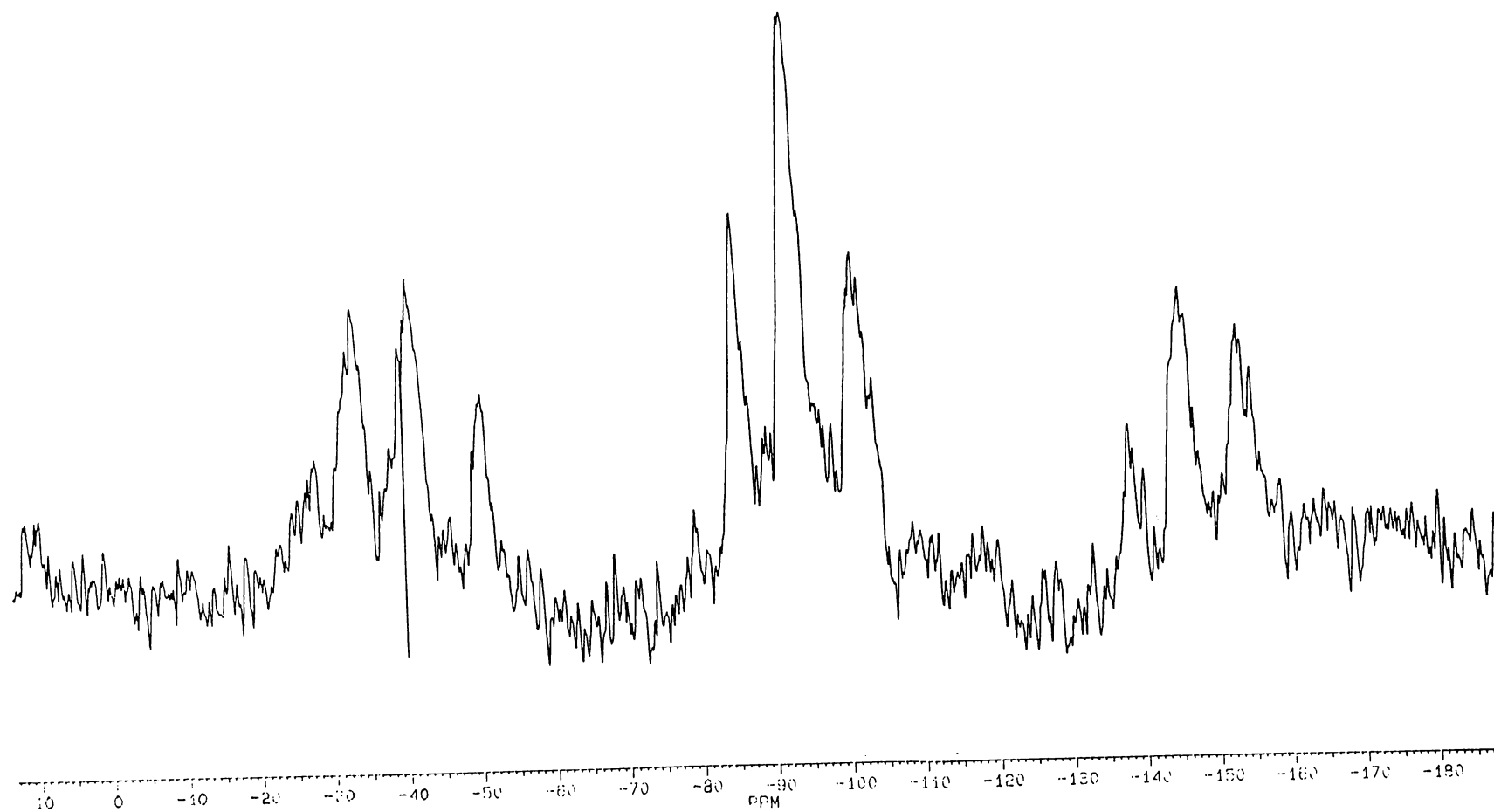
Table 7.23 lists the ^{119}Sn NMR data reported for $\text{Br}_n\text{SnCl}_{4-n}$ species ($n = 0-4$).

Table 7.23 ^{119}Sn NMR data for compounds of general formula $\text{Br}_n\text{SnCl}_{4-n}$ ($n = 0-4$) [189].

Compound	$\delta \text{ }^{119}\text{Sn}$ (ppm)
SnCl_4	-150
BrSnCl_3	-265
Br_2SnCl_2	-382
Br_3SnCl	-502
Br_4Sn	-623

All recorded in CS_2 at -30°C .

Figure 7.14. ^{119}Sn NMR spectrum of the product mixture obtained from the reaction of $\text{Br}_3\text{SnCo(CO)}_4$ with $\text{Et}_4\text{NSnCl}_3$. Recorded in CH_2Cl_2 .



The spectra of these compounds show a regular pattern of low field shifts by an average 118 ppm on substitution of a chlorine by a bromine.

It may be assumed that the various peaks in the ^{119}Sn NMR spectrum of the product mixture result from the different anions observed in the mass spectrum. From the latter it appears that the anions containing more bromine than chlorine are the most abundant. Using this feature, together with the anticipated direction of the δ ^{119}Sn shifts on replacing Br by Cl taken from table 7.23, some tentative assignments may be made. For example, the most intense peak at -92.6 δ is assigned to the two tins of the symmetrical anion $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$ while the two peaks at 101.1 δ and -145.3 δ , being of similar intensity, are assigned to Sn^1 and Sn^2 of $[(\text{Br}_2\text{ClSn}^1)\text{Co}(\text{CO})_3(\text{Sn}^2\text{Br}_3)]^-$.

There are also some peaks of intensity only slightly above that of the noise level. These may result from those anions containing mainly Cl rather than Br. These are treated as genuine and are included in table 7.24 which repeats the spectrum and shows the tentative assignments which have been made. Unfortunately, the spectrum did not cover the region above $+13$ δ where the remainder of the peaks resulting from Cl_3Sn groups would be expected.

Table 7.24 ^{119}Sn NMR spectrum of the product mixture from the reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Br}_3\text{SnCo}(\text{CO})_4$ with tentative assignments.

δ ^{119}Sn (ppm)	Relative Intensity	Assignment
-153.0	52	$[(\text{Br}_3\text{Sn})_2\text{Co}(\text{CO})_3]^-$
-145.2	57	Br_3Sn of $[(\text{Br}_3\text{Sn})\text{Co}(\text{CO})_3(\text{SnBr}_2\text{Cl})]^-$
-138.0	36	Br_3Sn of $[(\text{Br}_3\text{Sn})\text{Co}(\text{CO})_3(\text{SnBrCl}_2)]^-$
-133.0	15	Br_3Sn of $[(\text{Br}_3\text{Sn})\text{Co}(\text{CO})_3(\text{SnCl}_3)]^-$
-101.1	64	Br_2ClSn of $[(\text{Br}_2\text{ClSn})\text{Co}(\text{CO})_3(\text{SnBr}_3)]^-$
-92.6	100	$[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$
-85.1	71	Br_2ClSn of $[(\text{Br}_2\text{ClSn})\text{Co}(\text{CO})_3(\text{SnCl}_2\text{Br})]^-$
-79.0	15	Br_2ClSn of $[(\text{Br}_2\text{ClSn})\text{Co}(\text{CO})_3(\text{SnCl}_3)]^-$
-50.7	44	BrCl_2Sn of $[(\text{BrCl}_2\text{Sn})\text{Co}(\text{CO})_3(\text{SnBr}_3)]^-$
-41.0	61	BrCl_2Sn of $[(\text{BrCl}_2\text{Sn})\text{Co}(\text{CO})_3(\text{SnClBr}_2)]^-$
-33.4	56	$[(\text{BrCl}_2\text{Sn})_2\text{Co}(\text{CO})_3]^-$
-27.7	22	BrCl_2Sn of $[(\text{BrCl}_2\text{Sn})\text{Co}(\text{CO})_3(\text{SnCl}_3)]^-$
+10.0	15	Cl_3Sn of $[(\text{Cl}_3\text{Sn})\text{Co}(\text{CO})_3(\text{SnBr}_3)]^-$
>10	region not observed	

7.6.2.6. X-ray crystal structure determination of $\text{Et}_4\text{N}[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]$.

(i) Preliminary study and data refinement.

Crystals suitable for study were grown from an Et_2O solution of the product mixture cooled to -30°C . A thin orange plate was mounted on a glass fibre in tap grease. Preliminary precession photography indicated monoclinic symmetry with systematic absences appropriate for $\text{P}2_1/\text{c}$. The crystal was then sent to the University of Canterbury for data collection. Table 7.25 gives the crystal data obtained.

Table 7.25 Crystal data obtained for $\text{Et}_4\text{N}[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]$.

Formula:	$\text{Br}_4\text{C}_{11}\text{Cl}_2\text{CoH}_{20}\text{NO}_3\text{Sn}_2$		
Mr:	901.02		
Space group:	Monoclinic, $\text{P}2_1/\text{c}$		
	$a = 10.508 \text{ (5)}$	$b = 10.298 \text{ (4)}$	$c = 22.90 \text{ (1) \AA}$
		$\beta = 101.98 \text{ (5)}^\circ$	
$U = 2424 \text{ (2) \AA}^3$			
$D_{\text{calc}} = 2.59 \text{ g/cm}^3$	$D_{\text{obs}} > 2.3 \text{ g/cm}^3$		
$Z = 4$			
$F(000) = 1764$	$\mu \text{ (Mo-}k\alpha) = 70.25 \text{ cm}^{-1}$		
$T = -150^\circ\text{C}$	$\lambda \text{ (Mo-}k\alpha) = 0.7107 \text{ \AA}$		
Crystal dimensions:	$0.18 \times 0.25 \times 0.06 \text{ mm}^3$		

A total of 3164 unique reflections in the range $4^\circ < 2\theta < 45^\circ$ were collected with $0 < h < 12$, $0 < k < 12$, $-25 < l < 25$. Of these, the 2112 with $I > 2\sigma(I)$ were used in all calculations. The intensity data were corrected for Lorentz, polarisation and absorption effects. The transmission factors were $\text{max} = 0.808$ and $\text{min} = 0.691$.

Solution of the structure was achieved by direct methods. The heavy atoms of the unique molecule were found with ease while subsequent refinements and difference maps gave the positions of the carbonyl groups and the nitrogen and carbon atoms of the tetraethylammonium cation. The six halogen atoms attached to the two tin atoms were revealed as peaks of approximately equal height. When these were refined with Br scattering factors the temperature factors were markedly larger than those of any other atom present. It was therefore assumed that each halogen site was randomly occupied by Br or Cl in the stoichiometric ratio - 2:1 from electron probe analysis. Refinement was continued using Br scattering factors but final site occupancies of 0.74, corresponding to $[\frac{2}{3}\text{Br} + \frac{1}{3}\text{Cl}]$ based on Z^2 values. That is $[\frac{2}{3}(35)^2 + \frac{1}{3}(17)^2]/(35)^2 = 0.74$. This model gave sensible

temperature factors. A similar situation was recently reported [205] for the X-ray crystal structure determination of $[\text{SnCl}_2\text{Br}(\text{OH})(\text{THF})]_2 \cdot 2\text{THF}$ where the halogen atoms could not be distinguished. This structure was solved using a procedure much the same as that employed here.

All atoms were then assigned anisotropic temperature factors and the hydrogens of the cation were placed in calculated positions. Full matrix least squares refinement to convergence gave $R = 0.069$, $R_w = 0.068$ with $w = [\sigma^2 F + 0.0015 F^2]^{-1}$. At this point the largest parameter shift other than the carbons of the cation was 0.033. The highest peak of the final difference map, having $2.003 \text{ e}/\text{\AA}^3$, was adjacent to a halogen atom.

The final positional and anisotropic thermal parameters, and a table of calculated hydrogen positions for $\text{Et}_4\text{N}[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]$, are shown in appendix 3 together with a complete list of the bond lengths and angles determined for this molecule. Structure factors have been archived by the University of Waikato.

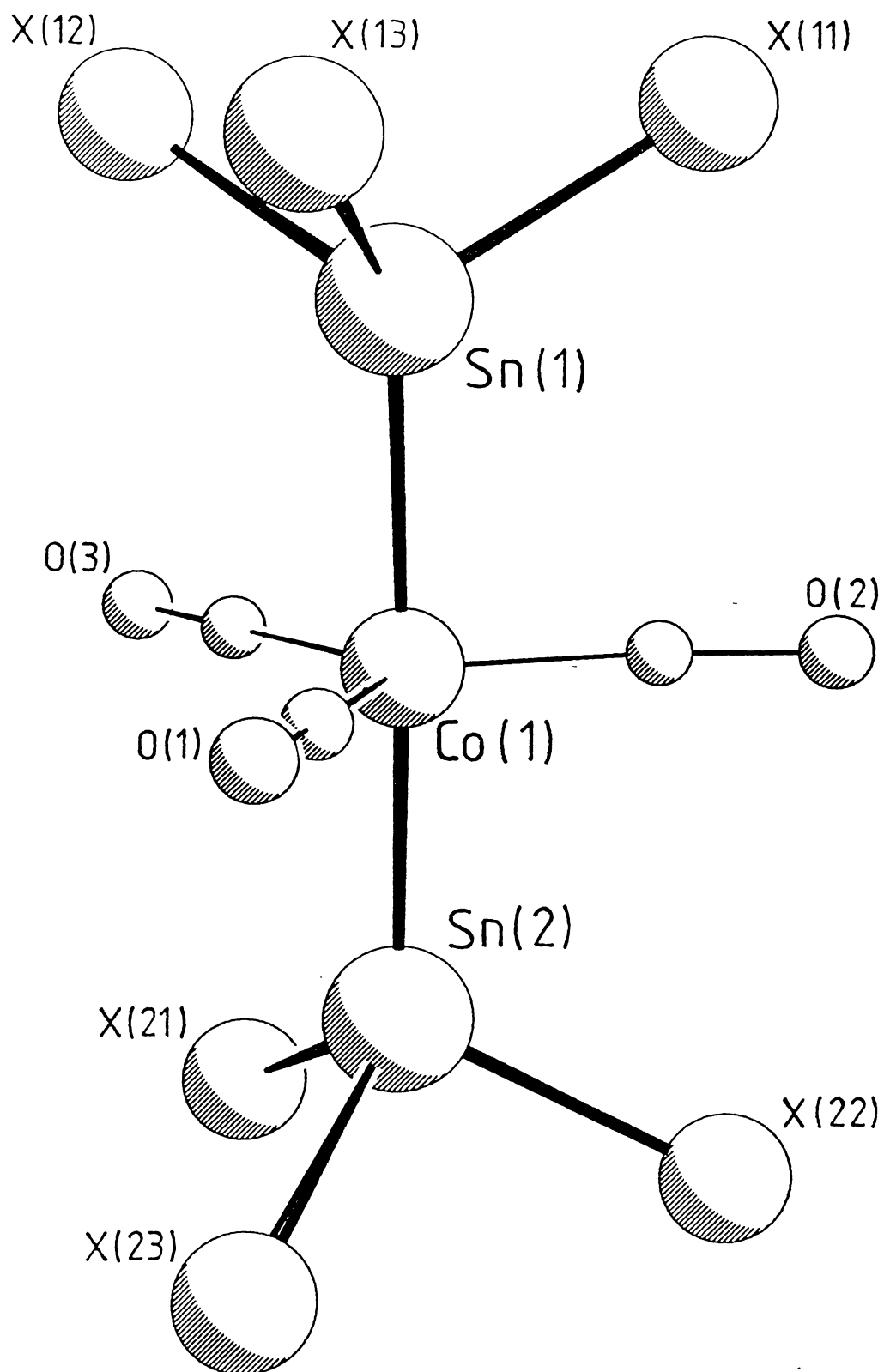
(ii) Discussion of the structure of $\text{Et}_4\text{N}[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]$.

The crystal lattice consists of discrete $[\text{Et}_4\text{N}]^+$ cations and $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$ anions.

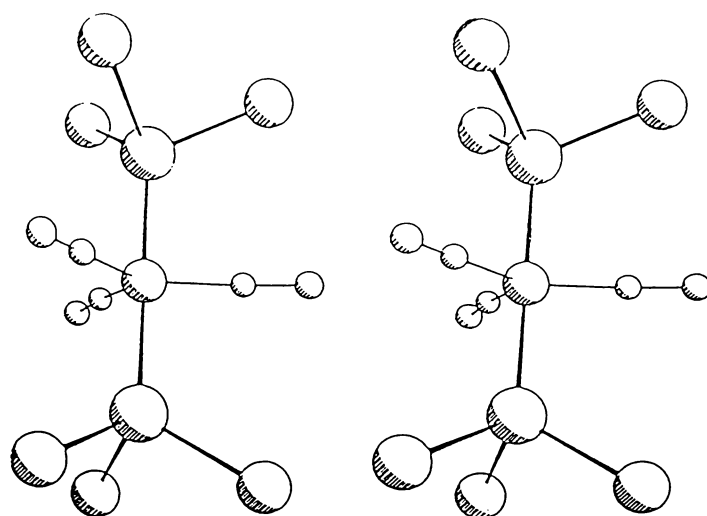
A perspective view of $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$ is shown in figure 7.15. which shows the labelling system used. Figure 7.16 depicts a stereo view of this anion.

From the crystal structure analysis it is not possible to definitely determine if the disorder of the halogen atoms was caused by anions of formula $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$ with random occupancy of the halide positions by Cl and Br, or by a lattice containing various anions of general formula $[\text{Sn}_2\text{Co}(\text{CO})_3\text{Br}_x\text{Cl}_y]^-$ ($x + y = 6$) occupying each anion site. However, it is felt that the former case is more likely since the two tin atoms showed no complications during refinement of the structure which would be expected if this were the average of several different anions. Also, the ^{119}Sn NMR spectrum showed the most abundant anion to be a symmetrical species, probably $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$. Thus, for the course of this discussion the anion will be referred to as $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$.

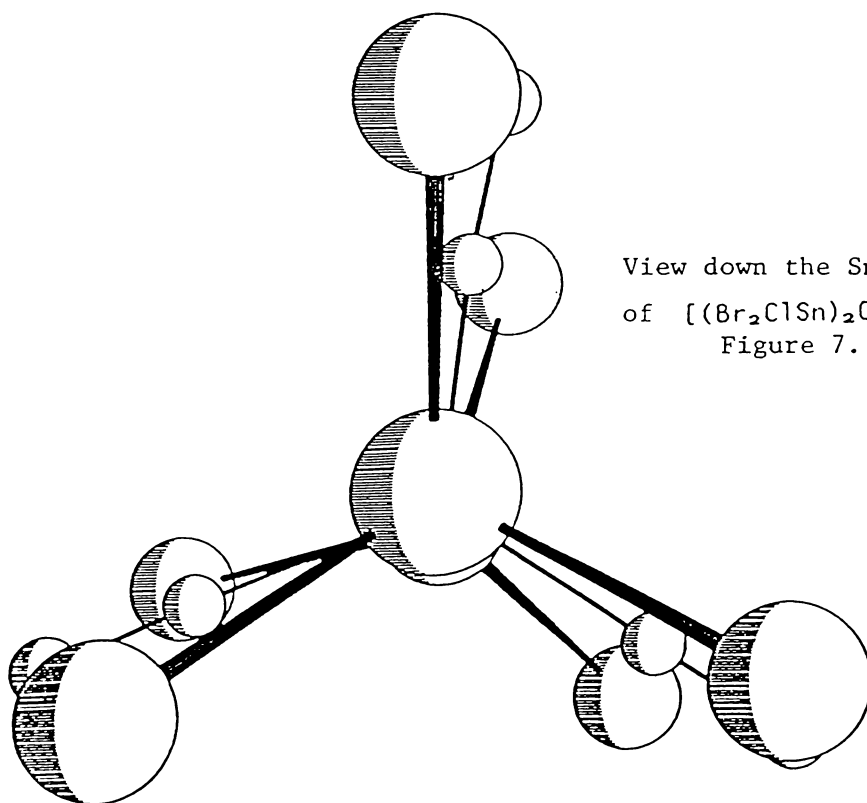
Selected bond lengths and angles of the anion are shown in table 7.26 where X denotes a halogen atom.



Perspective view of $[\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$
Figure 7.15.



Stereo view of $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$
Figure 7.16.



View down the Sn-Co-Sn axis
of $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$
Figure 7.17.

Table 7.26 Selected bond lengths and angles for $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$.

Bond	length (Å)	Bond angle	Angle(°)
Sn(1)-Co(1)	2.463(4)	Sn(1)-Co(1)-Sn(2)	178.0(2)
Sn(2)-Co(1)	2.466(4)	X(11)-Sn(1)-Co(1)	119.4(1)
Sn(1)-X(11)	2.486(3)	X(21)-Sn(2)-Co(1)	116.5(1)
Sn(1)-X(12)	2.512(3)	X(11)-Sn(1)-X(12)	102.6(1)
Sn(1)-X(13)	2.490(4)	X(21)-Sn(2)-X(22)	98.5(1)
Sn(2)-X(21)	2.490(4)	Sn(1)-Co(1)-C(1)	90.1(8)
Sn(2)-X(22)	2.542(3)	Sn(2)-Co(1)-C(2)	89.9(7)
Sn(2)-X(23)	2.469(4)		
Co(1)-C(1)	1.75(3)		
Co(1)-C(2)	1.74(2)		
Co(1)-C(3)	1.85(3)		

The anion has a very similar structure to that determined for $[(\text{Cl}_3\text{Sn})_2\text{Co}(\text{CO})_3]^-$ [94] where the Sn(1)-Co(1)-Sn(2) angle is almost 180° . The Sn-Co bond lengths, however, are lengthened from an average 2.442 Å for the all-chlorine containing anion to an average 2.465 Å for the anion where four of the six chlorine substituents have been replaced by bromine atoms. This is consistent with the replacement of substituents by less electronegative groups.

The Sn-X bond lengths and angles cannot be discussed in any detail because of the disorder, however it can be stated that the average bond length of 2.498 Å is closer to that expected for Sn-Br (eg 2.501 Å for $\text{Br}_3\text{SnFe}(\text{CO})_2\text{Cp}$ [167]) than for Sn-Cl (eg 2.35 Å for $[(\text{Cl}_3\text{Sn})_2\text{Co}(\text{CO})_3]^-$ [94]). Although there are slight differences in the lengths of the Sn-X bonds the average values to each tin are the same and these differences are not expected to be chemically significant.

Figure 7.17 shows a view of the anion down the Sn-Co-Sn axis. The halogen atoms and the carbonyl groups are virtually eclipsed which was also observed for the anion $[(\text{Cl}_3\text{Sn})_2\text{Co}(\text{CO})_3]^-$ [94]. This indicates there is little steric interaction between these groups which, in turn, suggests a low barrier to rotation about the Sn-Co-Sn axis.

The Co-C bond lengths are normal being an average 1.77 Å while the Sn-Co-C bond angles show the carbonyl groups to be perpendicular to the Sn-Co-Sn backbone.

The tetraethylammonium cation is normal with C-N bond lengths ranging from 1.482 to 1.588 Å and C-C bond lengths ranging from 1.484 to 1.567 Å. The C-N-C bond angles range from 103 to 114° and C-C-N angles from 111.6 to 114.9° .

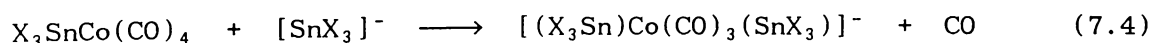
7.6.3. Discussion of the Reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Br}_3\text{SnCo(CO)}_4$.

The reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Br}_3\text{SnCo(CO)}_4$ provided a mixture of tin-cobalt carbonyl anions differing by the number of contained chlorine and bromine atoms. These appear to be of the form $[(\text{Br}_x\text{Cl}_{3-x}\text{Sn})\text{Co(CO)}_3(\text{SnCl}_{3-y}\text{Br}_y)]^-$ ($x, y = 0-3$). Clearly halogen exchange is occurring in solution.

This process is observed for simple $\text{SnX}_n\text{Y}_{4-n}$ species ($X, Y = \text{halogen}$, $n = 1-3$) which are impossible to separate from each other as halogen exchange continuously occurs to provide a steady state concentration of every possible arrangement [189]. However, this has not been reported for any more complex mixed halide tin species.

Although the crystal structure of the anion $[(\text{Br}_2\text{ClSn})_2\text{Co(CO)}_3]^-$ was obtained, disorder was present between the chlorine and bromine atoms of each tin. This could have resulted from free rotation of Br_2ClSn groups about the Sn-Co axis but it is also possible that anions of varying composition form an isomorphous set and all co-crystallised, thus the electron density of the halogen atoms was averaged over all unit cells. It should be noted, however, that $\text{Et}_4\text{N}[(\text{Cl}_3\text{Sn})_2\text{Co(CO)}_3]$ is not isomorphous with the structure discussed here.

It cannot be distinguished from the reaction whether the exchange occurs in the starting materials or once the anion has been formed. Nevertheless, it is still likely that the formation of the anions occurs by replacement of an axial carbonyl ligand of $\text{X}_3\text{SnCo(CO)}_4$ by $[\text{SnX}_3]^-$ as depicted in equation 7.4.



Replacement of an axial carbonyl ligand would be preferred for steric reasons.

7.6.4. Discussion of the Other Reactions of Trihalogenocobalt tetracarbonyl Substituted Group 14 Compounds with $\text{Et}_4\text{NSnCl}_3$.

7.6.4.1. Discussion of the reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Cl}_3\text{GeCo(CO)}_4$.

It was unfortunate that the major product of the reaction between $\text{Et}_4\text{NSnCl}_3$ and $\text{Cl}_3\text{GeCo(CO)}_4$ could not be fully characterised during the course of this work. However, it seems evident from the results obtained

that $[\text{Cl}_3\text{Sn}]^-$ will react with $\text{Cl}_3\text{GeCo}(\text{CO})_4$ to replace a carbonyl group as anticipated.

The reaction was monitored by infrared spectroscopy and at no time was the formation of $[\text{Co}(\text{CO})_4]^-$ observed. This seems to suggest that the reaction was comparatively straightforward and the most likely product would be the anion $\{[\text{Cl}_3\text{Ge}]\text{Co}(\text{CO})_3[\text{SnCl}_3]\}^-$.

The infrared spectrum of the major product is listed in table 7.27 together with the data reported for $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ [94].

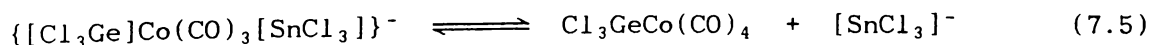
Table 7.27 Carbonyl region infrared data for the product of reaction between $[\text{SnCl}_3]^-$ and $\text{Cl}_3\text{GeCo}(\text{CO})_4$, together with that reported for $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ [94] (cm^{-1}).

Product from $[\text{SnCl}_3]^- + \text{Cl}_3\text{GeCo}(\text{CO})_4$	$\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ [94]
2120 m	
2050 s	
1996 vs, br	1991 vs, br

Both recorded in CH_2Cl_2 .

The major peak in the spectrum of the product of this reaction is observed at 1996 cm^{-1} . This is shifted by 5 cm^{-1} to higher frequency compared to the corresponding peak of $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ which is consistent with the replacement of a tin atom by a germanium. For example the carbonyl bonds in the infrared spectrum of $\text{Cl}_3\text{GeCo}(\text{CO})_4$ are shifted by an average 2 cm^{-1} to higher frequency compared to that of $\text{Cl}_3\text{SnCo}(\text{CO})_4$ [160].

The other bands observed in this product mixture are anticipated to result from the starting material, $\text{Cl}_3\text{GeCo}(\text{CO})_4$ (νcm^{-1} : 2123 (s), 2070 (s), 2050 (vs), 2012 (w) [160]). As this could not be removed by frequent washings with hexane it is possible that in solution the anionic product breaks down to some degree to exist in equilibrium with $\text{Cl}_3\text{GeCo}(\text{CO})_4$ and $[\text{SnCl}_3]^-$ (equation 7.5).

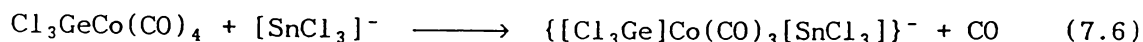


Obviously, for this process to occur a carbonyl group would have to be obtained from some source. At this stage it is not possible to state how this could be achieved.

The results obtained from this experiment suggest that the major product of reaction between $\text{Et}_4\text{NSnCl}_3$ and $\text{Cl}_3\text{GeCo}(\text{CO})_4$ is the anion

$\{[\text{Cl}_3\text{Ge}]\text{Co}(\text{CO})_3[\text{SnCl}_3]\}^-$. It is hoped that crystals of this species may be obtained in the near future to allow confirmation of this assignment.

If this characterisation is assumed to be correct then it is possible to propose a straightforward mechanism for this reaction, as shown in equation 7.6. Here the $[\text{SnCl}_3]^-$ acts to replace an axial carbonyl of $\text{Cl}_3\text{GeCo}(\text{CO})_4$ in an analogous manner to phosphine substitution [169].

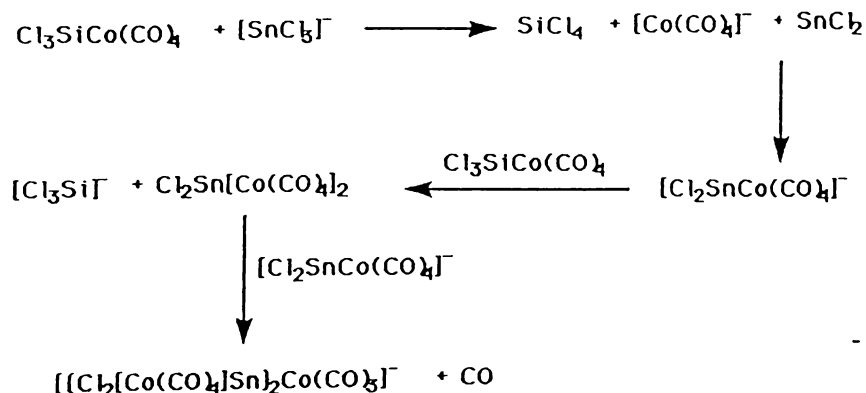


Also found as a minor product of this reaction was a white solid insoluble in both hexane and dichloromethane. This species showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull and its characterisation was not pursued.

7.6.4.2. Discussion of the reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Cl}_3\text{SiCo}(\text{CO})_4$.

The reaction of $[\text{SnCl}_3]^-$ with $\text{Cl}_3\text{SiCo}(\text{CO})_4$ proceeded at room temperature with very rapid initial production of $[\text{Co}(\text{CO})_4]^-$ as observed from the infrared spectrum of the mixture. Within 20 minutes, however, the produced $[\text{Co}(\text{CO})_4]^-$ had all reacted further.

This feature was observed in the reactions of the trialkyl cobalt tetracarbonyl substituted tin species with $[\text{Cl}_3\text{Sn}]^-$ (section 7.4.3) where it was suggested that the $[\text{SnCl}_3]^-$ displaced the $\text{Co}(\text{CO})_4$ unit of the $\text{R}_3\text{SnCo}(\text{CO})_4$ species and then formed $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. This could react further with the $[\text{SnCl}_3]^-$ finally providing the anion $\{[\text{Cl}_2\text{SnCo}(\text{CO})_4]_2\text{Co}(\text{CO})_3\}^-$. It appears that a similar process occurs in the reaction between $\text{Cl}_3\text{SiCo}(\text{CO})_4$ and $[\text{SnCl}_3]^-$ as shown in scheme 7.2.



Scheme 7.2

During one experiment $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ was found as a minor product of this reaction which supports its formation as an intermediate in this process.

It is also possible that the produced $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ will react with $[\text{SnCl}_3]^-$ directly, rather than just with $[\text{Cl}_2\text{SnCo}(\text{CO})_4]^-$, to produce the unsymmetrical anion $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}\text{Co}(\text{CO})_3\{\text{SnCl}_3\}]^-$. This reaction has been reported [94] although the product was not fully characterised. The presence of this species would account for the apparent mixture of products in the final solution. A slow reaction in the refrigerator could then provide $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ as the sole product.

The absence of silicon in these products is perhaps a result of its ready hydrolysis. The presence of even small amounts of water in the solution would remove the silicon from the reaction, and this process probably accounts for the insoluble white powder observed on work-up.

7.7. Related studies.

Three other experiments related to the work of this chapter have been carried out. They do not fit into any of the preceding sections thus they are described separately here. The first is a study of the reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Et}_4\text{NSnCl}_3$. This was carried out to determine if $[\text{SnCl}_3]^-$ will react in an analogous fashion to SnCl_2 by inserting into the Co-Co bond yielding $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, or if a more complicated reaction would take place. The second experiment was conducted to find if $\text{Co}_2(\text{CO})_8$ will react with $\text{Et}_4\text{N}^+\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ to produce other anions of this series. Finally, a study was carried out on the reaction of $\text{Cl}_3\text{SnCo}(\text{CO})_4$ with Ph_3SnLi . It was hoped that $[\text{Ph}_3\text{Sn}]^-$ would react in an analogous fashion to $[\text{Cl}_3\text{Sn}]^-$ and that this reaction would provide an unsymmetrical anion of the form $[\{\text{Ph}_3\text{Sn}\}\text{Co}(\text{CO})_3\{\text{SnCl}_3\}]^-$.

7.7.1. Experimental Details and Results.

7.7.1.1. Reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Et}_4\text{NSnCl}_3$.

$\text{Et}_4\text{NSnCl}_3$ (0.074 g; 0.21 mmol) in CH_2Cl_2 (5 ml) was added to a stirred solution of $\text{Co}_2(\text{CO})_8$ (0.072 g; 0.21 mmol) in CH_2Cl_2 (10 ml). On mixing, the colour of the solution did not appear to change greatly from the original light brown, although during the course of the reaction it could be seen to be darkening to a deep red-brown colour. Immediate change was apparent in the carbonyl region infrared spectrum, however, as a band resulting from $[\text{Co}(\text{CO})_4]^-$ was obvious, together with a new band at around

2025 cm^{-1} . After two hours the bridging carbonyl band of $\text{Co}_2(\text{CO})_8$ had completely disappeared and the new band at 2025 cm^{-1} had increased in intensity to become very strong. The solution was worked up. The hexane extracts were characterised by carbonyl region infrared spectroscopy and by mass spectroscopy to be $\text{ClSn}[\text{Co}(\text{CO})_4]_3$. The Et_2O soluble products gave a burgundy solution in CH_2Cl_2 . The carbonyl region infrared spectra of these products, together with that reported for $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ are listed in table 7.24. Also present was an insoluble blue powder which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be CoCl_2 .

Table 7.28 Carbonyl region infrared data for the products of reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Et}_4\text{NSnCl}_3$ and that reported for $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ [184] (cm^{-1}).

$\text{ClSn}[\text{Co}(\text{CO})_4]_3$ (a) [184]	Hexane extracts (a)	Et_2O extracts (b)
2110 vw	2096 vw	
2088 s	2088 s	
	2068 w	2067 w
2049 w	2048 sh, w	2049 m, br
2043 m	2042 m	2029 m, sh
2028 s	2026 s	2013 s, br
2001 w	2000 w	2005 m, sh
	1970 sh, w	1967 m, sh

(a) Recorded in hexane.

(b) Recorded in CH_2Cl_2 .

7.7.1.2. Reaction of $\text{Co}_2(\text{CO})_8$ and $\text{Et}_4\text{N}^+\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$

$\text{Co}_2(\text{CO})_8$ (0.017 g; 0.05 mmoles) in CH_2Cl_2 (10 mls) was added to a stirred solution of $\text{Et}_4\text{N}^+\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ (0.036 g; 0.05 mmoles) in CH_2Cl_2 (10 mls). On mixing the solution changed from a bright yellow to a deep orange-brown. The carbonyl region infrared spectrum of the solution became much sharper and the main band of $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ (1991 cm^{-1} [94]) was shifted to 2010 cm^{-1} . No $[\text{Co}(\text{CO})_4]^-$ was observed. After 2 hours the reaction mixture was worked up. A trace of hexane soluble species was found and by carbonyl region infrared spectroscopy was characterised as $\text{Cl}_3\text{SnCo}(\text{CO})_4$ (2120 (m-s), 2067 (m), 2045 (vs) [150]). The remaining soluble products were dissolved in Et_2O and a carbonyl region infrared spectrum of these in CH_2Cl_2 solution showed the main carbonyl containing species to be $\text{Et}_4\text{N}^+\{[\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$. The carbonyl bands of this product, together with

those reported for this anion are listed in table 7.29. Also present was a fairly large amount of an insoluble blue powder which showed no carbonyl vibrations in an infrared spectrum recorded as a nujol mull. This was assumed to be CoCl_2 .

Table 7.29 Carbonyl region infrared data for the major product of reaction between $\text{Co}_2(\text{CO})_8$ and $\text{Et}_4\text{N}^+\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ together with that for $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ (cm^{-1}).

Product of run 7.7.1.2.	$[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$
2097 w	2094 m
2089 s	2087 s
2054 sh, w	2052 m
2037 sh, m	2034 m
2011 vs, br	2010 s, br
1967 m, br	1967 m, br

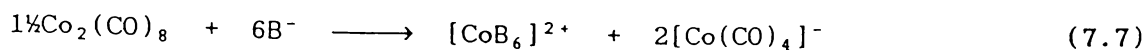
7.7.1.3. Reaction of Ph_3SnLi with $\text{Cl}_3\text{SnCo}(\text{CO})_4$.

Ph_3SnLi (ca. 0.95 mmoles from its preparation) in Et_2O (10 mls) was added to a stirred solution of $\text{Cl}_3\text{SnCo}(\text{CO})_4$ (0.390 g; 0.98 mmoles) in Et_2O (10 mls). On mixing the solution changed from a pale yellow to an orange-brown. A light coloured solid was suspended in this mixture. During the reaction the solution became deep red in colour while the solid was deposited at the bottom of the flask and could be seen to be an orange powder. Monitoring by carbonyl region infrared spectroscopy showed an instant reduction in intensity of the bands resulting from $\text{Cl}_3\text{SnCo}(\text{CO})_4$ (2120 (m-s), 2067 (m), 2045 (vs) [150]) on addition of Ph_3SnLi . No $[\text{Co}(\text{CO})_4]^-$ was observed. No $\text{Cl}_3\text{SnCo}(\text{CO})_4$ remained after 3 hours of reaction and the solvent was removed. No hexane soluble species were observed. Neither the products in the red Et_2O solution nor the insoluble orange powder could be identified since they both readily decomposed on even the slightest contact with air and were also caused to decompose to a white powder during attempts at separation by filtration.

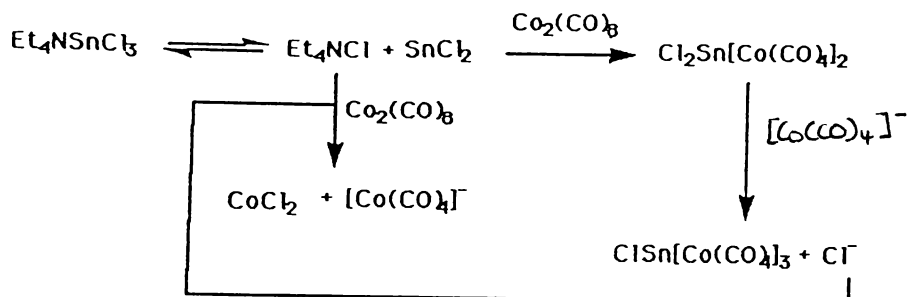
7.7.2. Discussion of these Related Reactions.

7.7.2.1. Discussion of the reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Et}_4\text{NSnCl}_3$.

The major products of this reaction were $\text{ClSn}[\text{Co}(\text{CO})_4]_3$, the unidentified anionic species and CoCl_2 . It is known that $\text{Co}_2(\text{CO})_8$ will react with a base as shown in equation 7.7.



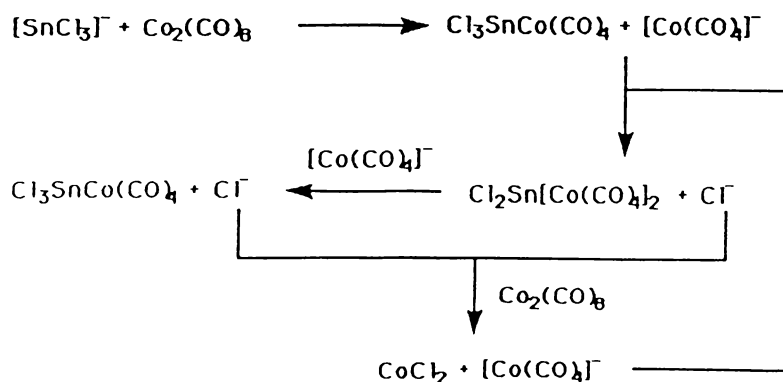
If Cl^- is considered to act as a base in this reaction then the process outlined in scheme 7.3 could be envisaged.



Scheme 7.3

The insertion of SnCl_2 into the Co-Co bond of $\text{Co}_2(\text{CO})_8$ is a well established reaction [12] thus this scheme could conceivably account for the formation of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ and CoCl_2 from this reaction.

Alternatively, $[\text{SnCl}_3]^-$ may have reacted directly with $\text{Co}_2(\text{CO})_8$ initially producing $\text{Cl}_3\text{SnCo}(\text{CO})_4$ and $[\text{Co}(\text{CO})_4]^-$ as shown in scheme 7.4.



Scheme 7.4

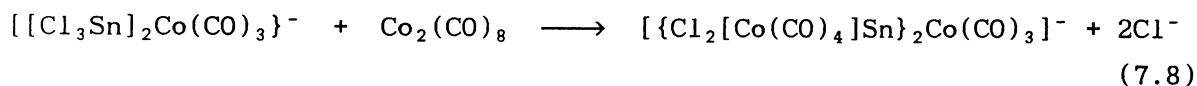
It is unfortunate that, as yet, the anionic species have not been characterised. It may be hoped that their identification will give further insight into the mechanism of this reaction. The carbonyl region infrared spectrum of these new products is not of particular help since the bands are very broad and ill-resolved. Attempts at the crystallisation of this product under various conditions were unsuccessful which could suggest this

to be a mixture but any proposals of the exact nature of these species are purely speculation at this stage.

7.7.2.2. Discussion of the reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Et}_4\text{N}^+[(\text{Cl}_3\text{Sn})_2\text{Co}(\text{CO})_3]^-$.

This reaction was carried out to find if the chlorine atoms of $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ could be replaced by $\text{Co}(\text{CO})_4$ units to provide anions of the form $\{[\text{Cl}_{3-n}[\text{Co}(\text{CO})_4]_n\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ ($n = 1 - 3$). From the results of this experiment it appears that this is possible, and may, in fact, be a promising synthetic route to these anions.

A simple balanced equation may be written for this process to give the observed anionic product, as shown in equation 7.8.



This equation, however does not account for the fairly large quantity of produced CoCl_2 , nor for the presence of a trace of $\text{Cl}_3\text{SnCo}(\text{CO})_4$. CoCl_2 is presumably formed by the reaction of Cl^- with $\text{Co}_2(\text{CO})_8$, while $\text{Cl}_3\text{SnCo}(\text{CO})_4$ is probably produced by the breakdown of a small amount of $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ caused by the complicated nature of the processes occurring in the reaction mixture.

In any event, it is clear that the major product of the reaction between $\{[\text{Cl}_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ and $\text{Co}_2(\text{CO})_8$ is $\{[\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$. As a progression of this, it could be suggested that the reaction of $\{[\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ with $\text{Co}_2(\text{CO})_8$ will provide $\{[\text{Cl}[\text{Co}(\text{CO})_4]_2\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$ and then further reaction of the latter with $\text{Co}_2(\text{CO})_8$ should give $\{[(\text{CO})_4\text{Co}]_3\text{Sn}]_2\text{Co}(\text{CO})_3\}^-$. It appears that this may be a useful synthetic route to these tin-cobalt carbonyl anions and it could be speculated that the use of a larger proportion of $\text{Co}_2(\text{CO})_8$ to the starting anion may give the higher cobalt tetracarbonyl substituted anions directly.

7.7.2.3. Discussion of the reaction of Ph_3SnLi with $\text{Cl}_3\text{SnCo}(\text{CO})_4$.

It is unfortunate that the extreme air sensitivity of the products of this reaction prevented their identification. It is, thus, not possible to say a great deal about this system, other than that it is clear that

$[\text{Ph}_3\text{Sn}]^-$ does not displace an axial carbonyl group in an analogous fashion to $[\text{SnCl}_3]^-$.

It is possible that Ph_3SnLi reacts with a carbonyl group in a similar manner to MeLi as depicted in figure 7.18.

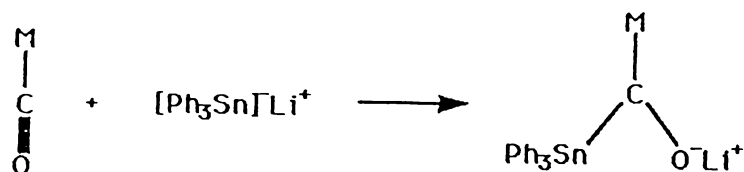


Figure 7.18

The limited time available, however, prevented any further study of this system.

7.8. Conclusion.

The chlorotin-cobalt carbonyl anion $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ was found as the major product of the reactions between $[\text{Cl}_3\text{Sn}]^-$ and $\text{R}_3\text{M}'\text{Co}(\text{CO})_4$. (R = alkyl, aryl group, $\text{M}' = \text{Sn}, \text{Ge}$; $\text{R} = \text{Cl}$, $\text{M}' = \text{Si}$) as well as from the reaction of $[\{\text{Cl}_3\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ with $\text{Co}_2(\text{CO})_8$. This anion is obviously a favoured structure and formation of unsymmetrical tin-cobalt carbonyl anions of the form $[\{\text{R}_3\text{M}^1\}\text{Co}(\text{CO})_3[\text{M}^2\text{R}'_3]]^-$ could not be established.

The X-ray crystal structure of $\text{Et}_4\text{N}^+[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ has been determined and compared with that reported for $\{\text{HB}(\text{pz})_3\}_2\text{Co}\}[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]$ [94]. This has shown that the cation has very little influence on the structure of the anion. An X-ray crystal structure determination of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ has also been performed and a comparison of this with that of $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ has shown that replacement of an axial carbonyl on $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ by $[\text{Cl}_2\text{SnCo}(\text{CO})_4]^-$ results in a contraction of the internal Sn-Co bonds and a lengthening of the external Sn-Co and Sn-Cl bonds. These changes have been attributed mainly to σ -bonding effects. A vibrational analysis of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]^-$ has been carried out, as well as a study of the ^{119}Sn NMR spectra of some chloro tin-cobalt carbonyl species.

The reaction of $\text{Et}_4\text{NSnCl}_3$ with $\text{Br}_3\text{SnCo}(\text{CO})_4$ provides a mixture of anions of general formula $[\text{Br}_x\text{Cl}_y\text{Sn}_2\text{Co}(\text{CO})_3]^-$ ($x + y = 6$). This mixture has been characterised by carbonyl region infrared spectroscopy, FAB MS, ^{119}Sn NMR spectroscopy and electron probe analysis. An X-ray crystal determination has also been carried out for $\text{Et}_4\text{N}[\{\text{Br}_2\text{ClSn}\}_2\text{Co}(\text{CO})_3]$ which has shown a lengthening of the Sn-Co bonds on replacement of Cl by Br.

CHAPTER 8: Concluding Remarks.

Although each chapter of this thesis has been treated as an individual piece of work there are some noticeable features which apply to several of the areas covered. These are thus brought together for discussion in this chapter.

8.1. Experimental limitations.

In previous work molecules with from 3 to 9 heavy atoms e.g. $\text{GeCo}_4(\text{CO})_{14}$ (*B*) and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (*E*) have been characterised in substantial detail by spectroscopy. Mass spectroscopy was particularly valuable giving the molecular weight and the number of carbonyl groups. Where mass spectroscopy was not feasible for species such as anions e.g. $[\text{GeCo}_5(\text{CO})_{16}]^-$ (*L*) and $[\text{GeCo}_7(\text{CO})_{20}]^-$ (*N*), or for very high molecular weight compounds e.g. $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (*G*) it was fortunate that these molecules yielded single crystals allowing the molecular structure to be determined by X-ray crystallography.

In this thesis, many of the investigations reported have led to molecules which are larger than those previously studied. For example, in Chapter 4 the reaction of Me_2GeH_2 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ was suggested to provide $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (*F*). Similarly, in Chapter 6 the reaction of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ with $[\text{Co}(\text{CO})_4]^-$ gave an anionic species suspected to be of the form $[\text{Ge}_3\text{Co}_9(\text{CO})_n]^-$. Also, where the hydride MeGeH_3 was used in reactions with neutral clusters (Chapters 3 and 4) the unsymmetrical nature of the reacting germanium group led to the possibility of mixtures of isomers. This has caused difficulties in characterisation of these new products since in the majority of cases single crystals suitable for X-ray crystallography were not obtained by the standard methods employed. These methods generally used various mixtures of solvents such as CH_2Cl_2 , Et_2O and hexane as well as diffusion of one of these solvents into a concentrated solution of the product in a more polar solvent. It might be worthwhile for future workers to attempt crystallisations from other solvents, such as toluene or acetonitrile.

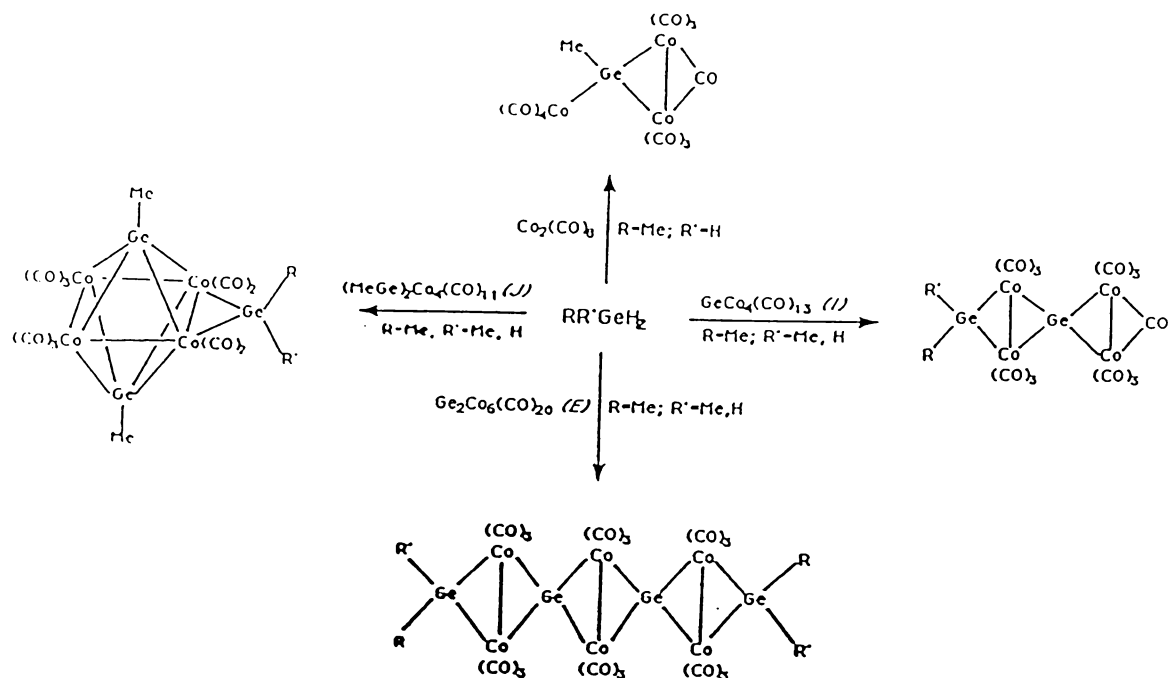
Difficulties in characterisation were also found for these new molecules since most had a molecular weight beyond the limits of the mass spectroscopy resources at the University of Waikato. Here, the highest possible mass observed is 1000 m.u. (see A1.4.3.). Recently some fast atom bombardment mass spectra were recorded of samples from this work at the University of Adelaide. Unfortunately, four out of the six samples sent

for this purpose did not survive transportation. If such facilities become available to this University there would be major improvements in the characterisation of at least some of the new products obtained in this work.

There are other features which could aid in the identification of these species which future workers might consider. For example, in the reactions of neutral clusters with substituted germanium hydrides, the use of hydrides such as $t\text{Bu}_2\text{GeH}_2$ or Ph_2GeH_2 , rather than Me_2GeH_2 as used in this work, could aid the crystallisation of the resulting products. The presence of the larger hydrocarbon groups on these extended chain molecules would alter the solubility of these species and would also sterically hinder them so that their conformation is locked. Mesityl or "supermesityl" groups could also be considered for this purpose. Similarly, for the new anionic species, it might be of advantage to use larger cations, such as alkali metals encapsulated in crown ethers. Of course, both of these suggestions involve the possible disadvantage of changing the chemistry of the reactions, thus not providing analogous products and it would be preferable to first attempt the modified crystallisation techniques mentioned above.

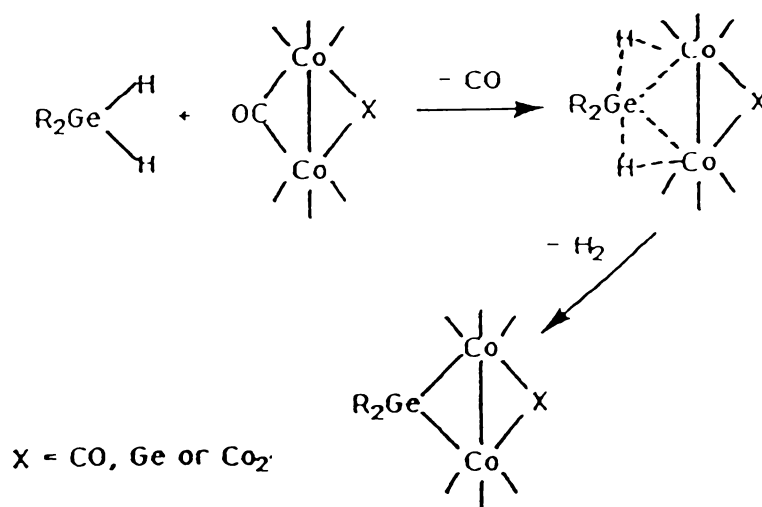
8.2. Reactions of substituted germanium hydrides with a bridging carbonyl group.

The results of Chapters 2, 3 and 4 show that a germanium hydride possessing a GeH_2 unit will replace a bridging carbonyl group across a Co-Co bond giving a GeCo_2 triangle. This occurs with retention of the basic cluster framework whatever the environment of the Co-Co bond. Some examples of this are shown in scheme 8.1.



Scheme 8.1.

In the reactions where incondensable gas evolution was monitored it appeared that CO release predominated in the early stages of reaction while H_2 evolution took over later. As discussed in Chapter 1 (section 1.2.1.) this observation was also reported for the reactions of GeH_4 or Ge_2H_6 with $Co_2(CO)_8$ [19]. This indicates that the bridging carbonyl ligand is released before the hydrogens from the replacing germanium group are lost. A general reaction pathway for this process is now proposed as shown in scheme 8.2.



Scheme 8.2.

The exact nature of the major intermediate in this process is unknown and the broken lines indicate that the positions of the hydrogens in this species cannot be determined at this stage.

It is interesting that in the most of these reactions of MeGeH_3 the third functional hydrogen does not appear to react further by abstracting a Co(CO)_4 unit from the cluster. This suggests that the germanium-cobalt framework is strong compared to the simple Co-Co bond of $\text{Co}_2(\text{CO})_8$. In some reactions, however, a product fraction soluble only in CH_2Cl_2 was also obtained which would indicate that some intramolecular reaction to form a *closa* species occurs.

8.3. A comparison of the reactivity of the homologues $\text{GeCo}_4(\text{CO})_{14}(\text{B})$, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}(\text{G})$.

From the work of Chapters 3, 4 and 6 it is apparent that the reactivities of $\text{GeCo}_4(\text{CO})_{14}(\text{B})$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}(\text{E})$ are quite similar when differences such as solubility are taken into account, while $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ appears to react by quite different pathways.

In the reactions of these clusters with an excess of MeGeH_3 or Me_2GeH_2 both $\text{GeCo}_4(\text{CO})_{14}$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ provided the disubstituted species, $[\text{MeGeR}]_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ or $[\text{MeGeR}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$ respectively, as the major product. For $\text{GeCo}_4(\text{CO})_{14}$, and probably for $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, the reaction proceeded *via* the monosubstituted compound, $[\text{MeGeR}]\text{GeCo}_4(\text{CO})_{13}$ or $[\text{MeGeR}]\text{Ge}_2\text{Co}_6(\text{CO})_{19}$, respectively. For $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ however, the reaction with MeGeH_3 appeared to provide $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ in only low yields (average 28%) and the major product appeared to be a *closa* hydrido cluster.

Similarly, in Chapter 6 the reaction of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ paralleled the analogous reaction of $\text{GeCo}_4(\text{CO})_{14}$ [28, 29] (see section 1.3.2.2) where condensation to $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ preceded reaction with the anion to yield $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-(\text{M})$. In contrast, $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ reacted readily with $[\text{Co}(\text{CO})_4]^-$ at room temperature and no evidence for an intermediate condensed species was found. It was thus apparent that a different pathway was involved in this process as compared to the former two, although the product which was thought to be of the form $[\text{Ge}_3\text{Co}_9(\text{CO})_n]^-$, may still be suggested to be the higher homologue to $[\text{GeCo}_5(\text{CO})_{16}]^-$ and $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^-$.

8.4. Reactions of the *closo* hexanuclear clusters, $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ where $\text{R} = \text{Me}, \text{Co}(\text{CO})_4$.

Until the work of this thesis was carried out, very little attention had been paid to the chemistry of the two *closo* hexanuclear clusters first prepared in this laboratory, $(\text{Me}_2\text{Ge})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ [87] and $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ [19]. The only feature which had been studied was the thermal stability of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ where it was found that this cluster decomposed above 70°C [21]. It was thus thought useful to gather all the results of experiments involving these two clusters into one section. These are shown in table 8.1.

Table 8.1. Results of experiments involving the *closo* hexanuclear clusters $(RGe)_2Co_4(CO)_{11}$ ($R = Me, Co(CO)_4$).

Cluster	Reagent	Solvent	Temperature (°C)	Duration	Products	Section
$(MeGe)_2Co_4(CO)_{11}$	Me_2GeH_2 (xs)	hexane	R.T.	16 weeks	Probably $(MeGe)_2Co_4(CO)_{10}[GeMe_2]$ + ?	4.8.1.
$(MeGe)_2Co_4(CO)_{11}$	$MeGeH_3$ (xs)	hexane	R.T.	28 weeks	Probably $(MeGe)_2Co_4(CO)_{10}[MeGeH]$ + ?	4.8.1.
$[(CO)_4CoGe]_2Co_4(CO)_{11}$	Me_2GeH_2 (xs)	CH_2Cl_2	R.T.	19 weeks	?	4.8.2.
$[(CO)_4CoGe]_2Co_4(CO)_{11}$	$MeGeH_3$ (xs)	CH_2Cl_2	R.T.	21 weeks	?	4.8.2.
$(MeGe)_2Co_4(CO)_{11}$	CO (30 atm)	CH_2Cl_2	R.T.	16 hours	Possibly $(MeGe)_2Co_4(CO)_{12}$	5.4.
$[(CO)_4CoGe]_2Co_4(CO)_{11}$	CO (30 atm)	CH_2Cl_2	R.T.	16 hours	Possibly $[(CO)_4CoGe]_2Co_4(CO)_{12}$	5.4.
$(MeGe)_2Co_4(CO)_{11}$	PPh_3 (1:1)	hexane	40	2 hours	$[Ph_3PCo(CO)_3]_2$ + low yield of possibly $(MeGe)_2Co_4(CO)_{10}PPh_3$ + decomposition product	5.5.
$[(CO)_4CoGe]_2Co_4(CO)_{11}$	PPh_3 (1:1)	hexane	40	3 hours	$[Ph_3PCo(CO)_3]_2$ + decomposition product	5.5.

Table 8.1. continued

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	$\text{P}(\text{OEt})_3(1:1)$	hexane	50	3½ hours	$[(\text{EtO})_3\text{PCo}(\text{CO})_3]_2$ + low yield of possibly $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11-n}-$ $[\text{P}(\text{OEt})_3]_n$ (n = 1-4) + decomposition product	5.5.
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$	$\text{P}(\text{OEt})_3(1:1)$	hexane	50	4 hours	$[(\text{EtO})_3\text{PCo}(\text{CO})_3]_2$ + low yield of possibly $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11-n}-$ $[\text{P}(\text{OEt})_3]_n$ (n = 1-4) + decomposition product	5.5.
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	$\text{PPh}_3(1:1)$ (ETC)	THF	R.T.	5 mins	$[\text{Ph}_3\text{PCo}(\text{CO})_3]_2$ + probably $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{PPh}_3$ + decomposition product	5.6.
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	$\text{PPh}_3(1:5)$ (ETC)	THF	R.T.	5 mins	$[\text{Ph}_3\text{PCo}(\text{CO})_3]_2$ + low yield of probably $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{PPh}_3$ + decomposition product	5.6.
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	$\text{P}(\text{OEt})_3(1:5)$ (ETC)	THF	R.T.	5 mins	Probably $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}\text{P}(\text{OEt})_3$	5.6.

Table 8.1. continued

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	$\text{P}(\text{OEt})_3(1:5)$ (ETC)	THF	R.T.	5 mins	$[(\text{EtO})_3\text{PCo}(\text{CO})_3]_2$ + low yield of probably $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11-n}$ $[\text{P}(\text{OEt})_3]_n$ ($n = 1-3$) + decomposition product	5.6.
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	$^t\text{BuNC}$	hexane	R.T.	1 hour	Possibly insertion product + $[\text{Co}(\text{CO})_4]^-$ + decomposition product	5.7.
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	$^t\text{BuNC}$	THF	R.T.	15 mins	Possibly insertion product + $[\text{Co}(\text{CO})_4]^-$ + decomposition product	5.7.
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	XyNC	THF	R.T.	5 mins	$[\text{Co}(\text{CO})_4]^-$ + decomposition product	5.7.
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$	$\text{Et}_4\text{N}[\text{Co}(\text{CO})_4]$	CH_2Cl_2	R.T.	3 hours	$\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}](M)$ + Co(II) species	6.4.
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$	$\text{PPN}[\text{Mn}(\text{CO})_5]$	CH_2Cl_2	R.T.	3 hours	Possibly $\text{PPN}[\text{Ge}_2\text{Co}_6\text{Mn}(\text{CO})_{22}]$ + $\text{Mn}_2(\text{CO})_{10}$ + $[\text{Co}(\text{CO})_4]^-$	6.4.
$[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$	$\text{Na}_2[\text{Fe}(\text{CO})_4]$	CH_2Cl_2	50	24 hours	No reaction	6.6.
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{12}$	$\text{PPN}[\text{Co}(\text{CO})_4]$	CH_2Cl_2	50	6 hours	Unidentified anionic species	6.5.

These studies have been concerned with the substitution of the apical groups, of the bridging carbonyl ligands or of the terminal carbonyl ligands. It is apparent that the most promising system is the replacement of the bridging carbonyl group by a germanium hydride species, since this gave worthwhile yields of reasonably well characterised products. Substitution of the apical group of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}(\text{K})$ by $[\text{Mn}(\text{CO})_5]^-$ appeared to also result in addition to the cluster providing an anionic species which has not yet been formally identified. Thus it would appear that a more suitable method for the preparation of clusters of the form $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ (R = for example $\text{Mn}(\text{CO})_5$, $\text{Fe}(\text{CO})_2\text{Cp}$) is by using disubstituted digermanes in the original preparation (ie. $(\text{CO})_5\text{MnGeH}_2\text{GeH}_2\text{Mn}(\text{CO})_5$ or $\text{Cp}(\text{CO})_2\text{FeGeH}_2\text{GeH}_2\text{Fe}(\text{CO})_2\text{Cp}$). The reaction of RGe_2H_5 species (R = $\text{Co}(\text{CO})_4$, $\text{Mn}(\text{CO})_5$, Me , Et) with $\text{Co}_2(\text{CO})_8$ has provided mixed terminal clusters of the form $(\text{RGe})\text{Co}_4(\text{CO})_{11}[\text{GeCo}(\text{CO})_4]$ [39] while reaction of $\text{MeGeH}_2\text{GeH}_2\text{Me}$ yielded $(\text{Me}_2\text{Ge})_2\text{Co}_4(\text{CO})_{11}$ (see section 3.8). Ligand substitution of the terminal carbonyl groups was generally found to result in large scale degradation of the cluster, even when conducted under relatively mild conditions, and formation of disubstituted dicobaltcarbonyl species appeared to be very favourable.

In most cases the reactivity of the two clusters is similar. The only occasion where there is an obvious difference is in the reactions with $[\text{Co}(\text{CO})_4]^-$. Here $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ reacted readily at room temperature while $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ required heating to 50°C . This may be rationalised by the anticipated involvement of the terminal $\text{Co}(\text{CO})_4$ units of $[(\text{CO})_4\text{CoGe}]_2\text{Co}_4(\text{CO})_{11}$ in this reaction, while $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ must react by a different pathway. In those systems where the products and conditions are similar it may be assumed that the pathway does not involve the terminal groups and is confined to the metal core.

8.5. General conclusions.

The work of this thesis has provided new routes to the known clusters $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}(\text{J})$ (section 3.8), $\text{Et}_4\text{N}[\text{Ge}_2\text{Co}_7(\text{CO})_{21}](\text{M})$ (section 6.4.1) and $\text{Et}_4\text{N}[\{\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn}\}_2\text{Co}(\text{CO})_3]$ (section 7.4).

The new clusters $[\text{MeGeR}]_2\text{GeCo}_4(\text{CO})_{12}(\text{D})$ (R = Me , H) have been synthesised and fully characterised (section 3.4).

A new tin-cobalt carbonyl anion of probable formation $[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]^-$ has been synthesized and spectroscopically and

crystallographically examined (section 7.6).

Reasonably good, though incomplete, evidence for the formation of $[\text{MeGeR}]_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}(\text{F})$ has been obtained (section 4.4.1). Similarly, fairly strong evidence for a species of the form $[\text{Ge}_2\text{MnCo}_6(\text{CO})_{22}]^-$ was found (section 6.4.2.).

Clear indications of several new products - $[\text{MeGeH}]_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ (4.4.2), $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{MeGeR}]$ ($\text{R} = \text{Me}, \text{H}$) (4.8.1), $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}[\text{P}(\text{OEt})_3]$ (5.6), $[\text{Ge}_3\text{Co}_9(\text{CO})_n]$ (6.4.5) and $\{[\text{Cl}_3\text{Sn}]\text{Co}(\text{CO})_3\{\text{GeCl}\}_3\}^-$ (7.6) - have been obtained together with suggestions of several other unidentified new species.

Many of the new neutral clusters are more stable to oxidation than the parent clusters, however the majority of the anionic germanium-cobalt carbonyl species are very sensitive to handling making their further study less attractive. However, this worker hopes that, in the future, at least some of the compounds observed in this work will be identified and fully characterised.

APPENDICES.

APPENDIX 1: General Experimental Procedures

A1.1. Manipulations of Materials

The compounds in this work were generally sensitive to oxidation and/or hydrolysis, making the exclusion of air essential. Standard vacuum line techniques were employed in the manipulation of volatile compounds. Involatile species were handled under a nitrogen atmosphere and stored in nitrogen flushed glassware or glove-boxes. The less air sensitive nature of some of the higher molecular mass compounds dealt with meant that they could be handled in air for relatively long periods without appreciable decomposition.

Apiezon 'M' or 'N' grease was used to lubricate joints and taps exposed to high vacuum. These hydrocarbon greases have a low vapour pressure and are thus used extensively in vacuum line work.

All glassware was rigourously acid washed to avoid the decomposition of compounds that may result from alkaline impurities [193].

A1.2 Fractionation

Volatile mixtures were separated by passage through a series of progressively colder traps, selectively condensing each of the components. Where compounds had high mutual solubility or similar pressures, repeated fractionations were necessary to obtain enriched fractions.

The constant temperatures required for this process were achieved using slush baths. Compounds suitable for this purpose are listed in table A1.1

Table A1.1. Constant temperature (slush) baths

Constituent	Temperature (°C)
ice/water/salt	0 to -20
carbon tetrachloride	- 22
chlorobenzene	- 45
chloroform	- 63
ethyl acetate	- 82
toluene	- 96
n-propanol	-127
liquid nitrogen	-196

A1.3 Purification of Solvents

A variety of organic solvents were used in this work. Where solvents were redistilled before use LR grade proved of sufficient purity, however for those solvents which were purified simply by standing over sodium wire, AR grade was used. Table A1.2 lists the commonly used solvents and their particular purification technique.

Table A1.2. Solvent purification techniques.

Solvent	Purification technique
Hexane/pentane	Dried over Na wire and distilled from CaH_2 under a nitrogen atmosphere.
Benzene	Dried over Na wire.
Dichloromethane	Distilled from phosphorus pentoxide under a nitrogen atmosphere.
Diethyl ether/ Tetrahydrofuran	Dried over Na wire and distilled from Na/benzophenone under a nitrogen atmosphere.
Di-n-butyl ether	Dried over sodium wire.

Solvents used for NMR spectroscopy, commonly deuterio-chloroform or deuterobenzene, were of spectroscopic grade.

A1.4. Instrumental Techniques.

A1.4.1. Infrared spectroscopy

Infrared spectroscopy was used in sample identification and characterisation, and to monitor sample purity. Routine spectra were recorded on a PYE UNICAM Pu9510 spectrophotometer ($4000\text{--}200\text{ cm}^{-1}$) while definitive spectra were recorded on a Perkin-Elmer 180 spectrophotometer ($4000\text{--}180\text{ cm}^{-1}$).

Gaseous samples, which were usually reagents for reactions, or the product of some intermediate step in a reaction sequence, were contained within a gas cell of 10 cm path length and 5 cm diameter KBr windows. Sample pressures of 1-2 cm Hg were generally used. A cell with a cold finger attachment was employed for small samples or those of low volatility.

Involatile compounds were analysed as solids or in solution. The region of particular interest was the carbonyl stretching region between 2150 and 1750 cm^{-1} , which was calibrated against HCl/DCI [2]. Solutions were contained within a standard 0.1 mm solution cell with KBr windows. Solid samples were prepared as nujol mulls in a nitrogen glove-box, and were held between KBr windows.

A1.4.2. Raman spectroscopy.

Raman spectra were recorded by either Dr Tony Cartner, Miss Jacky Carroll or Mr Brett Loper on a SPEX 1403 0.85 m Double Spectrometer. For the compounds used in this work the He-Ne laser line at 632.8 nm proved the most convenient.

Samples were either single crystals or fine powders. These were packed into glass capillaries under N_2 and then sealed.

A1.4.3. Mass spectroscopy.

(i) Standard mass spectroscopy.

Mass spectroscopy was a useful tool in sample identification and characterisation. Samples were prepared in the laboratory and transported to Ruakura Agricultural Research Centre, Hamilton, where their mass spectra were recorded on a Varian CH5 mass spectrometer (range 30-1000 mass units). Volatile samples were introduced as gases through the reservoir, while involatile samples were introduced as solids or solutions (the solvent being removed using instrument pumps) through the probe. The preparation (i.e. mounting on the gold cup of the spectrometer probe) and transportation of solid, and solution samples, together with their insertion into the spectrometer probe, were carried out in a plastic bag fitted with gloves for sample manipulation, under a nitrogen or argon atmosphere to avoid possible decomposition.

Spectra were computer calibrated using polyfluorokerosene as a reference. Although accurate at low mass units, higher mass species were sometimes found to differ from the known values by one or two mass units. This limited accuracy for high mass compounds made it difficult to distinguish, for example, between the loss of one CO unit (of 28 m.u.) and the loss of two methyl groups (30 m.u.). It was also impossible to distinguish between CH_4 , CH_3 or CH_2 loss from a molecule. However this technique is of particular use in determining the metal skeleton of a new compound. As described in Chapter 1, section 1.4.4., the five naturally

occurring isotopes of germanium give rise to characteristic intensity patterns depending on how many Ge atoms are present in a molecule. These patterns facilitated the identification of compounds through the analysis of their mass spectra. It should be noted that while in the early part of this work the machine worked reasonable well, the standard of the spectra obtained has deteriorated until recently they were of little use.

(ii) FAB mass spectroscopy.

Recently attempts have been made to obtain fast atom bombardment mass spectra for some of the compounds synthesised in this work. This technique is particularly useful in the identification of high molecular weight species or of ionic compounds. Six samples were sent overseas for this purpose but unfortunately only two survived transportation.

The FAB mass spectra were recorded by M.J. Liddell at the University of Adelaide on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA, with ion accelerating potential 8 kV. Samples were dissolved in CH_2Cl_2 (ca. 0.5M) and a drop of this solution was added to a drop of matrix (3-nitrobenzyl alcohol or dithioerythritol/dithiothreitol (1/6)), the volatile solvent evaporated and the resulting solution applied to the FAB probe tip.

A1.4.4. Nuclear magnetic resonance spectroscopy

(i) ^1H NMR spectroscopy.

^1H NMR Spectroscopy was used to characterise some compounds and to follow the progress of certain reactions. ^1H NMR studies were carried out on a JEOL 90 MHz Multinuclear Fourier transform spectrometer, under normal operating conditions. This instrument was also fitted with a variable temperature option which was used for reaction studies. All samples were run in sealed tubes of 5 mm o.d. as either CDCl_3 or C_6D_6 solutions. The solvent was also used as the internal standard.

The NMR tubes containing reacting mixtures were opened under vacuum to enable complete recovery of the contents for further characterisation.

(ii) ^{119}Sn NMR spectroscopy

^{119}Sn NMR spectroscopy was used to characterise some compounds produced in this work. All ^{119}Sn NMR spectra, other than that of $\text{Cl}_3\text{SnCo}(\text{CO})_4$ were recorded by Dr. Jan Coddington at Auckland University on a Bruker AM 400 Multinuclear Fourier Transform spectrometer. The ^{119}Sn NMR spectrum of $\text{Cl}_3\text{SnCo}(\text{CO})_4$ was recorded by Mr Ralph Thomson on a JEOL FX90Q spectrometer. In all cases the samples were run as CH_2Cl_2 solutions in sealed 8 mm o.d. tubes within 10 mm o.d. tubes. On both machines 90° tip angles and 1 second pulse delays were used. The other conditions used on each machine are outlined in table A1.3.

Table A1.3. Conditions used for ^{119}Sn NMR spectroscopy.

Spectrometer	Observation frequency (MHz)	Sweep width (Hz)	Decoupling	External Standard (w.r.t. Me_4Sn as 0ppm)
FX90Q	33.35	20000	Gated	Et_4Sn :0.4ppm
AM400	149.21	83333	No ^1H decoupling	$^n\text{Bu}_3\text{SnCl}$:150ppm

A1.4.5. Electron probe analysis.

Electron probe analysis was used for heavy element identification. This technique uses a high energy beam of electrons to displace core electrons in the target atoms. These are then identified by the emission spectra produced when the excited atoms return to the ground state. Since the electron beam can be focussed onto an area as small as 10^{-8} cm^2 extremely small samples can be studied, and multiple analysis of the same sample can be performed.

All electron probe analyses were performed by Mr Stephen Stokes on an ORTEC Energy-dispersive X-ray analyser attached to a JEOL JS-M35 scanning electron microscope, used to locate the sample site to be analysed. The use of the computer package RATIO allowed determination of approximate elemental ratios which were usually accurate to about 10%.

A1.5. Measurement of incondensable gases.

The volume of incondensable gas evolved in a reaction was measured using a Toepler pump fitted with a gas burette. A travelling microscope was used to accurately measure pressure differences and repeated measurements on the same gas quantity were made to improve the accuracy of the result. This was usually reliable to within 1%. The proportion of H_2 and CO present was determined by the average molecular weight method - the weight of a known pressure of gas within a known volume was determined and from this the average molecular weight calculated. The accuracy of this measurement depended on the weight of the gas relative to that of the vessel in which it was contained, and was optimised by using as high a pressure as possible. Usually the proportion of H_2 and CO present was accurate to 2-4%, however where the amount of gas was very small the error incurred could be as high as 10%. The total quantities of H_2 and CO evolved were obtained by relating the proportion of H_2 and CO back to the initial measurement of total gas quantity.

APPENDIX 2: Preparations of Mono- and Dimethylgermane

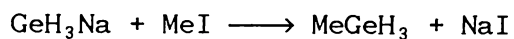
A2.1. General

Until recently mono- and dimethylgermane were prepared in this laboratory by the lithium aluminium hydride reduction of the appropriate methylgermanium chloride in di-n-butyl ether. However the rising cost of these chemicals made it desirable to find an alternative method. In particular, Me_2GeCl_2 is no longer stocked by any of the major chemical companies.

This appendix covers some of the available routes to these species which have been attempted here. This is not intended to be a complete review of all documented routes to MeGeH_3 and Me_2GeH_2 but it is hoped that this will be of use of further workers in this area.

A2.2. Preparations of Monomethylgermane.

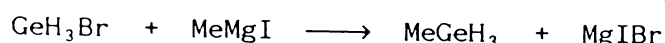
A2.2.1. By the reaction of germyl sodium with methyl iodide [194].



Germyl sodium was typically prepared by condensing liquid ammonia (12 mls) onto freshly cut sodium metal (0.12 g; 5.00 mmoles) in a 100 ml flask, and the sodium dissolved at -63.5°C . This solution was then frozen slowly to prevent splattering of the metal. Monogermane (3.00 mmoles by volume) was condensed into the flask and left to react at -63.5°C for $\frac{1}{2}$ - $\frac{3}{4}$ hour. The solution was frozen down, hydrogen pumped out and further GeH_4 (3.00 mmoles) condensed onto the solid. The solution was again left to react to completion (usually a further $\frac{1}{2}$ - $\frac{3}{4}$ hour) marked by the disappearance of the blue colour of the sodium/ammonia solution.

Unreacted GeH_4 and most of the ammonia was distilled off at -63.5°C and then methyl iodide (0.568 g; 4.00 mmoles) was condensed into the flask. This was then left to react at room temperature in the dark for 1 hour. The volatile material was then passed, in small batches, over concentrated sulphuric acid to remove the last traces of ammonia. Although a deficit of MeI was used, a small amount of unreacted MeI commonly remained. Fractionation was not suitable for its separation from the produced MeGeH_3 , and it was found that the best method for its removal was to pass the volatiles over a new amount of GeH_3Na which then increased the yield of MeGeH_3 . This method generally provided around 2 mmoles of MeGeH_3 which is a 40% yield based on initial GeH_4 .

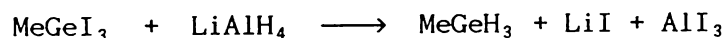
A2.2.2. By the reaction of bromogermane with methyl magnesium iodide.



Bromogermane was prepared by the direct reaction of bromine with a large excess of monogermane at -127°C [195]. At this temperature the reaction was very slow and could be monitored by leaving the flask open to the manometer on the vacuum line. The reaction was complete when the slush bath had reached room temperature, then the BrGeH_3 was separated from unreacted GeH_4 and produced HBr by fractionation. The yield of BrGeH_3 obtained was generally around 70%.

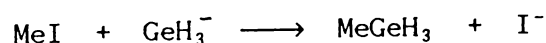
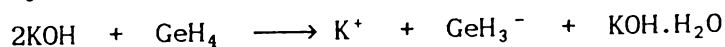
BrGeH_3 (0.462 g; 3.00 mmoles) was condensed onto a di-n-butyl ether solution of MeMgI (containing approximately 6 mmoles of Grignard reagent from 0.146 g, 6 mmoles Mg and 0.852 g, 6 mmoles MeI used in its preparation). The mixture was left to react for 3 hours and then all volatile material removed and fractionated. A low yield of MeGeH_3 (ca. 10% based on initial BrGeH_3) was obtained by this route.

A2.2.3. By reaction of germanium (II) iodide with methyl iodide and reduction of the produced MeGeI_3 [196]



This method was not attempted and is only summarised here: GeI_2 (10 g; 31 mmoles) is introduced into an ampoule capable of withstanding high gas pressures and air is removed. MeI (4.8 g; 33 mmoles) is condensed in and the ampoule sealed. The tube is heated in an oven at 110°C for at least 24 hours. After cooling the excess MeI is distilled out and then the product may be purified by vacuum distillation. (Bp of MeGeI_3 = 237°C at 252 mm; Mp. 48.5°C [196]). This method is reported to provide MeGeI_3 almost quantitatively [196]. This may then be reduced by lithium aluminium hydride in di-n-butyl ether to produce MeGeH_3 .

A2.2.4. By reaction of germyl potassium with methyl iodide [197].

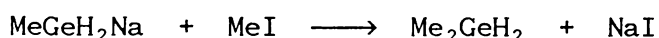


Again, this method was not attempted and is only summarised here: KOH powder (2.8 g; 49 mmoles) and 1,2-dimethoxyethane (10 mls) are placed in a 50 ml round-bottomed flask which is attached via a tap adaptor to the vacuum

line. The mixture is frozen down and thoroughly degassed. GeH_4 (2 mmoles) is condensed into the flask and the stopcock closed. The mixture is warmed to room temperature and is shaken vigorously for $\frac{1}{2}$ hour. The mixture is then frozen down again and any H_2 formed through the slow decomposition of GeH_3K is removed by pumping. MeI (3 mmoles) is condensed into the flask and this is then allowed to warm to about 15°C while shaking occasionally when a white precipitate should form. The precipitate is difficult to see in the presence of KOH . The reaction is then quenched in a -78°C bath. If the reaction is left too long secondary processes yielding Me_2GeH_2 and Me_2O occur. Produced MeGeH_3 is purified by fractionation and a yield of 80% is reported by this method [197].

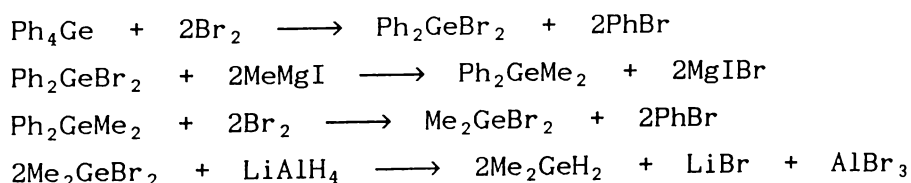
A2.3. Preparations of Dimethylgermane.

A2.3.1. By reaction of methylgermyl sodium with methyl iodide.



Methyl germyl sodium was prepared in an analogous fashion to germyl sodium (A2.2.1.) using an excess of MeGeH_3 with a sodium in ammonia solution held at -63.5°C . A deficit of MeI was added to the solid MeGeH_2Na after unreacted MeGeH_3 and most of the ammonia had been pumped away, and this was left to react at room temperature for 1 hour in the dark. All volatile material was distilled away from the solid residues and slowly passed over concentrated sulphuric acid to remove any remaining NH_3 . Any unreacted MeI was removed by either fractionation or by rereacting the volatile mixture with a fresh batch of MeGeH_2Na . This method provided a 25% yield of Me_2GeH_2 .

A2.3.2. By a multi-step process from tetraphenylgermane.



Tetraphenylgermane (10 g; 26 mmoles) and ethylene bromide (60 mls) were placed in a three-necked flask fitted with a condenser, a motor driven stirrer and a dropping funnel. The mixture was heated to reflux temperature and then bromine (8.78 g; 55 mmoles) was added dropwise to the refluxing solution. Refluxing was continued until there was no visible evidence of Br_2 vapour (ca. $\frac{1}{2}$ hour after the last addition of Br_2). The

ethylene bromide, bromobenzene and residual bromine were removed by distillation [198]. The residue was diluted with toluene (50 mls) and was then added dropwise to a stirred solution of MeMgI (ca. 60 mmoles) in Et₂O (100 mls) which had been prepared in situ. The Et₂O was then replaced by toluene through distillation and the mixture refluxed for 2 hours. Excess MeMgI was destroyed by the addition of dilute hydrochloric acid. The solution was then heated to boiling and the toluene layer separated while still hot. Most of the toluene was removed by distillation then the residue was returned to a three-necked flask fitted with a condenser, a motor driven stirrer and a dropping funnel. Ethylene bromide (60 mls) was added and the mixture brought up to reflux temperature. Bromine (8.78 g; 55 mmoles) was added dropwise and the mixture left refluxing as before. Ethylene bromide, bromobenzene and bromine were removed by distillation, then the residue was diluted with 10 mls of di-n-butyl ether. This was then transferred to a separating funnel attached to a third three-necked flask connected to a vacuum line. This flask contained LiAlH₄ (3.77 g; 100 mmoles) in d-n-butyl ether (80 mls) and was kept under vacuum. The Me₂GeBr₂ solution was added slowly and the produced Me₂GeH₂ removed at regular intervals. Also present among the final products were small amounts of Me₃GeH, and other phenyl substituted species but these were easily separated from Me₂GeH₂. Fortunately no MeGeH₃ was obtained - presumably as a result of the excess bromine used in the first step - which would be difficult to separate. The yield of Me₂GeH₂ obtained based on initial Ph₄Ge was 36%.

Note, direct bromination of Me₄Ge was attempted but no reaction occurred, even when using AlBr₃ as a catalyst.

A2.3.3. By selective methylation of germanium tetrachloride by tetramethylsilane.

According to Bordeaux *et al.* [199] using catalytic amounts of aluminium tribromide, selective mono-, di-, tri- or tetramethylation of GeCl₄ may be achieved in high yield with Me₄Si as the methylating reagent.

Three workers in this laboratory attempted the preparation of Me₂GeCl₂ using the route described in the above report. This stated the optimum conditions as 56 hours of reaction at 200°C using a 1:1 ratio of GeCl₄ to Me₄Si with 3-5 mol% AlBr₃. Unfortunately, none of the workers here obtained any Me₂GeCl₂ at all and it appeared that the germanium containing products were dimeric species of some sort.

APPENDIX 3: Structural Parameters Obtained From the X-ray Crystallographic
 Structure Determinations Carried Out in This Work.

Note: For $\text{Et}_4\text{N}[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]$ the disorder of the halogen atoms prevented the identification of individual bromines and chlorines. These are thus referred to in the tables as X(1), X(2) etc.

Table A3.1

Final positional parameters and equivalent thermal parameters
for $\text{Ge}[\text{Co}_2(\text{CO})_6(\mu\text{-GeMe}_2)]_2$

ATOM	x	y	z	Ueq
Ge(1)	0.2182(1)	0.2426(1)	0.7664(1)	0.036
Ge(2)	0.2009(1)	0.4238(1)	0.6265(1)	0.052
Ge(3)	0.4326(1)	0.1064(1)	0.8050(1)	0.047
Co(1)	0.3181(1)	0.3973(1)	0.8399(1)	0.044
Co(2)	0.0467(1)	0.3437(1)	0.7749(1)	0.043
Co(3)	0.1928(1)	0.0974(1)	0.8588(1)	0.042
Co(4)	0.2881(1)	0.1261(1)	0.6060(1)	0.041
C(11)	0.2938(8)	0.5099(6)	0.910(1)	0.061
C(12)	0.3584(9)	0.3637(6)	1.009(1)	0.064
C(13)	0.4748(9)	0.4080(6)	0.751(1)	0.063
C(21)	-0.0626(9)	0.2812(6)	0.635(1)	0.062
C(22)	-0.0036(9)	0.3008(5)	0.941(1)	0.061
C(23)	-0.0233(8)	0.4480(5)	0.8061(8)	0.053
C(31)	0.0063(9)	0.0872(5)	0.8171(8)	0.051
C(32)	0.1914(8)	-0.0241(6)	0.8536(9)	0.056
C(33)	0.2244(9)	0.1408(6)	1.041(1)	0.061
C(41)	0.3086(9)	0.0107(6)	0.5455(9)	0.058
C(42)	0.4277(9)	0.1977(6)	0.5359(9)	0.056
C(43)	0.131(1)	0.1222(6)	0.4970(9)	0.059
C(1)	0.236(1)	0.3676(7)	0.4398(9)	0.086
C(2)	0.190(1)	0.5517(6)	0.597(1)	0.086
C(3)	0.5218(9)	-0.0057(6)	0.803(1)	0.069
C(4)	0.5819(9)	0.2038(6)	0.888(1)	0.075
O(11)	0.2770(7)	0.5830(4)	0.9548(8)	0.091
O(12)	0.3906(8)	0.3490(5)	1.1210(7)	0.095
O(13)	0.5802(7)	0.4178(5)	0.6971(8)	0.095

O(21)	-0.1418(8)	0.2440(5)	0.5477(9)	0.103
O(22)	-0.0365(7)	0.2763(4)	1.0455(7)	0.088
O(23)	-0.0747(7)	0.5134(4)	0.8259(7)	0.077
O(31)	-0.1115(6)	0.0780(4)	0.7904(8)	0.085
O(32)	0.1891(7)	-0.1009(4)	0.8523(8)	0.093
O(33)	0.2400(8)	0.1629(5)	1.1588(7)	0.095
O(41)	0.3222(7)	-0.0623(4)	0.5038(7)	0.084
O(42)	0.5174(7)	0.2393(4)	0.4838(8)	0.089
O(43)	0.0368(8)	0.1157(5)	0.4224(7)	0.098

Table A3.2 Final positional and thermal parameters
of calculated hydrogen atoms for $\text{Ge}[\text{Co}_2(\text{CO})_6(\mu\text{-GeMe}_2)]_2$

ATOM	X/A	Y/B	Z/C	U11
H(11)	0.218(1)	0.3002(7)	0.4300(9)	0.130
H(12)	0.333(1)	0.3889(7)	0.4162(9)	0.130
H(13)	0.171(1)	0.3901(7)	0.3752(9)	0.130
H(21)	0.169(1)	0.5866(6)	0.685(1)	0.130
H(22)	0.117(1)	0.5547(6)	0.523(1)	0.130
H(23)	0.282(1)	0.5782(6)	0.566(1)	0.130
H(31)	0.4719(9)	-0.0627(6)	0.751(1)	0.130
H(32)	0.5470(9)	-0.0169(6)	0.900(1)	0.130
H(33)	0.6076(9)	0.0154(6)	0.755(1)	0.130
H(41)	0.5539(9)	0.2649(6)	0.893(1)	0.130
H(42)	0.6541(9)	0.1998(6)	0.818(1)	0.130
H(43)	0.6200(9)	0.1934(6)	0.981(1)	0.130

Table A3.3 Thermal parameters for $\text{Ge}[\text{Co}_2(\text{CO})_6(\mu\text{-GeMe}_2)]_2$

ATOM	U11	U22	U33	U23	U13	U12
Ge(1)	0.0369(4)	0.0322(4)	0.0415(4)	0.0050(3)	0.0048(3)	0.0078(3)
Ge(2)	0.0582(5)	0.0453(5)	0.0554(5)	0.0164(4)	0.0113(4)	0.0121(4)
Ge(3)	0.0403(5)	0.0506(5)	0.0531(5)	0.0094(4)	0.0026(4)	0.0140(4)
Co(1)	0.0433(6)	0.0367(6)	0.0520(6)	0.0019(5)	0.0069(5)	0.0032(5)
Co(2)	0.0413(6)	0.0354(6)	0.0563(7)	0.0085(5)	0.0083(5)	0.0114(5)
Co(3)	0.0411(6)	0.0383(6)	0.0487(6)	0.0117(5)	0.0080(5)	0.0099(5)
Co(4)	0.0423(6)	0.0384(6)	0.0428(6)	0.0030(4)	0.0046(5)	0.0110(5)
C(11)	0.048(5)	0.044(5)	0.085(7)	0.001(5)	0.002(4)	-0.002(4)
C(12)	0.069(6)	0.055(6)	0.061(6)	-0.006(5)	0.006(5)	-0.003(5)
C(13)	0.056(6)	0.057(6)	0.075(6)	0.009(5)	0.012(5)	0.000(4)
C(21)	0.051(5)	0.042(5)	0.095(7)	0.003(5)	-0.003(5)	0.013(4)
C(22)	0.058(6)	0.045(5)	0.083(7)	0.011(5)	0.020(5)	0.016(4)
C(23)	0.058(5)	0.050(5)	0.054(5)	0.016(4)	0.010(4)	0.012(4)
C(31)	0.054(5)	0.034(4)	0.064(5)	0.007(4)	0.002(4)	-0.002(4)
C(32)	0.048(5)	0.062(6)	0.063(5)	0.020(5)	0.010(4)	0.014(4)
C(33)	0.071(6)	0.056(5)	0.063(6)	0.025(5)	0.008(5)	0.020(5)
C(41)	0.059(5)	0.058(6)	0.054(5)	-0.004(4)	0.004(4)	0.011(5)
C(42)	0.058(5)	0.052(5)	0.065(6)	0.013(4)	0.019(5)	0.024(4)
C(43)	0.075(6)	0.055(5)	0.047(5)	-0.004(4)	0.005(5)	0.019(5)
C(1)	0.121(9)	0.081(7)	0.068(6)	0.023(6)	0.020(6)	0.040(7)
C(2)	0.116(9)	0.056(6)	0.098(8)	0.033(6)	0.030(7)	0.027(6)
C(3)	0.068(6)	0.078(7)	0.072(6)	0.023(5)	0.007(5)	0.036(5)
C(4)	0.062(6)	0.071(7)	0.094(7)	0.007(6)	-0.010(5)	0.020(5)
O(11)	0.086(5)	0.052(4)	0.126(6)	-0.029(4)	-0.002(4)	0.010(4)
O(12)	0.124(6)	0.102(6)	0.049(4)	0.004(4)	-0.008(4)	-0.008(5)
O(13)	0.061(4)	0.106(6)	0.115(6)	0.011(5)	0.032(4)	-0.007(4)
O(21)	0.089(5)	0.070(5)	0.140(7)	-0.013(5)	-0.047(5)	0.010(4)
O(22)	0.110(6)	0.073(5)	0.094(5)	0.030(4)	0.055(4)	0.025(4)

O(23)	0.090(5)	0.056(4)	0.095(5)	0.009(3)	0.019(4)	0.038(4)
O(31)	0.039(4)	0.085(5)	0.132(6)	0.021(4)	0.001(4)	0.008(3)
O(32)	0.108(6)	0.045(4)	0.135(6)	0.031(4)	0.020(5)	0.018(4)
O(33)	0.138(7)	0.097(6)	0.050(4)	0.003(4)	0.007(4)	0.021(5)
O(41)	0.096(5)	0.048(4)	0.105(5)	-0.013(4)	0.010(4)	0.017(4)
O(42)	0.078(5)	0.080(5)	0.118(6)	0.032(4)	0.042(4)	0.016(4)
O(43)	0.086(5)	0.129(7)	0.079(5)	-0.017(4)	-0.025(4)	0.038(5)

Bond lengths and angles for $\text{Ge}[\text{Co}_2(\text{CO})_6(\mu\text{-GeMe}_2)]_2$

Bond Lengths (Å).

Ge(1) ---Co(1)	2.367(1)	Co(3) ---Co(4)	2.644(1)
Ge(1) ---Co(2)	2.387(1)	Co(3) ---C(31)	1.801(8)
Ge(1) ---Co(3)	2.383(1)	Co(3) ---C(32)	1.791(9)
Ge(1) ---Co(4)	2.372(1)	Co(3) ---C(33)	1.78(1)
Ge(2) ---Co(1)	2.378(1)	Co(4) ---C(41)	1.787(8)
Ge(2) ---Co(2)	2.349(1)	Co(4) ---C(42)	1.769(9)
Ge(2) ---C(1)	1.939(9)	Co(4) ---C(43)	1.790(9)
Ge(2) ---C(2)	1.961(8)	C(11) ---O(11)	1.159(9)
Ge(3) ---Co(3)	2.363(1)	C(12) ---O(12)	1.14(1)
Ge(3) ---Co(4)	2.372(1)	C(13) ---O(13)	1.144(9)
Ge(3) ---C(3)	1.979(8)	C(21) ---O(21)	1.141(9)
Ge(3) ---C(4)	1.951(8)	C(22) ---O(22)	1.130(9)
Co(1) ---Co(2)	2.639(1)	C(23) ---O(23)	1.154(8)
Co(1) ---C(11)	1.782(8)	C(31) ---O(31)	1.136(9)
Co(1) ---C(12)	1.78(1)	C(32) ---O(32)	1.132(9)
Co(1) ---C(13)	1.745(9)	C(33) ---O(33)	1.128(9)
Co(2) ---C(21)	1.753(9)	C(41) ---O(41)	1.141(9)
Co(2) ---C(22)	1.806(9)	C(42) ---O(42)	1.137(9)
Co(2) ---C(23)	1.778(8)	C(43) ---O(43)	1.115(9)

Bond Angles (°).

Co(1) -Ge(1) -Co(2)	67.5(1)	C(21) -Co(2) -C(22)	109.6(4)
Co(1) -Ge(1) -Co(3)	138.3(1)	C(21) -Co(2) -C(23)	103.9(4)
Co(1) -Ge(1) -Co(4)	133.1(1)	C(22) -Co(2) -C(23)	95.9(3)
Co(2) -Ge(1) -Co(3)	125.4(1)	Ge(1) -Co(3) -Ge(3)	82.6(1)
Co(2) -Ge(1) -Co(4)	138.5(1)	Ge(1) -Co(3) -Co(4)	56.0(1)
Co(3) -Ge(1) -Co(4)	67.6(1)	Ge(1) -Co(3) -C(31)	87.3(2)

Co(1) -Ge(2) -Co(2)	67.9(1)	Ge(1) -Co(3) -C(32)	156.0(3)
Co(1) -Ge(2) -C(1)	123.8(3)	Ge(1) -Co(3) -C(33)	96.9(3)
Co(1) -Ge(2) -C(2)	117.4(3)	Ge(3) -Co(3) -Co(4)	56.2(1)
Co(2) -Ge(2) -C(1)	120.7(3)	Ge(3) -Co(3) -C(31)	155.0(3)
Co(2) -Ge(2) -C(2)	121.1(3)	Ge(3) -Co(3) -C(32)	85.9(2)
C(1) -Ge(2) -C(2)	103.9(4)	Ge(3) -Co(3) -C(33)	96.1(3)
Co(3) -Ge(3) -Co(4)	67.9(1)	Co(4) -Co(3) -C(31)	99.3(3)
Co(3) -Ge(3) -C(3)	119.0(3)	Co(4) -Co(3) -C(32)	100.2(3)
Co(3) -Ge(3) -C(4)	124.1(3)	Co(4) -Co(3) -C(33)	140.8(3)
Co(4) -Ge(3) -C(3)	119.2(3)	C(31) -Co(3) -C(32)	94.5(3)
Co(4) -Ge(3) -C(4)	121.6(3)	C(31) -Co(3) -C(33)	107.8(4)
C(3) -Ge(3) -C(4)	103.3(4)	C(32) -Co(3) -C(33)	105.2(4)
Ge(1) -Co(1) -Ge(2)	82.6(1)	Ge(1) -Co(4) -Ge(3)	82.7(1)
Ge(1) -Co(1) -Co(2)	56.6(1)	Ge(1) -Co(4) -Co(3)	56.4(1)
Ge(1) -Co(1) -C(11)	148.6(3)	Ge(1) -Co(4) -C(41)	154.8(3)
Ge(1) -Co(1) -C(12)	88.5(3)	Ge(1) -Co(4) -C(42)	96.3(2)
Ge(1) -Co(1) -C(13)	101.8(3)	Ge(1) -Co(4) -C(43)	90.3(2)
Ge(2) -Co(1) -Co(2)	55.5(1)	Ge(3) -Co(4) -Co(3)	55.9(1)
Ge(2) -Co(1) -C(11)	87.2(3)	Ge(3) -Co(4) -C(41)	84.7(3)
Ge(2) -Co(1) -C(12)	164.3(3)	Ge(3) -Co(4) -C(42)	91.9(3)
Ge(2) -Co(1) -C(13)	87.9(3)	Ge(3) -Co(4) -C(43)	158.7(3)
Co(2) -Co(1) -C(11)	93.3(3)	Co(3) -Co(4) -C(41)	98.5(3)
Co(2) -Co(1) -C(12)	108.7(3)	Co(3) -Co(4) -C(42)	137.5(3)
Co(2) -Co(1) -C(13)	137.3(3)	Co(3) -Co(4) -C(43)	103.6(3)
C(11) -Co(1) -C(12)	93.8(4)	C(41) -Co(4) -C(42)	105.9(4)
C(11) -Co(1) -C(13)	107.5(4)	C(41) -Co(4) -C(43)	93.7(4)
C(12) -Co(1) -C(13)	106.7(4)	C(42) -Co(4) -C(43)	108.9(4)
Ge(1) -Co(2) -Ge(2)	82.8(1)	Co(1) -C(11) -O(11)	179.5(7)
Ge(1) -Co(2) -Co(1)	55.9(1)	Co(1) -C(12) -O(12)	174.5(8)
Ge(1) -Co(2) -C(21)	95.2(3)	Co(1) -C(13) -O(13)	176.9(8)
Ge(1) -Co(2) -C(22)	87.1(2)	Co(2) -C(21) -O(21)	174.7(8)

Ge(1) -Co(2) -C(23)	158.3(3)	Co(2) -C(22) -O(22)	178.0(7)
Ge(2) -Co(2) -Co(1)	56.6(1)	Co(2) -C(23) -O(23)	176.9(7)
Ge(2) -Co(2) -C(21)	94.7(3)	Co(3) -C(31) -O(31)	178.0(7)
Ge(2) -Co(2) -C(22)	154.4(3)	Co(3) -C(32) -O(32)	178.8(7)
Ge(2) -Co(2) -C(23)	85.5(2)	Co(3) -C(33) -O(33)	175.4(8)
Co(1) -Co(2) -C(21)	138.8(3)	Co(4) -C(41) -O(41)	178.4(8)
Co(1) -Co(2) -C(22)	98.4(3)	Co(4) -C(42) -O(42)	175.6(8)
Co(1) -Co(2) -C(23)	102.5(3)	Co(4) -C(43) -O(43)	175.2(8)

Table A3.5

Final positional parameters for $\text{Et}_4\text{N}^+[(\text{Cl}_2[\text{Co}(\text{CO})_4]\text{Sn})_2\text{Co}(\text{CO})_3]^-$.

ATOM	x	y	z	ATOM	x	y	z
Sn(1)	0.8730(1)	0.1310(1)	0.2593(1)	C(22)	1.132(2)	0.0705(5)	0.092(1)
Co(1)	0.8793(2)	0.2500(1)	0.2525(1)	O(22)	1.124(1)	0.0763(4)	-0.0169(8)
Co(2)	1.1440(1)	0.0579(1)	0.2631(1)	C(23)	1.335(1)	0.0065(5)	0.2760(9)
Cl(1)	0.7208(2)	0.0999(1)	0.4425(2)	O(23)	1.4530(8)	-0.0275(3)	0.2831(8)
Cl(2)	0.6682(3)	0.0855(1)	0.0955(2)	C(24)	0.998(1)	-0.0019(4)	0.3166(8)
C(11)	0.648(1)	0.2500(1)	0.220(1)	O(24)	0.9081(8)	-0.0417(3)	0.3513(6)
O(11)	0.497(1)	0.2500(1)	0.2014(9)	N	0.567(1)	0.250(0)	0.7758(8)
C(12)	0.966(1)	0.2500(1)	0.417(1)	C(1)	0.678(2)	0.2060(6)	0.693(1)
O(12)	1.0219(9)	0.2500(1)	0.5244(7)	C(111)	0.686(2)	0.2068(7)	0.867(1)
C(13)	1.020(1)	0.2500(1)	0.1242(9)	C(2)	0.448(2)	0.2102(7)	0.679(1)
O(13)	1.1096(9)	0.2500(1)	0.0430(7)	C(211)	0.464(2)	0.2113(9)	0.867(2)
C(21)	1.240(1)	0.1171(5)	0.370(1)	C(3)	0.812(1)	0.1663(4)	0.7815(9)
O(21)	1.3085(8)	0.1574(4)	0.4324(9)	C(4)	0.320(1)	0.1662(5)	0.769(1)

Table A3.6 Thermal parameters
of $\text{Et}_4\text{N}^+ \{ [\text{Cl}_2\{\text{Co}(\text{CO})_4\}\text{Sn}\}_2\text{Co}(\text{CO})_3 \}^-$.

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ATOM	U11	U22	U33	U23	U13	U12
Sn(1)	0.0219(4)	0.0241(4)	0.0277(4)	0.0027(2)	0.0011(2)	-0.0033(2)
Co(1)	0.0140(7)	0.0239(8)	0.0246(8)	0.0000(0)	-0.0001(6)	0.0000(0)
Co(2)	0.0314(6)	0.0244(7)	0.0438(7)	0.0004(5)	0.0093(5)	0.0019(5)
Cl(1)	0.029(1)	0.045(1)	0.039(1)	0.0114(9)	0.0092(8)	0.0004(9)
Cl(2)	0.052(1)	0.040(1)	0.039(1)	0.004(1)	-0.0133(9)	-0.020(1)
C(11)	0.022(7)	0.042(7)	0.031(6)	0.000(0)	0.001(5)	0.000(0)
O(11)	0.018(5)	0.081(7)	0.062(6)	0.000(0)	-0.002(4)	0.000(0)
C(12)	0.014(5)	0.031(6)	0.039(7)	0.000(0)	0.006(5)	0.000(0)
O(12)	0.025(4)	0.051(5)	0.022(4)	0.000(0)	-0.004(3)	0.000(0)
C(13)	0.020(5)	0.025(6)	0.023(5)	0.000(0)	0.001(5)	0.000(0)
O(13)	0.024(4)	0.054(6)	0.038(5)	0.000(0)	0.008(4)	0.000(0)
C(21)	0.025(5)	0.044(6)	0.085(7)	-0.019(5)	-0.001(5)	0.022(4)
O(21)	0.031(4)	0.079(6)	0.158(8)	-0.067(6)	-0.014(4)	0.017(4)
C(22)	0.081(7)	0.045(6)	0.054(6)	0.009(5)	0.028(6)	0.016(6)
O(22)	0.128(7)	0.097(7)	0.061(5)	0.004(5)	0.033(5)	0.045(6)
C(23)	0.040(5)	0.040(6)	0.072(6)	-0.005(5)	0.025(5)	-0.005(5)
O(23)	0.041(4)	0.033(4)	0.121(6)	0.001(4)	0.023(4)	0.009(3)
C(24)	0.034(5)	0.033(5)	0.050(5)	0.000(4)	-0.001(4)	0.015(4)
O(24)	0.039(3)	0.037(4)	0.082(5)	0.020(3)	0.007(3)	-0.007(3)
N	0.016(4)	0.030(5)	0.024(4)	0.000(0)	-0.003(4)	0.000(0)
C(1)	0.021(8)	0.020(8)	0.023(7)	-0.017(6)	0.004(6)	0.000(6)
C(111)	0.038(9)	0.035(9)	0.023(8)	0.008(7)	-0.004(7)	0.007(7)
C(2)	0.014(7)	0.028(9)	0.037(8)	-0.009(7)	-0.002(6)	-0.010(6)
C(211)	0.050(8)	0.05(1)	0.05(1)	0.000(9)	0.000(7)	0.000(7)
C(3)	0.024(4)	0.040(5)	0.070(6)	0.002(5)	0.003(4)	0.014(4)
C(4)	0.039(6)	0.047(7)	0.14(1)	0.002(7)	0.024(6)	-0.021(5)

Table A3.7 Bond Lengths and Angles for
 $\text{Et}_4\text{N}^+ \{ [\text{Cl}_2\{\text{Co}(\text{CO})_4\}\text{Sn}\}_2\text{Co}(\text{CO})_3 \}^-$.

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Bond Lengths (Å).

Sn(1) ---Co(1)	2.474(1)	C(12) ---O(12)	1.16(1)
Sn(1) ---Co(2)	2.561(1)	C(13) ---O(13)	1.13(1)
Sn(1) ---Cl(1)	2.394(2)	C(21) ---O(21)	1.15(1)
Sn(1) ---Cl(2)	2.396(2)	C(22) ---O(22)	1.13(1)
Co(1) ---C(11)	1.76(1)	C(23) ---O(23)	1.14(1)
Co(1) ---C(12)	1.77(1)	C(24) ---O(24)	1.15(1)
Co(1) ---C(13)	1.78(1)	N ---C(1)	1.55(1)
Co(2) ---C(21)	1.77(1)	N ---C(2)	1.54(2)
Co(2) ---C(22)	1.78(1)	C(1) ---C(1)	1.83(3)
Co(2) ---C(23)	1.80(1)	C(1) ---C(2)	1.75(2)
Co(2) ---C(24)	1.788(9)	C(2) ---C(2)	1.65(3)
C(11) ---O(11)	1.15(1)		

Bond Angles (°).

Co(1) -Sn(1) -Co(2)	125.2(1)	Co(1) -C(12) -O(12)	179.7(4)
Co(1) -Sn(1) -Cl(1)	107.7(1)	Co(1) -C(13) -O(13)	179.9(2)
Co(1) -Sn(1) -Cl(2)	112.8(1)	Co(2) -C(21) -O(21)	175(1)
Co(2) -Sn(1) -Cl(1)	105.8(1)	Co(2) -C(22) -O(22)	177(1)
Co(2) -Sn(1) -Cl(2)	104.5(1)	Co(2) -C(23) -O(23)	177.9(8)
Cl(1) -Sn(1) -Cl(2)	97.1(1)	Co(2) -C(24) -O(24)	177.8(7)
Sn(1) -Co(1) -C(11)	89.1(1)	C(1) -N -C(1A)	71.0(8)
Sn(1) -Co(1) -C(12)	88.8(1)	C(1) -N -C(2)	69.0(7)
Sn(1) -Co(1) -C(13)	92.0(1)	C(1) -N -C(2A)	111.6(9)
C(11) -Co(1) -C(12)	117.8(5)	C(1) -N -C(1)	72(1)
C(11) -Co(1) -C(13)	121.0(5)	C(2) -N -C(1A)	111.7(8)
C(12) -Co(1) -C(13)	121.2(4)	C(2) -N -C(2A)	78.9(9)
Sn(1) -Co(2) -C(21)	83.5(2)	C(2) -N -C(2)	65(1)
Sn(1) -Co(2) -C(22)	85.8(3)	N -C(1) -C(1A)	54.2(7)

Sn(1) -Co(2) -C(23)	176.6(3)	N	-C(1) -C(2)	55.1(7)
Sn(1) -Co(2) -C(24)	83.9(2)	N	-C(1) -C(3)	110.5(9)
C(21) -Co(2) -C(22)	120.1(5)	C(2)	-C(1) -C(1A)	91.8(9)
C(21) -Co(2) -C(23)	94.4(4)	C(2)	-C(1) -C(3)	133(1)
C(21) -Co(2) -C(24)	121.6(4)	N	-C(2) -C(1)	55.9(6)
C(22) -Co(2) -C(23)	97.6(4)	N	-C(2) -C(2A)	49.9(6)
C(22) -Co(2) -C(24)	115.5(4)	N	-C(2) -C(4)	105(1)
C(23) -Co(2) -C(24)	95.0(4)	C(1)	-C(2) -C(2A)	86.6(8)
Co(1) -C(11) -O(11)	178(1)	C(1)	-C(2) -C(4)	123(1)

Table A3.8

Final positional parameters for Cl₂Sn[Co(CO)₄]₂

ATOM	x	y	z	ATOM	x	y	z
Sn(1)	0.77920(4)	0.16874(4)	0.64690(3)	O(3)	1.2297(5)	0.1730(6)	0.9500(5)
Co(1)	0.9864(1)	0.1726(1)	0.7896(1)	C(4)	0.9420(6)	0.0389(7)	0.8395(6)
Co(2)	0.5747(1)	0.1869(1)	0.6738(1)	O(4)	0.9186(5)	-0.0461(5)	0.8727(5)
Cl(1)	0.7811(2)	0.3139(2)	0.5152(2)	C(5)	0.5165(6)	0.1704(7)	0.5262(6)
Cl(2)	0.7717(2)	-0.0030(2)	0.5430(2)	O(5)	0.4804(5)	0.1607(6)	0.4336(4)
C(1)	1.0387(6)	0.1718(6)	0.6696(6)	C(6)	0.4296(6)	0.1961(6)	0.6944(6)
O(1)	1.0735(4)	0.1732(5)	0.5978(4)	O(6)	0.3390(5)	0.2017(5)	0.7081(6)
C(2)	0.9417(6)	0.3134(7)	0.8304(6)	C(7)	0.6190(6)	0.0601(7)	0.7594(6)
O(2)	0.9173(5)	0.4009(5)	0.8540(5)	O(7)	0.6410(5)	-0.0200(5)	0.8135(5)
C(3)	1.1356(6)	0.1734(7)	0.8892(6)	C(8)	0.6209(6)	0.3312(8)	0.7240(7)
				O(8)	0.6451(5)	0.4239(6)	0.7533(6)

Table A3.9

Thermal parameters for $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$

ATOM	U11	U22	U33	U23	U13	U12
Sn(1)	0.0325(2)	0.0439(3)	0.0412(2)	-0.0009(2)	0.0092(2)	-0.0011(2)
Co(1)	0.0352(4)	0.0482(6)	0.0432(5)	-0.0001(4)	0.0083(3)	0.0002(4)
Co(2)	0.0335(4)	0.0497(6)	0.0489(5)	-0.0043(4)	0.0101(4)	-0.0006(4)
Cl(1)	0.064(1)	0.089(2)	0.071(1)	0.034(1)	0.018(1)	0.003(1)
Cl(2)	0.061(1)	0.070(1)	0.082(1)	-0.033(1)	0.022(1)	-0.004(1)
C(1)	0.039(3)	0.049(5)	0.061(4)	0.003(4)	0.013(3)	0.004(3)
O(1)	0.055(3)	0.090(4)	0.072(3)	-0.004(3)	0.034(3)	-0.002(3)
C(2)	0.047(4)	0.061(6)	0.048(4)	-0.009(4)	0.009(3)	-0.008(4)
O(2)	0.074(4)	0.058(4)	0.109(5)	-0.032(4)	0.028(3)	0.000(3)
C(3)	0.049(4)	0.079(6)	0.065(5)	-0.001(4)	0.008(4)	0.004(4)
O(3)	0.051(3)	0.132(6)	0.095(4)	0.007(4)	-0.015(3)	-0.001(4)
C(4)	0.044(4)	0.067(6)	0.064(5)	0.010(4)	0.010(4)	0.012(4)
O(4)	0.083(4)	0.066(4)	0.113(5)	0.036(4)	0.026(4)	-0.003(3)
C(5)	0.038(4)	0.091(6)	0.060(5)	0.003(4)	0.013(3)	-0.003(4)
O(5)	0.068(4)	0.152(6)	0.052(3)	-0.006(4)	-0.002(3)	-0.014(4)
C(6)	0.044(4)	0.062(5)	0.071(5)	-0.009(4)	0.014(4)	-0.003(4)
O(6)	0.052(3)	0.100(5)	0.127(5)	-0.011(4)	0.042(3)	0.000(3)
C(7)	0.038(4)	0.062(5)	0.062(5)	0.003(4)	0.013(3)	-0.005(3)
O(7)	0.070(4)	0.077(5)	0.095(4)	0.027(4)	0.011(3)	-0.009(3)
C(8)	0.042(4)	0.063(6)	0.090(6)	-0.014(5)	0.020(4)	0.005(4)
O(8)	0.070(4)	0.058(4)	0.171(7)	-0.037(4)	0.020(4)	0.000(3)

Table A3.10

Bond Lengths and Angles for Cl₂Sn[Co(CO)₄]₂

Bond Lengths (Å).

Sn(1) ---Co(1)	2.533(1)	Co(2) ---C(7)	1.796(8)
Sn(1) ---Co(2)	2.535(1)	Co(2) ---C(8)	1.798(9)
Sn(1) ---Cl(1)	2.373(2)	C(1) ---O(1)	1.114(7)
Sn(1) ---Cl(2)	2.363(2)	C(2) ---O(2)	1.112(8)
Co(1) ---C(1)	1.821(7)	C(3) ---O(3)	1.130(8)
Co(1) ---C(2)	1.825(8)	C(4) ---O(4)	1.132(8)
Co(1) ---C(3)	1.808(7)	C(5) ---O(5)	1.128(8)
Co(1) ---C(4)	1.802(9)	C(6) ---O(6)	1.130(8)
Co(2) ---C(5)	1.799(8)	C(7) ---O(7)	1.130(8)
Co(2) ---C(6)	1.804(7)	C(8) ---O(8)	1.134(8)

Bond Angles (°).

Co(1) -Sn(1) -Co(2)	129.3(1)	Sn(1) -Co(2) -C(6)	178.5(2)
Co(1) -Sn(1) -Cl(1)	106.0(1)	Sn(1) -Co(2) -C(7)	84.9(2)
Co(1) -Sn(1) -Cl(2)	106.0(1)	Sn(1) -Co(2) -C(8)	86.1(2)
Co(2) -Sn(1) -Cl(1)	105.0(1)	C(5) -Co(2) -C(6)	95.5(3)
Co(2) -Sn(1) -Cl(2)	106.0(1)	C(5) -Co(2) -C(7)	119.5(3)
Cl(1) -Sn(1) -Cl(2)	101.3(1)	C(5) -Co(2) -C(8)	116.2(4)
Sn(1) -Co(1) -C(1)	84.0(2)	C(6) -Co(2) -C(7)	93.6(3)
Sn(1) -Co(1) -C(2)	85.7(2)	C(6) -Co(2) -C(8)	94.9(3)
Sn(1) -Co(1) -C(3)	178.7(3)	C(7) -Co(2) -C(8)	122.3(4)
Sn(1) -Co(1) -C(4)	85.5(2)	Co(1) -C(1) -O(1)	178.0(6)
C(1) -Co(1) -C(2)	116.6(3)	Co(1) -C(2) -O(2)	177.6(7)
C(1) -Co(1) -C(3)	94.8(3)	Co(1) -C(3) -O(3)	178.6(8)
C(1) -Co(1) -C(4)	120.3(3)	Co(1) -C(4) -O(4)	177.4(7)
C(2) -Co(1) -C(3)	95.5(3)	Co(2) -C(5) -O(5)	179.5(6)
C(2) -Co(1) -C(4)	120.8(3)	Co(2) -C(6) -O(6)	179.5(6)

C(3)	-Co(1)	-C(4)	94.5(3)	Co(2)	-C(7)	-O(7)	176.4(6)
Sn(1)	-Co(2)	-C(5)	84.9(2)	Co(2)	-C(8)	-O(8)	177.0(7)

Table A3.11

Final positional and parameters for Et₄N[(Br₂ClSn)₂Co(CO)₃]

ATOM	x	y	z	U11	U22	U33	U23	U13	U12
Sn(1)	0.2501(2)	-0.0324(2)	0.4401(1)	0.031(1)	0.019(1)	0.024(1)	-0.0002(8)	0.0095(8)	-0.0047(8)
Sn(2)	0.1642(2)	-0.3728(2)	0.5781(1)	0.030(1)	0.015(1)	0.025(1)	0.0024(8)	0.0065(8)	-0.0020(8)
Co(1)	0.2072(3)	-0.1997(3)	0.5104(1)	0.029(2)	0.013(2)	0.024(2)	0.000(2)	0.010(2)	-0.003(2)
X(11)*	0.3883(3)	0.1574(3)	0.4786(1)	0.026(2)	0.012(2)	0.026(2)	0.001(1)	0.006(2)	-0.009(1)
X(12)*	0.3436(3)	-0.1046(3)	0.3530(1)	0.033(2)	0.023(2)	0.012(2)	-0.002(1)	0.020(2)	-0.001(2)
X(13)*	0.0595(4)	0.0855(3)	0.3807(2)	0.036(2)	0.026(2)	0.030(2)	0.005(2)	0.008(2)	0.000(2)
X(21)*	0.2914(3)	-0.5770(3)	0.5787(2)	0.033(2)	0.016(2)	0.032(2)	0.000(2)	0.004(2)	0.001(2)
X(22)*	0.2157(3)	-0.3273(3)	0.6896(1)	0.024(2)	0.012(2)	0.008(2)	-0.002(1)	0.003(1)	0.001(1)
X(23)*	-0.0595(3)	-0.4541(3)	0.5711(1)	0.030(2)	0.023(2)	0.027(2)	0.000(2)	0.005(2)	-0.005(2)
O(1)	-0.071(2)	-0.160(2)	0.4674(7)	0.03(1)	0.03(1)	0.03(1)	0.010(9)	-0.002(9)	-0.01(1)
O(2)	0.332(2)	-0.041(2)	0.6129(8)	0.08(1)	0.03(1)	0.03(1)	0.01(1)	0.01(1)	-0.02(1)

O(3)	0.363(2)	-0.386(2)	0.455(1)	0.07(2)	0.02(1)	0.08(2)	-0.02(1)	0.06(1)	0.01(1)
C(1)	0.039(3)	-0.178(2)	0.485(1)	0.04(2)	0.00(1)	0.02(1)	0.00(1)	0.00(1)	0.01(1)
C(2)	0.286(2)	-0.106(2)	0.570(1)	0.03(1)	0.02(1)	0.01(1)	0.00(1)	0.00(1)	-0.01(1)
C(3)	0.305(3)	-0.315(3)	0.476(1)	0.07(2)	0.02(2)	0.00(1)	-0.01(1)	0.00(1)	-0.06(2)
N(1)	0.728(2)	-0.324(2)	0.739(1)	0.03(1)	0.03(1)	0.05(1)	0.02(1)	0.02(1)	-0.01(1)
C(11)	0.685(3)	-0.306(2)	0.674(1)	0.05(2)	0.02(1)	0.02(2)	0.00(1)	0.00(1)	0.00(1)
C(12)	0.568(3)	-0.386(3)	0.645(1)	0.06(2)	0.02(2)	0.03(2)	-0.01(1)	0.02(1)	-0.03(1)
C(21)	0.772(3)	-0.468(2)	0.757(1)	0.04(2)	0.02(1)	0.04(2)	0.01(1)	0.00(1)	0.00(1)
C(22)	0.876(3)	-0.514(3)	0.726(1)	0.07(2)	0.02(2)	0.03(2)	-0.02(1)	0.03(2)	0.00(1)
C(31)	0.845(3)	-0.227(3)	0.761(1)	0.03(2)	0.02(1)	0.06(2)	0.01(1)	0.01(1)	-0.02(1)
C(32)	0.909(3)	-0.247(3)	0.825(1)	0.03(2)	0.03(2)	0.03(2)	0.00(1)	-0.02(1)	0.00(1)
C(41)	0.623(2)	-0.297(2)	0.774(1)	0.02(1)	0.03(2)	0.04(2)	0.01(1)	0.01(1)	-0.01(1)
C(42)	0.556(3)	-0.161(3)	0.760(2)	0.04(2)	0.03(2)	0.08(2)	0.02(2)	0.02(2)	0.02(2)

* X is 0.66 Br/ 0.33 Cl

Table A3.12 Final positional and thermal parameters
of calculated hydrogen atoms for $\text{Et}_4\text{N}[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]$

ATOM	X/A	Y/B	Z/C	U11
H(111)	0.663(3)	-0.214(2)	0.666(1)	0.010
H(112)	0.757(3)	-0.330(2)	0.655(1)	0.010
H(121)	0.543(3)	-0.371(3)	0.602(1)	0.030
H(122)	0.494(3)	-0.364(3)	0.663(1)	0.030
H(123)	0.592(3)	-0.477(3)	0.653(1)	0.030
H(211)	0.697(3)	-0.526(2)	0.747(1)	0.010
H(212)	0.806(3)	-0.471(2)	0.800(1)	0.010
H(221)	0.893(3)	-0.600(3)	0.744(1)	0.030
H(222)	0.953(3)	-0.458(3)	0.739(1)	0.030
H(223)	0.859(3)	-0.521(3)	0.682(1)	0.030
H(311)	0.911(3)	-0.241(3)	0.737(1)	0.010
H(312)	0.812(3)	-0.138(3)	0.756(1)	0.010
H(321)	0.962(3)	-0.170(3)	0.839(1)	0.030
H(322)	0.963(3)	-0.325(3)	0.834(1)	0.030
H(323)	0.836(3)	-0.251(3)	0.845(1)	0.030
H(411)	0.556(2)	-0.365(2)	0.765(1)	0.010
H(412)	0.663(2)	-0.299(2)	0.817(1)	0.010
H(421)	0.496(3)	-0.153(3)	0.787(2)	0.030
H(422)	0.508(3)	-0.154(3)	0.718(2)	0.030
H(423)	0.622(3)	-0.092(3)	0.768(2)	0.030

Table A3.13

Bond Lengths and Angles for $\text{Et}_4\text{N}[(\text{Br}_2\text{ClSn})_2\text{Co}(\text{CO})_3]$

Bond Lengths (Å).

Sn(1) ---Co(1)	2.463(4)	O(1) ---C(1)	1.16(3)
Sn(1) ---X(11)	2.486(3)	O(2) ---C(2)	1.21(3)
Sn(1) ---X(12)	2.512(3)	O(3) ---C(3)	1.13(3)
Sn(1) ---X(13)	2.490(4)	N(1) ---C(11)	1.48(3)
Sn(2) ---Co(1)	2.466(4)	N(1) ---C(21)	1.59(3)
Sn(2) ---X(21)	2.490(4)	N(1) ---C(31)	1.59(3)
Sn(2) ---X(22)	2.542(3)	N(1) ---C(41)	1.53(3)
Sn(2) ---X(23)	2.469(4)	C(11) ---C(12)	1.51(3)
Co(1) ---C(1)	1.75(3)	C(21) ---C(22)	1.50(3)
Co(1) ---C(2)	1.74(2)	C(31) ---C(32)	1.48(3)
Co(1) ---C(3)	1.85(3)	C(41) ---C(42)	1.57(3)

Bond Angles (°).

Co(1) -Sn(1) -X(11)	119.4(1)	Sn(2) -Co(1) -C(3)	89.5(7)
Co(1) -Sn(1) -X(12)	117.9(1)	C(1) -Co(1) -C(2)	118(1)
Co(1) -Sn(1) -X(13)	117.5(1)	C(1) -Co(1) -C(3)	123(1)
X(11) -Sn(1) -X(12)	102.6(1)	C(2) -Co(1) -C(3)	118(1)
X(11) -Sn(1) -X(13)	98.9(1)	Co(1) -C(1) -O(1)	177(2)
X(12) -Sn(1) -X(13)	96.6(1)	Co(1) -C(2) -O(2)	175(2)
Co(1) -Sn(2) -X(21)	116.5(1)	Co(1) -C(3) -O(3)	178(2)
Co(1) -Sn(2) -X(22)	118.0(1)	C(11) -N(1) -C(21)	113(2)
Co(1) -Sn(2) -X(23)	120.0(1)	C(11) -N(1) -C(31)	107(2)
X(21) -Sn(2) -X(22)	98.5(1)	C(11) -N(1) -C(41)	114(2)
X(21) -Sn(2) -X(23)	102.5(1)	C(21) -N(1) -C(31)	109(2)
X(22) -Sn(2) -X(23)	97.4(1)	C(21) -N(1) -C(41)	103(2)
Sn(1) -Co(1) -Sn(2)	178.0(2)	C(31) -N(1) -C(41)	108(2)

Sn(1) -Co(1) -C(1)	90.1(8)	N(1) -C(11) -C(12)	114(2)
Sn(1) -Co(1) -C(2)	90.2(8)	N(1) -C(21) -C(22)	111(2)
Sn(1) -Co(1) -C(3)	88.8(7)	N(1) -C(31) -C(32)	113(2)
Sn(2) -Co(1) -C(1)	89.9(7)	N(1) -C(41) -C(42)	112(2)
Sn(2) -Co(1) -C(2)	91.6(8)		

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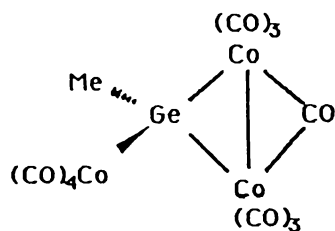
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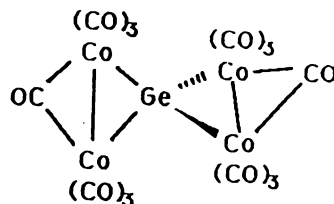
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Molecular Structures of Commonly Cited Clusters.

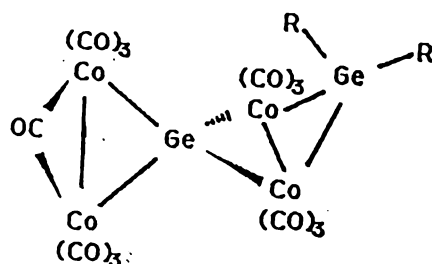
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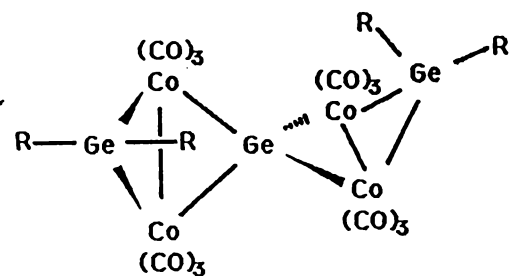
B $\text{GeCo}_4(\text{CO})_{14}$



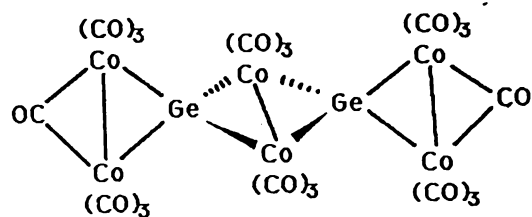
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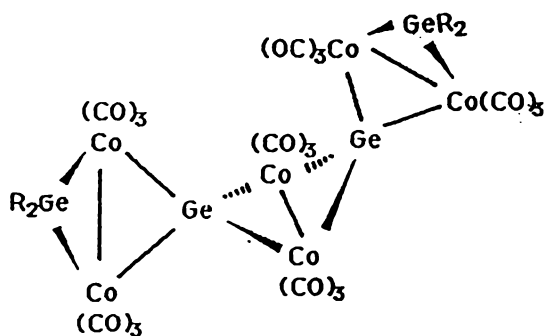
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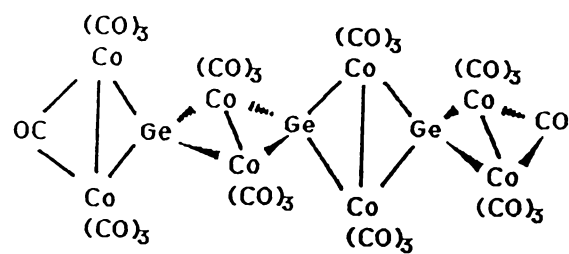
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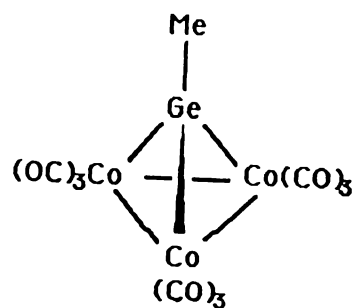
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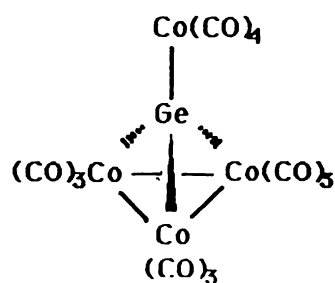
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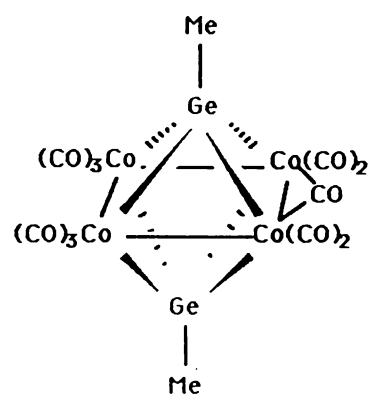
H $\text{MeGeCo}_3(\text{CO})_9$



I $\text{GeCo}_4(\text{CO})_{13}$



J $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$



K $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$

