GERMANIUM DERIVATIVES OF COBALT CARBONYL

A thesis

submitted to the

University of Waikato

for the degree of

Doctor of Philosophy

by

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University of Waikato

December , 1978

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ACKNOWLEDGEMENTS

I am extemely grateful to my supervisor, Dr.K.M. Mackay, who initiated my interest in this field and whose help and guidance have been invaluable.

I would like to thank a number of the technical staff of the university; particularly Mr.G. Purdy, the glassblower, Mr.F. Bailey and Mrs.D. Whitehead of the draughting department, and the university photographer, Mr.R. Julian. Thanks are also due to Miss.O. Johnson and Mr.A. Brennan for their help in recording mass spectra.

For their helpful discussions during this research, I am also grateful to our department staff Drs. B.K. Nicholson and D.W. Smith and my contemporaries Dr.F.S. Wong and Mr.N. Duffy.

I thank the University Grants Committee for a Post - Graduate Scholarship, which was held during the course of this work.

Finally, I would like to thank my mother for all her efforts in preparing the typescript and my wife Jill, for her patience over the years.

ABSTRACT

This work reports the reactions of $NaCo(CO)_4$ with $GeCl_4$, $GeBr_4$, $MeGeCl_3$, $MeGeBr_3$, and Me_2GeCl_2 and of $Co_2(CO)_8$ with germanium hydride derivatives, along with the isolation and characterisation of their products. Amongst these are the new compounds $ClGe[Co(CO)_4]_3$, $Br_2Ge[Co(CO)_4]_2$, $BrGe[Co(CO)_4]_3$, $MeGeCl_2Co(CO)_4$, $MeGeBr_2Co(CO)_4$, $MeGeCl[Co(CO)_4]_2$, $MeGeBr[Co(CO)_4]_2$, $GeCo_4(CO)_{14}$ and $Ge[Co(CO)_4]_4$. There have also been indications of $MeGe[Co(CO)_4]_3$ and some spectroscopic data have been collected for $Me_2GeBrCo(CO)_4$.

The proposed configuration for $GeCo_4(CO)_{14}$ is a novel extension of the already-established germanium - bridged dicobalt carbonyl derivatives. The relationships between and interconversions of three tetracobalt derivatives of Germanium are discussed.

A review of Group IVB - Cobalt carbonyl derivatives is presented along with a discussion of the mass and infrared spectra of compounds prepared in this work.

Some of the chlorogermyl cobalt carbonyl derivatives prepared in this work have been reacted with $NaMn(CO)_5$. Under this competition situation, metal carbonyl exchange has been found to be favoured over alkali halide elimination. e.g. :

$$ClGe[Co(CO)_4]_3 + 3NaMn(CO)_5 \longrightarrow ClGe[Mn(CO)_5]_3 + 3NaCo(CO)_4$$

However, this system is subject to substituent effects.

Preliminary studies on the Germanium derivatives of Rhenium and Vanadium carbonyls are also reported.

ABBREVIATIONS

The following abbreviations have been used as defined below in various parts of the text :

Me	=	Methyl , CH_3
Et	=	Ethyl , C_2H_5
Pr	=	Propyl , C_3H_7
Bu	=	Butyl , C_4H_9
Ph	=	Phenyl , C_6H_5
α-Np	=	α-Naphthyl , $C_{10}H_7$
acac	=	Acetylacetonate , $C_5H_7O_2$
Cp	=	Cyclopentadienyl , C_5H_5
TMS	=	Tetramethylsilane , $(CH_3)_4Si$
Et_2O	=	Diethyl ether , $(C_2H_5)_2O$
THF	=	Tetrahydrofuran , C_4H_8O
diglyme	=	Diethyleneglycol dimethyl ether , $CH_3O(CH_2CH_2O)_2CH_3$
nmr	=	Nuclear Magnetic Resonance
ESR	=	Electron Spin Resonance
NQR	=	Nuclear Quadrupole Resonance
P^+	=	Parent ion
M'	=	Group IVB atom
R.T.	=	Room temperature
M.P.	=	Melting point
hr	=	Hour
d	=	Day
v	=	Very
s	=	Strong
m	=	Medium
w	=	Weak
br	=	Broad
sh	=	Shoulder

CHAPTER ONE

Introduction to Group IVB - Cobalt Carbonyl derivatives

1.1 General

The amount of recent work in the field of Transition Metal Carbonyl chemistry and, more specifically, Main Group-substituted Transition Metal carbonyls is reflected in part by the reviews which have appeared over recent years. (1,2,3,4,5,6). Year - by - year reviews for specific elements or groups update this information e.g.(7,8,9).

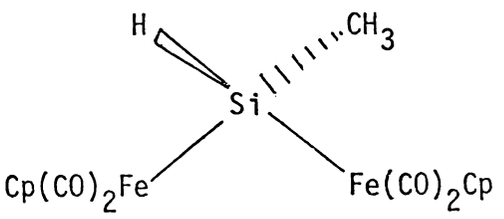
The investigation of cobalt carbonyl derivatives has gone hand - in - hand with their extended use in other areas. Thus, the application of $Co_2(CO)_8$, in particular, to the catalysis of several reaction systems e.g.(10,11,12) has been vigorously pursued, along with work on its structural (13,14) spectroscopic (15,16) and reactivity aspects (17).

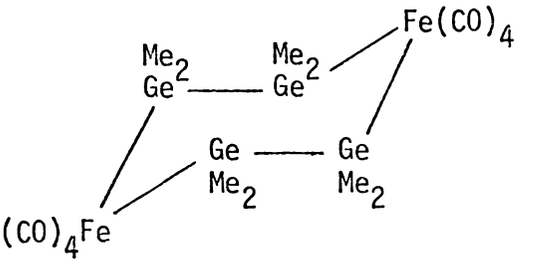
The anion $Co(CO)_4^-$ is widely used in the syntheses of cobalt carbonyl substituted compounds. The reactions of the whole range of metal carbonyl anions have been quite thoroughly reviewed e.g.(18,19,30,31). Preparations of these carbonyl anions with a number of counter ions have been reported, along with syntheses which overcome specific problems. e.g.(20,21,22,23,24,25,26,27). The basicity (28) or nucleophilicity (29) of $Co(CO)_4^-$ relative to a number of other metal carbonyl anions has been determined.

The syntheses of cobalt carbonyl derivatives of the Group IVB elements have been extensively reviewed in the past e.g.(1,2,3) and will not be dealt with further. Most derivatives discussed here have been prepared by reaction of $Co(CO)_4^-$ or $Co_2(CO)_8$ with Group IVB hydrides or halides.

Tables 1.2 (p *8*) and 1.3 (p*12*) give the preparative methods for known polycobalt carbonyl - Group IVB derivatives.

The neighbouring iron triad, (as reviewed recently by Bonny (36) presents some very interesting analogues of the compound - types discussed in this work. Derivatives (32,33) with bridging silicon or germanium provide interesting structural and bonding comparisons with those found for cobalt. i.e. :





Butler et al.(34) have made vibrational studies of some direct analogues of cobalt derivatives. Thorn and Hoffman (35) have reported detailed calculations of bonding in $M_2(CO)_6$(ligand) complexes, where M is either iron or cobalt. A direct analogy between the iron compounds $M'[Fe(CO)_4]_4$ (M' = Sn,Ge) reported in (37) and (38) and a new cobalt derivative prepared here is made in Section 3.4.

In contrast, the Group IVB- rhodium- and iridium carbonyl derivatives show little analogy with those of cobalt. (1,2,3)

1.2 Monocobalt Derivatives of Germanium

Unlike the polycobalt derivatives described in the next section, monocobalt carbonyl derivatives of Group IVB elements are not subject to steric hindrance and show only a single structure. Microwave and electron diffraction structural data (e.g. 39,40) show results typified by $GeH_3Co(CO)_4$:

Co-C (mean) = 180.0 pm

Co-Ge = 241.6 pm

Co-$\hat{Ge}$-H = 109.1°

C_{eq}-$\hat{Co}$-Ge = 83.8°

At least one carbonyl in $-Co(CO)_4$ can be substituted by phosphines, giving derivatives of the type $X_3M'Co(CO)_3PR_3$ (where X = H, organo- or halo- group ; M' = Group IVB element ; R = alkyl, aryl).(1,2,3). We will only be concerned with $-Co(CO)_4$ derivatives here. Table 1.1 lists the mono-(cobalt tetracarbonyl) derivatives of the Group IVB elements. (A number of related silicon ions and adducts are listed in (5))

Amongst the numerous reports on these compounds, studies include :

i) ^{59}Co NQR and low temperature ^{13}C nmr studies of $X_3SnCo(CO)_4$ derivatives (67)

ii) Kinetics of iodine cleavage of Sn-Co in $Me_3SnCo(CO)_4$ (68)

iii) An ESR study of anions formed by high energy radiation of $Ph_3PbCo(CO)_4$ (69)

iv) Products arising from the reaction of $GeCl_3^-$ and $SnCl_3^-$ with $Co_2(CO)_8$ (70)

Though not directly analogous to this class of compounds, an interesting recent extension of them involves the "superreduction" of $NaCo(CO)_4$ by sodium in liquid ammonia, naphthalene - THF or hexamethylphosphoramide. (71) Reaction of the resultant $Na_3Co(CO)_3$ with $Ph_3M'Cl$ (M' = Ge,Sn,Pb) has produced $[(Ph_3M')_2Co(CO)_3]^-$, isolated as the tetraethyl-ammonium salt.

Table 1.1

Mono-($Co(CO)_4$)Derivatives of the Group IVB Elements

Compound	References (a)
$R_3SiCo(CO)_4$ (R = H,Me,Et,Ph,OMe,OEt)	41,42,43,44
$X_3SiCo(CO)_4$ (X = F,Cl,C_6F_6)	42,43,45
$MeSiX_2Co(CO)_4$ (X = H,F)	46,47
$RMeSiPhCo(CO)_4$ (R = α-Np , neo-C_5H_{11})	48
$Ph_2SiHCo(CO)_4$	44
$PhSiCl_2Co(CO)_4$	44
$R_3GeCo(CO)_4$ (R = H,Me,Et,Ph)	49,50,57,65
$X_3GeCo(CO)_4$ (X = Cl,Br,I)	51,52
$MeGeX_2Co(CO)_4$ (X = I , H)	51,53
$Me_2GeXCo(CO)_4$ (X = Cl , H)	51,54
$PhGeX_2Co(CO)_4$ (X = Cl , I)	51
$Ph_2GeXCo(CO)_4$ (X = Cl , I)	51
$(CO)_5MnGePh_2Co(CO)_4$	55
$GeH_3GeH_2Co(CO)_4$	72
$(CO)_4CoGeH_2GeH_2Co(CO)_4$	72

Table 1.1 Contd.

Compounds	References
$R_3SnCo(CO)_4$ (R = Me,Et,Bu,Ph)	50,56,57,58
$X_3SnCo(CO)_4$ (X = Cl,Br,I)	52
$MeSnX_2Co(CO)_4$ (X = Cl,Br,I)	59,60
$Me_2SnXCo(CO)_4$ (X = Cl,Br,I)	52,60
$Bu_aSnCl_bCo(CO)_4$ (a = 1, 2 ; b = 2, 1)	52,59
$PhSnX_2Co(CO)_4$ (X = Cl,Br,I)	52
$Ph_2SnXCo(CO)_4$ (X = Cl,Br,I)	52
$(CO)_5MnSnX_2Co(CO)_4$ (X_2 = Ph_2 , PhCl)	61,62
$(acac)_2SnClCo(CO)_4$ (b) (acac = $C_5H_7O_2$)	63
$R_3PbCo(CO)_4$ (R = Me,Et,Ph,C_6H_{11})	66,50,51,58

Notes:

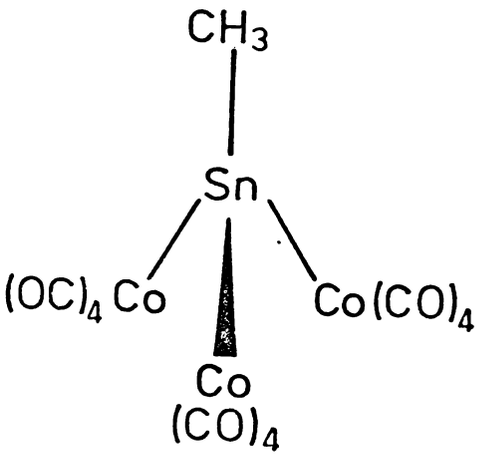
a) See also the reviews (1,2,3) for details of spectra and Preparations.

b) This is an example of six - co-ordinate tin , other compounds of which are further discussed in reference (64).

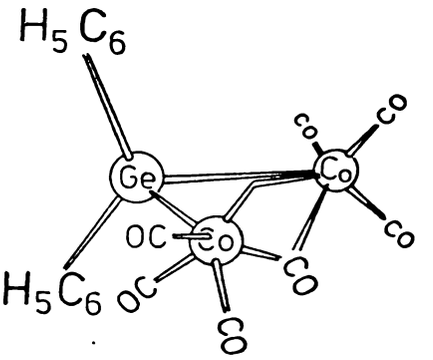
Figure 1.1

Structural Types for Poly-(Cobalt carbonyl)-Group IVB Derivatives

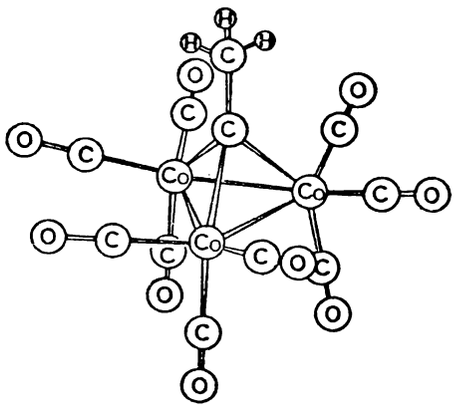
Figure 1.1 Structural Types for Poly-(Cobalt carbonyl)-Group IVB Derivatives



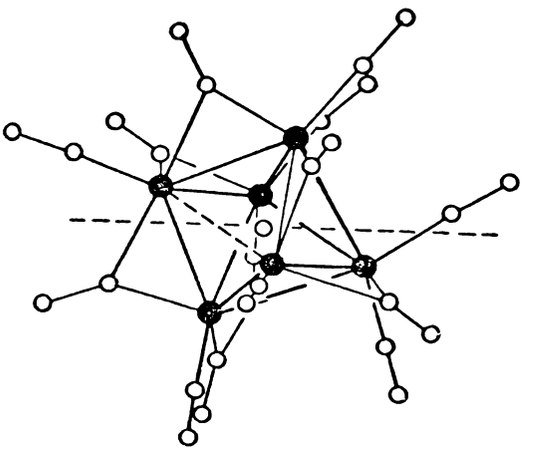
A $MeSn[Co(CO)_4]_3$ (82)



B $Ph_2GeCo_2(CO)_7$ (87)



C $CH_3CCo_3(CO)_9$ (94)



D $[Co_6(CO)_{14}C]^-$ (74)

1.3 Polycobalt Derivatives of Germanium

Polycobalt carbonyl derivatives of Main Group elements fall into four main structural types, examples of which can be seen in Figure 1.1

A) Those containing n terminal $-Co(CO)_4$ groups (n = 2,3,4).

B) Those containing n μ-R_2M' groups replacing the bridging carbonyls in $Co_2(CO)_8$ (n = 1,2). A subclass of tricobalt derivatives is formed when one of the above R groups = $Co(CO)_4$.

C) Those containing a cluster of $LM'Co_3(CO)_9$ of the type shown in Figure 1.1C, where the three cobalt atoms and the Group IV atom form a tetrahedron. A subclass of tetracobalt derivatives is formed when L = $-Co(CO)_4$.

D) This class covers the larger cobalt clusters which enclose one or more Main Group atoms (normally carbon). These are typified by examples given in (73) and (74) and will not be further discussed here.

Nearly all the Main Group derivatives in class A are those of Group IVB. However, Patmore and Graham have reported a number of Group IIIB derivatives also.(75) Table 1.2 lists the known Group IVB compounds in this class.

Derivatives from class B are well established and many of the iron analogues are also known to exist. Series of this type have been reported for numerous non - Group IVB compounds e.g.(35,84,105). A list of Group IVB derivatives in this class is presented in Table 1.3.

The $RCCo_3(CO)_9$ structures in class C have been thoroughly investigated.(92,93) A recent review by Schmid (94) has covered the more general cases $L_nECo_3(CO)_9$, where E can be a number of possible elements with ligands, L. The silicon derivatives in this class are nearly all of the type: $R_3Si\text{-}O\text{-}CCo_3(CO)_9$. (92,95). The notable exception is

Table 1.2

Poly-(Tetracarbonyl cobalt)-Group IVB Derivatives

Compound	Preparative Method (a)	Yield (%)	Characterisation (b)	Reference
$R_2M'[Co(CO)_4]_2$:				
M' = Si , R_2 = H_2	3			104
M' = Ge , R_2 = Cl_2	1, 10	72	EA,IR	51,37
I_2(c)	2	30	EA,IR	76
Me_2	3		EA,IR,nmr,MS(d)	51,77
I and Me	1	69	EA,IR	51
Ph_2	3		EA	78
M' = Sn , R_2 = Cl_2	2	50,20	EA,IR	59,76,83
Br_2	2	22	EA,IR	76,83
I_2	2	25	EA,IR	76,83
Me_2	3	53	EA,IR,nmr	51,57,59,82,91
Ph_2	3, 8	43	EA,IR,Mag,MW	51,83,58

Table 1.2 Contd.

Compound		Preparative Method (a)	Yield (%)	Characterisation	Reference
	Me and Cl	3	59	EA,IR	51,59
	Ph and Cl	3		EA,IR	51
	$(n\text{-}Pr)_2$	3		FIR	59
	n-Pr and Cl	3		FIR	59
	$(n\text{-}Bu)_2$	3		FIR	57,59
	n-Bu and Cl	3		EA,IR	51,59
	$(CH_2{=}CH)_2$	1a			82
	$(CH_2{=}CH)$ and Cl	3		EA,IR	51,79
	$(CH_3CO_2)_2$	2a		EA,IR,MW,MS(d)	52
	$(C_5H_7O_2)_2$ (= acac)	11		EA,IR,MS(d)	63
M' = Pb , R_2 =	Ph_2	3	76	EA,MW,Mag	58
$RM'[Co(CO)_4]_3$:					
M' = Ge , R =	Ph (f)	9		IR	86

Table 1.2 Contd.

Compound		Preparative Method (a)	Yield (%)	Characterisation (b)	Reference
M' = Sn , R =	F	2	25	EA,IR,nmr,MS(e)	52
	Cl	1, 4	75	EA,IR,XR,MS(D)	59,79,80
	Br	1,4,5,6	64	EA,IR,MS(d)	59,79
	I	1	73	EA,IR,MS(d)	79
	Me	1	53	EA,IR,MS(e)	59,79,82
	Et	1		FIR	59
	n-Bu	1, 3		EA,IR,MS(d)	59,79
	Ph	3		EA,IR,MS(e)	79
	$(CH_2=CH)$	3		EA,IR,MS(d)	79
	(CH_3CO_2)	2a		EA,IR,MS(d)	52
Others					
$Sn[Co(CO)_4]_4$		1,4a,7	12,48,14	EA,IR,MW,MS(d)	52,81
$Pb[Co(CO)_4]_4$		7	92	EA,IR,MS(d)	81

Table 1.2 Contd.

Notes

a) 1 = Reaction of M'(IV) halide with $Co_2(CO)_8$ 1a = Reaction of $Sn(CH{=}CH_2)_4$ with $Co_2(CO)_8$

2 = Reaction of M'(II) halide with $Co_2(CO)_8$ 2a = Reaction of $Sn(CH_3CO_2)_2$ with $Co_2(CO)_8$

3 = Reaction of M'(IV) halide with $NaCo(CO)_4$ 4 = Reaction of $X_2Sn[Co(CO)_4]_2$ with $Co_2(CO)_8$

4a = Reaction of $ClSn[Co(CO)_4]_3$ with $Co_2(CO)_8$ 5 = Reaction of $Br_2Sn[Co(CO)_4]_2$ with $TlC_5H_7O_2$

6 = Reaction of $Br_2Sn[Co(CO)_4]_2$ with $NaCo(CO)_4$ 7 = Reaction of activated metal with $Co_2(CO)_8$

8 = Reaction of $Cl_2Sn[Co(CO)_4]_2$ with PhMgBr 9 = High pressure CO reaction with $PhGeCo_3(CO)_{11}$

10 = Reaction of $GeCl_3^-$ with $Co_2(CO)_8$ 11 = Reaction of $(acac)_2SnCl_2$ with $NaCo(CO)_4$

b) EA = Elemental analysis ; IR = Infrared spectrum ; FIR = Far infrared data only ;
nmr = Nuclear magnetic resonance data ; MS = Mass spectrum ; MW = Molecular Weight measurements;
XR = X-ray crystal structure ; Mag = Magnetic susceptibility measurements.

c) This was the first reported compound containing a Ge-Co bond.

d) The mass spectrum shows *no* parent ion : mention of key fragments only.

e) The mass spectrum *does* show a parent ion. Only key fragments are mentioned.

f) This product has been identified only by its carbonyl infrared spectrum. It rapidly loses CO to reform $PhGeCo_3(CO)_{11}$.

Table 1.3

Group IVB Derivatives of $Co_2(CO)_6$

Compound	Preparative Method (a)	Characterisation (b)	Reference
$(\mu\text{-}R_2M')(\mu\text{-}CO)Co_2(CO)_6$			
M' = Si , R_2 = Ph_2	1	IR	85,86
$PhCo(CO)_4$	1	IR	85,86
M' = Ge , R_2 = Ph_2	1, 2	EA,MS,IR,XR	87,99
Me_2	2	MS,IR,nmr	77
$MeCo(CO)_4$	1	IR,MS,nmr	53
$PhCo(CO)_4$	1	EA,MS,IR,XR	86
M' = Sn , R_2 = Me_2 (C)	2	MS	91
$(C_5H_7O_2)_2$ (= acac)	4	EA,MS,IR,nmr	63

Table 1.3 Contd.

Compound	Preparative Method (a)	Characterisation (b)	Reference
$(\mu\text{-}R_2M')_2Co_2(CO)_6$			
M' = Ge , R_2 = Me_2	1, 3	EA,MS,IR,nmr	77,88,89,90
M' = Sn , R_2 = Me_2	1, 2	EA,MS,IR,nmr	90,91

Notes

a) 1 = Reaction of Group IVB hydride with $Co_2(CO)_8$

2 = Photolysis of $R_2M'[Co(CO)_4]_2$

3 = Photolysis of $Me_2GeClCo(CO)_4$

4 = Reaction of $(acac)_2SnCl_2$ with $NaCo(CO)_4$

b) IR = Infrared data ; EA = Elemental Analysis ; MS = Mass spectral parent ions and important envelopes ; nmr = Nuclear magnetic resonance data ; XR = X-ray crystal structure.

c) This compound only arose from a low temperature reaction, melts below 0^oC and is exceedingly unstable. As a result, completely pure samples have not been made.

$(CO)_4CoSiCo_3(CO)_9$, whose characterisation includes a crystal structure. (96). Only limited work has been done with the germanium analogues:

$PhGeCo_3(CO)_9$ (a) ----- (86)

$(CO)_4CoGeCo_3(CO)_9$ (b) ----- (97)

a) Prepared by reflux of $[(Co)_4Co]PhGeCo_2(CO)_7$ and characterised by EA, IR, MS.

b) Prepared in 60% yield from reaction of $GeBr_4$ with $NaCo(CO)_4$. Characterised by EA, IR, MS and XR.

A report by Ibekwe and Newlands (98) of the formation of $n\text{-}BuSnCo_3(CO)_9$ is contrary to the findings of later work. (82). From this and more recent work (94) it seems fairly clear that polycobalt derivatives of tin will not close up to form $RSnCo_3(CO)_9$ clusters.

The above tabulations illustrate some interesting features of Group IVB - cobalt carbonyl chemistry. Silicon is notable for its single contribution to Table 1.2. Because of its size it is much better suited to form the condensed $-Co_2(CO)_6$ or cluster - type of derivative. The steric congestion of terminal $-Co(CO)_4$ groups is apparently only relieved enough when the other two substituents on silicon are hydrogen. As discussed below for tin, the size of the silicon atom is also not really suited for the apical position of the tetrahedral clusters, as in $(CO)_4CoSiCo_3(CO)_9$ (96). This is reflected by the yields of the carbon, silicon and germanium analogues of this compound: 0 , 5 , 60% , respectively (97).

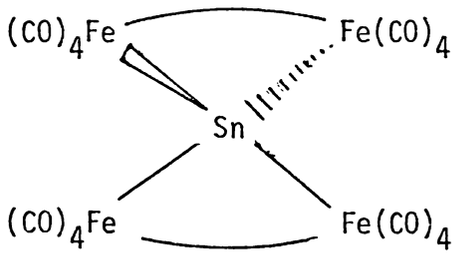
In the case of tin, the opposite situation holds true. All the derivatives $X_aSn[Co(CO)_4]_{4-a}$ (a = 0 to 4) are known for a number of different X - substituents. The ready formation of such derivatives is illustrated by the extreme

case (a = 0) , which can not only be made by the usual halide substitution, but also by the direct action of activated tin with $Co_2(CO)_8$. (81). The intermediate bridging configuration, though known for tin, is not a particularly favourable one. Triplett and Curtis (91) have discussed this in terms of the size of tin (as compared to germanium) as a bridging atom. (N.B. Covalent radii (pm) for Group IVB are (94) : C = 77 ; Si = 111 ; Ge = 122 ; Sn = 141 ; Pb = 147) Attempts by Schmid (81) to make clustered tin derivatives have failed. Only $Sn[Co(CO)_4]_4$ was formed. This too has been explained in terms of the size of tin. (94) With largely constant Co - Co bond lengths and Co - $\widehat{Co}$ - Co bond angles in the tricobalt clusters, the size of the possible hetero-atoms is limited to 130 pm. Tin exceeds this limit. This is further reflected by the formation of the six co-ordinate tin derivatives $(acac)_2SnCo_2(CO)_7$ and $(acac)_2Sn[Co(CO)_4]_2$ (63). Both have been isolated from the same reaction system as air-sensitive solids. They are examples of a series - type which is discussed and expanded in (64).

Like tin, lead forms $Pb[Co(CO)_4]_4$ instead of clustered derivatives. (81) Though the number of lead derivatives of cobalt is very limited, the ones that have been made suggest the same sort of behaviour as tin. This is to be expected from an extension of the size arguments for M'. The limitation on lead derivatives is probably due to the restriction to Pb(II) compounds as reagents, rather than to the instability of derivative - types. The tin / lead size difference can be seen by the additional solvent co-ordination possible for $Pb[Co(CO)_4]_4$ but not for $Sn[Co(CO)_4]_4$. (81)

Two iron analogues have been reported which are of direct interest to this work. (37,38). $Sn[Fe(CO)_4]_4$ has been isolated

from the products of $Na_2Fe(CO)_4$ or $Fe(CO)_5$ reacted with a number of chlorotin derivatives. Its crystal structure shows approximate D_{2d} molecular symmetry, with two long Fe - Fe bonds, (as expected to complete the 18-electron configuration.)



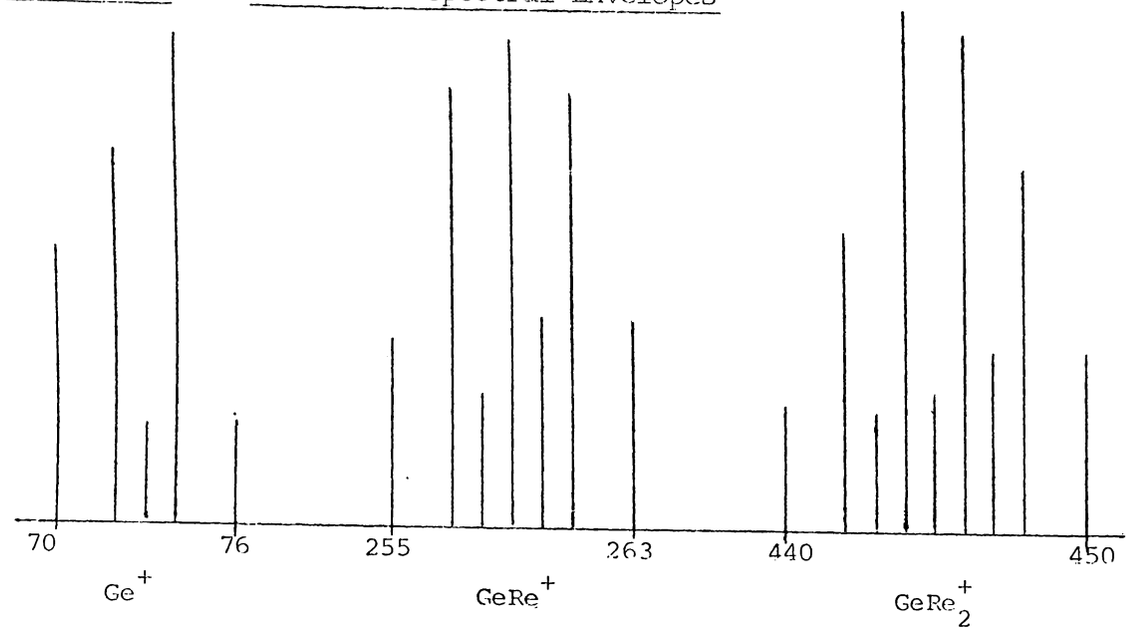
$Ge[Fe(CO)_4]_4$ has been made by the reactions $GeCl_3^-$ / $Fe(CO)_5$ and $Fe(CO)_4^{2-}$ / $GeCl_4$. Infrared data indicates the same structure as $Sn[Fe(CO)_4]_4$.

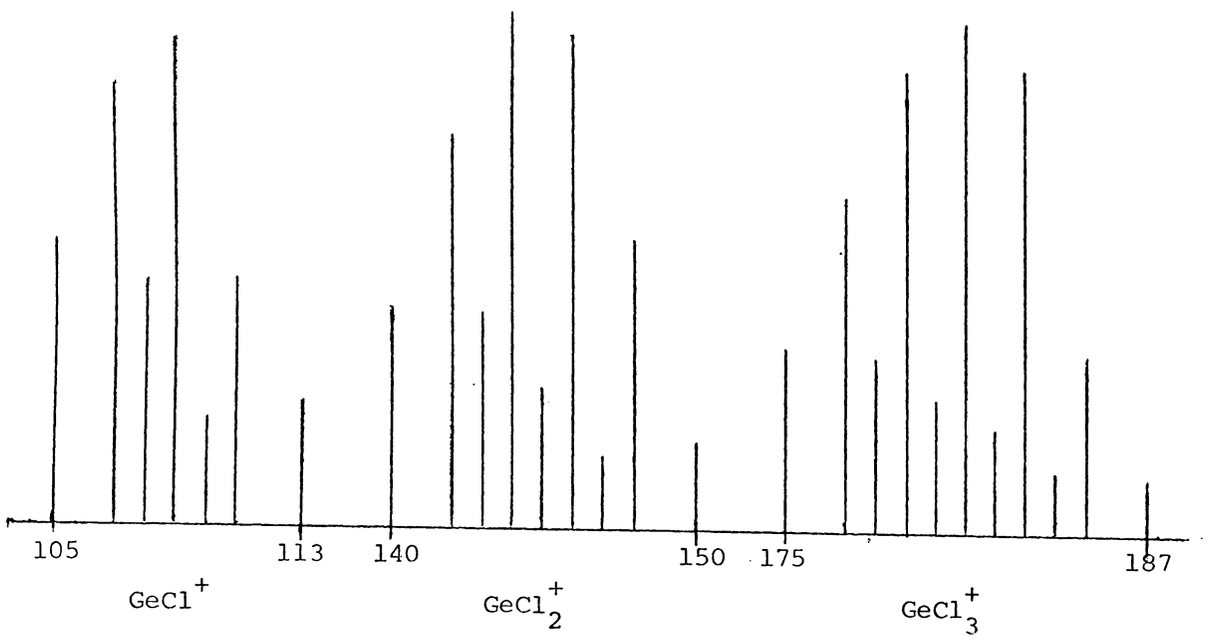
These two extremes of behaviour, set by silicon and tin, would be expected to set limits for the behaviour of germanium. However, few data are available on the germanium system. Since both terminal- and clustered cobalt carbonyl derivatives of germanium are known, it is obviously intermediate between the silicon and tin cases. One of the aims of this work is to better establish the nature of the polycobalt derivatives of germanium with respect to the other Group IVB derivatives.

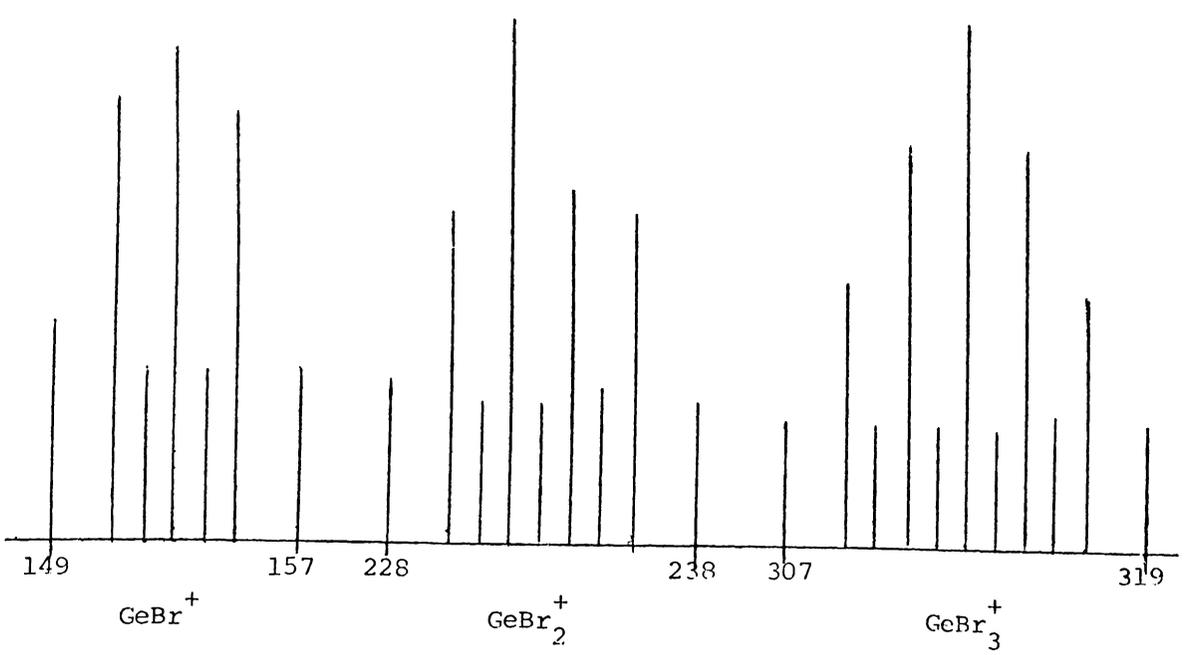
1.4 Mass Spectral Studies

The mass spectra of germanium - containing compounds are characterised by ion envelopes containing the five naturally occurring isotopes : (^{70}Ge = 20.52% ; ^{72}Ge = 27.43% ; ^{73}Ge = 7.76% ; ^{74}Ge = 36.54% ; ^{76}Ge = 7.76%) The basic pattern is modified by the addition of Cl (^{35}Cl = 75.53% ; ^{37}Cl = 24.47%) , Br (^{79}Br = 50.54% ; ^{81}Br = 49.46%) or Re (^{185}Re = 37.5% ; ^{187}Re 62.5%) as shown in Figure 1.2 for most of the combinations dealt with in this work. In

Figure 1.2 Basic Mass Spectral Envelopes







spectra of the simple metal carbonyls ($M_a(CO)_n$) of mono-isotopic cobalt and manganese, the main ion peaks (m/e = x) are also accompanied by a ^{13}C peak (m/e = x + 1) at n x 1.11% intensity and an ^{18}O peak (m/e = x + 2) at n x 0.204% intensity.

Most papers report mass spectra very briefly with only the parent ion (where applicable) and a comment on the major fragments. For Main Group derivatives of metal carbonyls, the major fragmentation series is that due to carbonyl loss from the parent ion. When available for a number of similar compounds, more detailed mass spectral data have wider application. There can be a clear relationship between fragmentation patterns and structures (103). Though one must be careful about inferring relative stabilities from mass spectral data, such arguments are more reasonable if made by comparing similar compounds run under the same conditions. e.g. (100). Information on appearance- and ionization potentials makes calculation of relative bond energies possible. This has been done for a number of Group IVB - Transition metal derivatives. e.g. (101)

General data on the fragmentations of substituted metal carbonyls (e.g. (100) , (103) and references therein), along with metastable-supported fragmentations of alkyl and aryl germanium derivatives (102) have been used as support for the fragmentation reactions inferred from the mass spectra obtained in this work.

1.5 Infrared studies

In the field of metal carbonyl chemistry, vibrational studies have proved to be one of the most useful techniques for analysis and characterisation. The large intrinsic intensities of carbonyl stretching absorptions in the infrared

mean that only very small samples are required and purity can be monitored to a high degree. Symmetry predictions aid the identification of products from their carbonyl stretches. Similarly, the intense Raman absorptions for metal - metal stretches and related modes extends the useful range of vibrational spectroscopy.

Infrared spectroscopy was important in this work for further reasons. These result from the "failures" of other techniques. As noted in Chapter Eight, the mass spectra of most bis- and tris- terminal cobalt carbonyls show no parent ion. While this may be expected and accounted for, no molecular weight characterisation can be made on these compounds as a consequence. No characterisation by ^{1}H nmr could be made on most derivatives since they contained no hydrogen. As noted in Section 2.2.4 microanalyses for carbonyl carbon were found to be unsatisfactory. These limitations on other techniques meant that a lot of emphasis had to be placed on accurate determination of infrared data.

Most initial preparative reports of Group IVB - metal carbonyl derivatives include a fairly full discussion of infrared data. Further analyses on isolated classes of compounds have also been carried out independently. It is convenient here to draw the references to vibrational analyses of Group IVB - cobalt tetracarbonyl derivatives together:

i) Silicon cobalt carbonyls : 3,50,66,106,107,108

ii) Mono-(cobalt carbonyl) germanium derivatives: 49,50,51,52,66,77,106,107,108,109,110

iii) Poly-(cobalt carbonyl) germanium derivatives: 51,76,77,86,87,88,90,97,99

iv) Mono-(cobalt carbonyl) tin derivatives : 49,50,51,52,59,60,66,106,107,108,109,110

v) Poly-(cobalt carbonyl) tin derivatives :

51,52,59,76,79,81,82,83,90,91

vi) Lead cobalt carbonyls : 50,51,66,81

1.6 Prolegomena

The layout of this thesis, as related to the work mentioned so far, is discussed below.

1.6.1 Chapter Two is a brief description of the practical and spectroscopic techniques used in this work. It includes a description of the preparation and reaction techniques for metal carbonyl anions. While the basic techniques for this are quite common (see Section 1.1), the specific conditions applied here must be quoted for reasonable comparison with literature reports.

1.6.2 Chapter Three describes the cobalt carbonyl derivatives of $GeCl_4$. As noted, germanium is intermediate between silicon and tin, with respect to bonding in the polycobalt carbonyl derivatives. To date, the available information indicates that both of the "extreme" bonding situations occur for germanium. On the one hand, the derivatives $Cl_3GeCo(CO)_4$ and $Cl_2Ge[Co(CO)_4]_2$ have been prepared in reasonable yields (57, 72% respectively) from the reaction of $GeCl_4$ with $NaCo(CO)_4$ or $Co_2(CO)_8$ in THF.(51). On the other hand, Schmid reports the preparation of $(CO)_4CoGeCo_3(CO)_9$ in 62% yield from the reaction of $GeBr_4$ with $NaCo(CO)_4$.(97). He has since reported its crystal structure.(94). It would appear from the available data that the germanium atom is well suited in size to fit the apex of the tricobalt cluster. (This is also supported by the report of the preparation of $PhGeCo_3(CO)_9$ (86)).

This ambivalent behaviour of germanium toward cobalt

carbonyl substitution makes it the most interesting element of its group, from this point of view. However, as noted, only the extremes of its behaviour have so far been observed. Formation of the intermediate and "transitional" species in this series of compounds is required to complete the available information in this intermediate bonding situation for the cobalt carbonyl derivatives. To this end Chapter Three describes the synthesis and characterisation of the whole series of compounds resulting from stepwise substitution of $GeCl_4$.

1.6.3 From pilot studies with $GeBr_4$, it appeared that the bromine substituents enhanced the formation of higher cobalt-substituted derivatives. The only compound in this series prepared until now is $Br_3GeCo(CO)_4$.(52). The 16% yield of this preparation compared with the 57% yield for the chloro-analogue (51) further supports the difference between these two systems. Similarly, the effect of bromine substituents in the tin system can be seen by comparing the yields for the preparations of $Br_xSn[Co(CO)_4]_{4-x}$: i.e. 30% , 50% , 64% for x = 3, 2, 1, respectively.

In parallel to the chloro - system studies, Chapter Four reports the preparation and characterisation of $Br_3GeCo(CO)_4$ and the new compounds $Br_2Ge[Co(CO)_4]_2$ and $BrGe[Co(CO)_4]_3$.

1.6.4 The work described in Chapter Five deals with the cobalt carbonyl derivatives of the methylhalogermanes. An extension of the problem described in 1.6.5 arose in trying to assign spectra containing $Me_2Ge[Co(CO)_4]_2$. The literature infrared data are given in Table 1.4a . Again, for assignment purposes in complex spectra, the inconsistent data could not be used and this compound was separately prepared and characterised. The first attempts to prepare $Me_2Ge[Co(CO)_4]_2$

Table 1.4

Literature Infrared Data for

Dimethylgermyl Cobalt Carbonyl Derivatives

(All units are cm^{-1})

a) $Me_2Ge[Co(CO)_4]_2$

(i)	(ii)
2098 (3.5)	2105 (2)
2081 (9.8)	2090 (6)
2033 (3.5,sh)	2035 (sh)
2027 (7.4)	2025 (6.5)
2019 (9.8)	
2006 (10)	2010 (7)
1997 (7.2)	1995 (4.5)

(i) = reference (51) in cyclohexane

(ii) = reference (77) in cyclohexane

b) $Me_2GeClCo(CO)_4$

(i)	(ii)
2100 (7.4)	2110 (8)
2041 (8.3)	2050 (8)
2021 (9.9)	2030 (8.5)
2004 (10)	2005 (9)

i) = reference (51) in cyclohexane

(ii) = reference (77) in cyclohexane

Table 1.4 Contd.

c) $(Me_2Ge)_2Co_2(CO)_6$

(i)	(ii)	(iii)
2072 (s)	2075 (1.5)	2063 (s)
2035 (vs)	2035 (4)	2028 (vs)
2014 (vs)	2010 (4)	2002 (vs)
1994 (vs)		1990 (m,sh)
1984 (m)	1985 (4.5)	1960 (m,sh)

(i) = reference (90) in cyclohexane

(ii) = reference (77) in cyclohexane

(iii) = reference (88) in CS_2

directly yielded only $Me_2GeClCo(CO)_4$. In assigning this reaction product, the same problem arose with the reported infrared data , shown in Table 1.4b . Thus, $Me_2GeClCo(CO)_4$ was also isolated and characterised.

These characterisations were particularly important in the work in Section 5.2 , which describes the preparations of the analogous monomethylgermyl derivatives. In this case, the commercial $MeGeCl_3$ contained a large percentage of Me_2GeCl_2 (extremely difficult to separate), so all preparations with these two components proceeded in parallel. The data from the dimethyl system were needed to sort out the very complex infrared spectra resulting from these reaction systems.

The only monomethylgermyl cobalt carbonyl derivatives established are :

$MeGeI_2Co(CO)_4$ (51)

$MeGeH_2Co(CO)_4$ (53)

$MeGeI[Co(CO)_4]_2$ (51)

The extension of this series of compounds is also described in this chapter, along with a comparison with the analogous halogermyl derivatives described in Chapters Three and Four.

1.6.5 Chapter Six discusses substitution reactions at Ge - H centres. These provide useful syntheses for mono- , di-, tri- and tetra-substituted germanes, as illustrated by the following sequence:

$$MeGeH_3 \xrightarrow{Co_2(CO)_8} MeGeH_2Co(CO)_4 + HCo(CO)_4 \quad ----1$$

$$\longrightarrow MeGeH[Co(CO)_4]_2 + HCo(CO)_4 \quad ----2$$

$$\longrightarrow MeGeCo_3(CO)_{11} + HCo(CO)_4 \quad ----3$$

This sequence was studied by B.W.L.Graham (53) , who separately prepared $MeGeH_2Co(CO)_4$ and followed the reaction from there. He only identified product 2 as $MeGeHX_2$, by nmr, as a transient intermediate. The tricobalt product was

characterised by comparison with $PhGeCo_3(CO)_{11}$, whose crystal structure is known. (86) (cf. see Figure 1.1B. p.6)

This system has been further studied to observe the relative stabilities of all three products. (N.B. The proposed dicobalt intermediate could be $MeGeH[Co(CO)_4]_2$ or $MeGeHCo_2(CO)_7$ or possibly both species may arise ; (see Figure 1.1A,B)

In the analogous dimethylgermyl system, one less Ge-H centre eliminates further reaction to a tricobalt product. Thus, it was hoped to elucidate the nature of the dicobalt final products and relate this back to the monomethyl system.

Both systems produce $HCo(CO)_4$. MacDiarmid et al. report that methylsilanes react with $HCo(CO)_4$ to form silicon - cobalt bonded species. (125,126). This prompted repeating this reaction for Ge-H-containing analogues. Any "interference" from such side reactions would alter the proposed reaction schemes for the above system.

The final products from the $Me_2GeH_2/Co_2(CO)_8$ reaction ($Me_2Ge[Co(CO)_4]_2$, $Me_2GeCo_2(CO)_7$ and $(Me_2Ge)_2Co_2(CO)_6$)have been independently prepared and characterised. (51,77,88,90) The infrared data that were available for $(Me_2Ge)_2Co_2(CO)_6$ are given in Table 1.4c).
For the assignment of the closely related products in the $Me_2GeH_2/Co_2(CO)_8$ system, the inconsistencies made these data useless. Thus $(Me_2Ge)_2Co_2(CO)_6$ was separately prepared and characterised.

The extreme cases of having all- and no-hydride substituted germanes in reaction with $Co_2(CO)_8$ are also reported.

1.6.6 While numerous mono-(pentacarbonyl manganese) derivatives of silicon, germanium and tin have been reported (e.g. *135, 136, 137* and references therein), not a lot of

attention has been given to the higher members of these series. Exceptions to this include the long-established $H_2Ge[Mn(CO)_5]_2$, from the reaction of GeH_4 with $HMn(CO)_5$ *(138)* and the more recent $X_2Si[Mn(CO)_5]_2$ (X = H, D, halogen) prepared from SiH_2I_2 or SiD_2I_2 / $NaMn(CO)_5$ and subsequent reactions.*(139)* Thompson and Graham*(141)* have also prepared a series of bis- and tris- pentacarbonyl manganese derivatives of tin, while Curtis et al. have prepared and photolysed some germanium and tin derivatives to form Group IVB-bridged species.

e.g. $Me_2GeClMn(CO)_5 \xrightarrow{h\nu} (Me_2Ge)_2Mn_2(CO)_8$

Recent work in this laboratory *(53, 54, 140)* has established part of an exchange series in which $-Mn(CO)_5$ displaces $-Co(CO)_4$ in reactions of the type :

$$Me_2GeHCo(CO)_4 + NaMn(CO)_5 \longrightarrow Me_2GeHMn(CO)_5 + NaCo(CO)_4$$

In the manganese system, in terms of near-quantitative yields, this reaction is comparable with the corresponding alkali halide elimination. However, these two reactions have yet to be compared in a competition situation.

With this in mind, and a desire to make a direct comparison of the $X_zM'[Mn(CO)_5]_y$ derivatives with the cobalt analogues, reactions of $ClGe[Co(CO)_4]_3$, $Cl_3GeCo(CO)_4$ and $Me_2GeClCo(CO)_4$ with $NaMn(CO)_5$ were studied as described in Chapter Seven.

1.6.7 Chapter Eight gives the tabulated mass spectral data for the new and recharacterised compounds from this work, along with a discussion of specific points of note and general trends for series.

While the infrared data for all compounds have been presented as they arise, the reproduction of spectra and a general discussion of the data is also presented in Chapter

Eight. Here the series of derivatives are compared with one another and with analogous compounds from the literature.

1.6.8 Appendices 1 and 2 give brief accounts of initial approaches made in the preparative fields of the germanium derivatives of rhenium and vanadium carbonyls.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES

2.1 General

Most of the compounds dealt with in this work are air-sensitive. Thus, where volatility allowed, a standard vacuum line was used. Involatile, air-sensitive compounds were handled in a nitrogen-flushed glovebox. (This included the initial handling of all new compounds). A constant flow of nitrogen was supplied from a dewar of liquid nitrogen, using a partially immersed copper rod as the "heat source" to vaporise it. The last traces of water and oxygen were removed with large surface areas of P_2O_5 and finely cut sodium. Bench handling of less air-sensitive materials was carried out in nitrogen-flushed glassware. Volatiles incondensible at -196°C (normally CO, H_2) were handled with a Toepler pump and gas burette.

2.2 Analytical Techniques

2.2.1 Infrared Spectroscopy

Infrared spectra were routinely run on either a Shimadzu IR 27G or a Beckman IR 20A. Definitive spectra were run on a Perkin Elmer 180. Spectra were calibrated with polystyrene, HCl/DCl and CO_2 (111), either directly or by calibration of the internal wavenumber marker. This marker was found to be accurate and reproducible. ($\pm$ 0.1 cm^{-1} in the region 2300 cm^{-1} to *ca.* 1950 cm^{-1}). Definitive spectra were run under the following conditions:

Spectral Slit Width (Resolution) = 0.5 cm^{-1}

Scan Speed = 0.1 cm^{-1}/sec

Abscissa Scale (Carbonyl region) = 1 cm^{-1}/mm

Absorption maxima were pinpointed with the wavenumber readout (which activates the wavenumber marker). With this technique, a combination of machine and reading errors gives an accuracy of ca. ± 0.3 cm^{-1} for absorptions in the carbonyl region.

Gas phase spectra were run in a 10 cm gas cell. Solution spectra were run in a 0.1 mm standard solution cell. Solid state spectra were run either as nujol mulls or in a cold cell at -196°C. In all cases KBr windows were used.

All relative intensities reported in this work were taken from peak heights rather than peak areas. Although this method has the disadvantage of enhancing the relative contributions from shoulders and weak absorptions which share base area with nearby strong modes, it has been found to be the most useful method for reproducing spectra. Since visual representation of spectra was found to be very useful in this work, the carbonyl stretching regions of most of the compounds discussed here are reproduced in Chapter Eight.

2.2.2 Mass Spectrometry

Mass spectra were run by Miss O.Johnson and Mr A. Brennan on a Varian CH5 instrument at Ruakura Agricultural Research Centre. Nearly all samples were introduced as solids, though gas sampling was also possible. All samples were kept cold and in the dark for as long as possible before sampling and initial spectra were run at the lowest probe temperature required to obtain a spectrum of satisfactory intensity. Spectra were then also run at higher and then lower temperatures to check for spectral changes. In some cases, this was repeated using different filament currents, particularly if a mixture of products was thought

to be present. This was to check for fragmentation differences as the ionizing-electron density was altered.

Routine, low resolution spectra were produced with computer-subtracted background and calibration marks every 50 m/e units. This was not available for normal resolution spectra, which were calibrated from the background mercury lines (relative intensities in brackets):
$^{196}Hg^+$ (5), $^{198}Hg^+$ (30), $^{199}Hg^+$ (60), $^{200}Hg^+$ (80), $^{201}Hg^+$ (50) $^{202}Hg^+$ (100), $^{204}Hg^+$ (20) .
The series of Hg^{2+} ions also appear at half these mass values. Calibration could be further checked with the very strong m/e = 28 peak corresponding to CO^+ and N_2^+ .

2.2.3 Nuclear Magnetic Resonance

Spectra were recorded on a J.E.O.L. C-60 HL instrument with standard (5mm o.d.) sample tubes which were adapted with B10 cones to fit the vacuum frame. Where possible, samples were run as neat liquids. Most solids were dissolved in benzene, with 5% tetramethylsilane (TMS) as reference. In handling reaction mixtures requiring both glovebox manipulations and vacuum line distillations, tap-adapted sample tubes were used. The instrument was also fitted with a variable temperature option which was used for reaction studies.

2.2.4 Microanalyses

These were done by Professor A.Campbell and his associates at the University of Otago on a Perkin Elmer CHN analyser. Routine analyses for carbonyl carbon were found to give erratic results. (eg. 43.7% C when 23.2% expected and 13.4% C when 16.7% expected ; both from the same batch of analyses.) Halogen analyses for the same samples were quite good, so this was most probably a technique problem and no

further carbon analyses were obtained.

Analysis for carbonyl was attempted in this laboratory, using destruction with bromine, followed by accurate measurement of the evolved CO. Reaction in thoroughly degassed solutions (hexane or diethyl ether) was found to give the best results, but even these could not be reproduced reliably enough on standards. The direct reaction of bromine with the solid compounds was found to give consistently low returns of CO, probably due to a surface-limiting effect as a $CoBr_2$ coating formed on the solid.

2.3 Starting Materials

2.3.1 Solvents

All organic solvents were thoroughly dried with and stored over sodium wire. Where necessary they were also dried with $LiAlH_4$. The $SiCl_4$ used in the nmr reactions described in Chapter Six was fractionated on the vacuum line to remove any HCl formed from hydrolysis.

2.3.2 Sodium

B.W.L. Graham (53) found that yields of metal-metal coupling reactions using alkali-halide elimination were adversely affected by alkaline impurities in the alkali metal. For this reason, all sodium used in amalgam preparations was purified by heating under vacuum in a glass tube with one or two side arms. This allowed the molten sodium to be poured or boiled away from the contaminants, which remained on the glass.

2.3.3 Metal Carbonyls

a) Cobalt Carbonyl ($Co_2(CO)_8$):

This was supplied by Pressure Chemical Company, vacuum

sublimed at 40-45°C and stored at -25°C. All handling was carried out in a glovebox.

b) $M_2(CO)_{10}$ (M = Mn,Re) :

These were supplied by Pressure Chemical Company and Strem Chemicals Inc.,respectively.

$Mn_2(CO)_{10}$ was kept in a fridge and used without further treatment. $Re_2(CO)_{10}$ was kept at room temperature and handled as a non-air-sensitive compound.

c) Vanadium Carbonyl ($Na[CH_3O(CH_2CH_2O)_2CH_3]_2V(CO)_6$) :

This was supplied by Pressure Chemical Company as the diglyme-stabilized sodium salt. When fresh it has a mustard yellow appearance but forms a brown surface coating after extended storage (even at -25°C). All handling of the bulk sample was done in a glovebox.

2.3.4 Germanium Halides

a) $GeCl_4$ and $GeBr_4$

These were both supplied by Koch-Light Laboratories Ltd. (U.K.) and could be freed from any hydrolysis contaminants by vacuum line fractionation.

b) $MeGeCl_3$:

This was supplied by Alpha Products in 40% purity (as monitored by nmr). The bulk of the 60% "contaminant" was Me_2GeCl_2 which was found extremely difficult to separate, even with very long fractionation times. Gas/liquid chromatography on a 25 foot preparative column, with 10% SE30 on Chromosorb W as packing, only succeeded in separating a small component of Me_3GeCl.

Analytical work with 1% OV 17 on Chromosorb W gave reasonable separation. However, this was only available in an analytical column set up for destructive Flame Ionization

detection. Largely due to vacuum line fractionations, the $MeGeCl_3$ proportion was improved to 60%. It was used in this form in the work described in Section 6.2.

c) Me_2GeCl_2:

This was supplied by Alpha Products with purity levels of 85-90%. The remaining component was $MeGeCl_3$ which could be reduced to a few percent by vacuum line fractionation at -45^oC over long periods. As with the $MeGeCl_3$ above, this compound was stored under vacuum in a fridge, using a teflon-tapped glass tube.

d) $MeGeBr_3$:

As supplied by Laramie Chemical Company, this chemical was 90% $MeGeBr_3$ and 10% Me_2GeBr_2 (by nmr). The latter was easily removed by vacuum line fractionation. It was kept as described above for the chlorides.

2.3.5 Germanium Hydrides

a) Monogermane (GeH_4):

This was prepared by Jolly's method (112):

$$GeO_2 \xrightarrow[H^+]{BH_4^-} GeH_4$$

No N_2 carrier gas was used and 50% H_3PO_4 was used with a 3:1 BH_4^- : Ge(IV) ratio.

b) Dimethylgermane (Me_2GeH_2) :

This was prepared by:

$$Me_2GeCl_2 \xrightarrow{BH_4^-} Me_2GeH_2$$

and characterised by infrared and nmr spectra, with reference to the literature (113,114).

c) $MeGeH_2Br$, Me_2GeHBr and GeH_3Br :

These were prepared in high yield using the low temperature reaction described by Geisler *et al.* (115):

$$Me_xGeH_{4-x} + Br_2 \xrightarrow{-127^\circ \text{ to } -100^\circ C} Me_xGeH_{3-x}Br + HBr$$

Allowing the n-propanol bath used for the overnight reaction to warm up much higher than $-100^\circ C$ was found to increase the dibromide yields. Infrared and nmr checks on these compounds could be made with reference to the literature (114, 116, 117, 118).

d) GeH_3I :

This was prepared by the sealed pressure-tube reaction described by Anderson et al. (119) :

$$GeH_4 + I_2 \longrightarrow GeH_3I + HI$$

When carried out at room temperature, in the dark, with a deficit of I_2, yields of GeH_3I were almost quantitative.

2.3.6 Silyl Halides

a) SiH_3I :

This was prepared in low yields by the method described by Emeléus et al. (120) :

$$SiH_4 + HI \xrightarrow[AlI_3]{80^\circ C} SiH_3I + H_2$$

All preparations formed some $(SiH_3)_2O$ and no samples of SiH_3I were obtained completely free of this, as monitored by infrared spectra. (121,122).

b) SiH_3Br :

This was prepared by Ward's method (123) :

$$C_6H_5SiCl_3 \xrightarrow[Et_2O]{LiAlH_4} C_6H_5SiH_3 \xrightarrow[-78^\circ C]{HBr} C_6H_6 + SiH_3Br$$

and product identification made from the infrared spectra. (122).

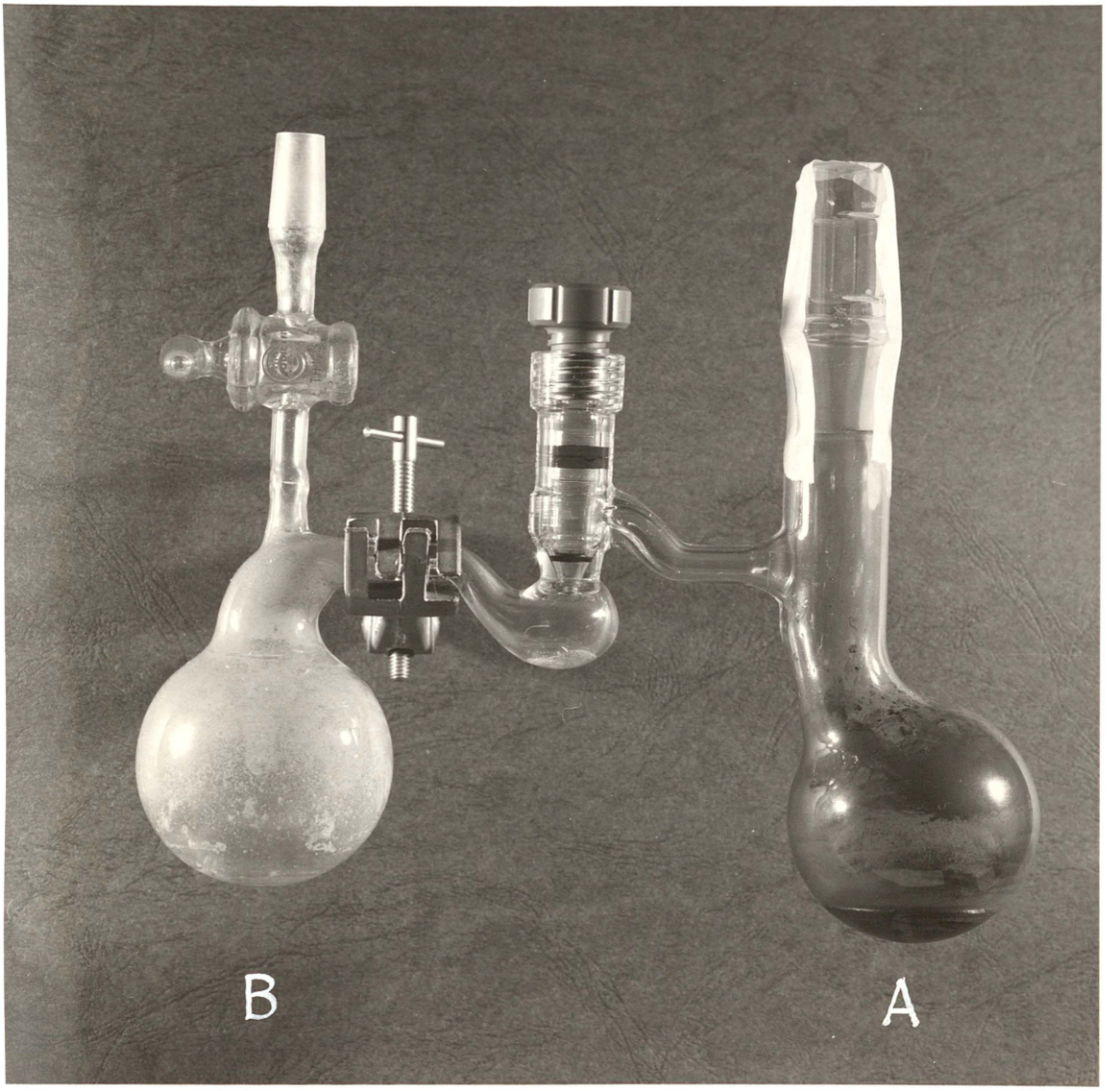
2.4 Preparative Techniques

The general method of preparation and reaction described in Chapters Three, Four, Five and Seven is common to them all and will be described here.

All production and reaction of $NaCo(CO)_4$ and $NaMn(CO)_5$ was carried out in the vessel pictured in Figure 2.1. The whole vessel is initially evacuated and flamed under vacuum. Both taps are closed prior to transfer to a glovebox. (N.B. The central tap has O-rings resistant to polar solvents). In the glovebox, the stopper in Bulb A is removed against the vacuum in that part only, admitting nitrogen. A measured quantity of $Co_2(CO)_8$ is added and dissolved in ca. 30 mls of diethyl ether. Sodium amalgam excess (typically ca. 10-15 mls at 1% concentration) and a magnetic follower are added before restoppering and taping up the stopper. The vessel is removed from the glovebox and left stirring for ca. 3 hours or until the ether solution is completely clear. The sludge of finely divided mercury is allowed to settle before decanting the solution from the amalgam. Using the vacuum still in bulb B, the solution is drawn into that part of the vessel via the O-ring tap.

If the other reactant is a volatile one, the ether is condensed out of bulb B, leaving white $NaCo(CO)_4$ which is pumped to remove any volatile impurities (e.g.any unreduced $Co_2(CO)_8$) Fresh,dry solvent (usually Et_2O or THF) is then condensed into bulb B, followed by the volatile reactant. This reaction side of the vessel can be warmed up for reaction without contact with the amalgam in bulb A. For most reactions the vessel is swirled at room temperature for ca. 15-20 minutes. Solvent is then condensed out of the reaction bulb at room temperature (or below, if any products are volatile.) Volatile components are then pumped out through a U-trap at $-196^{o}C$ before condensing 5-10 mls of extraction solvent (usually pentane or hexane) back into bulb B. This solution is then pipetted out of the reaction vessel in a glovebox,

Figure 2.1 Reduction / Reaction Vessel



from which point handling and purification is carried out as described for individual cases.

When the other reactant is involatile, this is pipetted into bulb B as a solution, before anion solution is decanted. The solvent is removed, leaving the bulb under vacuum as before. In these cases, the reaction is carried out directly, as the anion solution is drawn through from bulb A.

Further points about this system include:

1) Only Et_2O was used as solvent for the reductions, as THF was found to give suspensions of the amalgam sludge which would not settle completely, resulting in some of the material coming through into the reaction bulb.

2) Involatile reactants were added before decanting the anion solution because exposure of the latter even to normal glovebox atmosphere generally resulted in some reoxidation. This could be seen by red or brown discolouration. Combined with 1) above, this meant that all reactions of involatiles were carried out in Et_2O.

3) Most reaction systems used excess $NaCo(CO)_4$, since there is no convenient way to monitor the yield from this reduction. In those systems requiring more exact quantities of $NaCo(CO)_4$, after the initial decanting the Et_2O is recondensed onto the amalgam and any remaining $NaCo(CO)_4$ is rinsed through to bulb B.

4) In some $NaCo(CO)_4$ preparations, concentrated ether solutions form a brown etherate, which comes down as an oil. However, removal of all the ether from the system returns the pure, white salt.

In the case of the preparation of $NaMn(CO)_5$, the same procedure was used, with the following minor exceptions:

a) Reduction times are much shorter (generally 15

minutes to 1 hour) and give rise to a pale green solution from the yellow $Mn_2(CO)_{10}$ solution).

b) $Mn_2(CO)_{10}$ generally turns up in the reaction products, due to halogen exchange with the germyl halide, followed by salt elimination:

$$NaMn(CO)_5 + R_3GeX \longrightarrow R_3GeNa + XMn(CO)_5$$

$$XMn(CO)_5 + NaMn(CO)_5 \longrightarrow Mn_2(CO)_{10} + NaX$$

(In the cobalt system, the formation of the much less stable $XCo(CO)_4$ is not significant.)

CHAPTER THREE

Cobalt Carbonyl Derivatives of $GeCl_4$

3.1 Reactions of $GeCl_4$ with $NaCo(CO)_4$

In a typical reaction, $Co_2(CO)_8$ (970 mg ; 2.8 mmoles) was reduced with Na/Hg as described in Section 2.4 and reacted in Et_2O with $GeCl_4$ (1050 mg ; 4.9 mmoles) at room temperature for 10 minutes. After removal of the solvent, residues were extracted with hexane. An infrared spectrum of this crude extract showed $Cl_3GeCo(CO)_4$, $Cl_2Ge[CO(CO)_4]_2$ and $ClGe[Co(CO)_4]_3$ to be present (as identified below).

Sublimation at 6°C gave $Cl_3GeCo(CO)_4$ (1020 mg ; 60%) as a pale yellow solid (M.P. = 69° - 72°C in a sealed capillary). (N.B. Sublimation was found to be a more efficient technique than successive recrystallisations from hexane).

After removal of this component, further sublimation at 10°- 30°C gave $Cl_2Ge[Co(CO)_4]_2$ (an orange solid with a melting point of 100° - 102°C with decomposition) as a minor product. N.B. The yield of this compound rose to ca. 15% only at 8 : 1 $Co(CO)_4^-$ / $GeCl_4$ ratio.

Crude physical separation of the $ClGe[Co(CO)_4]_3$ component of the product mixture was possible due to the decreasing hexane solubility of these compounds in hexane with additional $-Co(CO)_4$ substitution. Thus, $ClGe[Co(CO)_4]_3$ was deposited as a deep red outer ring, surrounding the orange $Cl_2Ge[Co(CO)_4]_2$ and yellow $Cl_3GeCo(CO)_4$. The pure $ClGe[Co(CO)_4]_3$ was isolated in ca. 30% yield (as estimated from infrared data - see discussion) by crystallisation from hexane at -20°C over a day or so. Alternatively, after removal of the $Cl_3GeCo(CO)_4$ and $Cl_2Ge[Co(CO)_4]_2$ components by sublimation the

$ClGe[Co(CO)_4]_3$ could be sublimed from the residues at 40°C over a period of several hours , as a deep red solid. (M.P. = 73-75°C in a sealed capillary ; Analysis : Calculated for Cl : 5.72% ; Found : 5.76%)

The reaction was also carried out at 4 : 1 and 8 : 1 $Co(CO)_4^-/GeCl_4$ ratios. Yields from these reactions (which gave the same mixture of products) were estimated by infrared absorption intensities as:

$Cl_3GeCo(CO)_4$	:	60 - 70%
$Cl_2Ge[Co(CO)_4]_2$	:	$\leq$ 15%
$ClGe[Co(CO)_4]_3$	:	25 - 30%

3.2 Characterisation of $NaCo(CO)_4/GeCl_4$ Products.

3.2.1 Infrared Spectra.

The infrared spectra of $Cl_3GeCo(CO)_4$, $Cl_2Ge[Co(CO)_4]_2$ and $ClGe[Co(CO)_4]_3$ are given in Table 3.1 a, b and c, respectively. The former two compounds have already been reported and their assignments may be compared directly with the literature data.

$ClGe[Co(CO)_4]_3$ is a new compound whose tin analogue is known. The crystal structure of $ClSn[Co(CO)_4]_3$ has been done (80) and shows C_{3v} molecular symmetry. The close agreement of the spectra of the germanium and tin analogues (six of the $3A_1 + 4E$ modes predicted for C_{3v} are seen) supports the assignment of $ClGe[Co(CO)_4]_3$ as a C_{3v} species also. With a 0.1mm solution cell, full scale carbonyl absorptions could be obtained using concentrations of ca. 2.2 mg/ml (i.e. ca. 3.5×10^{-3}M).

The assignment of all spectra is discussed in Chapter Eight, while the carbonyl stretching regions are shown in Figures 8.1 (p.153) , 8.3 (p.159) and 8.5 (p.165) for

Table 3.1

Infrared Spectra of Products from $NaCo(CO)_4/GeCl_4$

a) Infrared Spectrum of $Cl_3GeCo(CO)_4$

Hexane Solution	Nujol Mull	Reference(109)(i)	Assignment (ii)
2122.6 (4.8)	2122.2 (5.3)	2123 (s)	νCO (A_1)
2068.6 (4.9)	2067.8 (5.1)	2070 (s)	νCO (A_1)
2050.1 (10)	2048.2 (10)	2052 (vs)	νCO (E)
	2027 (1.5)	2034 (sh)	$\nu^{13}CO$
2012.5 (0.8)	2009 (0.8)	2013 (w)	$\nu^{13}CO$
552 (2.0)	547 (2.3)	549 (vs)	δCo-C-O (A_1)
463 (0.9)	460 (1.5)	463 (s)	νCo-C, δCo-C-O(E)
409 (1.1)	406 (w)	405 (s)	νGeCl (E)
390 (1.1)	387 (w)	390 (s)	νGeCl (A_1)

Notes

i) Cyclohexane solution.

ii) Symmetry assignments are those given in (109).

iii) Other literature infrared data for this compound appear in (51,66,110,112)

b) Infrared Spectrum of $Cl_2Ge[Co(CO)_4]_2$

Hexane Solution	Nujol Mull	Reference(51)(i)	Assignment
2117.8 (1.6)	2116.8 (1.2)	2117 (0.1)	νCO (A_1)
2100.1 (9.9)	2099.0 (9.4)	2100 (9.6)	νCO (B_1)
2058.1 (7.3)	2056.9 (5.8)	2058 (6.7)	νCO) $2A_1$
2054.5 (4.7,sh)	2054 (5.5,sh)	2054 (3.8,sh)	νCO) +
2044.8 (10)	2042.9 (10)	2044 (10)	νCO) $2B_1$
2027.8 (6.9)	2026.1 (5.1)	2026 (4.4)	νCO) +
2015.7 (2.9)	2013.8 (2.9)	2016 (2.4)	νCO) B_2

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Table 3.1 contd.

Hexane Solution	Nujol Mull	Assignment
548 (2.3)	548 (2.6)	δCo-C-O (A_1+B_1)
536 (2.5)	536 (2.5)	
	402 (w)	νGeCl (B_1)
362 (0.8)	360 (vw)	νGeCl (A_1)
336 (0.5)	329 (vw)	δCo-C-O (A_1+B_1)
308 (0.6)	320 (vw)	

Note

i) In cyclohexane solution

c) Infrared Spectrum of $ClGe[Co(CO)_4]_3$

Hexane Solution	Nujol Mull	$ClSn[Co(CO)_4]_3$(i)	Assignment
2109.2 (0.9)	2109 (0.5,br)	2110 (vw)	νCO (A_1)
2088.2 (9.8)	2087.2 (9.7)	2088 (s)	νCO (E)
2049.1 (7.8)	2047.8 (5.7)	2049 (mw)	νCO ($2A_1$ + 3E)
2044.7 (7.0,sh)		2043 (mw,sh)	νCO
2028.5 (10)	2028.4 (10)	2028 (s)	νCO
2003.1 (4.6)	2000.0 (3.1)	2001 (w)	νCO
537 (3.2)	546 (2.2,sh)		δCo-C-O (A_1+E)
	536 (2.8)		
483 (w)			δCo-C-O, νCo-C (A_1+E)
	402 (w)		νGe-Cl (E)

Note

i) Reference (79) in cyclohexane.

$Cl_3GeCo(CO)_4$, $Cl_2Ge[Co(CO)_4]_2$ and $ClGe[Co(CO)_4]_3$, respectively.

3.2.2 Mass Spectra

The mass spectrum of $Cl_3GeCo(CO)_4$ shows a weak parent ion envelope (m/e = 346-358) and the expected fragments corresponding to carbonyl loss. Similar, weaker series of fragments arise from $(P-Cl)^+$. The whole spectrum is listed in Table 8.1 (p.*136*).

The mass spectrum of $Cl_2Ge[Co(CO)_4]_2$ shows no parent ion, but does show envelopes corresponding to both $(P-CO)^+$ and $(P-Cl)^+$. The expected carbonyl loss fragments from each of these ions form the predominant part of the spectrum, which is listed in Table 8.2 (p.*137*).

The spectrum of $ClGe[Co(CO)_4]_3$ shows no parent ion, but $(P-CO)^+$ and the fragments due to carbonyl loss from this are seen. The whole spectrum is listed in Table 8.3. (p.*138*).

The discussion of all mass spectra is given in Sections 8.1 and 8.2.

3.2.3 Handling

$ClGe[Co(CO)_4]_3$ has been kept under nitrogen in a refrigerator for several months without any sign of change. Routine bench handling in air resulted in no detectable oxidation or decomposition. Similar handling was possible for the deep red hydrocarbon solutions.

3.3 Reactions of $NaCo(CO)_4/GeCl_4$ Products

3.3.1 Reaction with $LiAlH_4$

An attempted reduction with $LiAlH_4$ of a 1:1:1 mixture of $Cl_3GeCo(CO)_4$, $Cl_2Ge[Co(CO)_4]_2$ and $ClGe[Co(CO)_4]_3$ was carried out in Et_2O at room temperature, under vacuum. Immediate gas evolution was evident. This ceased in ca.

10 minutes. Residues were hexane insoluble and an Et_2O extract showed no infrared carbonyl absorptions. $LiAlH_4$ apparently causes decomposition of all three compounds, though there is no indication of the fate of the germanium in this system.

3.3.2 Reactions with HgX_2

a) Reaction of $Cl_3GeCo(CO)_4$ with $HgCl_2$:

In hexane solution, under vacuum, after 3 hours at room temperature no visible change had occurred. The infrared spectra showed that no reaction had taken place. The reaction was repeated in THF to see whether a polar solvent had any effect, by dissolving more $HgCl_2$. The pale yellow solution colour was lost over ca. 24 hours but no infrared spectral changes were evident, even after 34 hours.

Discussion :

These results are interesting in the light of the quantitative Ge-Co cleavage found from reaction of $Me_xGeH_{3-x}Co(CO)_4$ (x = 0 to 3) with $HgCl_2$. (49,53,54,133). The apparent stabilization of the Ge-Co bond by $-GeX_3$ does not seem to show up as part of a trend with increased halogenation, in terms of reaction rate, when compared with the results of the analogous reactions in Chapter Four, where X = Br. This would imply that the effect is rather one of thermodynamic stabilization of the Ge-Co bond.

b) Reaction of $ClGe[Co(CO)_4]_3$ with HgI_2 :

The reaction :

$$BrGe[Co(CO)_4]_3 + HgBr_2 \longrightarrow Br_2Ge[Co(CO)_4]_2 + BrHgCo(CO)_4$$

(described in Chapter Four) suggested a synthetic route to asymmetric substitution on germanium in these systems. e.g.

$$ClGe[Co(CO)_4]_3 + HgI_2 \longrightarrow ClGeI[Co(CO)_4]_2 + IHgCo(CO)_4$$

Alternatively, the halogen atoms could redistribute to give a mixture of $Cl_2Ge[Co(CO)_4]_2$ and $I_2Ge[Co(CO)_4]_2$.

Solid HgI_2 was added to a hexane solution of $ClGe[Co(CO)_4]_3$ and warmed to room temperature under vacuum. The reaction was monitored by solution infrared sampling in a glovebox.

After 30 minutes : Weak infrared absorptions at ca. 2115, 2100 and 2044 cm^{-1}, characteristic of $X_2Ge[Co(CO)_4]_2$ species began to appear.

After 2.5 hours : Decomposition was noted by a 50% drop in carbonyl absorptions intensities. The following absorptions could be distinguished from the weakening $ClGe[Co(CO)_4]_3$ modes. (All values in cm^{-1}) :

Product	$Cl_2Ge[Co(CO)_4]_2$(i)	$I_2Ge[Co(CO)_4]_2$(ii)
2114.2	2117.8	2113
2098.5	2100.1	2096
2056.2	2058.1	2054
	2054.5 (sh)	2051 (sh)
2044.4	2044.8	2042
2028.2	2027.8	2025
2014.3	2015.7	2013

Notes

i) Values from this work in hexane. (See Table 3.1b, p.41)

ii) Reference (51) in cyclohexane.

After 11 hours : The dicobalt product intensities had stayed almost constant, but the $ClGe[Co(CO)_4]_3$ had been further consumed.

After 25 hours : No carbonyl absorptions could be seen.

Discussion :

The choice of starting materials was made to maximise

the separation of possible carbonyl infrared absorptions. From the above results it seems quite clear that the asymmetric compound (i.e. $ClGeI[Co(CO)_4]_2$) did form and showed no sign of redistribution. Rather, it seemed to decompose directly to a non-carbonyl-containing species. This process appeared to reach equilibrium with its formation from $ClGe[Co(CO)_4]_3$ as shown by its static concentration between 2.5 hours and 11 hours of reaction. Such an equilibrium would make isolation of the asymmetric product difficult. The decomposition route, apparently preferable to redistribution, is undetermined at this point.

3.3.3 Reflux Reactions

a) A 1:1:1 mixture of $Cl_3Co(CO)_4$, $Cl_2Ge[Co(CO)_4]_2$ and $ClGe[Co(CO)_4]_3$ was refluxed in hexane (69°C), under nitrogen, and monitored by infrared spectra. After 5 minutes, the amount of $ClGe[Co(CO)_4]_3$ was unchanged while the other two had diminished by ca. 30%. New carbonyl bands appeared at 2112 cm^{-1}(w) 2062 cm^{-1} (s) and 1844 cm^{-1}(m). After a further 10 minutes, decomposition had reduced all intensities ; more for $Cl_3GeCo(CO)_4$ and $Cl_2Ge[Co(CO)_4]_2$ than for $ClGe[Co(CO)_4]_3$ and the extra modes above. No carbonyl absorptions were evident after a further 5 minutes of reflux. The identiy of the component contributing the extra absorptions remains unknown.

b) Reflux of $ClGe[Co(CO)_4]_3$:

After 2 hours of reflux in pentane (36°C) had shown no changes, 10 minutes of reflux in hexane (69°C) changed the red solution to yellow/brown. Infrared spectra showed the formation and subsequent decomposition of bridged-carbonyl species whose absorptions were deduced to include :

2111 cm^{-1}(w) , 2081 cm^{-1}(w-m) , 2062 cm^{-1}(s) , 2045 cm^{-1}(vs) ca. 2030 cm^{-1}(s) , 1845 cm^{-1}(m) , 1828 cm^{-1}(w). While some of these modes are possibly contributed to by $GeCo_4(CO)_{14}$ (2079 (vs) , 2061 (vs) , 2040 (m) , 2032 (s) , 2023 (m) , 2005 (w) , 1848 (m)) and $(CO)_4CoGeCo_3(CO)_9$ (2112 (w) , 2083 (s) , 2045 (vs) , 2029 (m) , 2008 (vw) , 1991 (vw)) (See Section 3.5), not all of the relative intensities of the observed absorptions can be accounted for in this way. As with the case above, the remaining component in this system remains unassigned.

3.3.4 Reaction with $NaCo(CO)_4$

a) Reaction of $Cl_3GeCo(CO)_4$ with $NaCo(CO)_4$:

$NaCo(CO)_4$, prepared from $Co_2(CO)_8$ (470 mg ; 1.4 mmoles), was reacted in Et_2O at room temperature with $Cl_3GeCo(CO)_4$ (160 mg ; 0.46 mmoles) for 20 minutes. The residues from the deep red reaction solution were only slightly soluble in hexane. The composition of successive hexane extracts was as follows :

Extract	Composition
1	$ClGe[Co(CO)_4]_3$ > $GeCo_4(CO)_{14}$ >> $Co_2(CO)_8$
2	$GeCo_4(CO)_{14}$ >> $ClGe[Co(CO)_4]_3$
3	$Ge[Co(CO)_4]_4$ > $ClGe[Co(CO)_4]_3$, $Co_2(CO)_8$
4	$Ge[Co(CO)_4]_4$ >> $Co_2(CO)_8$

Identifications were made on the basis of infrared spectra, using the data reported in Section 3.5 and reference (124).

b) Reaction of $ClGe[Co(CO)_4]_3$ with $NaCo(CO)_4$:

$ClGe[Co(CO)_4]_3$ (160 mg ; 0.26 mmoles) was reacted at room temperature in Et_2O with large excess of $NaCo(CO)_4$ for 20 minutes. The bulk of the dark red residues was hexane insoluble. The hexane extracts showed $GeCo_4(CO)_{14}$(See Section 3.5) and a little $Co_2(CO)_8$. The former came out of solution

in the refrigerator as a red/black solid. A further Et_2O extract showed only $Co_2(CO)_8$, while a subsequent hexane extract showed only $Co_4(CO)_{12}$ (by infrared and mass spectra).

3.4 Discussion

The reactions of $GeCl_4$ with $NaCo(CO)_4$ clearly show the stepwise substitution of chlorine by $-Co(CO)_4$. This is supported by the further reactions of the partially substituted derivatives with $Co(CO)_4^-$, which produce higher members of the series, including some tetracobalt species, discussed in the next section.

W.A.G. Graham prepared $Cl_3GeCo(CO)_4$ using either 1:1 $GeCl_4/NaCo(CO)_4$ or 23 : 19 $GeCl_4/Co_2(CO)_8$ reactant ratios in THF with 57%, 60% yields respectively. (51). (Using these routes, other authors have made further reports on this compound, including vibrational analyses (66,109,110,112), force field calculations (108) and an X-ray crystal structure. (132)) However, using a 5.9 : 2.3 $Co_2(CO)_8/GeCl_4$ ratio, Graham also reports the preparation of $Cl_2Ge[Co(CO)_4]_2$ in THF in 72% yield.(51). No comments were made about the other products from these reactions. Thus, it would seem that the products formed from these preparations were dependent upon the reaction ratios only. As noted above, using $GeCl_4/Co(CO)_4^-$ ratios of 1:1 , 1:4 and 1:8 in Et_2O, the 60 - 70% product each time was $Cl_3GeCo(CO)_4$. $Cl_2Ge[Co(CO)_4]_2$ was only a minor product in these systems, which produced $ClGe[Co(CO)_4]_3$ as the secondary product. Reported data for this and the analogous tin systems (51,52,79) indicate that THF seems to make the substitution reactions much more sensitive to reactant ratios (whether $Co(CO)_4^-$ or $Co_2(CO)_8$ is used). Possibly the better solvation of $GeCl_4$ by THF enhances the relative reactivity

of the chlorine substituents as successive $-Co(CO)_4$ groups are added. e.g. A stronger positive inductive effect would be expected to make better leaving groups of the chlorine substituents.

The low yields of $Cl_2Ge[Co(CO)_4]_2$ in the Et_2O system are interesting. Even in the $Cl_3GeCo(CO)_4/NaCo(CO)_4$ system. where only monosubstitution was required, no $Cl_2Ge[Co(CO)_4]_2$ was seen at all and only further substituted derivatives were seen. This must be compared with the 72% yield for $Cl_2Ge[Co(CO)_4]_2$ and 50% yield for $Cl_2Sn[Co(CO)_4]_2$ reported by Graham in the THF system.(51). While the difference between the two $Cl_2Ge[Co(CO)_4]_2$ preparations may be considered in terms of the better adduct formation in THF conferring greater solution stability on this product, the distinction between it and the mono- or tris-cobalt species in solution is unclear. As noted in the next Chapter, yields of $Br_2Ge[Co(CO)_4]_2$ are good, at the expense of $Br_3GeCo(CO)_4$. This would seem to rule out a configurational instability, while the "high" yield formation of the tris-cobalt products rules out possible steric hindrance in $Cl_2Ge[Co(CO)_4]_2$.

An interesting and useful point arising from the infrared monitoring of $GeCl_4/Co(CO)_4^-$ reaction products was the relationship between absorption intensities and concentrations of $Cl_xGe[Co(CO)_4]_{4-x}$. (x = 1, 2, 3). Amounts of each required to give full scale absorptions of the chosen modes in hexane solution are :

$Cl_3GeCo(CO)_4$ (2123 cm^{-1}) = 6.4 mg/ml (1.8×10^{-2}M)

$Cl_2Ge[Co(CO)_4]_2$ (2100 cm^{-1}) = 2.0 mg/ml (4.1×10^{-3}M)

$ClGe[Co(CO)_4]_3$ (2088 cm^{-1}) = 2.2 mg/ml (3.5×10^{-3}M)

These modes were chosen as being :

i) due to comparable vibrations in all compounds. (See Chapter Eight)

ii) of comparable relative intensities in the spectra of the pure compounds (See Table 3.1, p. 41)

iii) well clear of the main, lower energy envelope of absorptions and readily resolved.

The above data was useful for the semi-quantitative analysis of crude product mixtures in this reaction system.

3.5 Preparation, Characterisation and Reactions of $GeCo_4(CO)_x$ Species

3.5.1 Preparation of $Ge[Co(CO)_4]_4$

This compound was isolated from the reaction products of $Cl_3GeCo(CO)_4/NaCo(CO)_4$ by successive hexane extractions. (See Section 3.3.4). This was the least hexane soluble of the carbonyl products and was largely separable from other reaction products on this basis. In a refrigerator overnight, the product came out of the deep red hexane solution as a black solid.

3.5.2 Characterisation of $Ge[Co(CO)_4]_4$

a) Infrared Spectrum :

This is given in Table 3.2a and the carbonyl absorptions are shown in Figure 8.7 (p.171). The spectrum compares very closely with that of the established $Sn[Co(CO)_4]_4$ (52). Under full tetrahedral symmetry , both compounds have the following predicted carbonyl stretching modes : $2A_1 + E + T_1 + 3T_2$. Of these only the T_2 modes are infrared active. Thus, the observation of only two strong modes in both spectra is an indication that these molecules are close to this symmetry. The significance of the weak modes is further discussed in Chapter Eight.

Table 3.2

Infrared Spectra of $GeCo_4(CO)_x$ Derivatives

a) Infrared Spectrum of $Ge[Co(CO)_4]_4$

Hexane Solution (i)		Nujol Mull (ii)		$Sn[Co(CO)_4]_4$ (iii)
2078.9	(8.1)	2081.2	(s)	2079 (9.8)
2067	(1.0)(iv)	2069	(m) (iv)	
2042	(2.0)(iv)	2038	(m) (iv)	
2032	(2.2,sh)			2032 (3.0)
2019,8	(10)	2019.7	(vs)	2018 (10)
2000	(0.7,br)	2001	(m)	1999 (0.5,sh)
				1994 (2.3)
		541	(s)	
		508	(s)	

Notes

i) See Figure 8.7 ,p.*171* for the carbonyl stretching region spectrum.

ii) Numerical relative intensities were not taken due to significant baseline drift.

iii) Reference (52) in cyclohexane

iv) These seemed to be impurity absorptions which varied in relative intensities between samples. (e.g. compare the nujol and hexane solution intensities of these modes). They became more predominant over long storage periods. The most likely decomposition product giving rise to these modes is $Co_2(CO)_8$.(124).

Table 3.2 Contd

b) Infrared Spectrum of $GeCo_4(CO)_{14}$

Hexane Solution (a)	Nujol Mull (b)
2079.3 (9.7)	2077.4
2061.3 (10)	2059.0
2040.4 (4.7)	2038.8
2032.0 (6.7)	2029.3
2022.8 (3.6)	2020.5
2004.7 (1.0)	2000.0
1848 (3.4)	1843

Notes

a) See Figure 8.7 (p.*171*).

b) Relative intensities for this sample have been omitted due to significant baseline drift over the region.

b) Mass Spectrum :

The highest mass ion seen in this spectrum is $GeCo_4(CO)_{14}^+$. Though this may be expected and reconcilable (as discussed in Sections 8.1 and 8.2) and similar to that seen for the tin analogue, the observation of $(P-2CO)^+$ is not of direct use in the initial characterisation of this compound. The full spectrum seen for this species is listed in Table 8.4 (p.*139*).

c) Handling :

$Ge[Co(CO)_4]_4$ is a black solid with low hexane solubility, giving a deep red solution at low concentrations. The compound was found to decompose under room temperature handling, but did not seem to be affected by short manipulations in air. These observations concur with those made about $Sn[Co(CO)_4]_4$ (52,81). Further comments made about that compound are also likely to apply to $Ge[Co(CO)_4]_4$.

3.5.3 Preparations of $GeCo_4(CO)_{14}$

a) This product first became evident in samples of $ClGe[Co(CO)_4]_3$ (before recrystallisation) prepared from the reaction of $GeCl_4$ with $NaCo(CO)_4$. The observation of extra, weak absorptions in the spectra of these samples could be assigned in retrospect to $GeCo_4(CO)_{14}$.

b) A sample of $GeCo_4(CO)_{14}$ was isolated as the only tetracobalt derivative of germanium from the reaction of $ClGe[Co(CO)_4]_3$ with $NaCo(CO)_4$. (Section 3.3.4b)

c) $GeCo_4(CO)_{14}$ was isolated as the second of three products in the $Cl_3GeCo(CO)_4/NaCo(CO)_4$ reaction system. (Section 3.3.4a) It was the major of the two tetracobalt species.

d) The 15 week room temperature reaction of GeH_4 with $Co_2(CO)_8$ gave $GeCo_4(CO)_{14}$ as the major product, along with one other tetracobalt compound. (Section 6.*1* , p. *98*)

e) Though not isolated from the $GeBr_4/NaCo(CO)_4$ systems discussed in Chapter Four, the fourth component of these was most probably $GeCo_4(CO)_{14}$, from the infrared data.

3.5.4 Characterisation and Reactions of $GeCo_4(CO)_{14}$

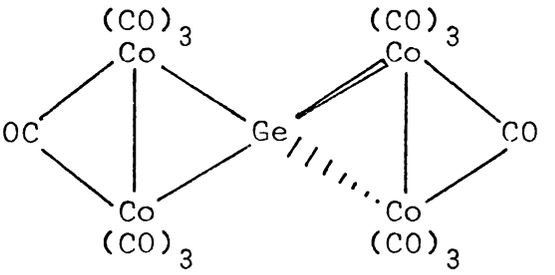
a) Mass Spectrum :

This shows a highest mass envelope at m/e = 698-704 , corresponding to $GeCo_4(CO)_{14}^+$. Successive loss of 14 carbonyls from this forms the major fragmentation pattern in this spectrum. The spectrum is listed in Table 8.4 (p.*139*) and further discussed in Sections 8.1 and 8.2.

b) Infrared Spectrum :

This is listed in Table 3.2b and the carbonyl region is shown in Figure 8.7 (p.*171*). The presence of the bridging carbonyl mode eliminates the "all-terminal" configuration discussed in the previous section.($Ge[Co(CO)_4]_4$). A carbonyl stretching mode analysis for possible $GeCo_4(CO)_{14}$ or $GeCo_4(CO)_{15}$ configurations from the infrared and mass spectral data above predicts :

$(CO)_7Co_2GeCo_2(CO)_7$ (D_{2d}):



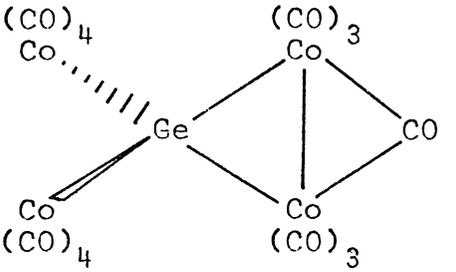
Terminal : $2A_1 + A_2 + B_1 + 2B_2 + 3E$; Bridging : $A_1 + B_2$

(Of these, only the B_2 and E modes are infrared active).

$[Co(CO)_4]_2GeCo_2(CO)_7$ (C_s) :

Terminal : 7A' + 7A"

Bridging : A'



(All modes are infrared active).

The simplicity of the infrared spectrum observed suggests the D_{2d} formulation as the more likely of the two. However, the observation of six terminal modes, where five are predicted may preclude this. On the other hand, the eight terminal modes not seen for the C_s molecule implies a great deal of accidental degeneracy, overlap and vanishing intensities. This is further discussed in Chapter Eight.

c) Carbonyl Determinations :

At this point with no certain identification of this product, CO analysis using Br_2 destruction of the molecule was investigated. Several attempts, including standardisation runs using $Co_2(CO)_8$ gave unsatisfactory results for both CO yield (typically 70 - 80%) and reproducibility. (N.B. Accuracy to within 5% was required to be able to distinguish the 15 and 14 carbonyl-containing derivatives.

d) Thermal Decomposition :

An attempted recrystallisation of $GeCo_4(CO)_{14}$, using hot hexane was found to cause its decomposition to $(CO)_4CoGeCo_3(CO)_9$, identified by its infrared spectrum. (97). Since this compound had also been established by its mass spectrum and crystal structure, it served as a useful reference point in determining the exact composition of the product under analysis here.(i.e. the CO evolution on decomposition could be monitored to determine whether one or two carbonyls are lost in forming $GeCo_4(CO)_{13}$).

Using the crude solid product from the $GeH_4/Co_2(CO)_8$ reaction, known to contain some non-carbonyl impurity,13.5 mg was heated in a black-painted, teflon-tapped glass tube, under vacuum, in an oil bath. No CO was evolved in two hours at 45°C so subsequent heating was at 50°C ($\pm$ 3°C). Table 3.3 shows the results from this reaction, which are plotted in Figure 3.1.

Table 3.3

CO Evolution with Time in the Thermal Decompositon of $GeCo_4(CO)_{14}$

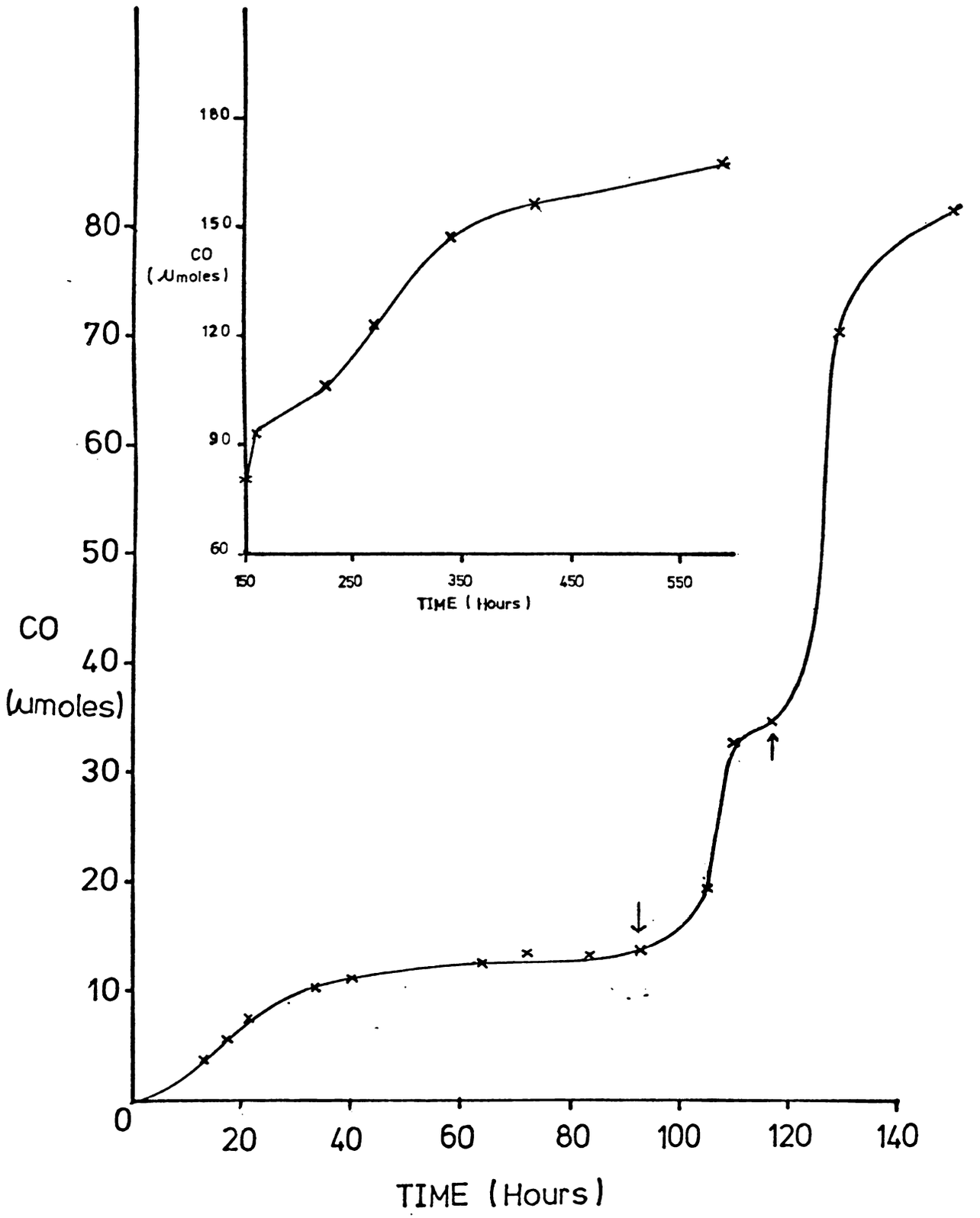
Time (hours)	1.0	13	17	21	33.5
CO evolved (μmoles)	0.5	3.8	5.6	7.5	10.3
Time (hours)	40	64	72 *	83	93
CO evolved (μmoles)	11.1	12.5	13.4	13.2	13.9
Time (hours)	105	110	117	129	150
CO evolved (μmoles)	19.3	32.8	34.7	70.1	81.4
Time (hours)	162	225	270	342	418
CO evolved (μmoles)	93.8	106.6	123.3	148.4	157.0
Time (hours)	591	870	900		
CO evolved (μmoles)	168.2	173.3	174.1		

* This result seems to be a reading error, as seen by the following, smaller cumulative CO total.

After 93 hours, when the curve in Figure 3.1 started its upward turn, hexane was condensed into the vessel and a small volume of deep red/purple solution was removed for an infrared spectrum. (c.f. deep red/brown solution of starting material in hexane). The spectrum obtained is given below, along with that of $(CO)_4CoGeCo_3(CO)_9$ reported by Schmid. (97). As evident from the weak appearance of the very strong 2061 cm^{-1} mode of the starting material, conversion of the sample was not quite complete.

Continued heating after removal of the solvent resulted in a sharp rise in CO evolution, which then tailed off. The addition of solvent had apparently exposed fresh reaction surface.

Figure 3.1 Thermal Decomposition of $GeCo_4(CO)_{14}$



Arrows mark infrared solution sampling points.

Hexane Extract from $GeCo_4(CO)_{14}$ Thermal Decomposition	$(CO)_4CoGeCo_3(CO)_9$ (97) (hexane)
2111.4 (w)	2112 (w)
2082.0 (s)	2083 (s)
2061.1 (w)	
2043.7 (vs)	2045 (vs)
2027.0 (m)	2029 (m)
2007.1 (w)	2008 (vw)
1990 (vw)	1991 (vw)

This was confirmed by adding further solvent after 117 hours, to resample the product. Again, there was a sharp increase in CO evolution after solvent removal. This then tailed off again. The infrared sample at this point showed only $(CO)_4CoGeCo_3(CO)_9$ in reduced quantity. After 150 hours, 2-3 mls of hexane were condensed into the tube and all further reaction was carried out with solvent present.

After 342 hours most of the solution colour had gone and CO evolution was clearly tailing off. By 900 hours no further carbonyl could be detected in solution. Thus the asymptote to the curve in Figure 3.1 at its upper limit is at ca. 175 μmoles of evolved CO. This implies ca. 12.5 μmoles of pure $GeCo_4(CO)_{14}$ or ca. 11.7 μmoles of pure $GeCo_4(CO)_{15}$. i.e. Formation of $GeCo_4(CO)_{13}$ requires 12.5 and 23.4 μmoles of CO evolution, respectively. (N.B. No allowance is made here for the removal of the two infrared samples in the course of this decomposition. This would depress the expected amounts of CO evolved slightly.)

The clear plateau in Figure 3.1 at ca. 13 μmoles of evolved CO, along with the infrared observation that decomposition to $GeCo_4(CO)_{13}$ was virtually complete at this

stage is a clear indication that the product under analysis here is $GeCo_4(CO)_{14}$.

Another decomposition done completely in solution at 55° - 60°C gave almost complete conversion to $(CO)_4CoGeCo_3(CO)_9$ in 2 hours as monitored by its infrared spectrum. In this case 5.5 mg of hexane soluble product only had evolved 6.6 μmoles of CO at this point, where complete conversion of pure product is predicted to give 7.8 μmoles. Decomposition was largely complete in 69 hours.

This thermal decomposition, taken along with the infrared and mass spectral data establishes the compound as $GeCo_4(CO)_{14}$ and points strongly to its proposed configuration. (p. *54*). This is supported to some extent by the reports of the compounds $Sn[Fe(CO)_4]_4$ and $Ge[Fe(CO)_4]_4$ (37,38), whose configuration was shown in Chapter One (p. *16*). i.e. the Group IVB atom occupies a bridging position between two pairs of iron atoms in much the same way as proposed for the cobalt compound above. However, the exact configuration of $GeCo_4(CO)_{14}$ still needs to be established with certainty. The two obvious techniques to do this are X-ray crystallography and ^{13}C nmr.

e) Handling :

$GeCo_4(CO)_{14}$ is a deep red solid which has been kept for some months under nitrogen at -20°C, without decomposition. Solubility in aliphatic solvents is low and not much better in ethers. Solutions are deep red in colour. Neither solutions nor solid have shown signs of decomposition during short bench-handling in air. The melting point in a sealed capillary is 79-80°C with gas evolution evident from the partially melted solid. Chromatography on dry alumina (6 mm i.d. x 6 cm column) gave only $Co_2(CO)_8$. (c.f. $((Me_2Ge)_2Co_2(CO)_6$, discussed in

Chapter Six.

3.5.5 Preparation of $(CO)_4CoGeCo_3(CO)_9$

An attempted preparation of this compound using Schmid's method (97) was unsuccessful. i.e. :

$$GeBr_4 + 4NaCo(CO)_4 \xrightarrow[\text{2.5 hrs R.T.}\\ \text{20 hrs } 55^oC]{\text{2:1 Pet. Ether/benzene}} (CO)_4CoGeCo_3(CO)_9 + 4NaBr$$

However, as described in the previous section, this compound was derived virtually quantitatively from the thermal decomposition of $GeCo_4(CO)_{14}$. This type of reaction was probably also responsible for the presence of small amounts of $(CO)_4CoGeCo_3(CO)_9$ from the reaction of GeH_4 with $Co_2(CO)_8$, which produced mainly $GeCo_4(CO)_{14}$. (See Chapter Six). Its very small yield in that case reflects the reaction rate at room temperature. (N.B. four days at 50°C were required for the near-completion of this reaction. See the previous section). The $(CO)_4CoGeCo_3(CO)_9$ prepared in this work has been characterised by infrared and mass spectra, both of which agree closely with that reported by Schmid (97). Its infrared spectrum is reproduced (as obtained here) in Figure 8.7 (p.171).

3.6 Discussion

The work of this Chapter set out to establish the position of germanium - cobalt derivatives, as compared to the silicon and tin analogues known, with respect to structural classification and spectroscopic properties. The latter will be summarised as part of an overall picture of a larger group of related compounds in Chapter Eight.

Each member of the series $Cl_xGe[Co(CO)_4]_{4-x}$ (x = 0 - 4) has now been prepared and independently characterised. This fact in itself places germanium apart from silicon, whose size

determines that it will form clustered compounds when the higher members of the series are attempted to be prepared. While this series of compounds is directly analogous to the known tin series, germanium again sets itself apart in the formation of two additional $GeCo_4$ species. While $Sn[Co(CO)_4]_4$ is the only $SnCo_4$ product so far observed, it has been found that $Ge[Co(CO)_4]_4$ is a much less favoured compound, probably due to the increased steric interactions with the smaller germanium as the central atom. Rather, under room temperature conditions, the germanium system prefers to relieve this interaction by closing up the cobalt substituents into two pairs, forming $(CO)_7Co_2GeCo_2(CO)_7$, where $GeCo_2(CO)_7$ takes the place of the second bridging carbonyl in the basic $Co_2(CO)_8$ structure. The preference for this configuration over the crowded $Ge[Co(CO)_4]_4$ is seen in the mass spectrum of the latter species, where spectrometer conditions cause it to condense, with loss of two carbonyl groups, to form $GeCo_4(CO)_{14}^+$.

Under higher temperature conditions, the favoured conformation becomes the cluster compound $(CO)_4CoGeCo_3(CO)_9$, analogous to the silicon system. The mechanism of this decomposition is interesting in that it must involve cleavage of a cobalt - cobalt bond (after terminal/bridging CO exchange, possibly, as discussed by Job and Curtis (77)) to form the tricobalt cluster. As mentioned in Chapter One, the size of germanium seems to be more suited to this configuration than silicon, as reflected in yields of similar preparations. This result is also affected by the great affinity of silicon for oxygen, which results in the majority of its compounds binding through a carbonyl oxygen , e.g. $R_3SiOCCo_3(CO)_9$.

The relative stabilities of $GeCo_4(CO)_{13}$ and $GeCo_4(CO)_{14}$

under mass spectral conditions is seen from the fact that the parent ions for both are seen. This can be contrasted with $Ge[Co(CO)_4]_4$, $ClGe[Co(CO)_4]_3$ and $Cl_2Ge[Co(CO)_4]_2$, all of which show highest mass ions corresponding to carbonyl loss. However, this effect is not peculiar to germanium, as each of the tin analogues is found to do the same. (See Chapter Eight).

Overall, the stepwise substitution of $GeCl_4$ is found to favour $Cl_3GeCo(CO)_4$ and $ClGe[Co(CO)_4]_3$ at the expense of $Cl_2Ge[Co(CO)_4]_2$. This would seem to be related to mechanism of formation, since the stability of the isolated $Cl_2Ge[Co(CO)_4]_2$ is no different from the other two. For the tetracobalt species, while $GeCo_4(CO)_{14}$ is the favoured room temperature product, the overall stability order is :

$$Ge[Co(CO)_4]_4 \; < \; (CO)_7Co_2GeCo_2(CO)_7 \; < \; (CO)_4CoGeCo_3(CO)_9$$

The interrelationship of the tetracobalt derivatives seen here is an interesting extension of the reports of similar behaviour for the di- and tricobalt derivatives of germanium. In a system directly analogous to the thermal decomposition of $GeCo_4(CO)_{14}$ reported above, Graham (86) has reported that under reflux in hexane, $[Co(CO)_4]GePhCo_2(CO)_7$ condenses to form the clustered compound $PhGeCo_3(CO)_9$. Under high pressures of CO, $PhGeCo_3(CO)_{11}$ forms $PhGe[Co(CO)_4]_3$ which rapidly loses CO to reform the undecacarbonyl.

A similar transformation of this type is reported by O'Brien *et al.* (87). Under CO pressure, $Ph_2GeCo_2(CO)_7$ is converted to the stable $Ph_2Ge[Co(CO)_4]_2$. An interesting feature of this system is that the required conditions for the reverse reaction (which should be more favourable in terms of the stability order noted above) have not been found. In contrast, the energy barrier for the conversion

of $GeCo_4(CO)_{14}$ to $GeCo_4(CO)_{13}$, as discussed above, has been quite closely defined by the observed 45°-$50^{\circ}C$ cut-off temperature.

The importance of steric considerations in these interconversions is seen from the relative stabilities of $PhGe[Co(CO)_4]_3$ and $Ph_2Ge[Co(CO)_4]_2$. As expected from such considerations, the stability of the proposed $MeGe[Co(CO)_4]_3$ (discussed in Chapter Five) is intermediate between these two compounds. However, electronic effects have also been seen as the dominant feature in product stability toward interconversion. The derivatives $XGe[Co(CO)_4]_3$ (X = halogen) provide a direct contrast with the methyl and phenyl derivatives mentioned above. They are quite stable in the "tris-terminal" configuration. Also, no halogen-substituted Group IVB-bridged derivatives of cobalt carbonyl have yet been reported.

Chapter Four

Cobalt Carbonyl Derivatives of $GeBr_4$

4.1 Reaction of $GeBr_4$ with $NaCo(CO)_4$

Using the general method described in Chapter Two, a typical reaction was carried out as follows :

$GeBr_4$ (1420 mg ; 3.6 mmoles) was reacted in Et_2O with $NaCo(CO)_4$ (produced from $Co_2(CO)_8$; 2360 mg ; 6.9 mmoles) at room temperature for twenty minutes. The ether was removed and residues were extracted with n - hexane.

Sublimation of this extract at 6°C for several hours gave pale lemon - yellow $Br_3GeCo(CO)_4$ (170 mg ; 0.35 mmoles ; 10% yield).

After removal of the above component, successive sublimations between room temperature and 50°C were found to be gradually concentrating the $Br_2Ge[Co(CO)_4]_2$ component from the product mixture. However, complete separation of this compound was not found to be possible with this technique. A facile purification of $Br_2Ge[Co(CO)_4]_2$ from the 35° - 50°C sublimate mixtures involved washing the sublimate lightly with hexane while still on the cold finger. This removed an outer red/brown layer of solid, leaving a much more tightly packed layer of orange/yellow solid. The former was found to contain a mixture of all remaining products. The solid remaining on the probe was pure $Br_2Ge[Co(CO)_4]_2$ (604 mg ; 1.05 mmoles ; 29% ; N.B.This was isolated yield. Reaction yield was estimated by infrared at *ca.* 40%). While this suggests that this compound was coming up onto the probe first, infrared spectra of these sublimates in the early stages showed that $Br_2Ge[Co(CO)_4]_2$, $BrGe[Co(CO)_4]_3$ and a tetracobalt

species were all present.

Separation of $BrGe[Co(CO)_4]_3$ from the reaction residues was not readily achieved by sublimation. The most successful isolation of pure $BrGe[Co(CO)_4]_3$ involved crystallising this product out of the concentrated crude hexane extract from the reaction over a period of days in a refrigerator at $-20^{o}C$. (Yield ; 40%, based on $GeBr_4$ used).

A further component observed in the product mixture contained bridging carbonyl and was distinguished by infrared absorptions at : 2112 (w) , 2079 (m) , 2062 (s) , 1844 (m). This compound could not be isolated from product mixtures, but its handling properties and the likeness of the above absorptions to those seen in the $GeCl_4$ system suggest strongly that this component is a tetracobalt - substituted germanium derivative.

The reaction of $GeBr_4/NaCo(CO)_4$ in 2 : 1 petroleum ether/benzene under vacuum was first sampled after 10 hours at room temperature, for an infrared spectrum. There was no sign of $Br_3GeCo(CO)_4$. The $Br_2Ge[Co(CO)_4]_2$ component was estimated at 30% of the carbonyl-containing products, while the major product was $BrGe[Co(CO)_4]_3$ at *ca*. 40%. The remaining carbonyl compound was the unidentified bridged species.N.B. While the similar concentration/absorption relationships for $Br_2Ge[Co(CO)_4]_2$ and $BrGe[Co(CO)_4]_3$ could be determined from the isolated compounds, the unidentified species could only be determined by elimination. Further reaction at room temperature was found to decompose all carbonyl-containing products by *ca*. 140 hours of reaction time.

4.2 Characterisation of $GeBr_4/NaCo(CO)_4$ Products

4.2.1 Infrared Spectra

The spectra for $Br_3GeCo(CO)_4$, $Br_2Ge[Co(CO)_4]_2$ and

$BrGe[Co(CO)_4]_3$ are given in Tables 4.1 a, b and c , respectively. The carbonyl stretching regions are shown in Figures 8.1 (p.*153*) , 8.3 (p.*159*) and 8.5 (p.*165*).

The analysis of the spectrum of $Br_3GeCo(CO)_4$ has already been reported in some detail. (51,109,111,112).

$Br_2Ge[Co(CO)_4]_2$ is a new compound and has been assigned in parallel with the tin analogue. C_{2v} molecular symmetry predicts $3A_1 + A_2 + 3B_1 + B_2$ carbonyl stretching modes. (Of these, A_2 is infrared inactive). Seven absorptions are seen in agreement with this prediction and with the result found for $Br_2Sn[Co(CO)_4]_2$.(51).

$BrGe[Co(CO)_4]_3$ is also a new compound and can be assigned by close analogy with $BrSn[Co(CO)_4]_3$. (79). In this case, C_{3v} molecular symmetry predicts $3A_1 + A_2 + 4E$ carbonyl stretching modes. (Again, A_2 is infrared inactive). The observation of six of the seven modes expected is consistent with this symmetry.

The assignment of each of these compounds is discussed in more detail in Chapter Eight.

4.2.2 Mass Spectra

The mass spectrum of $Br_3GeCo(CO)_4$ is given in Table 8.5 (p.*140*). The notable feature of this spectrum is that no parent ion is seen. However, both $(P-CO)^+$ and $(P-Br)^+$ occur, along with the fragments due to carbonyl loss from these ions.

The mass spectrum of $Br_2Ge[Co(CO)_4]_2$ is listed in Table 8.6 (p.*142*) and also shows no parent ion. $(P-CO)^+$ is the highest mass fragment seen and the major envelopes are due to carbonyl loss from this.

Once again no parent ion is seen in the mass spectrum of $BrGe[Co(CO)_4]_3$, (Table 8.7 , p.*143*) but $(P-CO)^+$ and the other carbonyl loss fragments are seen.

Table 4.1

Infrared Spectra of Products from $GeBr_4/NaCo(CO)_4$

a) Infrared Spectrum of $Br_3GeCo(CO)_4$

Hexane Solution	Nujol Mull	Reference(109)(i)	Assignment(ii)
2119.2 (5.2)	2118.7 (6.6)	2119 (s)	νCO (A_1)
2066.0 (4.8)	2065.3 (5.3)	2067 (s)	νCO (A_1)
2048.0 (10)	2045.7 (10)	2050 (vs)	νCO (E)
	2007 (0.7)	2011 (w)	ν^{13}CO
544 (2.1)	542 (2.5)	547 (s)	δCo-C-O (E)
458 (0.8)	457 (1.0)	460 (m)	νCo-C, δCo-C-O(E)

Notes

i) Cyclohexane solution.

ii) Symmetry assigments follow those in (109).

b) Infrared Spectrum of $Br_2Ge[Co(CO)_4]_2$

Hexane Solution	Nujol Mull	$Br_2Sn[Co(CO)_4]_2$(i)	Assigment
2116.6 (2.1)	2115.8 (2.0)	2113 (0.1)	νCO (A_1)
2098.7 (9.7)	2097.9 (10)	2096 (9.7)	νCO (B_1)
2057.0 (6.4)	2055.9 (6.2)	2055 (4.5)	νCO } $2A_1$
2055* (5.3,sh)	2053* (4.6,sh)	2050 (2.8,sh)	νCO } +
2044.4 (10)	2042.5 (10)	2040 (10)	νCO } $2B_1$
2026.1 (6.0)	2024.9 (4.9)	2026 (3.3)	νCO } +
2015.0 (2.5)	2013.2 (2.9)	2016 (2.2,sh)	νCO } B_2
549	546		δCo-C-O
536	536		(A_1 + B_1)

Notes

i) Reference (51) in cyclohexane

*) This shoulder is not as clear as its analogue in $Cl_2Ge[Co(CO)_4]_2$ (See Figure 8.3, p.*159*) and can only be seen on a scale of 2 cm^{-1}/mm or larger.

Table 4.1 contd.

c) Infrared Spectrum of $BrGe[Co(CO)_4]_3$

Hexane Solution	Nujol Mull	$BrSn[Co(CO)_4]_3$ (i)	Assignment
2111.8 (0.4)		2108 (vw)	νCO (A_1)
2087.8 (10)	2086.9 (10)	2086 (s)	νCO (E)
2049.0 (5.1)	2048.0 (3.3)	2048 (m)	νCO } $2A_1$ + 3E
2044.8 (3.2,sh)		2042 (mw)	νCO } $2A_1$ + 3E
2028.0 (10)	2028.3 (9.2)	2026 (s)	νCO } $2A_1$ + 3E
2002.2 (3.6)	2000.0 (2.4)	2000 (m)	νCO } $2A_1$ + 3E
	536 (2.8)		$\delta Co-C-O$

Note

i) Reference (79) in cyclohexane.

The significance of the lack of parent ions in these spectra, along with other features observed are discussed in Sections 8.1 and 8.2 for each of these compounds.

4.2.3 Microanalyses

a) $Br_2Ge[Co(CO)_4]_2$: Found : Br = 25.4%

Calculated : Br = 27.8%

A check of the infrared spectrum of the sample used for analysis showed the strongest mode of $BrGe[Co(CO)_4]_3$ at 2088 cm^{-1} as a weak shoulder on the 2099 cm^{-1} mode of $Br_2Ge[Co(CO)_4]_2$. It was estimated that ca. 10% impurity of $BrGe[Co(CO)_4]_3$ would have been present in the sample analysed. This reduces the amount of bromine expected and gives better agreement of the calculated and experimental values.

b) $BrGe[Co(CO)_4]_3$ Found : Br = 13.07%. 12.90%

Calculated : Br = 12.02%

4.2.4 Handling

$Br_2Ge[Co(CO)_4]_2$ is a pale orange solid with a melting point of 104°-106°C (with decomposition) in a sealed capillary.

$BrGe[Co(CO)_4]_3$ is a deep brown/red solid with a melting point of 79°-81°C in a sealed capillary.

Both compounds are readily sublimed above room temperature. All three bromo-derivatives from this preparation have been stored under nitrogen in a refrigerator for some months without decomposition. No oxidation or decomposition was noted during short bench-handling in air.

4.3 Reaction of $GeBr_4/NaCo(CO)_4$ Products

4.3.1 Reaction with MeMgI

A mixture consisting of ca. 80% $Br_3GeCo(CO)_4$ and ca. 10% of each of $Br_2Ge[Co(CO)_4]_2$ and $BrGe[Co(CO)_4]_3$ was reacted with excess MeMgI in Et_2O in a glovebox. The resultant dark brown

reaction residue was barely soluble in ether or alkane solvents. Infrared sampling showed it to be completely devoid of carbonyl. i.e. Complete decomposition had taken place in ca. 5 minutes at room temperature.

4.3.2 Reactions with $HgBr_2$

a) Reaction of $HgBr_2$ with $Br_3GeCo(CO)_4$:

This was carried out under vacuum in hexane solution, using $Br_3GeCo(CO)_4$ in mixture with $Br_2Ge[Co(CO)_4]_2$. In contrast with the latter compound (discussed below), no changes in the $Br_3GeCo(CO)_4$ were observed over 57 hours at room temperature, in the light. It did not seem to be related to the $Br_2Ge[Co(CO)_4]_2$ quantity at all.

b) Reaction of $HgBr_2$ with $Br_2Ge[Co(CO)_4]_2$:

In the reaction described in 4.3.2a above, loss of $Br_2Ge[Co(CO)_4]_2$ was evident from the infrared spectrum after 5 hours at room temperature, under vacuum, in hexane. This coincided with the first sign of the 2072 cm^{-1} and 2007 cm^{-1} modes of $Hg[Co(CO)_4]_2$. (124).The $Br_2Ge[Co(CO)_4]_2$ continued to diminish over the next several hours and was essentially all gone in 33 hours. Its disappearance was accompanied by a corresponding increase in the amount of $Hg[Co(CO)_4]_2$, also evident as a yellow coating on the glassware and remaining $HgBr_2$.

Discussion :

Initially it was thought that the reaction may be following the path :

$$Br_2Ge[Co(CO)_4]_2 \xrightarrow{HgBr_2} Br_3GeCo(CO)_4 + BrHgCo(CO)_4$$

$$\longrightarrow Br_4Ge + Hg[Co(CO)_4]_2$$

However, the observed independence of $Br_3GeCo(CO)_4$ from the reaction of $Br_2Ge[Co(CO)_4]_2$ does not really support this. When the reaction was monitored for a further day, no changes

in the quantities of $Br_3GeCo(CO)_4$ and $Hg[Co(CO)_4]_2$ occurred. Thus, rather than following a stepwise process as shown above, the reaction is essentially a one - step process :

$$Br_2Ge[Co(CO)_4]_2 + HgBr_2 \longrightarrow Br_4Ge + Hg[Co(CO)_4]_2$$

i.e. The constant concentration and persistence of the $Br_3GeCo(CO)_4$ seem to rule this out as an intermediate in this reaction.

However, work by Chipperfield et al. (134) has indicated that reactions of this type are stepwise. They report a number of isolated compounds corresponding to mono-substitution in transition metal carbonyls. e.g. :

$$Me_3GeMn(CO)_5 + HgBr_2 \longrightarrow Me_3GeBr + (CO)_5MnHgBr$$

(N.B. This study does not include cobalt carbonyl derivatives).

c) Reaction of $HgBr_2$ with $BrGe[Co(CO)_4]_3$:

A sample of $BrGe[Co(CO)_4]_3$ whose infrared spectrum showed a very small trace of $Br_2Ge[Co(CO)_4]_2$ was reacted with $HgBr_2$ in hexane, under vacuum, at room temperature. After one hour, $Br_2Ge[Co(CO)_4]_2$ had formed at the expense of $BrGe[Co(CO)_4]_3$. The 2072 cm^{-1} mode of $Hg[Co(CO)_4]_2$ was also evident. Thus :

$$BrGe[Co(CO)_4]_3 + HgBr_2 \longrightarrow Br_2Ge[Co(CO)_4]_2 + BrHgCo(CO)_4$$

The only suggestion of the bromomercury compound was an unassigned weak/medium absorption at 2079 cm^{-1}. This was supported by the fact that this absorption diminished as the amount of $Hg[Co(CO)_4]_2$ increased as would be expected with further substitution of the $BrHgCo(CO)_4$.

Spectra run after 2.5 and 4 hours showed the continued loss of $BrGe[Co(CO)_4]_3$ and increase in amount of $Br_2Ge[Co(CO)_4]_2$. The solution colour changed from its initial red/brown to orange during this reaction. After four hours

the amount of $Br_2Ge[Co(CO)_4]_2$ remained static, even as the last of the $BrGe[Co(CO)_4]_3$ reacted. This is consistent with the $Br_2Ge[Co(CO)_4]_2$ beginning to react itself, as seen in the previous section. (In that case, reaction was apparent after ca. 5 hours). No sign of $Br_3GeCo(CO)_4$ was detected in this period, supporting the observations in b) above. After 6.5 hours the only species left were $Br_2Ge[Co(CO)_4]_2$ and $Hg[Co(CO)_4]_2$.

4.4 Discussion

4.4.1 Reaction Products

The interesting feature of the $GeBr_4/NaCo(CO)_4$ reactions is the extent to which substitution takes place. This may be compared directly with the results of the analogous $GeCl_4$ reactions :

	Yields (%)	
	X = Cl	X = Br
$X_3GeCo(CO)_4$	60-70	10
$X_2Ge[Co(CO)_4]_2$	< 15	40
$XGe[Co(CO)_4]_3$	25-30	40
$GeCo_4(CO)_y$	traces	ca. 10

(N.B. The yield of the tetracobalt product in the $GeBr_4$ system is only an estimate, since this component was not isolated). It would seem that the bulk of the bromine sustituents (with consequent steric and electronic interactions) promotes higher substitution by $-Co(CO)_4$ groups. This is also seen from yields in the analogous tin system, as discussed in Chapter One. This is probably the reason for the low $Br_3GeCo(CO)_4$ yield, which was also found by Graham (52) using a $GeBr_4/Co_2(CO)_8$ reaction in THF. The close correspondence of the infrared absorptions of the tetracobalt derivative found here with those of the unassigned product

from the reflux reactions of $Cl_3GeCo(CO)_4$ and $ClGe[Co(CO)_4]_3$ (Sections 3.3.3 a,b) supports the idea of common tetracobalt products. This is expected from the stepwise substitution of X in GeX_4. N.B. This mode of reaction was further supported by the prolonged, mixed solvent reaction of $GeBr_4/Co(CO)_4^-$ which clearly enhanced the formation of tetracobalt product(s).

4.4.2 Characterisation

The characterisation by infrared and mass spectra is fully discussed in Chapter Eight. While the microanalysis figures obtained for the two new compounds in this chapter were not as close to the calculated values as would be hoped for, at within 1%, they are comparable with data reported for the tin analogues :

$Br_2Sn[Co(CO)_4]_2$	;	Br (calculated)	= 25.3%
(76)		Br (found)	= 26.5%
$BrSn[Co(CO)_4]_3$	;	Br (calculated)	= 24.8%
(79)		Br (found)	= 27.6%

Several similar correspondences are reported for a number of cobalt carbonyl derivatives of germanium and tin halides. (51,76,79,90).

4.4.3 Reactions with $HgBr_2$

Previous work (53,54) with monocobalt derivatives of germanium showed quantitative cleavage of the germanium - cobalt bond, using HgX_2. The work described here has introduced the need for the consideration of relative activation effects of substituents on the germanium atom in such reactions. Without having carried out any kinetic work, a comparison of relative rates of substitution for the compounds studied here must be treated with care. Chipperfield et al.(134) have shown in their mercuration studies of $R_3M'X$ (R = alkyl ;

M' = Si,Ge,Sn ; X = $Mn(CO)_5$, $Fe(CO)_2Cp$, $Mo(CO)_3Cp$) with $HgBr_2$ that the reaction rates are generally (but not always) first order in each of [$HgBr_2$] and [organometallic]. While the solution concentrations of $HgBr_2$ in these studies were probably nearly constant(saturated) the bromogermylcobalt concentrations were quite arbitrary. However, the overlap amongst the reactions reported here gives a fairly clear indication of the overall processes in the series of compounds i.e. :

$$BrGe[Co(CO)_4]_3 \xrightarrow{HgBr_2} Br_2Ge[Co(CO)_4]_2$$

$$Br_2Ge[Co(CO)_4]_2 \xrightarrow{HgBr_2} GeBr_4$$

$$Br_3GeCo(CO)_4 \xrightarrow{HgBr_2} \text{no reaction (or exceedingly slow reaction)}$$

The time scale for the first reaction is clearly much shorter than that of the second, and the former is virtually complete by the time the latter becomes significant. This makes this pair of reactions useful for the separation of $Br_2Ge[Co(CO)_4]_2$ from mixtures with $BrGe[Co(CO)_4]_3$, as was found to be the case in all preparations of the dibromide.

Also, as was investigated in 3.3.2b (p. *44*), these reactions provide a synthetic route to possible asymmetrically-substituted derivatives.

i.e. $XGe[Co(CO)_4]_3 \xrightarrow{HgX'_2} XGeX'[Co(CO)_4]_2$

($X \neq X'$). As a consequence of the next stepwise substitution not occurring, only a single product is formed and this can be isolated, assuming it is stable. Though X has been limited to halogens so far, if similar reactions are established for alkyl and aryl derivatives, this opens up the synthetic possibility for a wide range of asymmetrically-substituted compounds. The asymmetric compounds themselves are potentially useful synthetic tools and could be further substituted or reacted by metal exchange reactions of the type discussed in

Chapter Seven.

As seen from the two HgX_2 reactions in the previous chapter, the behaviour of the chlorogermyl cobalt carbonyl derivatives in this system is directly parallel to that of the bromine-substituted analogues. This is a reflection of the very smilar handling properties and reactivities found for the isolated compounds in the two series $X_aGe[Co(CO)_4]_{4-a}$ (X = Cl, Br for a = 1,2,3).

CHAPTER FIVE

Cobalt Carbonyl Derivatives of Methyl-halogermanes

5.1 Derivatives of Me_2GeCl_2

5.1.1 Preparation of $Me_2GeClCo(CO)_4$

$NaCo(CO)_4$ from $Co_2(CO)_8$ (1140 mg ; 3.3 mmoles) was reacted with Me_2GeCl_2 (577 mg ; 3.3 mmoles) in ca. 10 mls of Et_2O at room temperature, under vacuum, for 15 minutes. The ether was removed from the now orange/brown solution and residues were pumped through a U-trap at -45°C for ca. 5 hours. This removed a small amount of pale yellow solid whose pentane solution infrared spectrum was exactly the same as that of the remaining pentane-soluble residues; i.e. $Me_2GeClCo(CO)_4$ as identified below; (580 mg ; 57%). The product was repeatedly recrystallised from pentane to give a pale yellow solid, which only just moves under vacuum. It kept for some weeks at -20°C under nitrogen. Under vacuum, no decomposition occurs at room temperature in the light, but even minor air exposure causes the formation of a green surface coating on the solid. Similarly, all carbonyl infrared absorptions were lost from a hexane solution kept in a screwtop vial at room temperature overnight.

5.1.2 Characterisation of $Me_2GeClCo(CO)_4$

a) Infrared Spectrum :

This is given in Table 5.1a and may be compared with the literature data shown in Table 1.4b (p.22). The molecular symmetry is C_s and the assignment of the spectrum can be made as a direct parallel with $Me_2GeHCo(CO)_4$ (54).

Table 5.1

Infrared Spectra of Cobalt Carbonyl Derivatives of Me_2GeCl_2

a) Infrared Spectrum of $Me_2GeClCo(CO)_4$

Hexane Solution	Cyclohexane Solution	Solid(i)	Assignment
2100.0 (5.3)	2099.7 (7.7)	2101 (6)	νCO (A')
2041.1 (6.8)	2040.2 (9.2)	2040 (5)	νCO (A')
2020.4 (10)	2019.6 (10)	2006 (10) (vbr)	νCO (A'+
2003.6 (9.1)	2003.0 (9.6)		νCO A")
1981 (1)	1982 (1)		$\nu^{13}CO$
1962 (1)	1962 (0.7)		$\nu^{13}CO$
837 (2)		842 (2)	δCH_3 (A")
805 (3)		805 (3)	δCH_3 (A')
606 (1)		604 (2)	νGeC (A")
576 (1)		572 (2)	νGeC (A')
550 (8)		546 (7)	δCo-C-O(A'+A")
505 (1)			δCo-C-O +
480 (1)			νCo-C
376 (3)			νCo-C (A')

Note

i) Recorded in a cold cell at -196°C.

b) Infrared Spectrum of $Me_2Ge[Co(CO)_4]_2$ (i)

	Assignment
2099.0 (3.1)	νCO (A_1)
2081.3 (9.6)	νCO (B_1)
2032 (7.3,sh)	νCO $2A_1$
2024.7 (8.5)	νCO +
2018.8 (10)	νCO $2B_1$
2006.7 (9.9)	νCO +
1997.0 (6.1)	νCO B_2
1965 (0.4)	$\nu^{13}CO$

Table 5.1b contd.

	Assignment	
832 (0.6)	δCH_3	$(A_1 + B_1)$
796 (1.7)	δCH_3	
546 (4.3)	$\delta Co\text{-}C\text{-}O$	$(A_1 + B_1)$

Note

i) Recorded as a hexane solution.

(See Chapter Eight). The carbonyl stretching region is depicted in Figure 8.2 (p.*156*).

b) Nuclear Magnetic Resonance :

In benzene solution with TMS as internal reference, the chemical shift for $Me_2GeClCo(CO)_4$ was found to be 9.07 τ (c.f 9.17τ in deuterobenzene solution - (77)).

c) Reaction with $LiAlH_4$, $LiAlD_4$:

Both of these reactants caused immediate evolution of incondensible gas (probably CO), when added to an Et_2O solution of $Me_2GeClCo(CO)_4$. The dark brown residue was not carbonyl-containing.

5.1.3 Preparation of $Me_2Ge[Co(CO)_4]_2$

$Me_2GeClCo(CO)_4$ was reacted in a 1:1 ratio with $NaCo(CO)_4$, or with a slight excess of $NaCo(CO)_4$, in Et_2O for 15 minutes at room temperature. Solvent was removed from the yellow/orange solution and the residues were hexane extracted. Recrystallisation of this extract from hexane, or sublimation at 20-25°C gave yellow $Me_2Ge[Co(CO)_4]_2$. (ca. 60% yields).

$Co_4(CO)_{12}$, sometimes found as a decomposition product in these systems, was difficult to separate. Attempted separation using a column of alumina plus 8% water (4cm x 5mm i.d.) in a glovebox was found to destroy all carbonyl-containing species. Sublimation at room temperature was also ineffective in separating the $Co_4(CO)_{12}$.

Handling in air caused decomposition in a matter of minutes. However, the air-sensitivity of $Me_2Ge[Co(CO)_4]_2$ was not as marked as that of $Me_2GeClCo(CO)_4$. A hexane solution in a stoppered vessel still showed the infrared absorptions of $Me_2Ge[Co(CO)_4]_2$ after 3 weeks at room temperature. Beyond this time, the $Me_2Ge[Co(CO)_4]_2$ had

decomposed completely.

5.1.4 Characterisation of $Me_2Ge[Co(CO)_4]_2$

a) Infrared Spectrum :

This is given in Table 5.1b and may be compared directly with the literature data in Table 1.4a. All seven infrared active carbonyl stretching modes predicted for C_{2v} molecular symmetry are seen. The assignment of these is discussed in Chapter Eight and they are shown in Figure 8.3 (p.*159*)

b) Nuclear Magnetic Resonance :

The chemical shift for $Me_2Ge[Co(CO)_4]_2$ in benzene is 8.71 τ. (c f. 8.77 τ reported in deuterobenzene - (77)).

5.1.5 Discussion

The preparative method for $Me_2Ge[Co(CO)_4]_2$ reported by Patmore and Graham (51) uses a 2:1 $NaCo(CO)_4/Me_2GeCl_2$ ratio, reacted in THF for ten minutes. This apparently only differs from the preparation of $Me_2GeClCo(CO)_4$ in that a 7.6 : 4.6 $NaCo(CO)_4/Me_2GeCl_2$ ratio is reported (51). Job and Curtis (77) have noted that excess $NaCo(CO)_4$ gives predominantly $Me_2GeClCo(CO)_4$ in these preparations. In addition they found that Me_2GeCl_2 gave better results than Me_2GeBr_2. In contrast Cleland *et al*. (78) report the converse in their preparations of diphenylgermyl bis-metal carbonyls.

In this work, the reactions of Me_2GeCl_2 with $NaCo(CO)_4$ in either Et_2O or THF, covering a reactant ratio range from just over 1:2 to *ca*. 1:10 , gave $Me_2GeClCo(CO)_4$ almost exclusively. The occasional presence of minor amounts of $Me_2Ge[Co(CO)_4]_2$ was indicated by the weak appearance in the infrared of the very strong 2081 cm^{-1} mode of that compound. It was necessary to react the isolated $Me_2GeClCo(CO)_4$ with further $NaCo(CO)_4$, to produce $Me_2Ge[Co(CO)_4]_2$. Under these circumstances, the product was formed quite readily.

The reasoning behind this reaction pattern is obscure at this stage. Cleland et al. (78) have suggested that halide displacement of one metal carbonyl group from a bis-metal carbonyl species could be responsible for the observation of only the mono-metal carbonyl derivative i.e. a redistribution between $Me_2Ge[Co(CO)_4]_2$ and Me_2GeCl_2. This is consistent with the observation that $Me_2Ge[Co(CO)_4]_2$ is formed from the isolated $Me_2GeClCo(CO)_4$ (free of Me_2GeCl_2). However, when further $NaCo(CO)_4$ was added directly to the untreated products of a $Me_2GeCl_2/NaCo(CO)_4$ reaction, $Me_2GeClCo(CO)_4$ was still the only final product.

5.2 Derivatives of $MeGeCl_3$

5.2.1 General

As noted in Chapter Two, the commercially available sample of $MeGeCl_3$ was actually 40 $MeGeCl_3$: 60 Me_2GeCl_2. Though the purification techniques mentioned were able to reverse this ratio, the initial identification of products from this system was very much dependent on knowing the data for the dimethylgermyl analogues described above. Though none of the compounds in this system could be prepared completely pure, the volatility difference between the mono- and dimethylgermyl derivatives, along with some crystallisation differentials, allowed the monomethyl products to be isolated at up to ca. 90% purity. The following notes will refer to the preparation and characterisation of the monomethyl compounds only, but all samples contained some of the dimethylgermyl analogue as impurity. As a result, the infrared data for the new compounds $MeGeCl_2Co(CO)_4$ and $MeGeCl[Co(CO)_4]_2$ are tabulated along with their closest established analogues.

5.2.2 Preparation of $MeGeCl_2Co(CO)_4$

$MeGeCl_3$ was reacted in THF with $NaCo(CO)_4$ at an approximate ratio of 1:1. The reaction solution was swirled at room temperature for 15 minutes. The solvent was removed and the orange residues were pumped for 12 hours. Very little solid was removed in this time. The hexane extract of the residue was sublimed at room temperature, giving $MeGeCl_2Co(CO)_4$ as a pale yellow solid with comparable handling properties to those described for $Me_2GeClCo(CO)_4$. (N.B. The compound appeared to be less volatile and less hexane soluble than its dimethylgermyl analogue).

5.2.3 Characterisation of $MeGeCl_2Co(CO)_4$

a) Infrared Spectrum :

This is given in Table 5.2a, along with that of $MeGeI_2Co(CO)_4$. (51) There is a close correspondence between the two compounds and the expected energy shifts for Cl- vs I- substituents is observed (See Chapter Eight). Both compounds show carbonyl stretching absorptions typical of C_s mono-(cobalt tetracarbonyl) derivatives. (See Figure 8.2, p.*156*).

b) Nuclear Magnetic Resonance :

The methyl chemical shift for $MeGeCl_2Co(CO)_4$ in benzene, relative to internal TMS is 8.75 τ.

5.2.4 Preparation of $MeGeCl[Co(CO)_4]_2$

$MeGeCl_2Co(CO)_4$ was reacted with excess $NaCo(CO)_4$ in Et_2O at room temperature for 15 minutes. The orange/brown hexane extract of the reaction residues was sublimed at room temperature. A hexane concentrate of this sublimate was left in a refrigerator at -20°C for two days. $MeGeCl[Co(CO)_4]_2$ crystallised out as a dark yellow solid.

Table 5.2

Infrared Spectra of Cobalt Carbonyl Derivatives of $MeGeCl_3$

a) Infrared Spectrum of $MeGeCl_2Co(CO)_4$

Hexane Solution	Solid(i)	$MeGeI_2Co(CO)_4$(ii)	Assignment
2112.6 (8)	2118 (8)	2106 (8.7)	νCO (A')
2057.4 (9)	2062 (7)	2053 (8.2)	νCO (A')
2037.6 (10)	2040-2020 (10)	2033 (9.8)	νCO (A' +
2024.4 (10)		2022 (10)	νCO A")
1989 (1)			$\nu^{13}CO$
801 (2)	806 (3)		δCH_3(A',A")
599 (1)	603 (2)		νGeC (A')
550 (6)	544 (8)		δCo-C-O
472 (2)	472 (3)		νCo-C (A',A")
391 (2,sh)	378 (2,sh)		νGeCl (A'
383 (3)	367 (3)		νGeCl + A")

Notes

i) Run in a cold cell at -196°C

ii) Reference (51) in cyclohexane

b) Infrared Spectrum of $MeGeCl[Co(CO)_4]_2$

Hexane Solution(i)	Nujol Mull	$MeGeI[Co(CO)_4]_2$(ii)	Assignment
2109.2 (3.5)[3.6]	2107.9 (2.4)	2106 (2.9)	νCO (A')
2091.1 (10) [10]	2089.6 (10)	2089 (10)	νCO (A")
2048.6 (5.2)[6.8]	2046.8 (4.4)	2046 (4.3)	νCO
2042.5 (5.4)[6.9]	2040.0 (4.5)	2040 (4.4)	νCO
2031.3 (9.3)[9.8]	2029.3 (9.2)	2030 (9.0)	νCO 3A' +
2024.6 (9.5)[10]	2022.5 (9.5)	2024 (9.2)	νCO 3A"
2014.4 (5.9)[8.6]	2012.5 (5.2)	2014 (4.9)	νCO
2001.7 (3.3)[5.7]	2000.7 (2.9)	2000 (2.9)	νCO
1980 (0.6)[0.6]			$\nu^{13}CO$

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Table 5.2b contd.

Hexane Solution(i)	Assignment
792 (0.7)	δCH_3 (A',A")
543 (3.2)	δCo-C-O (A',A")
501 (0.3)	δCo-C-O, νCo-C (A',A")

Notes

i) Figures in parentheses are relative intensities for the pure compound. Those in square brackets are intensities from the sample whose mass spectrum is reported in Section 5.2.5c).

ii) Reference (51) in cyclohexane

INSERT

The methyl chemical shift for $MeGeCl[Co(CO)_4]_2$ in benzene, relative to internal TMS is 8.64τ.

c) Mass Spectrum :

As was found for $Me_2Ge[Co(CO)_4]_2$, $Co_4(CO)_{12}$ was a fairly common contaminant. The handling properties of $MeGeCl[Co(CO)_4]_2$ were very much the same as those of $Me_2Ge[Co(CO)_4]_2$.

5.2.5 Characterisation of $MeGeCl[Co(CO)_4]_2$

a) Infrared Spectrum :

This is given in Table 5.2b and can be assigned by direct comparison with the established $MeGeI[Co(CO)_4]_2$. (51) Both compounds show the predicted eight carbonyl stretching modes for C_s molecular symmetry. (4A' + 4A"). The assignment of the spectrum is discussed in Chapter Eight and the carbonyl stretching modes are shown in Figure 8.4.(p.*162*).

b) Nuclear Magnetic Resonance :

The sample of $MeGeCl[Co(CO)_4]_2$ whose mass spectrum was run was that which showed the carbonyl stretching mode relative intensities given in square brackets in Table 5.2b. Apart from a small component of $Me_2Ge[Co(CO)_4]_2$ known to be present (and already subtracted from the infrared spectrum), the major component in the mass spectrum was $MeGeCl[Co(CO)_4]_2$. This is listed in Table 8.8 (p.*144*).

$MeGeCl[Co(CO)_4]_2$ shows no parent ion but $(P-CO)^+$ and the fragments due to carbonyl loss from this are observed.

The spectrum also contained another weak but distinct set of ions corresponding to $MeGeCo_3(CO)_x^+$ (x = 0 to 11). This result is discussed in Section 5.4, along with the inconsistent infrared relative intensities noted in Table 5.2b.

5.2.6 Reaction of $MeGeCl[Co(CO)_4]_2$ with $NaCo(CO)_4$

This reaction was carried out in Et_2O (using excess $NaCo(CO)_4$) for 15 minutes at room temperature. The hexane extract of the reaction residues showed largely

$MeGeCl[Co(CO)_4]_2$ and $Co_4(CO)_{12}$. However, there was some indication from absorptions at 2105, 2056, 1848 and 1836 cm^{-1} that there may have been a small amount of $[Co(CO)_4]GeMeCo_2(CO)_7$ formed from this reaction. (53). As they were minor effects in a complex spectrum, such an assignment is still quite speculative.

5.3 Derivatives of $MeGeBr_3$

5.3.1 General

While the results from the previous section established the two new monomethylgermyl derivatives in a general sense, many of the details remain uncertain, due to the contamination by the dimethylgermyl analogues. Also because of this, the products could not be characterised by elemental analysis.

$MeGeBr_3$ was available with a minor, readily separable Me_2GeBr_2 contaminant. This was used for a series of reactions parallel to those of the previous section. The following sections describe the preparation and characterisation of the new compounds $MeGeBr_2Co(CO)_4$ and $MeGeBr[Co(CO)_4]_2$, along with other products from this system.

5.3.2 Preparation of $MeGeBr_2Co(CO)_4$

$NaCo(CO)_4$ prepared from $Co_2(CO)_8$ (2380 mg , 7.0 mmoles) was reacted with $MeGeBr_3$ (1150 mg , 3.5 mmoles) in THF at room temperature for 15 minutes. The ether was removed, leaving yellow/orange residues. A hexane extract contained pure $MeGeBr_2Co(CO)_4$ (930 mg ; 63%) as a pale yellow solid. (M.P. = 78°-80°C in a sealed capillary).

The product is readily sublimable above ca. 10°C. It has been kept without change for a period of months, in a refrigerator, under nitrogen. After 30 hours in air, the solid shows some loss of colour but hexane solution infrared

intensities are still very strong. (The pale decomposition product formed on the solid surface is hexane insoluble).

An alternative preparation of $MeGeBr_2Co(CO)_4$ in Et_2O was much the same as that done in THF, but a small amount of $MeGeBr[Co(CO)_4]_2$ was also formed. This component could be removed by successive recrystallisations from hexane.

5.3.3 Characterisation of $MeGeBr_2Co(CO)_4$

a) Infrared Spectrum :

This is given in Table 5.3a, along with the data for $MeGeI_2Co(CO)_4$.(51). The correspondence between the two compounds is good and the carbonyl stretching modes conform to that expected for C_s molecular symmetry. (See Figure 8.2 p.*156*). The assignment is discussed in Chapter Eight.

b) Nuclear Magnetic Resonance :

In benzene, relative to internal TMS, $MeGeBr_2Co(CO)_4$ shows a methyl resonance at 8.43 τ.

c) Mass Spectrum :

This is listed in Table 8.9 (p.*145*) and is discussed in sections 8.1 and 8.2. The spectrum is notable for the absence of a parent ion. $(P-CO)^+$ is seen, along with the expected fragments due to carbonyl loss from this.

d) Microanalysis :

Found : Br = 39.03%, 38.62%, 37.32%

Calculated : Br = 38.19%

The first two analyses were done consecutively and the third on the following day. While all three are within the sort of limits found for this type of compound, the third result indicates that bromine was lost on standing, after the sample had been opened.

5.3.4 Partial Characterisation of $Me_2GeBrCo(CO)_4$.

This compound arose as a minor co-product, when

Table 5.3

Infrared Spectra of Cobalt Carbonyl Drivatives of $MeGeBr_3$

a) Infrared Spectrum of $MeGeBr_2Co(CO)_4$

Hexane Solution	Nujol Mull	$MeGeI_2$ $Co(CO)_4$(i)	Assignment
2110.1 (7.8)	2109.8 (7.8)	2106 (8.7)	νCO (A')
2055.8 (8.3)	2054.6 (7.4)	2053 (8.2)	νCO (A')
2035.9 (9.6)	2034.8 (9.8)	2033 (9.8)	νCO } A'
2023.7 (10)	2021.8 (10)	2022 (10)	νCO } + A"
1987 (0.4)			$\nu^{13}CO$
842 (0.2)			δCH_3
802 (0.8)	801 (1.0)		(A'+A")
595 (0.3)			νGeC (A')
549 (1.5)	546 (3.0)		δCo-C-O(A',A")
489 (0.3)			δCo-C-O,
473 (0.5)	470 (0.8)		νCo-C (A',A")

Note

i) Reference (51) in cyclohexane.

b) Infrared Spectrum of $MeGeBr[Co(CO)_4]_2$.

Hexane Solution	Nujol Mull	$MeGeI[Co(CO)_4]_2$(i)	Assignment
2108.4 (3.1)	2107.7 (3.2)	2106 (2.9)	νCO (A')
2090.5 (10)	2089.6 (10)	2089 (10)	νCO (A")
2048.6 (5.7)	2047.1 (5.0)	2046 (4.3)	νCO
2042.1 (5.7)	2040.8 (5.6)	2040 (4.4)	νCO 3A'
2031.4 (9.3)	2029.7 (9.4)	2030 (9.0)	νCO +
2024.8 (9.5)	2022.9 (9.8)	2024 (9.2)	νCO
2014.7 (6.1)	2013.5 (6.7)	2014 (4.9)	νCO 3A"
2001.4 (3.5)	2000.7 (4.5)	2000 (2.9)	νCO

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Table 5.3 contd.

Hexane Solution	Nujol Mull	$MeGeI[Co(CO)_4]_2$(i)	Assignment
794 (0.5)	792 (0.7)		δCH_3 (A',A")
541 (3.7)	539 (3.5)		δCo-C-O (A',A")
500 (0.9)	509 (1.2)		δCo-C-O,νCo-C (A',A")

Note

i) Reference (51) in cyclohexane.

Me_2GeBr_2 as impurity was reacted with $NaCo(CO)_4$ as in Section 5.3.2. As a minor product, it was not isolated and its infrared spectrum was seen as additional absorptions in the spectrum of $MeGeBr_2Co(CO)_4$. Those modes which could be distinguished are listed below, along with those of the analogue $Me_2GeClCo(CO)_4$:

$Me_2GeBrCo(CO)_4$		$Me_2GeClCo(CO)_4$(i)	Assignment
Hexane Solution	Nujol Mull	Hexane Solution	
2099.6 (6.4)	2098.8 (6.7)	2100.0 (5.3)	νCO (A')
2038 (sh)		2041.1 (6.8)	νCO (A")
		2020.4 (10)	νCO } A'
2004.2 (10)	2002.3 (10)	2003.6 (9.1)	νCO } + A"

Note.

i) See Table 5.1a (p.77)

Though the spectrum is incomplete and observed as a minor component, the two main absorption positions and their relative intensities are just as expected. The shoulder at 2038 cm^{-1} in the hexane solution was only evident as a discontinuity on the side of the very strong 2035.9 cm^{-1} mode of $MeGeBr_2Co(CO)_4$. Similarly, the absorption expected at ca. 2020 cm^{-1} is overlapped by a very strong $MeGeBr_2Co(CO)_4$ mode.

In the nmr, the $Me_2GeBrCo(CO)_4$ resonance was confirmed by monitoring signal integrals for different proportions of this as contaminant. In benzene solution, the chemical shift is 8.93 τ.

5.3.5 Preparation of $MeGeBr[Co(CO)_4]_2$.

$MeGeBr_2Co(CO)_4$ (340 mg , 0.8 mmoles) was reacted with $NaCo(CO)_4$ from $Co_2(CO)_8$ (720 mg ; 2.1 mmoles) in Et_2O at

room temperature for 20 minutes. Solvent was removed and the orange residues extracted with hexane. Two crystallisations from hexane at -63°C, followed by an overnight crystallisation at -20°C gave pale orange crystals of $MeGeBr[Co(CO)_4]_2$. (M.P. = 75°-77°C in a sealed capillary; Analysis : Found: Br = 15.55% ; Calculated : Br = 15.68%).The product is readily sublimed at > 30°C. Handling properties are very much the same as those for $MeGeBr_2Co(CO)_4$, though solubility in alkanes is lower, as has been generally found in this work for higher $-Co(CO)_4$ - substituted derivatives.

5.3.6 Characterisation of $MeGeBr[Co(CO)_4]_2$

a) Infrared Spectrum :

This is given in Table 5.3b and has been assigned in comparison with $MeGeI[Co(CO)_4]_2$(51). As with the chloro-analogue, the observation of eight carbonyl stretching modes is consistent with C_s molecular symmetry. This is most easily seen in Figure 8.4 (p.*162*). The assignment of this spectrum is discussed in Chapter Eight.

b) Nuclear Magnetic Resonance :

In benzene, relative to internal TMS, the methyl resonance of $MeGeBr[Co(CO)_4]_2$ occurs at 8.12 τ.

c) Mass Spectrum :

This is listed in Table 8.10 (p.*146*) and is discussed in Sections 8.1 and 8.2. No parent ion is seen, but $(P-CO)^+$ and the fragments due to carbonyl loss from this are prominent.

5.3.7 Reaction of $MeGeBr[Co(CO)_4]_2$ with $NaCo(CO)_4$

This was carried out in Et_2O at room temperature for 10 minutes, using excess $NaCo(CO)_4$. A yellow brown hexane extract was removed from the red reaction residues. Some $Co_2(CO)_8$ was sublimed out of the extract, leaving a residue

Table 5.4

Hexane Extract from $MeGeBr[Co(CO)_4]_2/NaCo(CO)_4$ Reaction

Hexane Extract	Assignment	$CH_3Sn[Co(CO)_4]_3$ (i)
2108 w	$MeGeBr[Co(CO)_4]_2$	
2104 w		2101 w
2099 w	$Me_2Ge[Co(CO)_4]_2$	
2091 m	$MeGeBr[Co(CO)_4]_2$	
2081 s	$Me_2Ge[Co(CO)_4]_2$ + ?	2079 s
2068 w-m	$Co_2(CO)_8$	
2063 m	$Co_4(CO)_{12}$	
2054 m	$Co_4(CO)_{12}$	
2042 m	$Co_2(CO)_8$ + ?	2040 w
2030 s,sh	$MeGeBr[Co(CO)_4]_2$ + ?	2028 w,sh
2023 vs	$MeGeBr[Co(CO)_4]_2$ + ?	2020 s
2014 vs		2010 s
2000 w-m,sh	$MeGeBr[Co(CO)_4]_2$ + ?	1992 w,sh
1997 w-m,sh	$Me_2Ge[Co(CO)_4]_2$ + ?	
1865 m	$Co_2(CO)_8$ + $Co_4(CO)_{12}$	
1855 w	$Co_2(CO)_8$	

Note

i) Reference (79) in cyclohexane.

with a very complex infrared carbonyl spectrum. This is listed in Table 5.4 with the fairly certain assignments and with the reported spectrum of $CH_3Sn[Co(CO)_4]_3$. (79).

$Me_2Ge[Co(CO)_4]_2$ was known to be a contaminant in the starting material. While the main feature of the reaction is that $MeGeBr[Co(CO)_4]_2$ was largely returned, there are some indications of the formation of $MeGe[Co(CO)_4]_3$. The intensities of the modes marked with a question mark in Table 5.4 appear to be too large for the assigned species only. Combined with the weak but obvious 2104 cm^{-1} and the very strong unassigned 2014 cm^{-1} absorptions, the analogy with the $MeSn[Co(CO)_4]_3$ becomes reasonable. Unfortunately, the isolation of this compound was not practical on the scale of the reaction. (See discussion in the next section).

5.4 Discussion

5.4.1 General

The failure of the reactions in this chapter to proceed directly to bis-cobalt derivatives is difficult to understand. The effects of both solvent and reactant ratios were checked without avail. In the chloro-system, minor impurities might have been called on to explain the difference from the reported behaviour.(51). However, the fact that the same results were found in the pure bromo-system seems to preclude such an explanation. The only other possibility here is that a specific, unreported reaction condition in the literature reactions is not being adhered to in the above reactions.

An interesting feature of the whole series of methyl-substituted halogermyl cobalt carbonyl derivatives is the marked increase in sensitivity toward oxidation and decomposition, as compared with the halide - only - substituted analogues reported in Chapters Three and Four. This

sensitivity does not seem to vary between the monomethyl and dimethyl derivatives, but there is a notable stability improvement in going from methylchlorogermyl- to methylbromogermyl-derivatives. This points toward a size effect of the substituents on germanium required to "balance" the cobalt carbonyl substituent(s). The destabilizing effect of the methyl groups seems to be better compensated for by bromine than chlorine.

Possibly the stability of the whole substituted - germanium molecule is dependent upon a π - interaction between the germanium and its substituents. Should such a π - interaction be important, the methyl groups, without the possibility for this interaction would become relatively destabilizing. The compensation for this by halogens would then be expected to be better with bromine, by $d\pi$ - $d\pi$ interaction, than with chlorine, by $p\pi$ - $d\pi$ interaction. That such interaction is certainly present can be seen from the increase in energy of the carbonyl stretching absorptions in the infrared upon changing from e.g. $R_3GeM(CO)_n$ to $X_3GeM(CO)_n$, (R = H, alkyl ; X = halogen ; M = Transition metal.). In this case, the electron - withdrawal by the halogens causes a shift in the transition metal d-orbital electron density toward the germanium 4d orbitals and out of the π^* antibonding orbitals on the carbonyl carbons. This increases the bonding interaction within the carbonyl groups, as reflected by the higher energy vibrational modes.

5.4.2 Nuclear Magnetic Resonance

It is convenient at this point to draw all the nmr data together in the form of Table 5.5.

Table 5.5

NMR Data for Methylgermyl Derivatives from this Work (i)

$MeGeCl_2Co(CO)_4$: 8.75 τ		$(Me_2Ge)_2Co_2(CO)_6$: 8.49 τ	
$MeGeCl[Co(CO)_4]_2$: 8.64 τ		$Me_2GeClCo(CO)_4$: 9.07 τ	
$MeGeBr_2Co(CO)_4$: 8.43 τ		$Me_2Ge[Co(CO)_4]_2$: 8.71 τ	
$MeGeBr[Co(CO)_4]_2$: 8.12 τ		$Me_2GeBrCo(CO)_4$: 8.93 τ	

Note

i) All resonances are in benzene, relative to internal TMS.

The table extends the pattern already noted (54) for metal carbonyl derivatives of the methyl germanes; viz. methyl chemical shifts fall into the following general regions with metal carbonyl substitution. (without halogen) (9.1 τ , 8.7 τ , 8.1 τ for one, two and three metal substituents on germanium, respectively). As expected, the addition of halogen substituents moves the corresponding shifts to lower field. In all, the downfield shift effect by substituents appears to follow the order :

$$-Co(CO)_4 \quad > \quad Br \quad > \quad Cl$$

(N.B. Me - substituents were found not to have any measurable effect - (54)).

5.4.3 Methylgermyltricobalt Derivatives

This work has shown that the formation of these derivatives is not favoured under normal alkali-halide elimination conditions. This was seen from the reactions of $MeGeCl[Co(CO)_4]_2$ and $MeGeBr[Co(CO)_4]_2$ with $NaCo(CO)_4$. (Sections 5.2.6 , 5.3.7 , respectively). These returned largely starting materials. However, both reactions showed some indications of tricobalt product formation. From the reaction of $MeGeCl[Co(CO)_4]_2$ / $NaCo(CO)_4$, there was some evidence for the formation of the established $MeGeCo_3(CO)_{11}$ (53), which is known to be a stable

compound. Its phenyl analogue has been reported to be formed from the rapid decomposition of the unstable $PhGe[Co(CO)_4]_3$. (86).

However, the mass spectrum of $MeGeCl[Co(CO)_4]_2$ indicated that some tricobalt species had also been formed as a minor product. The assignment of $MeGeCo_3(CO)_x^{\cdot+}$ (x = 0 to 11) is consistent with both $MeGeCo_3(CO)_{11}$ and $MeGe[Co(CO)_4]_3$. (See the mass spectral discussion in Chapter Eight). Checking the infrared spectrum of the sample used for the mass spectrum (See Table 5.2b,p.*83*), there is no support for the $MeGeCo_3(CO)_{11}$ modes : 2056 (s) , 2038 (s) , 1849 (w) , 1837 (w) (53). On the other hand, the abnormally high relative intensities of the 2001.7 , 2014.4 and 2024.6 cm^{-1} modes are consistent with overlap of a spectrum like that of $MeSn[Co(CO)_4]_3$ (2010 (s), 2020 (s) ; See Table 5.4,p.*92*) (N.B. the strong "2079 cm^{-1}" mode proposed for $MeGe[Co(CO)_4]_3$ is masked in the spectrum of "$MeGeCl[Co(CO)_4]_2$" by overlap from $Me_2Ge[Co(CO)_4]_2$, whose absorptions have been subtracted from the spectrum given in Table 5.2b). The assignment of $MeGe[Co(CO)_4]_3$ in this case is further supported by the reasonable correspondence of $MeSn[Co(CO)_4]_3$ with the minor product from the analogous $MeGeBr[Co(CO)_4]_2/NaCo(CO)_4$ reaction. (See Table 5.4)

On this basis, it seems reasonable to conclude that small amounts of $MeGe[Co(CO)_4]_3$ have been produced as minor products in these systems. That it has survived the handling for mass spectral sampling, sublimation and infrared solution sampling indicates that it is more stable than $PhGe[Co(CO)_4]_3$. (86). As in that case the decomposition product of $MeGe[Co(CO)_4]_3$ is probably $MeGeCo_3(CO)_{11}$, as tentatively identified from the products of

$MeGeCl[Co(CO)_4]_2/NaCo(CO)_4$. However, the extent of formation of $MeGe[Co(CO)_4]_3$ reflects its low stability, relative to the $XGe[Co(CO)_4]_3$ analogues reported in Chapters Three and Four. (X = Cl,Br). This is a further example of the stability of methyl- vs. halogen - substituted derivatives, discussed in Section 5.4.1.

Chapter Six

Cobalt Carbonyl Derivatives of Germanium Hydrides

6.1 Reaction of GeH_4 with $Co_2(CO)_8$

$Co_2(CO)_8$ (430 mg ; 1.26 mmoles) was sealed in a 20 ml high pressure glass tube with GeH_4 (c a. 0.65 mmoles) and 5 mls of hexane as solvent. It was wrapped in aluminium foil and kept at room temperature in a drawer for 15 weeks.

When the tube was opened, GeH_4 (ca. 0.08 mmoles) recovered. The hexane was removed and an Et_2O extract taken. Removal of the ether from this solution left two distinct regions of solid. The pale brown bulk was more Et_2O soluble and came down in the centre of the flask, surrounded by a dark brown ring. Manual separation in a glovebox gave the pale solid free of the dark material (but not vice versa).

A hexane solution infrared spectrum of the pale solid showed the following carbonyl absorptions: (cm^{-1}).

Et_2O Extract from $GeH_4/Co_2(CO)_8$	Assignment
2087 (w)	
2079 (vs)	$GeCo_4(CO)_{14}$
2068 (w)	$Co_2(CO)_8$
2061 (vs)	$GeCo_4(CO)_{14}$
2042 (sh)	$Co_2(CO)_8$
2040 (m)	$GeCo_4(CO)_{14}$
2032 (s)	$GeCo_4(CO)_{14}$
2023 (m)	$GeCo_4(CO)_{14}$
2005 (w)	$GeCo_4(CO)_{14}$
1865 (w)	$Co_2(CO)_8$
1848 (m)	$GeCo_4(CO)_{14}$

The small amount of $Co_2(CO)_8$ is consistent with the incomplete reaction of GeH_4, as noted. The assignment of $GeCo_4(CO)_{14}$ as the main component in this spectrum can be made by direct comparison with the spectrum of the isolated compound in Table 3.2b (p. *52*).

The mass spectrum of the pale solid was the same as listed in Table 8.*4* (p.*139*) further confirming the assignment as $GeCo_4(CO)_{14}$.

As extracted, this sample was known to contain some hexane insoluble, non - carbonyl - containing impurity.

The dark brown, secondary product from this reaction was largely freed from $GeCo_4(CO)_{14}$ by successive hexane washings. Complete purification by this method was not possible, due to the very small sample. However, the spectrum in hexane could be largely determined and is listed below along with the literature data for $(CO)_4CoGeCo_3(CO)_9$. (97): (cm^{-1}).

Dark Solid from $GeH_4/Co(CO)_8$	$(CO)_4CoGeCo_3(CO)_9$ (97)
2111.2 (w)	2112 (w)
2081.7 (s)	2083 (s)
2043.4 (vs)	2045 (vs)
2027.5 (s)	2029 (m)
	2008 (vw)
	1991 (vw)

The lower two modes could not be distinguished in the product spectrum due to overlap by impurity absorptions. However, the remaining modes show close correspondence with the literature data.

The mass spectrum of the dark solid confirmed its asssignment as $(CO)_4CoGeCo_3(CO)_9$, showing the same fragments

and relative intensities as reported by Schmid.(97).i.e. A parent ion (m/e = 670-676) and fragments due to loss of thirteen carbonyls from this.

6.2 Reaction of Me_2GeH_2 with $Co_2(CO)_8$

Cotton et al. (90) report the formation of $(Me_2Ge)_2Co_2(CO)_6$ by the dropwise addition of a toluene solution of Me_2GeH_2 to $Co_2(CO)_8$ (also in toluene). This preparation was followed, using 680 mg $Co_2(CO)_8$ (2.0 mmoles) in 50 mls of toluene and 4.4 mmoles Me_2GeH_2 in the same volume of that solvent. The $Co_2(CO)_8$ colour was not discharged after 3 hours of stirring at room temperature.

Chromatography of the concentrated toluene solution on alumina with 8% H_2O (8 cm x 2 cm i.d. column), in a glovebox gave two distinct hexane - eluted fractions. The first was mainly $Me_2GeCo_2(CO)_7$, with some $(Me_2Ge)_2Co_2(CO)_6$ and $Co_2(CO)_8$. The second showed only $(Me_2Ge)_2Co_2(CO)_6$ and a little $Co_4(CO)_{12}$.

The components of the first fraction could not be separated by sublimation, but chromatography on dry alumina gave pure $(Me_2Ge)_2Co_2(CO)_6$, eluted with hexane. Extraction of the column contents gave only $Co_2(CO)_8$.

6.2.1 Characterisation of $(Me_2Ge)_2Co_2(CO)_6$

a) Infrared Spectrum :

This is listed in Table 6.1a, and may be directly compared with the literature data in the same solvents, given in Table 1.4c (p. *23*). The assignment of the spectrum is discussed in Chapter Eight and the carbonyl stretching region is depicted in Figure 8.6 (p. *167*).

Though $Me_2GeCo_2(CO)_7$ was not obtained pure, its infrared

Table 6.1

Infrared Data for $Me_2GeH_2/Co_2(CO)_8$ Reaction Products

a) Infrared Spectrum of $(Me_2Ge)_2Co_2(CO)_6$

Hexane Solution	Cyclohexane Solution	CS_2 Solution
2066.0 (8.1)	2065.4 (8.5)	2063.2 (7.2)
2028.8 (10)	2028.4 (10)	2025.6 (10)
2008.8 (9.8)	2007.8 (9.8)	2004.3 (8.6)
1990.0 (9.5)	1988.8 (9.5)	1985.0 (8.1)
1981.3 (5.3)	1980.3 (5.5)	1976 (3.9,sh)
1945 (0.5)	1946.0 (0.5)	
840 w,br		
578 w,sh		
554 m		
519 m		

b) Infrared Spectrum of $Me_2GeCo_2(CO)_7$-Containing Fraction

Mixture (hexane)	$Me_2GeCo_2(CO)_7$ ((77) in C_6H_{12})	Assignment (i)
2087 (s)	2085 (7.5)	A
2066 (m)		B,C
2054 (w,sh)		C
2048 (vs)	2047 (9.5)	A
2028 (m,sh)		B
2025 (vs)	2024 (9.5)	A
2008 (vvs)	2006 (9.5)	A,B
1990 (m)	1998 (sh)	B
1981 (w-m)		B
1965 (w)	1971 (1)	A
1865 (vw)		C
1840 (s)	1844 (8)	A

Note i) A = $Me_2GeCo_2(CO)_7$; B = $(Me_2Ge)_2Co_2(CO)_6$; C = $Co_2(CO)_8$

absorptions could be deduced from the spectra of product mixtures. These are listed in Table 6.1b and show good correspondence with the data reported by Job and Curtis (77). The carbonyl stretching region for $Me_2GeCo_2(CO)_7$ is also shown in Figure 8.6.(p.*167*).

b) Mass Spectrum :

The highest mass envelope in the spectrum of $(Me_2Ge)_2Co_2(CO)_6$ is m/e = 486 - 498, corresponding to $C_{10}H_{12}O_6Ge_2Co_2^+$. Carbonyl loss fragments from this parent ion are predominant, with the base peak corresponding to $Me_4Ge_2Co_2(CO)^+$. Only a few of the ions due to methyl loss are seen. The spectrum is listed in Table 8.11 (p.*147*) and is further discussed in Sections 8.1 and 8.2.

c) Nuclear Magnetic Resonance :

In benzene solution, relative to internal TMS, the methyl resonance for $(Me_2Ge)_2Co_2(CO)_6$ occurs at 8.49 τ.

6.2.2 Discussion

The reported route to $(Me_2Ge)_2Co_2(CO)_6$ (90) :

$$2Me_2GeH_2 + Co_2(CO)_8 \longrightarrow (Me_2Ge)_2Co_2(CO)_6 + 2H_2 + 2CO$$

was found to be inefficient. Despite using excess Me_2GeH_2, not all of the $Co_2(CO)_8$ was reacted and the major product of the reaction was found to be $Me_2GeCo_2(CO)_7$. The purification of the $(Me_2Ge)_2Co_2(CO)_6$ using dry alumina chromatography was at the expense of destroying the $Me_2GeCo_2(CO)_7$. (N.B. It is possible that some of this latter compound may have converted to $(Me_2Ge)_2Co_2(CO)_6$ in the column but product yields indicated that this could only have been a minor process).

The ^1H nmr chemical shift data available for $(Me_2Ge)_2Co_2(CO)_6$ present some anomalies :

Shift (τ)	:	8.88	8.8	8.49	9.13
Solvent	:	$SiCl_4$	$2CF_2Cl_2/1CH_2Cl_2$	C_6H_6	C_6D_6
Reference	:	(54)	(88)	(This work)	(77)

Aromatic solvents generally give chemical shifts to low field of those in saturated solvents, for methyl-substituted germanium derivatives. (72). Combined with the trend in chemical shifts noted in the previous chapter for successive cobalt substitution on germanium, it would seem that the value of 9.13 τ in C_6D_6 is in error. This value would seem to be more appropriate for a compound with a single Ge-Co Bond.

6.3 Reactions of $Me_2GeHCo(CO)_4$

6.3.1 Reactions of $Me_2GeHCo(CO)_4$ with $Co_2(CO)_8$

$Co_2(CO)_8$ (29 mg ; 0.08 mmoles) was sealed in an nmr tube with $Me_2GeHCo(CO)_4$ (25 mg ; 0.09 mmoles), using $SiCl_4$ as solvent and 5% benzene as internal reference. The reaction was followed over several hours at temperatures between -40°C and 0°C.

The only reaction products observed were $HCo(CO)_4$ (21.5 τ) and a product giving rise to a poorly resolved methyl resonance centred at 8.72 τ. The tube was broken open under vacuum and the volatiles removed. Residues were extracted with hexane. This gave a sample whose infrared spectrum showed only $Me_2Ge[Co(CO)_4]_2$ (51) and $Co_4(CO)_{12}$.(124).

The reaction was repeated, using a 1:1 Co : GeH ratio and gave the same results. i.e.:

$$Me_2GeHCo(CO)_4 + Co_2(CO)_8 \longrightarrow Me_2Ge[Co(CO)_4]_2 + HCo(CO)_4$$

Discussion :

This reaction has been examined previously (54) and differed from the above in that reaction took place for half

an hour at room temperature and the products were sublimed out of the reaction residues. In that case both $Me_2GeCo_2(CO)_7$ and $(Me_2Ge)_2Co_2(CO)_6$ were identified as products. So far then, all three possible dicobalt products have been isolated from this reaction system, i.e. $Me_2GeCo_2(CO)_7$, $(Me_2Ge)_2Co_2(CO)_6$ and $Me_2Ge[Co(CO)_4]_2$. This is reasonable since each one has been separately prepared and all three are relatively stable compounds. (51,77,88,90).

The observation of $Co_4(CO)_{12}$ in the above reactions is consistent with other observations of this as a decomposition product in the preparations of $Me_2Ge[Co(CO)_4]_2$. (See section 5.1)

It must be noted at this point that no evidence has been found so far in these reaction systems for the formation of $MeGeCo_3(CO)_{11}$. Brooks and Graham have reported this as a product of the reaction of Me_2GeH_2 with $Co_2(CO)_8$ (128). However, no mention was made of reactant conditions, which must have been vigorous to effect Ge-C cleavage.

In view of the reports by MacDiarmid et al. (125,126) (See Section 1.6.5) there was a possibility that the course of the $Me_2GeHCo(CO)_4/Co_2(CO)_8$ reaction could be affected by side reaction with $HCo(CO)_4$. This was tested as described below.

6.3.2 Reaction of $Me_2GeHCo(CO)_4$ with $HCo(CO)_4$

$HCo(CO)_4$ (preparation based on the method reported in (129)) was sealed into an nmr tube with a sample of $Me_2GeHCo(CO)_4$, using $SiCl_4$ as solvent. No changes were observed in the nmr spectra over 7.25 hours at -20°C and 11 hours at 0°C.

Thus, under the reaction conditions described in the previous section, side-reactions involving $HCo(CO)_4$ may be

discounted. However, above 0°C, $HCo(CO)_4$ decomposes to H_2 and $Co_2(CO)_8$, which can further react with starting materials or primary products. This may have been an important factor in the formation of the different final products in previous work (54), noted above.

Since MacDiarmid's Si-Co coupling reactions were carried out at room temperature, it would seem that the observed difference in the behaviour of the silicon system (as compared to germanium) is probably an effect of $HCo(CO)_4$ decomposition.

6.4 Reactions of $MeGeH_2Co(CO)_4$ with $Co_2(CO)_8$

6.4.1 Cobalt Deficit

$Co_2(CO)_8$ (34 mg ; 0.1 mmole) was sealed into an nmr tube with $MeGeH_2Co(CO)_4$ (40 mg ; 0.15 mmoles), using $SiCl_4$ as solvent and 5% benzene as internal reference. The reaction was followed at various temperatures using ^1H nmr. Results are summarised in Table 6.2.

At the completion of reaction, the tube was opened under vacuum, volatile components removed and their nmr spectrum rerun. This showed the excess $MeGeH_2Co(CO)_4$ and the 8.60 τ signal seen weakly in both the earlier and latter stages of the reaction.

A hexane extract of the involatile products showed a complex carbonyl infrared spectrum, as shown in Table 6.3.

6.4.2 Cobalt Excess

$Co_2(CO)_8$ (35 mg ; 0.1 mmole) was sealed with $MeGeH_2Co(CO)_4$ (14 mg ; 0.05 mmole) in an nmr tube with $SiCl_4$ as solvent and 5% benzene as internal reference. The reaction was monitored as above and the nmr data are summarised in Table 6.4. When the reaction appeared to be complete, the

Table 6.2

Reaction of $2Co_2(CO)_8/3MeGeH_2Co(CO)_4$

a) Assigned Observations :

	Temperature (^oC)	Time	Compounds Observed (i)
1)	-40	0 hr	$MeGeH_2Co(CO)_4$
2)	-40	0.5 hr	$MeGeH_2Co(CO)_4$
			$MeGeHCo_2(CO)_x$ species
3)	-40	3.0 hr	
	-30	0.75 hr	$MeGeH_2Co(CO)_4$
			$MeGeHCo_2(CO)_x$
			$HCo(CO)_4$
4)	-40	3.0 hr	
	-30	1.0 hr	
	-20	0.5 hr	
	-10	0.5 hr	
	0	1.5 hr	$MeGeH_2Co(CO)_4$
			$MeGeHCo_2(CO)_x$
			$HCo(CO)_4$
			$MeGeCo_3(CO)_{11}$
5)	0	7 d	$MeGeH_2Co(CO)_4$ (3)
			$MeGeHCo_2(CO)_x$ (2)
			$MeGeCo_3(CO)_{11}$ (1)
			$HCo(CO)_4$ (m)
6)	20	2 d	No changes from 5) apart from loss of $HCo(CO)_4$

b) Assignments :

$MeGeH_2Co(CO)_4$: 9.15τ (triplet), 5.67τ (quartet) } J = 3.5Hz

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Table 6.2 Contd.

$MeGeHCo_2(CO)_x$	:	8.75τ 8.60τ	Probably doublets but coupling not determined.
$HCo(CO)_4$	:	21.2τ	(singlet)
$MeGeCo_3(CO)_{11}$	:	8.07τ	(singlet) (53)

Note

i) Compounds are first listed at the time at which they first appeared.

Table 6.3

Infrared Spectrum of Involatile Products from $MeGeH_2Co(CO)_4/Co_2(CO)_8$ Reaction (a)

Reaction Involatiles(b)	Assignments		
	$MeGeCo_3(CO)_{11}$ (53)	$Co_4(10)_{12}$ (124)	$MeGeH[Co(CO)_4]_2$ (c)
2105 (w)	2105 (w)		
2095 (m)			X
2085 (s)	2082 (s)		
2070 (w)			
2065 (w)	2064 (w,sh)	2064 (vs)	
2055 (s)	2056 (s)	2053 (vs)	
2045 (w)	2047 (w,sh)		X
2030 (vs)	2038 (s)	2038 (vw)	X
2020 (s,sh)	2017 (m)	2028 (vw)	
lower shoulders	2009 (m)		
(2020-2000)	2003 (w,sh)		X
1865 (w)		1867 (w)	
1850 (w)	1849 (w)		
1835 (w)	1837 (w)		

Notes

a) All units are cm^{-1}.

b) Values are $\pm$ 2 cm^{-1} due to the small abscissa scale used.

c) Tentative assignment ; see text and Figure 8.4 (p.*162*)

Table 6.4

Reaction of $2Co_2(CO)_8/1MeGeH_2Co(CO)_4$

a) Assigned Observations :

	Temperature(^oC)	Time	Compounds Observed (i)
1)	-30	0 hr	$MeGeH_2Co(CO)_4$
			$MeGeHCo_2(CO)_x$
2)	-30	1.5 hr	$MeGeH_2Co(CO)_4$
			$MeGeHCo_2(CO)_x$
			$MeGeCo_3(CO)_{11}$
3)	-30	1.5 hr	
	-20	1.0 hr	$MeGeH_2Co(CO)_4$
			$MeGeHCo_2(CO)_x$
			$MeGeCo_3(CO)_{11}$
			$HCo(CO)_4$
4)	-30	1.5 hr	
	-20	1.0 hr	
	-10	1.0 hr	
	0	18 hr	$MeGeHCo_2(CO)_x$ (3)
			$MeGeX_3$ species (2.5)
			$MeGeCo_3(CO)_{11}$ (1)
			$HCo(CO)_4$ (1)

b) Assignments :

$MeGeH_2Co(CO)_4$	:	9.14 τ	(triplet) J = 3.5 Hz
		5.65 τ	(quartet)
$MeGeHCo_2(CO)_x$	:	8.75 τ	(possibly a doublet: coupling not determined)
$MeGeCo_3(CO)_{11}$	:	8.05 τ	(singlet)
$HCo(CO)_4$	:	21.3 τ	(singlet)
$MeGeX_3$	:	8.42 τ	(singlet)
		8.22 τ	(singlet)

Note

i) Compounds are listed at the time at which they first appeared.

tube was opened under vacuum and 0.12 mmoles of incondensible gas were recovered. The volatile components were removed and their nmr spectrum showed:

8.46 τ	:	?	
9.12 τ	:	$MeGeH_2(Co(CO)_4$	(53)
9.82 τ	:	$MeGeH_3$	(127)

(The spectrum was too weak and poorly resolved to determine multiplicities and coupling constants, so assignments are made on the basis of chemical shifts only). Reaction residues showed the same infrared spectrum as in Table 6.3 as well as the excess $Co_2(CO)_8$.

6.4.3 Discussion

The assignment of $MeGeCo_3(CO)_{11}$ and $Co_4(CO)_{12}$ in the invotatile products (Table 6.2) can be made fairly certainly by reference to the literature (53,124). The former is also confirmed by its nmr identification (53). The assignment of $MeGeH[Co(CO)_4]_2$ is quite tentative and made by comparison with the analogues $MeGeX[Co(CO)_4]_2$ (X = Cl,Br : see Figure 8.4 p.*162*; X = I see (51)). Its assignment is also supported by the chemical shift of the remaining involatile component (8.78 τ), which is consistent with two cobalt substituents on germanium. (See (54) and Section 5.4). However, this implies that the volatile component (8.60 τ) is also a dicobalt species. At this stage there is no clear distinction between $MeGeH[Co(CO)_4]_2$ and $MeGeHCo_2(CO)_7$ with respect to possible volatilities and chemical shifts. Though the bridging carbonyl modes in the involatiles' extract could be accounted for without considering the possible $MeGeHCo_2(CO)_7$, the evidence does not rule out the heptacarbonyl. However,the relative intensities of the terminal carbonyl modes observed suggest $MeGeH[Co(CO)_4]_2$ as the more likely component in this

mixture.

The incondensibles found in the cobalt excess reaction (0.12 mmoles) exceed the ca. 0.05 mmoles expected from H_2 and CO loss from known products. The remaining incondensible must be due to the two unassigned products at 8.22 τ and 8.42 τ. Also, since the amount of $HCo(CO)_4$ produced is that expected for the formation of $MeGeH[Co(CO)_4]_2$ (i.e. one for one), the stoichiometry of the unassigned species must be such that no $HCo(CO)_4$ is produced. The appearance of $MeGeH_3$ and $MeGeH_2Co(CO)_4$ from decomposition or disproportionation of products during handling suggests (along with the above information) that possibly one of the unassigned products may have been based on a Ge - Co - Ge skeleton. (N.B. Graham (53) assigned the 8.42 τ signal seen in the work as $MeGeX_3$, on the basis of its chemical shift and the fact that it was a singlet).

In the low temperature, equimolar $MeGeH_2Co(CO)_4/Co_2(CO)_8$ reaction (53), Graham reports the initial formation of $MeGeHX_2$, which is consumed to form $MeGeCo_3(CO)_{11}$ via the reaction scheme in Section 1.6.5. In neither of the reactions described here did the final product ratio come near the 10 : 4 $MeGeCo_3(CO)_{11}/MeGeHX_2$ ratio reported for the equimolar reaction. Indeed, from the cobalt excess and deficit reactions alone, there is no evidence that the two products were not being formed by parallel reactions, at different rates. However, the work described in (54) and Section 6.3 support the idea of stepwise substitution of Ge-H and it is most likely that the above observations reflect an equilibrium situation in which the specific conditions of reaction determine relative rates and product ratios.

Under the conditions used here, the noted time lapse

between formation of the di- and tricobalt products could be useful in isolating the pure dicobalt species for characterisation. So far, separation from $MeGeCo_3(CO)_{11}$ using solvent and sublimation techniques have been unsuccessful.

6.5 Reaction of GeH_2Br_2 with $Co_2(CO)_8$

A small sample of GeH_2Br_2 (130) (ca. 0.1 mmole) was sealed into an nmr tube with $Co_2(CO)_8$ (37mg, 0.11 mmoles) using $SiCl_4$ as solvent and 5% TMS as internal reference. Table 6.5 summarises the nmr observations for this reaction. The excess GeH_2Br_2 showed in the infrared spectrum of the volatiles. The residues were extracted with hexane. This solution gave the carbonyl infrared spectrum shown in Table 6.6.

Overall, the observations are consistent with the stepwise substitutions seen in Sections 6.3,6.4. i.e. Initially :

$$GeH_2Br_2 + Co_2(CO)_8 \longrightarrow GeHBr_2Co(CO)_4 + HCo(CO)_4$$

4.25 τ 3.82 τ 21.2 τ

The next substitution , though not directly observable in the nmr, can be implied by the diminishing total intensities of the 4.25, 3.82 τ signals :

$$GeHBr_2Co(CO)_4 + Co_2(CO)_8 \longrightarrow Br_2Ge[Co(CO)_4]_2 + HCo(CO)_4$$

By comparing the GeH_2Br_2 : TMS relative intensities it is apparent that an equilibrium concentration of $GeHBr_2Co(CO)_4$ is reached before the further substitution to the bis cobalt compound starts. The latter process causes both GeH_2Br_2 and $GeHBr_2Co(CO)_4$ to diminish, relative to TMS.

The first process is faster than the second, as reflected by the decrease in GeH_2Br_2 with respect to $GeHBr_2Co(CO)_4$ as reaction proceeds. GeH_2Br_2 in the final products may indicate that this was in excess here. However, the presence of both

Table 6.5

Reaction of $GeH_2Br_2/Co_2(CO)_8$

a) Assigned Observations :

	Temperature (°C)	Time	Compounds Observed (i)
1)	-30	0	GeH_2Br_2 (vs)
2)	-30	0.5 hr	GeH_2Br_2
			$GeHBr_2Co(CO)_4$ (ii)
			$HCo(CO)_4$
3)	-30	1.0 hr	
	-20	0.5 hr	
	-10	5 hr	
	0	4 d	GeH_2Br_2 (m)
			$GeHBr_2Co(CO)_4$ (m)
			GeH_3Br (w) (iii)
			$HCo(CO)_4$ (m)

b) Assignments :

GeH_2Br_2	:	4.25 τ	(singlet)
$GeHBr_2Co(CO)_4$	:	3.82 τ	(singlet)
$HCo(CO)_4$	:	21.2 τ	(singlet)
GeH_3Br	:	4.40 τ	(singlet)

Notes

i) Compounds are first listed at the time at which they first appeared.

ii) Assigned as H-substituted rather than Br-substituted on the basis of the chemical shift value, reaction studies reported in the next section and the product analysis below.

iii) Possibly present all along as a small impurity in the GeH_2Br_2 but not observed until high power applied to record the diminishing spectrum.(130).

Table 6.6

Infrared Spectrum of Hexane Extract from $GeH_2Br_2/Co_2(CO)_8$(i)

Product (ii)	$Br_2Ge[Co(CO)_4]_2$ (iii)	$I_2Ge[Co(CO)_4]_2$ (iv)
2118 (7)	2117 (0.1)	2113 (4.1)
2105 (4)		
2096 (8)	2099 (9.7)	2096 (10)
2075 (2)		
2065 (8)		
2056 (8,sh)	2057 (4.5)	2054 (7.5)
	2055 (2.8,sh)	2051 (5.0,sh)
2042 (10)	2044 (10)	2042 (10)
2028 (8)	2026 (3.3)	2025 (5.4)
2015(4,sh)	2015 (2.2)	2013 (2.9)

Notes

i) All values are cm^{-1}

ii) These values are ca. $\pm$ 2 cm^{-1}

iii) A new compound prepared by an alternative route. (See Chapter Four and Figure 8.3, p.*159*)

iv) Reference (51) in cyclohexane. Intensity measurement method not stated.

GeH_2Br_2 and $GeHBr_2Co(CO)_4$ at completion supports the idea of a pair of equilibrium processes.

It seems fairly clear that the postulated product (i.e. $Br_2Ge[Co(CO)_4]_2$) is the main compound of the reaction involatiles, as expected. The other compound could not be assigned here since its absorptions are largely covered by those of $Br_2Ge[Co(CO)_4]_2$. Thus, the proposed $GeHBr_2Co(CO)_4$ can only be tentatively assigned on the basis of its nmr chemical shift. This compound would be an interesting one, being the first mixed hydride/halide-substituted germyl cobalt derivative.

6.6 Reactions of Non-Hydride Germane Derivatives with $Co_2(CO)_8$

As a comparison / contrast with the reactive hydride derivatives mentioned so far, it is useful to note the reactivity of non-hydride analogues under similar conditions.

Both Me_2GeCl_2 and $MeGeI_3$ were sealed in nmr tubes with $Co_2(CO)_8$, using $SiCl_4$ as solvent and TMS as internal reference. No reaction at all occurred over a period of two days at 0^oC.

$Cl_3GeCo(CO)_4$ was reacted with $Co_2(CO)_8$ at room temperature in Et_2O for one hour. Only reactants were returned, along with a little $Co_4(CO)_{12}$ from $Co_2(CO)_8$ decomposition during handling.

While the above examples reflect the general situation this unreactivity is not exclusive. Notably, both $GeCl_4$ and $GeBr_4$ are reported to react with $Co_2(CO)_8$ to form $Cl_3GeCo(CO)_4$, $Cl_2Ge[Co(CO)_4]_2$ and $Br_3GeCo(CO)_4$ (51,52). $MeGeI_3$ is also reported to form $MeGeI[Co(CO)_4]_2$. (51). Significant factors in these reactions are the use of THF

as solvent and reaction at room temperature. As noted in Chapters Three and Four solvation effects on GeX_4 are probably important and a change from $SiCl_4$ to THF as solvent would be expected to reflect this. Also, the disproportionation of $Co_2(CO)_8$ (amongst other binary carbonyls) in bases e.g. :

$$3/2\ Co_2(CO)_8 \xrightarrow{THF} [Co(THF)_6][Co(CO)_4]_2 + 4CO$$

is well established for a great range of bases. (131). In contrast, the same process in Et_2O is negligible. Thus reports of THF reactions of $Co_2(CO)_8$ (at room temperature) probably involve reaction of $Co(CO)_4^-$.

This effect can also be extended to the silicon and tin systems. In Et_2O, $Co_2(CO)_8$ was found not to react with the series Me_ySiX_{4-y} (X = halide) (95). Most of the tin analogues are also prepared in base solvents. (e.g. 51,52,79).

That the exceptions in the germanium system seem to be limited to high halide-content derivatives could be seen as an "activation" effect of these substituents upon reactivity with $Co_2(CO)_8$. (Or with low concentrations of $Co(CO)_4^-$ produced from its disproportionation). The reverse effect was noted in the $GeH_2Br_2/Co_2(CO)_8$ reaction in Section 6.5, where the substitution of Ge-H with $Ge\text{-}Co(CO)_4$ had a deactivating effect on the rate of further substitution. In that case, the effect is probably a steric one, whereas above, electronic effects are more likely.

CHAPTER SEVEN

Reactions of Chlorogermyl Cobalt Carbonyl Derivatives with $NaMn(CO)_5$

7.1 Reaction of $ClGe[Co(CO)_4]_3$ with $NaMn(CO)_5$

By analogy with Section 3.4; this reaction was investigated as a possible route to tetra- (metal carbonyl) substitution around germanium. The relative effectiveness of metal exchange and halide elimination will determine which derivatives are formed. The possible extreme situations are represented as :

$$ClGe[Co(CO)_4]_3 + NaMn(CO)_5 \longrightarrow (CO)_5MnGe[Co(CO)_4]_3 + NaCl$$

$$ClGe[Co(CO)_4]_3 + 3NaMn(CO)_5 \longrightarrow ClGe[Mn(CO)_5]_3 + 3NaCo(CO)_4$$

$$ClGe[Co(CO)_4]_3 + 4NaMn(CO)_5 \longrightarrow Ge[Mn(CO)_5]_4 + NaCl + 3NaCo(CO)_4.$$

The intermediate situationsto these alternatives are also possible.

7.1.1 Experimental

$NaMn(CO)_5$ from $Mn_2(CO)_{10}$ (185 ; 0.47 mmoles) was reacted at room temperature in Et_2O with $ClGe[Co(CO)_4]_3$ (ca. 0.2 mmoles) for 15 minutes. This resulted in a red/brown solution which left an orange ring and pale brown solid when the Et_2O was removed. A hexane extract was yellow and did not remove the orange residues. The infrared spectrum of the extract was very complex in the carbonyl region. It showed that no $ClGe[Co(CO)_4]_3$ was left and that the major component was $Mn_2(CO)_{10}$. Sublimation at room temperature and 35°C failed to separate this component. Crystallisation from hexane over three days in a refrigerator gave orange crystals. The infrared spectrum of the yellow hexane solution

of the isolated orange crystals was complex. (See Table 7.1)

On further standing in the refrigerator, this yellow solution deposited further orange solid. The remaining solution gave a yellow solid upon evaporation. The spectrum of this is also shown in Table 7.1.

7.1.2 Discussion

On the basis of the comparison with the infrared spectrum of $ClSn[Mn(CO)_5]_3$ (141), one of the components of the orange crystals was tentatively identified as $ClGe[Mn(CO)_5]_3$. Table 7.1 also shows that this component had been largely removed in the spectrum of the subsequent yellow solid, which showed mainly 2076, 2051, 2022 and 1998 cm^{-1}. Thus the orange component of the initially isolated solid was the assigned $ClGe[Mn(CO)_5]_3$. The relative simplicity of the infrared spectrum of the remaining component (i.e. essentially only four absorptions) suggests a compound of higher symmetry than $ClGe[Mn(CO)_5]_3$ (for a comparable mass - see below).

The mass spectrum of the initial orange crystals was made up of two partially overlapping fragmentation patterns, suggesting the presence of two components. This was confirmed when subsequent mass spectra of recrystallised products showed changes in the relative intensities of the partially overlapped fragments. The effect was also seen when a given sample was run at different temperatures and with different ionizing currents. Complete separation of the two components was not achieved but the "extremes" in the spectra gave definite indications of the individual components. (See Table 7.2). The two main sets of fragmentations seen correspond to carbonyl loss from the ions $GeMn_3(CO)_{15}^+$ and

Table 7.1

Infrared Spectra of Reaction Products from

$ClGe[Co(CO)_4]_3/NaMn(CO)_5$

Orange Crystals (a)	$ClSn[Mn(CO)_5]_3$ (b)	Yellow Solid (a)
	2093 (0.4)	
2081.7 (9.2)	2080 (8.3)	2081.6 (2.1)
2076.1 (7.7)		2076.1 (6.9)
2050.9 (2.2)		2051.0 (2.9)
2041.7 (4.0,sh)		
2038.9 (6.7)	2037 (5.8)	
2024.4 (9.9)	2030 (3.0,sh)	
2021.7 (10)	2020 (8.0)	2021.7 (10)
2010.0 (6.0)		2010.0 (4.2)
2004.8 (9.8)	2005 (10)	2005.0 (3.4)
1997.1 (9.5)		1997.5 (9.4)
1990.3 (8.1)	1989 (4.2)	1989.6 (3.3)
1964 (0.4)		
1960 (0.6)		1960 (0.4)

Notes

a) Hexane Solution.

b) Reference(141)in cyclohexane.

Table 7.2

Mass Spectrum of "Extreme" Product Samples from $ClGe[Co(CO)_4]_3$ / $NaMn(CO)_5$ Reaction (a)

m/e	Assignment	Relative Intensity (b)	
		A	B
	$GeMn_3(CO)_x^+$		
655-661	x=15	4	0.8
627-633	x=14	vvw	0.2
599-605	x=13	vvw	0.1
571-577	x=12	vvw	0.2
543-549	x=11	1	0.7
515-521	x=10	5	4
487-493	x=9	18	10
459-465	x=8	32	30
431-437	x=7	32	37
403-409	x=6	20	20
375-381	x=5	43	40
347-353	x=4	43	43
319-325	x=3	47	57
291-297	x=2	32	27
263-269	x=1	30	33
235-241	x=0	54	74
180-186	$GeMn_2^+$	93	100
125-131	$GeMn^+$	35	40
	$ClGeMn_3(CO)_x^+$		
550-558	x=10	9	1
522-530	x=9	29	4
494-502	x=8	80	7
466-474	x=7	23	3
438-446	x=6	33	7
410-418	x=5	28	4
382-390	x=4	50	6

Contd. Overpage.

Table 7.2 Contd.

	$ClGeMn_3(CO)_x^+$		
354-362	x=3	50	5
326-334	x=2	25	4
298-306	x=1	28	3
270-278	x=0	90	13
215-223	$ClGeMn_2^+$	45	6
160-168	$ClGeMn^+$	35	4
111	$Mn(CO)_2^+$	6	20
110	Mn_2^+	33	57
83	$Mn(CO)^+$	12	18
55	Mn^+	100	100

Notes

a) Probe temperature = 125°C.

b) The relative intensities here are those measured for the "extreme" samples :

A is the crude orange product, relatively enriched in $ClGeMn_3(CO)_{15}$.

B is the partially purified yellow product, with the proposed $Ge[Mn(CO)_5]_4$ as the main component.

$ClGeMn_3(CO)_{10}^+$. Both of these are consistent with $ClGe[Mn(CO)_5]_3$ fragmentations, particularly when compared with the intensity pattern reported in the mass spectrum of $ClSn[Mn(CO)_5]_3$. (141). There, in the $ClSnMn_3(CO)_x^+$ series, x = 12, 13, 14 fragments are absent and are flanked by weak envelopes for x = 15, 11, 10, 9, in very much the same sort of pattern as seen here. In this case, the ions $ClGeMn_3(CO)_x^+$ (x = 11 - 15) are too weak to see, while $GeMn_3(CO)_x^+$ (x = 12, 13, 14) ions can only just be seen.

However, the relative intensity changes on purification particularly in the higher mass region, indicate that two different compounds were present. This was confirmed by the infrared spectra of these fractions, which showed successive removal of the $ClGe[Mn(CO)_5]_3$ component. Table 7.2 shows this effect by comparing the intensities of the Cl-containing ions for the "extreme" samples. In contrast the $GeMn_3(CO)_x^+$ series does not show such a marked change, suggesting that these are common ions between the two products. This suggested that the second product was of equal or higher mass to the $ClGe[Mn(CO)_5]_3$.

On this basis and the indication from the infrared spectrum that the second product was of higher symmetry, a reasonable assignment for this product is $Ge[Mn(CO)_5]_4$.

i) The highest mass ion seen ($GeMn_3(CO)_{15}^+$) would correspond to $(P - Mn(CO)_5)^+$. If the steric congestion expected for such a compound follows the pattern of the cobalt analogue (See Section 3.4), it might be expected that at 125 ^oC in the mass spectrometer the parent molecule could relieve this congestion by loss of one terminal $-Mn(CO)_5$ substituent.

ii) As noted, the simpler infrared spectrum of the

second product from this reaction suggests a higher symmetry than $ClGe[Co(CO)_4]_3$. However, in mixed spectra, weak modes and shoulders may be missed completely. Thus the assignment of $Ge[Mn(CO)_5]_4$ is by no means certain from this point of view.

iii) The two products, postulated for this reaction are the most likely ones in view of the starting material ($ClGe[Co(CO)_4]_3$) and the reaction pattern seen in Section 7.3.

However, at this stage, without isolation and characterisation of these compounds, their assignments must remain tentative.

7.2 Reaction of $Cl_3GeCo(CO)_4$ with $NaMn(CO)_5$

$Cl_3GeCo(CO)_4$ (110 mg , 0.28 mmoles) was reacted for 20 minutes in Et_2O with $NaMn(CO)_5$ produced from $Mn_2(CO)_{10}$ (60 mg , 0.15 mmoles). The ether was removed and a hexane extract taken. This removed most of the reaction products, which were found largely to be $Cl_3GeCo(CO)_4$ and $Mn_2(CO)_{10}$. Other weak absorptions in the infrared suggested another component. Sublimation up to room temperature removed the $Mn_2(CO)_{10}$ and $Cl_3GeCo(CO)_4$, leaving orange residues. These showed a very complex infrared spectrum, suggesting several components. This is shown in Table 7.3, along with the spectra of $Cl_2Sn[Mn(CO)_5]_2$ and $ClSn[Mn(CO)_5]_3$. Though it is quite possible that the compounds $Cl_2Ge[Mn(CO)_5]_2$ and $ClGe[Mn(CO)_5]_3$ are present (as indicated by the correlation in Table 7.3), the spectrum is too complex for any meaningful assignment of individual components. An interesting feature of Table 7.3 is that there seems to be no correspondence with the spectrum for $Cl_3GeMn(CO)_5$. (137).

Table 7.3

Infrared Spectrum of Orange Reaction Product from $Cl_3GeCo(CO)_4/NaMn(CO)_5$

Orange Product (a)	$Cl_2Sn[Mn(CO)_5]_2$ (b)	$ClSn[Mn(CO)_5]_3$ (b)
2117.2 (1.0)	2119 (0.4)	
2114.0 (0.9,sh)		
2097.5 (4.7)	2093 (5.9)	2093 (0.4)
2088.6 (7.1)		
2081.5 (3.3)		2080 (8.3)
2078.4 (3.2)		
2072 (1.1)		
2058.7 (2.9)	2056 (2.0)	
2050.2 (6.0)		
2041.4 (6.3)		2037 (5.8)
2032.4 (10)	2030 (10)	3030 (3.0,sh)
2021.2 (6.4,sh)	2024 (4.0)	2020 (8.0)
	2011 (1.3)	
2004.7 (6.4)	2002 (3.9)	2005 (10)
2000.5 (5.4,sh)		
1990.5 (2.1)		1989 (4.2)
1980.0 (1.4)		

Notes

a) In hexane solution.

b) Reference (141) in cyclohexane.

7.3 Reaction of $Me_2GeClCo(CO)_4$ with $NaMn(CO)_5$

In view of the results suggested in Section 7.1, it was decided to carry out a competition of metal exchange and halide elimination. This was done on a one - to - one basis, using a monocobalt system, since the exchange has only been established for these so far. (53,54,140).

Thus, $Me_2GeClCo(CO)_4$ was reacted in Et_2O at room temperature with excess $NaMn(CO)_5$ for 20 minutes. (The starting material was known to contain a small impurity of $Me_2Ge[Co(CO)_4]_2$. The ether was removed and the solid products were extracted with hexane. The major component of the extract was identified by its infrared spectrum as $Mn_2(CO)_{10}$. (2045 (1), 2014 (2) and 1983 (1)). This component was removed by sublimation at 10°C over several hours. The resultant infrared spectrum is shown in Table 7.4 and could be completely assigned as a mixture of $Me_2Ge[Mn(CO)_5]_2$ (77) and $Me_2Ge[Co(CO)_4]_2$ (51). N.B. The possibility of $Me_2GeClMn(CO)_5$ could not be discounted from the infrared data, due to overlap.

7.4 Discussion

The incidence of $Mn_2(CO)_{10}$ as a major component of each of the above reaction products is probably not too significant. It is found to some extent with most alkali halide eliminations using $Mn(CO)_5^-$ because of the reasonably favourable halogen exchange reaction noted in Chapter Two.

The reaction of $ClGe[Co(CO)_4]_3$ showed that the metal exchange reaction takes priority over the halide elimination reaction. Even though some of the product was postulated to have involved both exchange and elimination, there was no evidence for the elimination - only products.

Table 7.4

Infrared Spectrum of Purified Products from

$Me_2GeClCo(CO)_4/NaMn(CO)_5$ Reaction

Reaction Products(a)	$Me_2Ge[Mn(CO)_5]_2$(b)	$Me_2Ge[Co(CO)_4]_2$(c)
2102.7 (w)	2105 (2.5)	
2099.0 (w)		2098 (3.5)
8081.5 (s)		2081 (9.8)
	2080 (8)	
2077.8 (s)		
	2045 (2)	
2034.0 (w,sh)		2033 (3.5,sh)
2027.7 (m,sh)		2027 (7.4)
possible shoulder		2019 (9.8)
2010.0 (vs,sh)	2010 (9.5)	
		2006 (10)
2002.9 (vs)	2000 (9.5)	
1996.8 (m)		1997 (7.2)
1991.3 (m)	1985 (8.5)	
1963 (vw)	1955 (2)	

Notes

a) In hexane.

b) Reference (77) in cyclohexane.

c) Reference (51) in cyclohexane.

(i.e. $(CO)_5MnGe[Co(CO)_4]_3$). In contrast, the exchange - only product ($ClGe[Mn(CO)_5]_3$) was seen. It is also interesting that there was no evidence for partial metal exchange.

The reaction of $Cl_3GeCo(CO)_4$ was notable for the limited extent to which anything at all happened. However, what little does react seems to have formed the higher exchange products. This suggests a fairly strong deactivating effect of the three chlorine substituents, making the first substitution the rate-determining step. After this, successive removal of chlorine substituents activates the compound, leading to the formation of higher - substituted derivatives.

A feature of the $Me_2GeClCo(CO)_4$ reaction was the apparent lack of reaction of the $Me_2Ge[Co(CO)_4]_2$ component. The exchange/elimination reaction of $Me_2GeClCo(CO)_4$ clearly went to completion. As in the case of $ClGe[Co(CO)_4]_3$, the single chlorine substituent had no apparent effect on the reaction, as expected from the discussion above. In terms of this relative activation effect, the $Me_2Ge[Co(CO)_4]_2$ component would be expected to be more likely to exchange. It is possible that some of the $-Co(CO)_4^-$ released when $Me_2GeClCo(CO)_4$ undergoes metal exchange eliminates -Cl from another molecule of $Me_2GeClCo(CO)_4$ to form $Me_2Ge[Co(CO)_4]_2$. However, the data presented here indicate that this would not be expected to compete favourably with the metal exchange reaction, particularly as a secondary process.

Though the mechanism of the metal exchange process has not been established, the effects of relative activation seen here suggest the possibility of a backside attack by the incoming metal carbonyl anion. Thus, more chlorine substituents increase the electron density in the vicinity of the germanium - substituent bonds, inhibiting possible

backside attack by $Mn(CO)_5^-$. Conversely, the positive inductive effect of methyl substituents would move electron density out of the path of the incoming anion and would help to make the metal carbonyl group already on the germanium a better leaving group.

Relative activation effects of the type observed and relative nucleophilicity of the metal carbonyl anions (29) determine the importance of the metal exchange reaction in a competition situation. Similarly, the importance of the alkali halide elimination in such situations is determined by the effective electrophilic behaviour of e.g. "$Me_2GeCo(CO)_4^+$" toward chlorine, as compared to that of Na^+. In the reaction systems studied here it seems fairly clear that the metal exchange reaction dominates over the alkali halide elimination. However, further investigation is necessary to determine the exact nature of substituent effects on both processes.

CHAPTER EIGHT

Mass and Infrared Spectral Studies of Germanium Derivatives of Cobalt Carbonyl

8.1 Mass Spectral Data

The mass spectra of the derivatives prepared in this work are listed in Tables 8.1 to 8.11 (p.p.*136-147*). Many of the features of the spectra are common and may be conveniently discussed together. Some of the more specific aspects of each spectrum will also be briefly mentioned below.

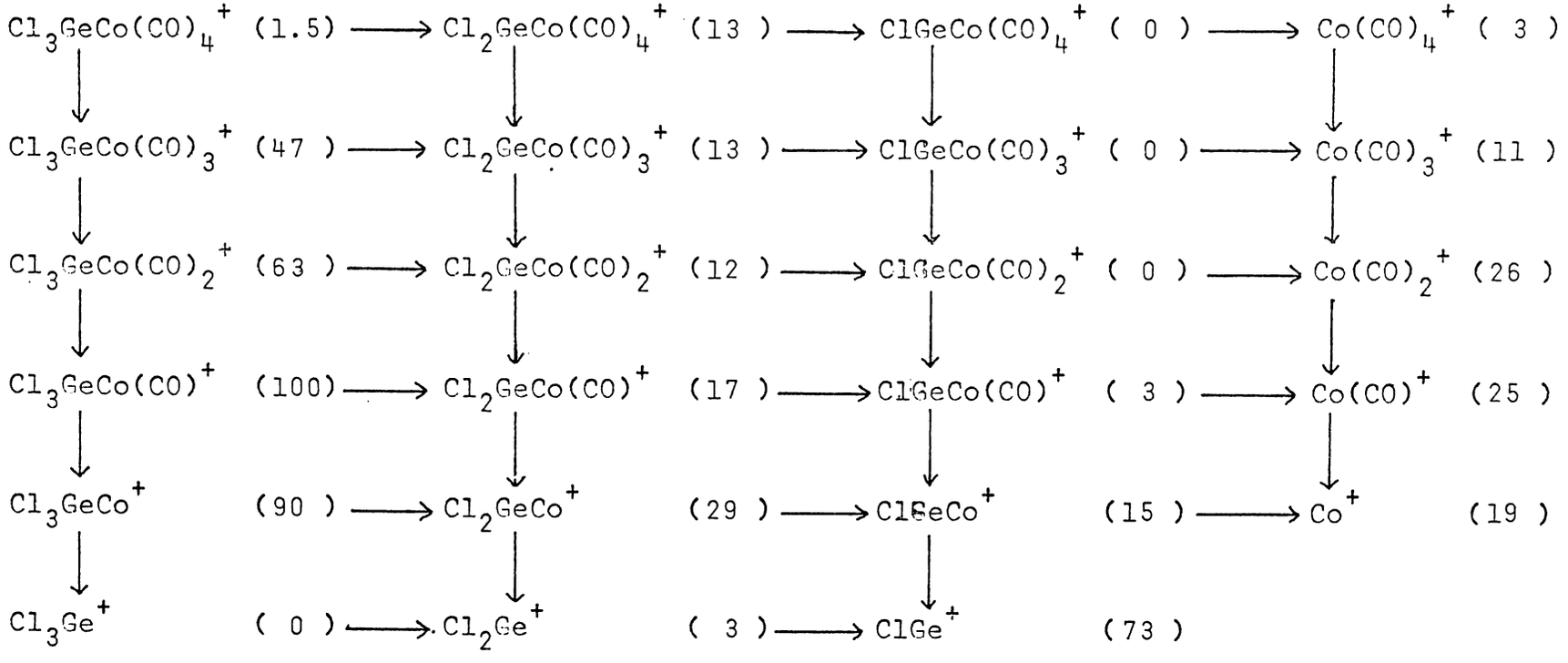
The basic fragmentation patterns are common to all spectra and are typified by the example given in Table 8A. i.e. The loss of carbonyl from the parent ion (or $(P-CO)^+$ if there is no parent ion) represents the major fragmentation process observed. This set of envelopes is overlapped to varying degrees by the series of fragments corresponding to carbonyl loss from (P - germanium sustituent)$^+$. These series are always much weaker and are often incomplete. As discussed in the next section, there is also some overlap of ions due to complete loss of the germanium moiety, but these are always weak.
N.B. The actual fragmentation processes as shown in the table can only be inferred without metastable support, but as mentioned in Section 1.4, these processes have been established in spectra of related compounds.

Another feature common to all these spectra is the unimportance of fragmentation below the germanium - cobalt-bonded unit. e.g. $Ge\text{-}Co^+$ for $X_3GeCo(CO)_4$ and $GeCo_2^+$ for $X_2Ge[Co(CO)_4]_2$ etc. This is tabulated and discussed in the next section.

The most striking feature of all the derivatives of the

TABLE 8A

Typical Mass Spectral Fragmentation Pattern for Germanium - Cobalt Carbonyl Derivatives (a)



Note :

a) ↓ = CO loss ; → = Cl loss

b) Relative intensities in parentheses.

type : $X_aGe[Co(CO)_4]_{4-a}$ (a = 0, 1, 2) is the lack of a parent ion. Graham (52,79) has found this for the analogous tin derivatives and has suggested that the observation of $(P-CO)^+$ in the spectrum of e.g. $XSn[Co(CO)_4]_3$ is due to the rearrangement of the molecule to the more stable (under conditions in the mass spectrometer) configuration of $[Co(CO)_4]SnXCo_2(CO)_7$. (See Figure 1.1B , p. *6*). He supports this with the evidence that ions based on Co_2^+ are also seen in these spectra. These would also require a rearrangement of this type in the parent molecule. Further support comes from the fact that the bridged-type of derivative has been found to be more stable under laboratory conditions, also. (e.g. $MeGeCo_3(CO)_{11}$ vs $MeGe[Co(CO)_4]_3$ - see (53) and Chapter Five). The mass spectral data available for the bridged derivatives in Table 1.3 (p.*12*) has indicated that all show parent ions. The results from this work directly parallel those from the tin analogues and lend further support to this type of possible rearrangement process.

As well as the general features mentioned above, the important features of the individual spectra are summarised below :

$Cl_3GeCo(CO)_4$ (Table 8.1 , p.*136*)

Though previously prepared, no mass spectral data was available for this compound. The spectrum shows a very weak parent ion, and may be compared with $Br_3GeCo(CO)_4$, which shows no parent ion.

$Cl_2Ge[Co(CO)_4]_2$ (Table 8.2 , p.*137*).

Again, though already reported, no mass spectral data was available. The highest mass envelope corresponds to $(P-CO)^+$. $(P-Cl)^+$ and fragments due to carbonyl loss from this are also seen (weakly) for all eight carbonyls.

$ClGe[Co(CO)_4]_3$ (Table 8.3 , p.138)

$(P-CO)^+$ is the highest mass envelope seen. If $ClGeCo_3(CO)_{11}^+$ represents a more stable entity than the parent ion, this reflects the difference between normal preparative conditions and those present in the mass spectrometer. i.e. no $XGeCo_3(CO)_{11}$ (X = halogen) species (as opposed to $XGe[Co(CO)_4]_3$) have yet been reported, even from reaction systems analogous to those used in the preparation of $RGeCo_3(CO)_{11}$(R = Me, Ph). No Ge^+ envelope is seen, reflecting the minimal fragmentation below $GeCo_3^+$.

$(CO)_7Co_2GeCo_2(CO)_7$ (Table 8.4 , p.139).

Increasing probe temperatures up to 120°C was found to to increase all the ion intensities without having any effect on relative intensities. In the light of the discussion above, the observation of the parent ion lends support to the proposed configuration for this compound as shown in Section 3.5.4 (p. 54). (Assuming that the proposed mass spectral rearrangement process is valid). i.e. it implies that none of the cobalt carbonyl substituents on germanium is in a terminal configuration. (See Figure 1.1A , p. 6).

The series of ions $GeCo_3(CO)_{7\,to\,2}^+$ were identified only by their ^{70}Ge and ^{72}Ge components, which showed weakly on the low mass side of the corresponding $GeCo_4(CO)_{5\,to\,0}^+$ envelopes.

There is some indication from the main set of envelopes ($GeCo_4(CO)_x^+$) of preferential loss of the first two carbonyls. While this is conveniently consistent with the expected ready removal of the bridging carbonyls in the proposed structure, such an argument remains speculative.

The loss of carbonyl oxygen in the spectrometer is generally not great in the higher mass regions for compounds of this type. Possible fragments of this type may often not

be seen due to overlap with other ions. The observation of $GeCo_3C^+$ and CoC^+ at low intensities is consistent with data published for $GeH_3Re(CO)_5$ (146) , $GeH_3Co(CO)_4$ (65) and $GeH_3Mn(CO)_5$ (145). Both these ions accompany strong $GeCo_3^+$ and Co^+ ions.

$\underline{Ge[Co(CO)_4]_4}$

The only difference found in the mass spectrum of this compound from that of $(CO)_7Co_2GeCo_2(CO)_7$ was that a probe temperature of 120°C gave a spectrum of similar intensity to that obtained for $(CO)_7Co_2GeCo_2(CO)_7$ at 90°C. As a check that decomposition of the $Ge[Co(CO)_4]_4$ was not taking place during handling, the infrared spectrum was run before and after the mass spectrum and showed no change. It would seem that the compound rearranges to $GeCo_4(CO)_{14}^+$ at the probe temperature required to volatilise the sample. If the observation of $(P-CO)^+$ does reflect the formation of a bridged ion, the observation of $(P-2CO)^+$ here could imply the rearrangement of $Ge[Co(CO)_4]_4$ to $(CO)_7Co_2GeCo_2(CO)_7^+$. i.e. the formation of a double bridging species.

In the case of the tin analogue ($SnCo_4(CO)_{16}$), $(P-CO)^+$ is the highest mass ion seen. An extension of the rearrangement argument (using the same premise) would then imply a semi-open, semi-bridged configuration of the type shown in Section 3.5.4 (p.*54*). This difference in behaviour between the germanium and tin analogues could be understood in terms of the larger tin atom coping with the steric congestion of the substituents better than germanium.

$\underline{(CO)_4CoGeCo_3(CO)_9}$

As reported in Section 3.3.5, the detailed mass spectral data reported by Schmid (97) compares closely with that obtained in this work. The data are therefore not tabulated

here.

$Br_3GeCo(CO)_4$ (Table 8.5 , p.*140*).

The mass spectrum of this compound has not been previously reported. The parent ion was not detected under a range of conditions. This may be compared with the very weak parent ion seen for the chloro-analogue. However, $(P-Br)^+$ is seen, along with loss of four carbonyls from this. The reason for the lack of a parent ion is obscure at this stage. Interestingly,the base peak for this compound does not appear in the parent $Br_3GeCo(CO)_x^+$ series (as with most of these compounds), but is $BrGe^+$. This is complemented by a moderate amount of $Co(CO)_x^+$. The rearrangement ions $BrCo(CO)_x^+$ are also readily observed in this simple spectrum.

$Br_2Ge[Co(CO)_4]_2$ (Table 8.6 , p.*142*).

The highest mass ion seen is $(P-CO)^+$, which appears at fairly low intensity. The series of ions due to carbonyl loss from $(P-Br)^+$ and $(P-2Br)^+$ are not important. Rearrangement ions are limited to $BrCo^+$.

$BrGe[Co(CO)_4]_3$ (Table 8.7 , p.*143*).

$(P-CO)^+$ is the highest mass ion seen. The weak appearance of Ge^+ in this spectrum is most probably the function of the high intensity of the whole spectrum, compared to that of $Br_2Ge[Co(CO)_4]_2$, which showed no Ge^+.

$MeGeCl[Co(CO)_4]_2$ (Table 8.8 , p.*144*).

This spectrum contained weak impurity envelopes due to $Me_2Ge[Co(CO)_4]_2$ and $MeGeCo_3(CO)_x^+$ (x = 0 to 11) which have been subtracted from that in the table. $(P-CO)^+$ is the highest mass envelope seen and no carbonyl-containing ions in the series due to fragmentation of $(P-Me)^+$ or $(P-Cl)^+$ were seen. Fragments containing both Me and Cl carried a high proportion of the total ion current.

$MeGeBr_2Co(CO)_4$ (Table 8.9 , p.145).

No parent ion was seen and $(P-CO)^+$ was the highest mass ion. $(P-Br)^+$ was also absent, but this is a relatively weak series anyway. As for $Br_3GeCo(CO)_4$, no reason for the lack of a parent ion in this compound has been established. Relative to the compounds above, $MeGeBr_2Co(CO)_4$ showed a large ion current due to low-mass ions.

$MeGeBr[Co(CO)_4]_2$ (Table 8.10 , p.146).

Again, $(P-CO)^+$ is the highest mass ion seen. A significant amount of ion current is carried by the series due to carbonyl loss from $(P-Me)^+$ in contrast with the situation noted above for the chloro-analogue. In all, a relatively high proportion of ion current is carried by ions other than those due to carbonyl loss from $(P-CO)^+$.

$(Me_2Ge)_2Co_2(CO)_6$ (Table 8.11 , p.147).

This spectrum appears to be consistent with the few comments noted with the reported literature preparations. (77,90). The parent ion is seen and as noted in the next section, a very high proportion of ion current is carried by ions not fragmented beyond $Ge_2Co_2^+$. Loss of methyl groups is not significant until all carbonyl groups have been removed. The loss of a complete (Me_2Ge) - bridging group gives rise only to weak envelopes, while Co_2^+, due to loss of both bridging groups, is very weak.

Table 8.1

Mass Spectrum of $Cl_3GeCo(CO)_4$ (a)

m/e	Assignment	Relative Intensity
	$Cl_3GeCo(CO)_x^+$	
346-358	x=4	1.5
318-330	x=3	47
290-302	x=2	63
262-274	x=1	100
234-246	x=0	90
	$Cl_2GeCo(CO)_x^+$	
311-321	x=4	13
283-293	x=3	13
255-265	x=2	12
227-237	x=1	17
199-209	x=0	29
192-200	$ClGeCo(CO)^+$	3
164-172	$ClGeCo^+$	15
129-135	$GeCo^+$	6
140-150	Cl_2Ge^+	3
105-113	$ClGe^+$	73
70-76	Ge^+	6
171	$Co(CO)_4^+$	3
143	$Co(CO)_3^+$	11
115	$Co(CO)_2^+$	26
87	$Co(CO)^+$	25
59	Co^+	19
150-152	$ClCo(CO)_2^+$	3
122-124	$ClCo(CO)^+$	7
94-96	$ClCo^+$	5

a) Probe temperature = 60°C

Table 8.2

Mass Spectrum of $Cl_2Ge[Co(CO)_4]_2$ (a)

m/e	Assignment	Relative Intensity
	$Cl_2GeCo_2(CO)_x^+$	
454-464	x=7	38
426-436	x=6	32
398-408	x=5	31
370-380	x=4	63
342-352	x=3	36
314-324	x=2	65
286-296	x=1	100
258-268	x=0	69
	$ClGeCo_2(CO)_x^+$	
447-455	x=8	6
419-427	x=7	2
391-399	x=6	1.5
363-381	x=5	1
335-343	x=4	4
307-315	x=3	4
379-387	x=2	3
251-259	x=1	4
223-231	x=0	13
227-237	$Cl_2GeCo(CO)^+$	7
199-209	Cl_2GeCo^+	9
140-150	Cl_2Ge^+	3
164-172	$ClGeCo^+$	13
129-135	$GeCo^+$	39
105-113	$ClGe^+$	12
70-76	Ge^+	3
188-194	$GeCo_2^+$	5

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Table 8.2 Contd.

143	$Co(CO)_3^+$	3
115	$Co(CO)_2^+$	11
87	$Co(CO)^+$	18
59	Co^+	18
181-183	$ClCo_2(CO)^+$	2
153-155	$ClCo_2^+$	6
118	Co_2^+	14

a) Probe temperature = 65°C.

Table 8.3

Mass Spectrum of $ClGe[Co(CO)_4]_3$ (a)

m/e	Assignment	Relative Intensity
	$ClGeCo_3(CO)_x^+$	
590-598	x=11	8
562-570	x=10	23
534-542	x=9	18
506-514	x=8	27
478-486	x=7	12
450-458	x=6	29
422-430	x=5	47
394-402	x=4	68
366-374	x=3	47
338-346	x=2	46
310-318	x=1	58
282-290	x=0	100
	$ClGeCo_2(CO)_{2-4}^+$	vw
251-259	$ClGeCo_2(CO)^+$	6
223-231	$ClGeCo_2^+$	27
164-172	$ClGeCo^+$	7

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Table 8.3 Contd.

247-253	$GeCo_3^+$	8
188-194	$GeCo_2^+$	44
129-135	$GeCo^+$	22
70-76	Ge^+	0
118	Co_2^+	20
115	$Co(CO)_2^+$	7
87	$Co(CO)^+$	44
59	Co^+	18

a) Probe temperature = 90°C

Table 8.4

Mass Spectrum of $(CO)_7Co_2GeCo_2(CO)_7$ (a)

m/e	Assignment $GeCo_4(CO)_x^+$	Relative Intensity
698-704	x=14	7
670-676	x=13	15
642-648	x=12	57
614-620	x=11	10
586-592	x=10	12
558-564	x=9	18
530-536	x=8	93
502-508	x=7	72
474-480	x=6	57
446-452	x=5	44
418-424	x=4	50
390-396	x=3	55
362-368	x=2	42
334-340	x=1	39
306-312	x=0	100

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Table 8.4 Contd.

	$GeCo_3(CO)_x^+$	
443-449	x=7	2
415-421	x=6	4
387-393	x=5	6
359-365	x=4	6
331-337	x=3	7
303-309	x=2	14
275-281	x=1	1
247-253	x=0	84
259-265	$GeCo_3C^+$	4
216-222	$GeCo_2(CO)^+$	1
188-194	$GeCo_2^+$	45
129-135	$GeCo^+$	20
118	Co_2^+	15
115	$Co(CO)_2^+$	8
87	$Co(CO)^+$	16
71	CoC^+	1
59	Co^+	19

a) Probe temperature = 90°C.

Table 8.5

Mass Spectrum of $Br_3GeCo(CO)_4$ (a)

m/e	Assignment $Br_3GeCo(CO)_x^+$	Relative Intensity
478-490	x=4	0
450-462	x=3	24
422-434	x=2	69
394-406	x=1	71
366-378	x=0	44

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Table 8.5 Contd.

	$Br_2GeCo(CO)_x^+$	
399-409	x=4	3
371-381	x=3	0
343-353	x=2	5
315-325	x=1	7
287-297	x=0	28
307-319	Br_3Ge^+	3
228-238	Br_2Ge^+	11
208-216	$BrGeCo^+$	16
149-157	$BrGe^+$	100
129-135	$GeCo^+$	15
70-76	Ge^+	17
194,196	$BrCo(CO)_2^+$	2
171	$Co(CO)_4^+$	2
166,168	$BrCo(CO)^+$	5
143	$Co(CO)_3^+$	8
138,140	$BrCo^+$	7
115	$Co(CO)_2^+$	27
87	$Co(CO)^+$	36
79,81	Br^+	9
59	Co^+	44

a) Probe temperature = 45°C.

Table 8.6

Mass Spectrum of $Br_2Ge[Co(CO)_4]_2$ (a)

m/e	Assignment $Br_2GeCo_2(CO)_x^+$	Relative Intensity
570-580	x=8	0
542-552	x=7	17
514-524	x=6	27
486-496	x=5	63
458-468	x=4	56
430-440	x=3	28
402-412	x=2	49
374-384	x=1	100
346-356	x=0	74
315-325	$Br_2GeCo(CO)^+$	9
287-297	Br_2GeCo^+	14
323-331	$BrGeCo_2(CO)_2^+$	2
295-303	$BrGeCo_2(CO)^+$	5
267-275	$BrGeCo_2^+$	14
236-244	$BrGeCo(CO)^+$	4
208-216	$BrGeCo^+$	20
149-157	$BrGe^+$	22
188-194	$GeCo_2^+$	5
129-135	$GeCo^+$	56
171	$Co(CO)_4^+$	1
143	$Co(CO)_3^+$	4
138,140	$BrCo^+$	4
118	Co_2^+	17
115	$Co(CO)_2^+$	19
87	$Co(CO)^+$	20
59	Co^+	28

a) Probe temperature = 80°C.

Table 8.7

Mass Spectrum of $BrGe[Co(CO)_4]_3$ (a)

m/e	Assignment	Relative Intensity
	$BrGeCo_3(CO)_x^+$	
662-670	x=12	0
634-642	x=11	18
606-614	x=10	45
578-586	x=9	25
550-558	x=8	48
522-530	x=7	8
494-502	x=6	22
466-474	x=5	79
438-446	x=4	78
410-418	x=3	49
382-390	x=2	65
354-362	x=1	59
326-334	x=0	100
267-275	$BrGeCo_2^+$	30
208-216	$BrGeCo^+$	8
149-157	$BrGe^+$	4
247-253	$GeCo_3^+$	4
188-194	$GeCo_2^+$	41
129-135	$GeCo^+$	21
70-76	Ge^+	2
171	$Co(CO)_4^+$	0.3
143	$Co(CO)_3^+$	2
138,140	$BrCo^+$	1
118	Co_2^+	15
115	$Co(CO)_2^+$	9
87	$Co(CO)^+$	15
59	Co^+	20

a) Probe temperature = 110°C.

Table 8.8

Mass Spectrum of $MeGeCl[Co(CO)_4]_2$ (a)

m/e	Assignment	Relative Intensity
	$MeGeClCo_2(CO)_x^+$	
462-470	x=8	0
434-442	x=7	30
406-414	x=6	44
378-386	x=5	15
350-358	x=4	37
322-330	x=3	30
294-302	x=2	100
266-274	x=1	63
238-246	x=0	85
179-187	$MeGeClCo^+$	9
223-231	$ClGeCo_2^+$	26
203-209	$MeGeCo_2^+$	19
188-194	$GeCo_2^+$	16
164-172	$ClGeCo^+$	8
144-150	$MeGeCo^+$	20
129-135	$GeCo^+$	17
118	Co_2^+	20
115	$Co(CO)_2^+$	11
105-111	$ClGe^+$	3
85-91	$MeGe^+$	7
87	$Co(CO)^+$	17
70-76	Ge^+	2
59	Co^+	16

a) Probe temperature = 50°C.

Table 8.9

Mass Spectrum of $MeGeBr_2Co(CO)_4$ (a)

m/e	Assignment $MeGeBr_2Co(CO)_x^+$	Relative Intensity
414-424	x=4	0
386-396	x=3	26
358-368	x=2	100
330-340	x=1	80
302-312	x=0	38
243-253	$MeGeBr_2^+$	1
371-381	$Br_2GeCo(CO)_3^+$	1
343-353	$Br_2GeCo(CO)_2^+$	6
315-325	$Br_2GeCo(CO)^+$	20
287-297	Br_2GeCo^+	32
228-238	Br_2Ge^+	1
279-287	$MeGeBrCo(CO)_2^+$	1
251-259	$MeGeBrCo(CO)^+$	5
223-231	$MeGeBrCo^+$	13
164-172	$MeGeBr^+$	1
264-272	$BrGeCo(CO)_2^+$	0.3
236-244	$BrGeCo(CO)^+$	2
208-216	$BrGeCo^+$	13
149-157	$BrGe^+$	27
144-150	$MeGeCo^+$	8
129-135	$GeCo^+$	10
85-91	$MeGe^+$	62
70-76	Ge^+	5
166,168	$BrCo(CO)^+$	1
138,140	$BrCo^+$	6

a) Probe temperature = 20°C.

Table 8.10

Mass Spectrum of $MeGeBr[Co(CO)_4]_2$ (a)

m/e	Assignment	Relative Intensity
	$MeGeBrCo_2(CO)_x^+$	
506-514	x=8	0
478-486	x=7	20
450-458	x=6	40
422-430	x=5	23
394-402	x=4	33
366-374	x=3	25
338-346	x=2	75
310-318	x=1	60
282-290	x=0	100
251-259	$MeGeBrCo(CO)^+$	10
223-231	$MeGeBrCo^+$	15
	$GeBrCo_2(CO)_x^+$	
407-415	x=5	6
379-387	x=4	10
351-359	x=3	5
323-331	x=2	3
295-303	x=1	4
267-275	x=0	35
208-216	$GeBrCo^+$	13
149-157	$GeBr^+$	10
203-209	$MeGeCo_2^+$	9
172-178	$MeGeCo(CO)^+$	1
144-150	$MeGeCo^+$	23
85-91	$MeGe^+$	12
188-194	$GeCo_2^+$	14
157-163	$GeCo(CO)^+$	4
129-135	$GeCo^+$	27

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Table 8.10 Contd.

70-76	Ge^+	3
138,140	$BrCo^+$	2
118	Co_2^+	22
115	$Co(CO)_2^+$	8
87	$Co(CO)^+$	19
59	Co^+	22

a) Probe temperature = 20°C.

Table 8.11

Mass Spectrum of $(Me_2Ge)_2Co_2(CO)_6$ (a)

m/e	Assignment	Relative Intensity
	$Me_4Ge_2Co_2(CO)_x^+$	
486-498	x=6	27
458-470	x=5	53
430-442	x=4	45
402-414	x=3	16
374-386	x=2	82
346-358	x=1	100
318-330	x=0	28
303-315	$Me_3Ge_2Co_2^+$	15
484-496	$Me_2Ge_2Co_2(CO)_6^+$	43
288-230	$Me_2Ge_2Co_2^+$	28
273-285	$MeGe_2Co_2^+$	72
258-270	$Ge_2Co_2^+$	98
218-224	$Me_2GeCo_2^+$	16
203-209	$MeGeCo_2^+$	19
188-194	$GeCo_2^+$	20
118	Co_2^+	4

a) Probe temperature = 45°C.

8.2 Mass Spectral Discussion

A further illustration of the care required in relating mass spectral data to normal stability comes from the observation of loss of carbonyl from the parent ion or $(P-CO)^+$ as the most important fragmentations. This does not indicate that CO is weakly bound to these dervivatives. Since the mass spectral data are related to ionized species, relative abundance may be kinetically controlled. Therefore conclusions about the thermodynamic stability of a neutral compound may not be valid. Also, only positive ions resulting from fragmentation are seen. Their relative intensities may be dependent upon the relative stabilities of the remaining negative ions or neutral species.

However, with the above points borne in mind, the comparison of spectra run under similar conditions, related to other data can still provide useful supportive information. Thus, in comparing the effect of bromine vs. chlorine substituents in $X_3GeCo(CO)_4$, the respective yields of 10% and 60% are supported by respective 52% and 69% values of ion current carried by Ge-Co-containing ions i.e. the replacement of Cl substituents by the larger Br is found to be less favourable as reflected by both the poor yields and the greater molecular break-up in the mass spectrometer.

For the polycobalt derivatives, there is a high incidence of ions containing the basic metal unit. (i.e. those containing $GeCo_2$ for the bis-cobalt derivatives ; those containing $GeCo_3$ for the tris-cobalt derivatives etc). Very little fragmentation occurs beyond these units, as can be seen from the tabulation below. This lists the percentage of total ion current carried by all ions containing the basic units.

Compound	Ions	Ion Current (% of total)	Ion Current due to all Ge-Co cont. fragments (% of total)
$Br_2Ge[Co(CO)_4]_2$	$\sum_{\text{all } n,x} (Br_nGeCo_2(CO)_x^+)$	67	86
$BrGe[Co(CO)_4]_3$	$\sum_{\text{all } n,x} (Br_nGeCo_3(CO)_x^+)$	78	92
$Cl_2Ge[Co(CO)_4]_2$	$\sum_{\text{all } n,x} (Cl_nGeCo_2(CO)_x^+)$	75	86
$ClGe[Co(CO)_4]_3$	$\sum_{\text{all } n,x} (Cl_nGeCo_3(CO)_x^+)$	72	87
$GeCo_4(CO)_{14}$	$\sum_{\text{all } x} (GeCo_4(CO)_x^+)$	73	94
$MeGeCl[Co(CO)_4]_2$	$\sum_{\text{all } m,n,x} (Me_mGeCl_nCo_2(CO)_x^+)$	71	87
$MeGeBr[Co(CO)_4]_2$	$\sum_{\text{all } m,n,x} (Me_mGeBr_nCo_2(CO)_x^+)$	75	85
$(Me_2Ge)_2Co_2(CO)_6$	$\sum_{\text{all } m,x} (Me_mGe_2Co_2(CO)_x^+)$	91	99+
$Br_3GeCo(CO)_4$			52
$Cl_3GeCo(CO)_4$			69

The right hand column shows that only a small amount of complete fragmentation occurs in these compounds. It is interesting to note that with the exception of $(Me_2Ge)_2Co_2(CO)_6$, all of the polycobalt derivatives carry about the same ion currents with fragments containing their respective basic units.(The high values for $(Me_2Ge)_2Co_2(CO)_6$ may be due to intrinsic stability or low sampling temperatures). When the compounds are further fragmented to Ge-Co-containing ions, similar results are seen. This contrasts with the results for the monocobalt derivatives, which not only differ from one another but also carry much less ion current with Ge-Co-containing ions than the polycobalt derivatives.

A consistent feature of all the spectra is the predominance of fragments due to carbonyl loss from the parent ion. More than this, it is quite notable that the strongest ion envelopes for all spectra occur in the low-carbonyl-content regions of these

series. This can be seen below, where the two most intense ion envelopes seen for each compound are listed.

Compound		
$Cl_3GeCo(CO)_4$	$Cl_3GeCo(CO)^+$	, Cl_3GeCo^+
$Cl_2Ge[Co(CO)_4]_2$	$Cl_2GeCo_2^+$	, $Cl_2GeCo_2(CO)_2^+$
$ClGe[Co(CO)_4]_3$	$ClGeCo_3^+$	, $ClGeCo_3(CO)_4^+$
$GeCo_4(CO)_{14}$	$GeCo_4^+$	, $GeCo_4(CO)_8^+$
$Br_3GeCo(CO)_4$	$BrGe^+$	, $Br_3GeCo(CO)^+$
$Br_2Ge[Co(CO)_4]_2$	$Br_2GeCo_2(CO)^+$	, $Br_2GeCo_2^+$
$BrGe[Co(CO)_4]_3$	$BrGeCo_3^+$	, $BrGeCo_3(CO)_5^+$
$MeGeCl[Co(CO)_4]_2$	$MeGeClCo_2(CO)_2^+$	, $MeGeClCo_2^+$
$MeGeBr_2Co(CO)_4$	$MeGeBr_2Co(CO)_2^+$	, $MeGeBr_2Co(CO)^+$
$MeGeBr[Co(CO)_4]_2$	$MeGeBrCo_2^+$	, $MeGeBrCo_2(CO)_2^+$
$(Me_2Ge)_2Co_2(CO)_6$	$Me_4Ge_2Co_2(CO)^+$	, $Ge_2Co_2^+$

As an exception, $Br_3GeCo(CO)_4$ has already been noted for its high degree of fragmentation relative to the other compounds. In nearly all cases, the parent ion with no carbonyl substituents is one of the most intense envelopes. This is consistent with the few literature reports which do note such data for related compounds. (77,79,97). An interesting comparison with the data for the tris-cobalt carbonyl tin derivatives can be made by using Figures 3 and 4 and Tables III and IV in reference (79). In both the alkyl/aryl and halide derivatives, Patmore and Graham report significant intensities at n = 0, 5, 11 in the $RSnCo_3(CO)_n^+$ and $XSnCo_3(CO)_n^+$ fragments. Neither $ClGeCo_3(CO)_{11}^+$ nor $BrGeCo_3(CO)_{11}^+$ show this trend. In fact, both are rather weak. However, the tabulation above shows that the two most intense fragments for $BrGeCo_3(CO)_n^+$ do arise at n = 0 and 5.

For $ClGe_3(CO)_n^+$ a slight deviation from this gives n = 0 and 4 as the most intense ions. Overall, it would seem that there is a close resemblance in the mass spectral behaviour of these analogues. The variation noted above for n = 11 could be construed as support for the argument that the larger tin atom can cope with the steric interactions of three cobalt substituents better than germanium.

An analysisof this type could also be carried out for the bis-cobalt carbonyl derivatives. A check on Tables 8.2, 8.6, 8.8 and 8.10 shows that all these germanium derivatives exhibit very much the same fragment abundance patterns for the series $X_2GeCo_2(CO)_n^+$. However, without the data for the analogous tin derivatives, no further support (or otherwise) for arguments of the type given above can be obtained.

8.3 Infrared Studies

8.3.1 General

Throughout this work, dealing with many similar compounds, it has been invaluable to refer directly to infrared spectra (or reproductions of them from the literature data), rather than just to tabulations of absorptions and relative intensities. This was especially important with product mixtures, which arose from all reaction systems. With such closely related compounds, the most useful part of these infrared spectra is the carbonyl stretching region. Thus, the carbonyl spectra obtained in this work are presented here in figure form, along with the positions of the absorption maxima on the facing pages. Included are references to the same compounds in the literature and data for related compounds.

The determinations of expected vibrational modes for the compounds discussed here were carried out by standard methods. (e.g. see 144). The following discussions all refer to solution spectra. In the solid state, crystal effects and site symmetries usually give rise to more complex spectra.

8.3.2 $X_3GeCo(CO)_4$ (Figure 8.1 , p.*153*).

Vibrational studies on these compounds, along with the silicon and tin analogues have been extensively reported. (See Section 1.5, p.*18*). Under C_{3v} symmetry, the predicted carbonyl absorptions are $2A_1 + E$, all of which are seen. It only remains to note the trends found with varying substitution. Replacing germanium by tin typically reduces most absorptions by 1-2 cm^{-1}. A larger downward change occurs on changing Cl to Br to I. This reflects decreasing electron withdrawal by the heavier halogens, leaving relatively more cobalt d-electron density between cobalt and carbon than cobalt and germanium. This results in more electron density

Figure 8.1

Infrared Spectra of $X_3GeCo(CO)_4$ from 1980cm^{-1} to 2140cm^{-1}

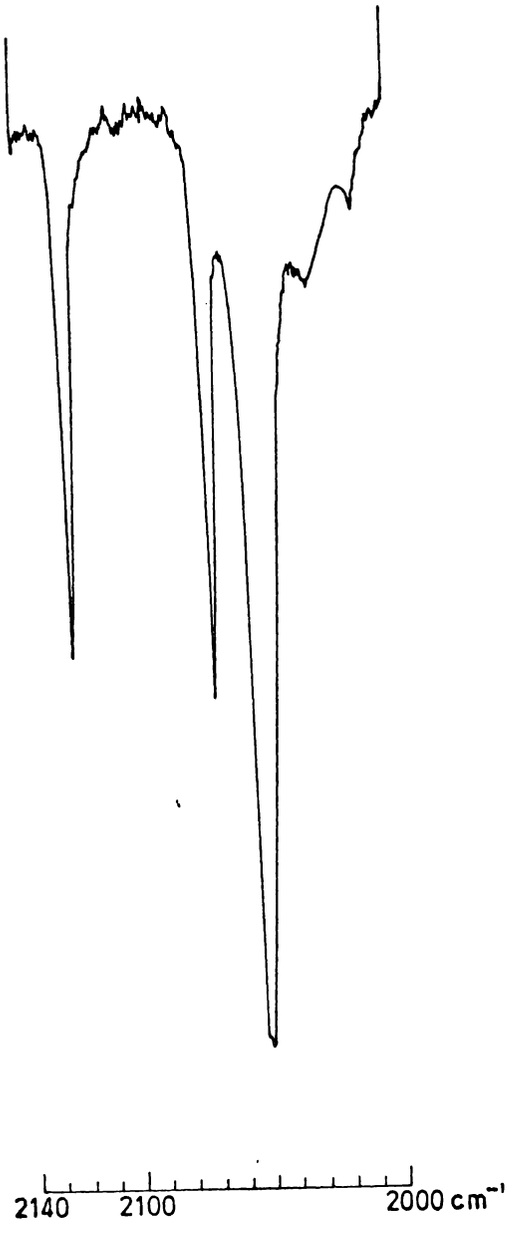
Figure 8.1

$X_3GeCo(CO)_4$ in Hexane

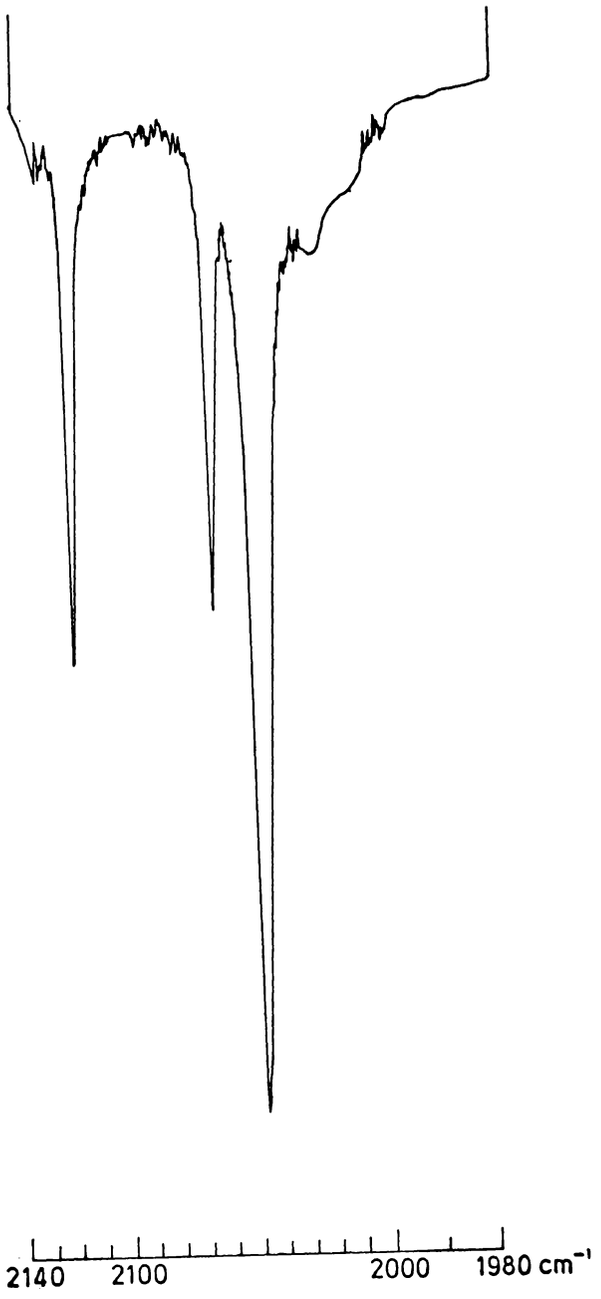
$Cl_3GeCo(CO)_4$		$Br_3GeCo(CO)_4$	
2122.6	(2120)	2119.2	(2116)
2068.6	(2068)	2066.0	(2063)
2050.1	(2048)	2048.0	(2043)

Values in parentheses are those for the tin analogues in cyclohexane. (51,52).

See also (66,110,112) for data on these and related derivatives.



$Cl_3 Ge Co(CO)_4$



$Br_3 Ge Co(CO)_4$

in the π^* antibonding orbitals on the carbonyl carbons, reducing the force constant and hence the energy of the observed absorptions.

8.3.3 $YGeX_2Co(CO)_4$ (Figure 8.2 , p.156).

In this case, the unsymmetric substitution on germanium reduces the molecular symmetry to C_s. Here, the A_1 modes of C_{3v} become A' and E becomes $A' + A''$. This latter splitting can be seen in Figure 8.2 for Y = Me , X = Cl,Br and Y = Cl, X = Me. The assignment of the two higher energy A' modes has been discussed by Graham (51) as a mixture of equatorial and axial carbonyl stretches, with the symmetric combination being the highest energy mode. Force field calculations (106) have shown this mixing to be 50%. A mixing effect of this sort is required to explain the finite intensity of what would otherwise be a weak or non-existent absorption corresponding to the symmetric stretch of the equatorial carbonyls only. This should cause no net dipole moment; even that moment arising from these carbonyls being bent toward the germanium (see Chapter One) would only be expected to give a weak absorption.

Apart from the trend seen for changing the halogen substituent, the effect of the halogen becomes even more obvious when comparing the two A' energies for the series $R_xCl_{3-x}GeCo(CO)_4$. e.g. For R = Ph , the high energy A' (or A_1) mode shows a drop of ca. 10 cm^{-1} for each of x = 0, 1, 2, 3. Similarly, the lower energy A' (or A_1) mode drops ca. 12 cm^{-1} per Cl removed. While the E and $(A' + A'')/2$ figures show a similar drop, this is not linear. Graham (51) has presented this as a linear plot versus the sum of the halogen electronegativities but took no account of the R - groups. These have since been shown to have a marked effect on the

Figure 8.2

Infrared Spectra of $YGeX_2Co(CO)_4$ from $1980cm^{-1}$ to $2140cm^{-1}$

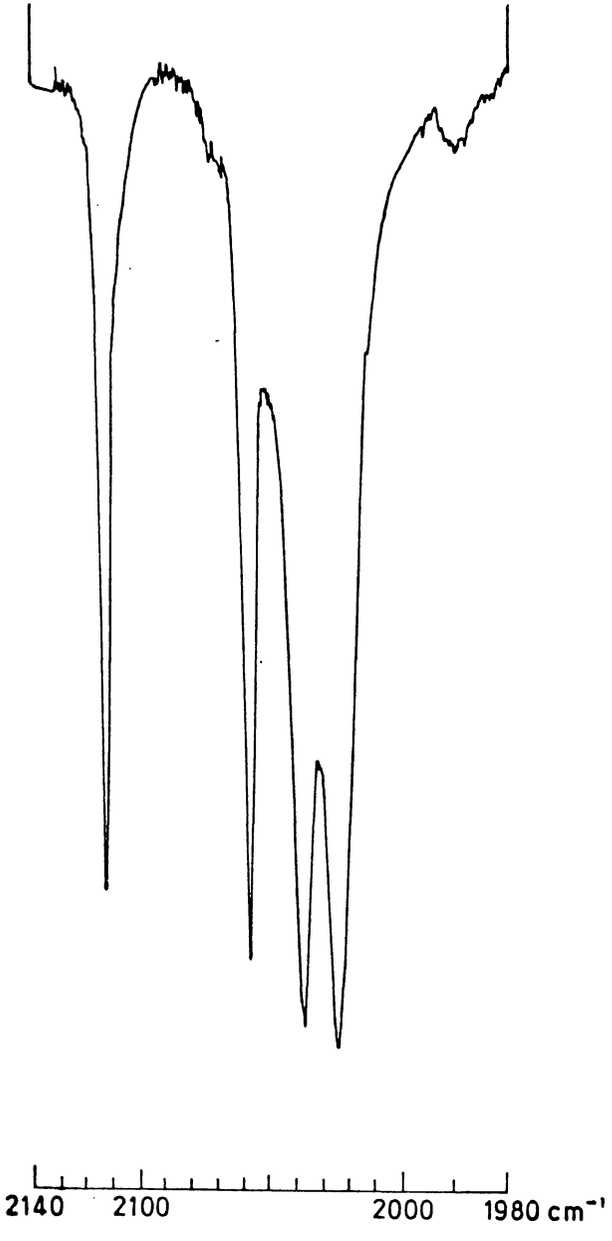
Figure 8.2

$YGeX_2Co(CO)_4$ in Hexane

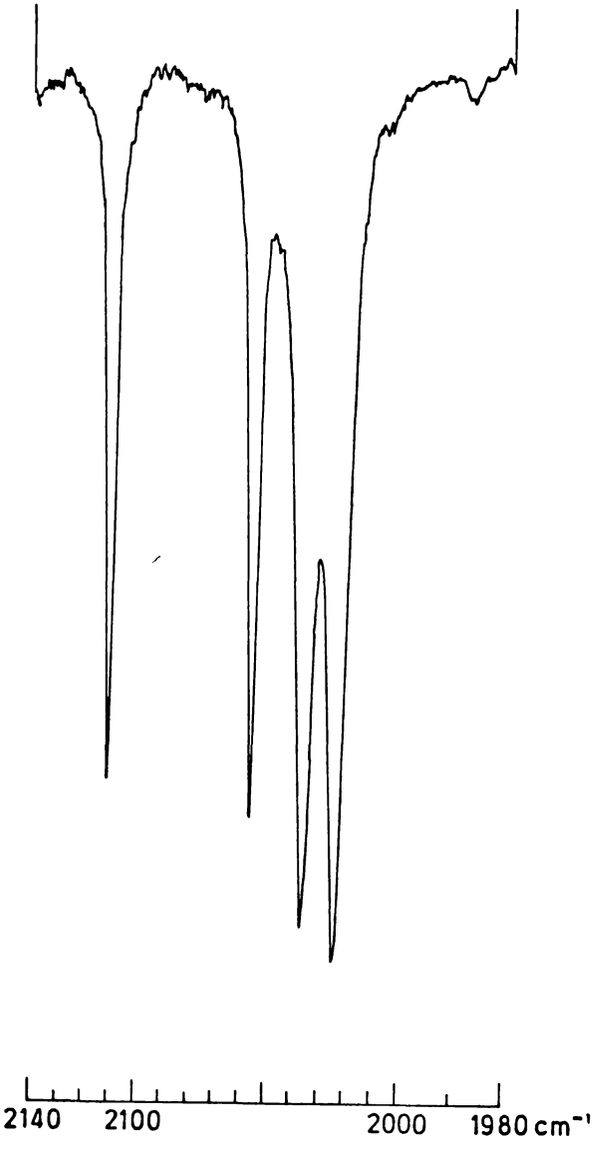
$MeGeCl_2Co(CO)_4$		$MeGeBr_2Co(CO)_4$		$Me_2GeClCo(CO)_4$	
2112.6	(2107)	2110.1	(2105)	2100.1	(2095)
2057.4	(2054)	2055.8	(2052)	2041.1	(2037)
2037.6	(2032)	2035.9	(2030)	2020.4	(2013)
2024.4	(2017)	2023.7	(2017)	2003.6	(1998)

Values in parentheses are those for the tin analogues in cyclohexane. (52,60).

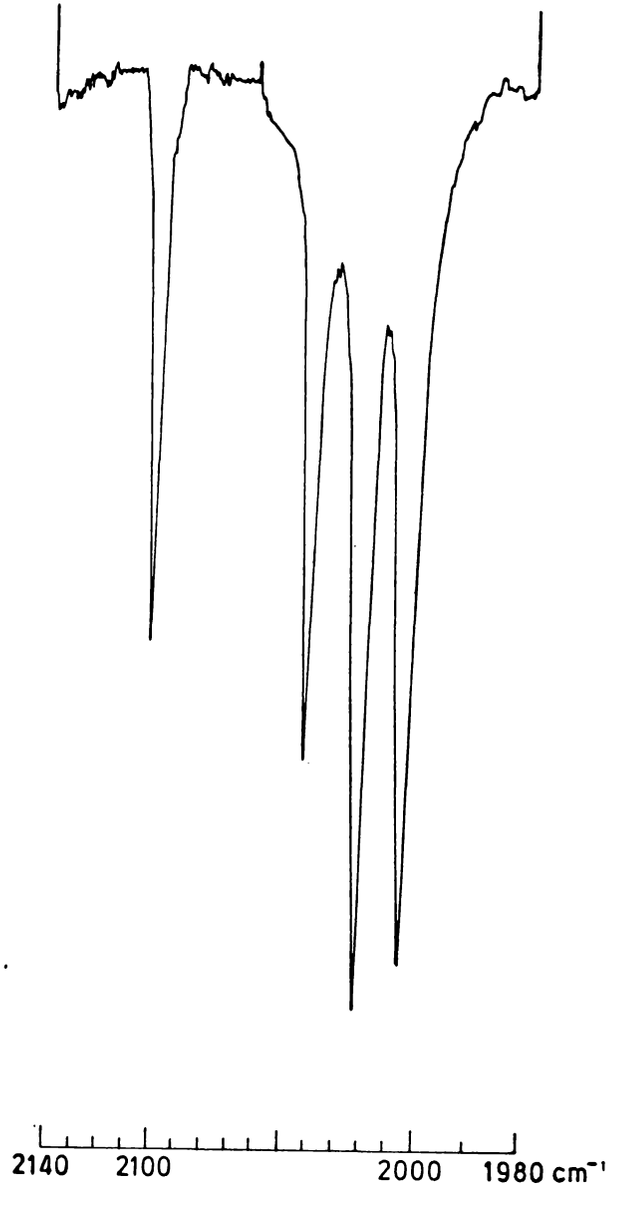
See also (51,53,54) for data on related derivatives.



$Me\,Ge\,Cl_2\,Co(CO)_4$



$Me\,Ge\,Br_2\,Co(CO)_4$



$Me_2\,Ge\,Cl\,Co(CO)_4$

energies of these modes (54) and such a simple relationship would seem dubious.

8.3.4 $X_2Ge[Co(CO)_4]_2$ (Figure 8.3 , p.159).

In the case where both X substituents are the same, C_{2v} molecular symmetry predicts seven infrared active carbonyl stretching modes. ($3A_1 + 3B_1 + B_2$). In all three examples studied here (X = Cl, Br, Me), as well as several other literature examples, all seven modes are seen, when shoulders are included. However,the use of the figures is clearly seen by comparing the methyl- and halogen-substituted derivatives shown in Figure 8.3. Not only is there a downward shift of ca. 20 cm^{-1} for each mode on changing from halogen to methyl substituents, but the main groupings of absorptions show quite different contours.

While the assignment of the large group of modes can not be made individually at this stage (especially without Raman data), the doubling up of the high energy A_1 (or A') mode from the original C_{3v} (or C_s) situation found for monocobalt derivatives seems fairly clear. i.e. The in- and out-of -phase combinations of this mode for the two terminal $-Co(CO)_4$ substituents give rise to this pair of absorptions. Of these two, the higher energy mode would be expected to be the in-phase combination of all eight carbonyls stretching together. Graham (51) has also discussed the resultant intensities of these modes in terms of Co-$\hat{M'}$-Co bond angles, as related to the partial cancellation of the terminal dipole moments making the high energy mode weaker, as seen for all derivatives in this class.

A similar series of shifts to that seen in the previous section is observed on replacement of the Group IVB atom or of the substituents on it. Once again, halogen substituents

Figure 8.3

Infrared Spectra of $X_2Ge[Co(CO)_4]_2$ from 1980cm^{-1} to 2140cm^{-1}

Figure 8.3

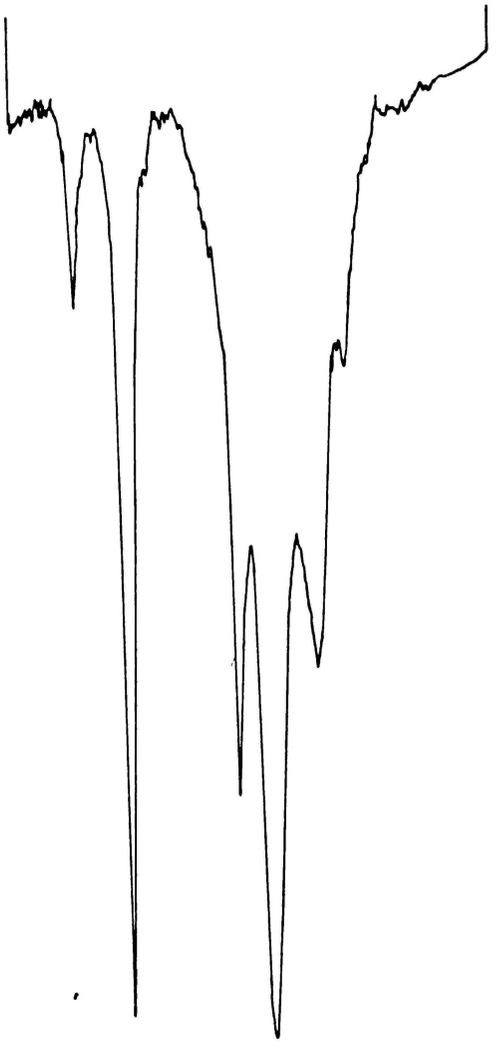
$X_2Ge[Co(CO)_4]_2$ in Hexane

$Cl_2Ge[Co(CO)_4]_2$		$Br_2Ge[Co(CO)_4]_2$		$Me_2Ge[Co(CO)_4]_2$	
2117.8	(2114)	2116.6	(2113)	2099.0	(2095)
2100.1	(2097)	2098.7	(2096)	2081.3	(2078)
2058.1	(2056)	2057.0	(2055)	2032 sh	(2031)sh
2054.5 sh	(2052)sh	2055 sh	(2050)sh	2024.7	(2024)
2044.8	(2040)	2044.4	(2040)	2018.8	(2013)
2027.8	(2023)	2026.1	(2026)	2006.7	(2002)
2015.7	(2016)	2015.0	(2016)	1997.0	(1992)

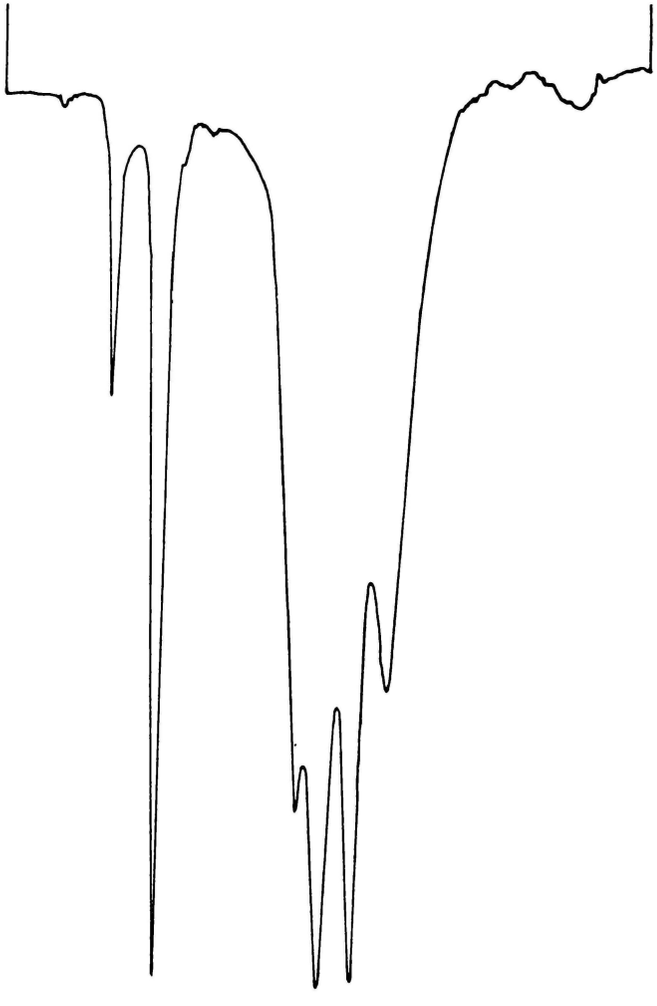
Values in parentheses are those for the tin analogues in cyclohexane. (51).

See also (37,76,77,78) for data on these and related derivatives.

$Cl_2Ge[Co(CO)_4]_2$



$Br_2Ge[Co(CO)_4]_2$



$Me_2Ge[Co(CO)_4]_2$

give the shift to higher energy already mentioned, for both germanium and tin analogues.

8.3.5 $MeGeX[Co(CO)_4]_2$ (Figure 8.4 , p.162)

Here, the symmetry of the molecules in the previous section has been reduced to C_s by the unsymmetric substitution on germanium. The expected carbonyl vibrations are $4A' + 4A''$. We now get a complete doubling up of the vibrations of $MeGeX_2Co(CO)_4$. (Compare with Figure 8.2). While this occurred to some extent for $X_2Ge[Co(CO)_4]_2$, the higher symmetry of those compounds removed one absorption. Here, the absorptions are clearly grouped into four pairs. The assignment of the two high energy modes is again to the in- and out-of-phase combinations of the symmetric carbonyl stretches of the two $-Co(CO)_4$ substituents. The lower absorptions will not necessarily follow the order of the monocobalt derivatives. (e.g. The 2048.6 and 2042.1 cm^{-1} modes of $MeGeBr[Co(CO)_4]_2$ are not necessarily the $A' + A''$ combination corresponding to the 2055.8 cm^{-1} A' mode in $MeGeBr_2Co(CO)_4$). Indeed, Graham (51) noted a consistent 17 cm^{-1} ($\pm$ 2 cm^{-1}) separation of the two higher energy modes for a number of bis-cobalt compounds. This is also borne out for the compounds described here. Should this order of energy difference between symmetric and asymmetric combinations apply to all the vibrational modes (as might be expected, intuitively, since all are of similar energy), then the pairing of modes for e.g. $MeGeBr[Co(CO)_4]_2$ might be expected to occur as :

	2108.4	2048.6	2042.1	2014.7
	2090.5	2031.4	2024.8	2001.4
Δcm^{-1}	17.9	17.2	17.3	14.3

Even though the figures show this symmetry in the spectra,

Figure 8.4

Infrared Spectra of $MeGeX[Co(CO)_4]_2$ from 1980cm^{-1} to 2140cm^{-1}

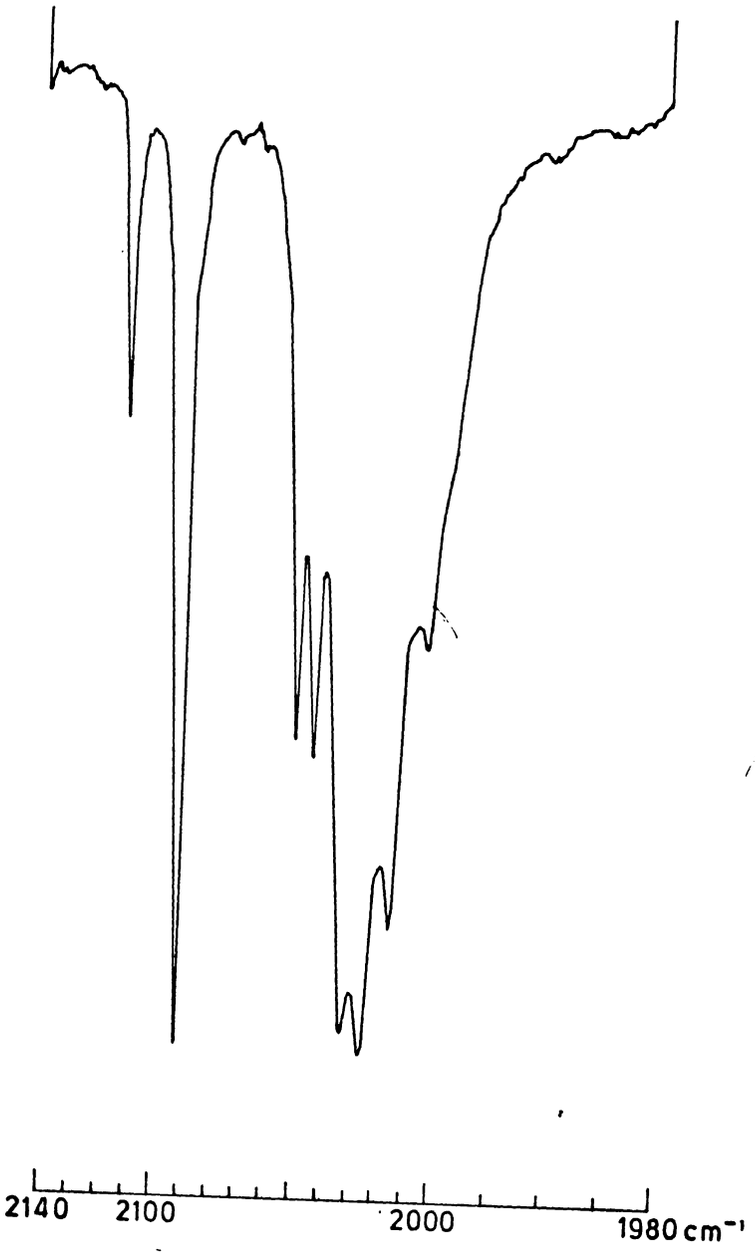
Figure 8.4

$MeGeX[Co(CO)_4]_2$ in Hexane

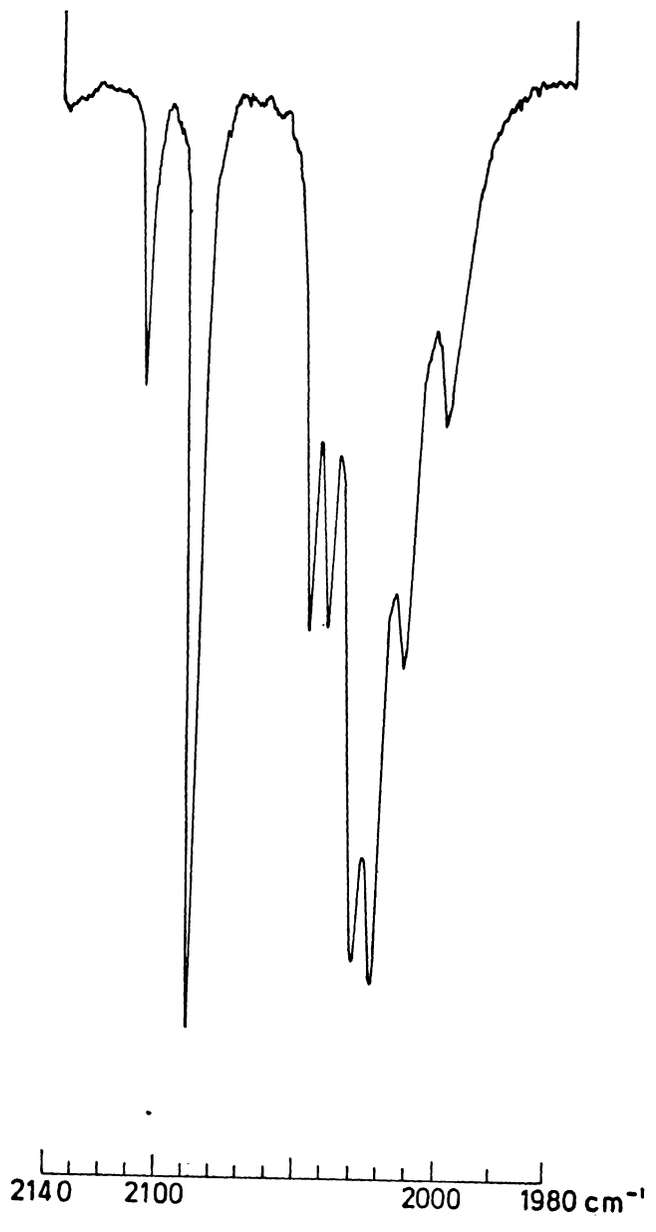
$MeGeCl[Co(CO)_4]_2$		$MeGeBr[Co(CO)_4]_2$	
2109.2	(2104)	2108.4	[2106]
2091.1	(2088)	2090.5	[2089]
2048.6	(2044)	2048.6	[2046]
2042.5	(2038)	2042.1	[2040]
2031.3	(2022)	2031.4	[2030]
2024.6	(2017)	2024.8	[2024]
2014.4	(2005)	2014.7	[2014]
2001.7	(1996)	2001.4	[2000]

Values in parentheses are those for $MeSnCl[Co(CO)_4]_2$ in cyclohexane. (51).

Values in square brackets are those for $MeGeI[Co(CO)_4]_2$ in cyclohexane. (51).



Me Ge Cl $[Co(CO)_4]_2$



Me Ge Br $[Co(CO)_4]_2$

the situation must be oversimplified, particularly for the large block of absorptions between 2050 cm^{-1} and 2000 cm^{-1}. The different modes of similar energy would certainly be expected to mix with one another, particularly at such low molecular symmetry. i.e each mode in this region has two others of the same symmetry available for mixing.

8.3.6 $XGe[Co(CO)_4]_3$ (Figure 8.5 , p.*165*).

Based on C_{3v} molecular symmetry, the predicted infrared-active modes are $3A_1 + 4E$. As before, the two higher energy modes represent the in- and out-of-phase stretching of all three terminal $-Co(CO)_4$ groups. In this case, the highest energy mode is even weaker than those seen previously, as expected for the in-phase stretch of all 12 CO groups. In view of the close grouping of the lower absorptions, it is reasonable that only six of the seven predicted modes are distinguished.

8.3.7 μ-(X)μ-(Y)$Co_2(CO)_6$ (Figure 8.6 , p.*167*).

The two compounds in this class prepared here are $Me_2GeCo_2(CO)_7$ and $(Me_2Ge)_2Co_2(CO)_6$. The point groups for these are C_s and C_{2v}, respectively, giving $2A_1 + 2B_1 + B_2$ infrared-active modes for $(Me_2Ge)_2Co_2(CO)_6$. All of these modes are seen in a clearly resolved spectrum showing virtually no overlap. The spectrum of $Me_2GeCo_2(CO)_7$ can be seen to be very much the same. C_s symmetry predicts $4A' + 3A''$ modes for this compound and all are seen. An interesting feature of this spectrum is the strong bridging carbonyl mode produced by the single bridging carbonyl. Its intensity relative to the terminal absorptions could be enhanced by the partial mutual cancelling of local dipole moments in the terminal carbonyl positions.

Figure 8.5

Infrared Spectra of $XGe[Co(CO)_4]_3$ from $1980cm^{-1}$ to $2140cm^{-1}$

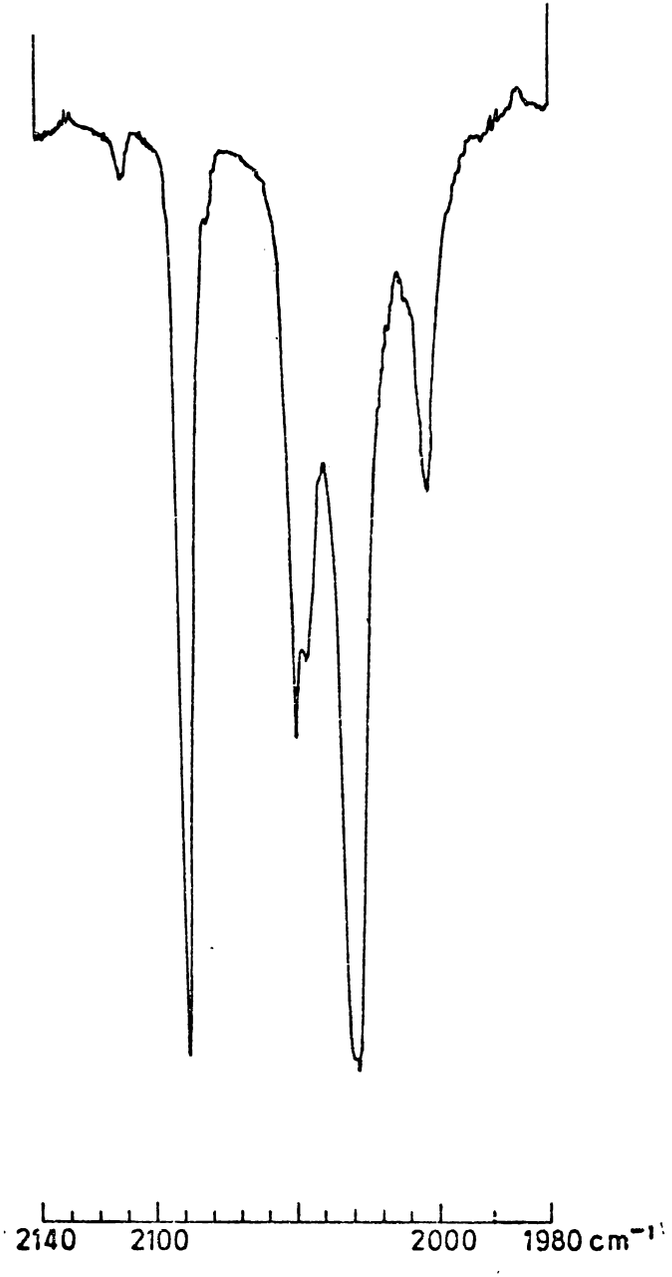
Figure 8.5

$XGe[Co(CO)_4]_3$ in Hexane

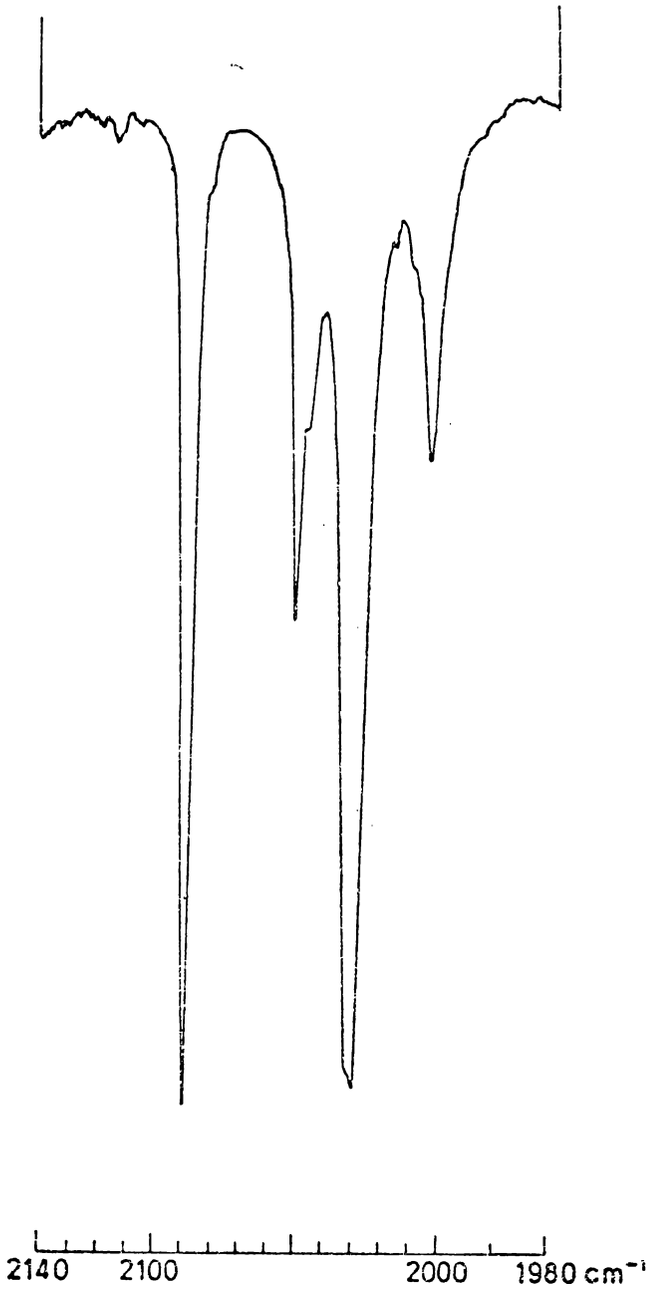
$ClGe[Co(CO)_4]_3$		$BrGe[Co(CO)_4]_3$	
2109.2	(2110)	2111.8	(2108)
2088.2	(2088)	2087.8	(2086)
2049.1	(2049)	2049.0	(2048)
2044.7sh	(2043)sh	2044.8sh	(2042)
2028.5	(2028)	2028.0	(2026)
2003.1	(2001)	2002.2	(2000)

Values in parentheses are those for the tin analogues in cyclohexane. (79).

The only other reported germanium derivative in this class is given in (86).



$Cl\,Ge[Co(CO)_4]_3$



$Br\,Ge[Co(CO)_4]_3$

Figure 8.6

Infrared Spectra of μ-(X)μ-(Y)$Co_2(CO)_6$ Derivatives

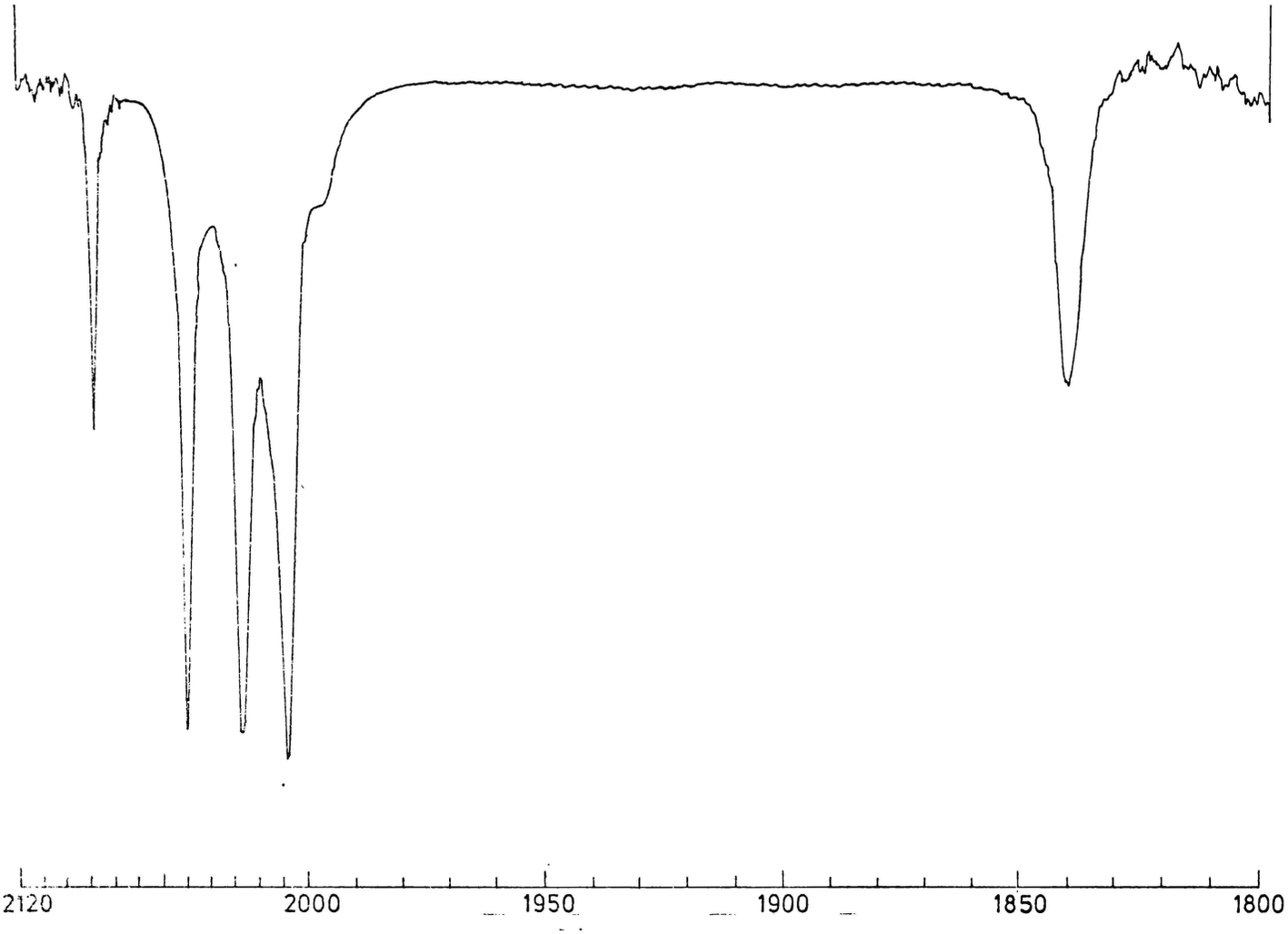
Figure 8.6

μ-(X)μ-(Y)$Co_2(CO)_6$ Derivatives in Hexane

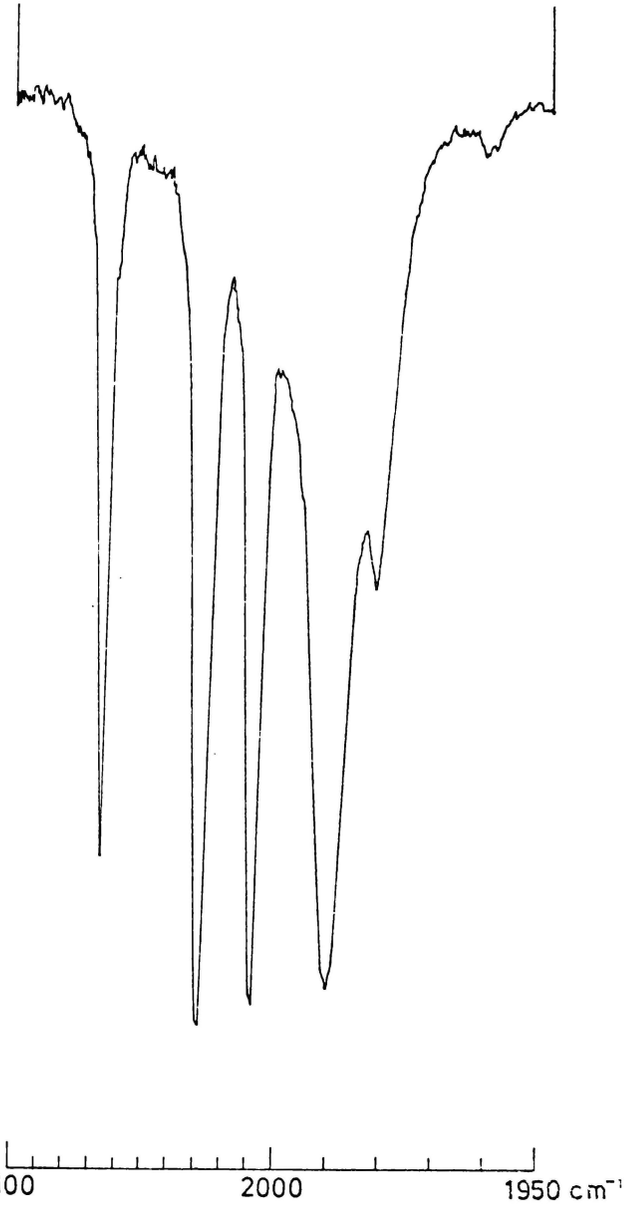
$Me_2GeCo_2(CO)_7$	$(Me_2Ge)_2Co_2(CO)_6$
2087	2066.0
2048	2028.8
2025	2008.8
2008	1990.0
1998sh	1981.3
1965	
1840	

See also (77).

See also (77,88,90)



$Me_2 Ge Co_2(CO)_7$



$(Me_2 Ge)_2 Co_2(CO)_6$

8.3.8 $(CO)_4CoGeCo_3(CO)_9$ (Figure 8.7 , p.171).

With the same molecular symmetry as that determined for $SiCo_4(CO)_{13}$ (96) (i.e. C_{3v}) the predicted infrared active modes for this compound are 4A, + 4E. Six of these are seen. With the mixture of terminal $-Co(CO)_4$ and cluster carbonyls present, assignment becomes very difficult. Without interaction from the cluster carbonyls, the $-Co(CO)_4$ group is expected to show the usual 2A, + E absorptions, as in the C_{3v} monocobalt derivatives. These would be expected in the regions shown below. Bor et al. (142) have also listed the regions and intensities typical for the clustered carbonyls in $XCCo_3(CO)_9$:

$YCo(CO)_4$	$XCCo_3(CO)_9$	$(Co)_4CoGeCo_3(CO)_9$
2100-2120 (5-7)	2101-2111 (0.2-1)	2111 (w)
2050-2070 (5-7)	2054-2066 (10)	2082 (s)
2030-2050 (10)	2038-2047 (4-5)	2044 (vs)
	2018-2034 (0.3-0.5)	2027 (m)
		2007 (w)
		1991 (vw)

Clearly there is a reasonable amount of mixing of the cluster and terminal $-Co(CO)_4$ carbonyl modes. Raman data would be useful in the assignment of the spectrum but this presents practical problems, since the solid is virtually black and even fairly weak solutions are deep red/purple.

8.3.9 $(CO)_7Co_2GeCo_2(CO)_7$ (Figure 8.7 , p.171).

As noted in 3.5.4b (p.54) only $2B_2$ + 3E terminal carbonyl modes are predicted for D_{2d} molecular symmetry, yet six are seen. The iron analogue ($Ge[Fe(CO)_4]_4$) (38) is reported to show approximate D_{2d} symmetry. Thus it is quite conceivable that the exact configuration in

$(CO)_7Co_2GeCo_2(CO)_7$ could be distorted away from the basic tetrahedral orientation around germanium enough for the E modes to split. The weak mode at 2004.7 cm^{-1} is the odd one out with regard to intensity and could be the result of such a splitting. On the other hand, it is possible that this could be a ^{13}C mode of the 2040.4 cm^{-1} absorption. These modes are generally found at ca. 35-40 cm^{-1} below the ^{12}C "parent" absorption. While the intensity of the 2004.7 cm^{-1} mode might be larger than usual for such a mode (c.f. 14 x 1.11% of the ^{12}C mode expected for a direct analogue) the symmetry reduction arising from one ^{13}C atom in the molecule could be responsible for some relative intensity changes.

At this stage this possibility can not be ruled out and the exact assignment of this spectrum remains uncertain.

8.3.10 $Ge[Co(CO)_4]_4$ (Figure 8.7 , p.*171*).

Under full tetrahedral symmetry, $3T_2$ infrared active carbonyl stretching modes are expected. In keeping with this, the spectrum shows two very strong modes at 2078.9, 2019.8 cm^{-1} as its main feature. However, the two weak modes observed at 2032, 2000 cm^{-1} would seem to rule out this assignment. While both absorptions are weak enough to be considered as ^{13}C modes, their positions relative to the strong modes seem to be incorrect for this. i.e. ^{13}C modes are generally seen 35-40 cm^{-1} below the ^{12}C analogues or 6-7 cm^{-1} below if they involve one mode mixing with another, which contains a ^{13}C atom. Thus, the (2019.8-2000 cm^{-1}) difference is intermediate between the values normally found, while the (2078.9-2032 cm^{-1}) difference comes outside the range.

If, in the T_d molecule, all $-Co(CO)_4$ groups are twisted

Figure 8.7

Infrared Spectra of $GeCo_4(CO)_x$ Derivatives

Figure 8.7

$GeCo_4(CO)_x$ Derivatives in Hexane

$(CO)_4CoGeCo_3(CO)_9$	$Ge[Co(CO)_4]_4$	
2111.4	2078.9	(2079)
2082.0	2032sh	(2032)
2043.7	2019.8	(2018)
2027.0	2000br	(1999)sh
2007.1		(1994)
1990		

See also (97).

Values in parentheses are those for $Sn[Co(CO)_4]_4$ (52)

X marks impurity bands.

$(CO)_7Co_2GeCo_2(CO)_7$

2079.3

2061.3

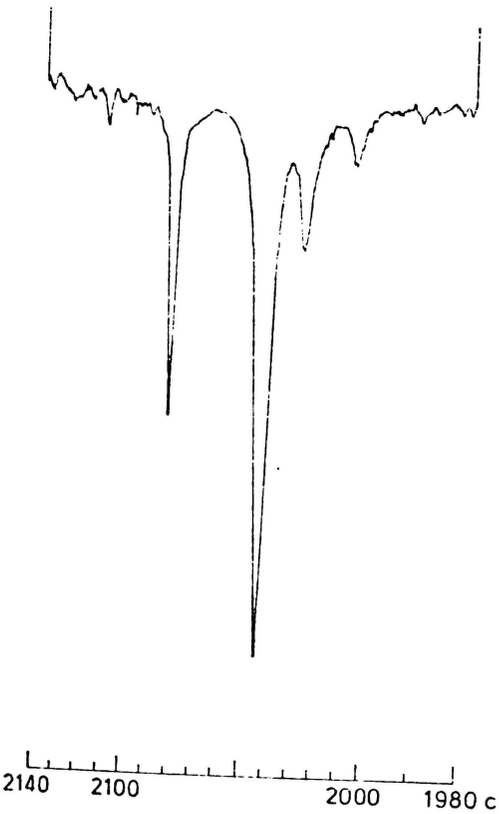
2040.4

2032.0

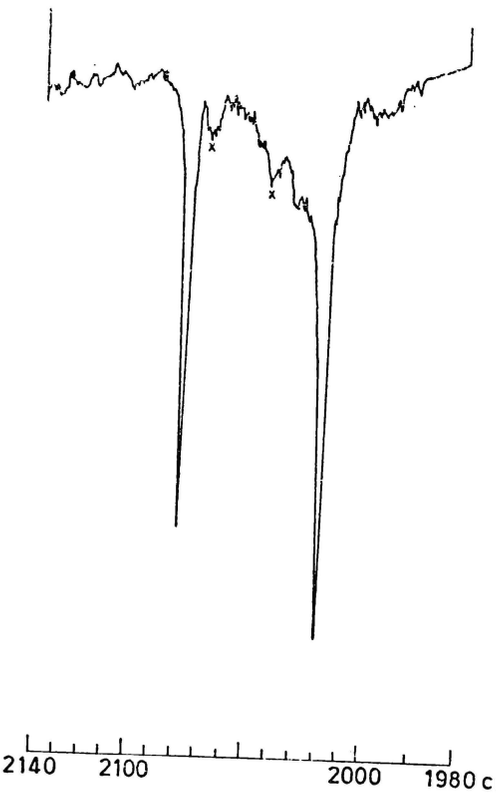
2022.8

2004.7

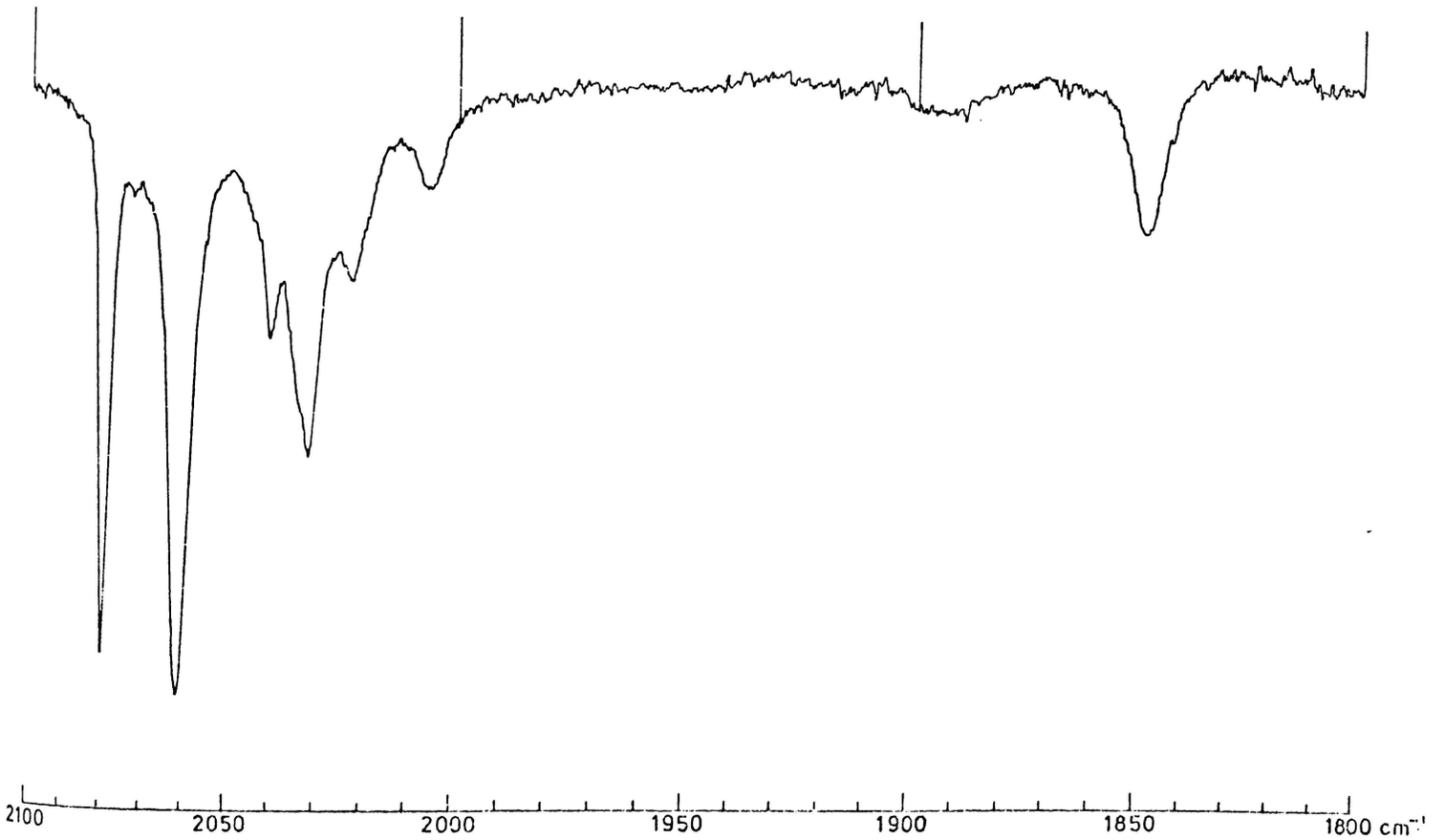
1848



$(CO)_4\,Co\,Ge\,Co_3\,(CO)_9$



$Ge[Co(CO)_4]_4$



$(CO)_7\,Co_2\,Ge\,Co_2(CO)_7$

about their Co-Co axis by an equal amount ($\alpha \neq 0^{o}$ or $n \times 60^{o}$), the molecule loses its planes of symmetry and takes up T molecular symmetry. In the T point group, the carbonyl stretching modes are represented by : $CO_{(ax)} = A + T$; $CO_{eq} = A + E + 3T$. Of these, only the T modes are infrared active. Under this symmetry, then, the four modes seen would fit with those predicted.

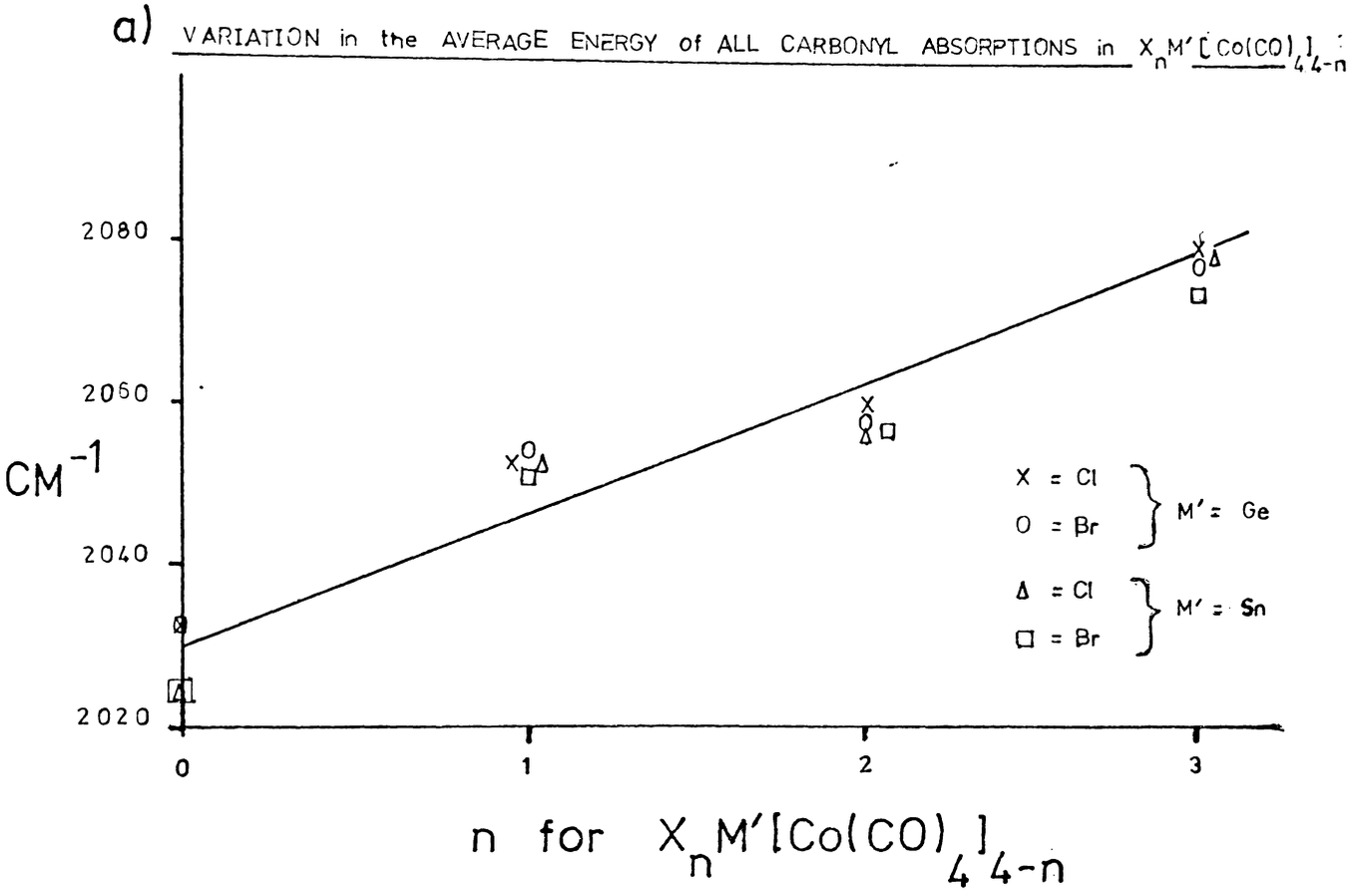
In their infrared analysis of $Sn[Co(CO)_4]_4$, Patmore and Graham (52) found 5 absorptions (including a shoulder). They suggested that a sterically favoured configuration, giving rise to C_{3v} symmetry was supported by the general similarity of the spectrum with that of $ClSn[Co(CO)_4]_3$ (apart from relative intensities). However, C_{3v} symmetry predicts $5A_1 + A_2 + 5E$ for the carbonyl stretching modes in this compound. (Of these, the A_2 is infrared inactive). This would imply that for $Sn[Co(CO)_4]_4$, 5 modes are absent from the spectrum. (In the case of $Ge[Co(CO)_4]_4$, 6 are absent). In such extremely simple spectra overlap problems are small, leaving accidental degeneracy and vanishing intensities to explain the absent modes. In view of this, it does not seem to be a likely possibility. Further, it does not seem likely that one $-Co(CO)_4$ group should be distinguished from the other three, as required to change from T_d to C_{3v}.

8.4 Discussion

This work completes a few series of analogous compounds and it is convenient at this point to draw together some of these results, as related to infrared spectroscopy. The carbonyl absorption spectra give a measure of substituent effects on bonding, as summarised on the plots in Figure 8.8.

FIGURE 8.8

Substituent Effects on Carbonyl Stretch Energies



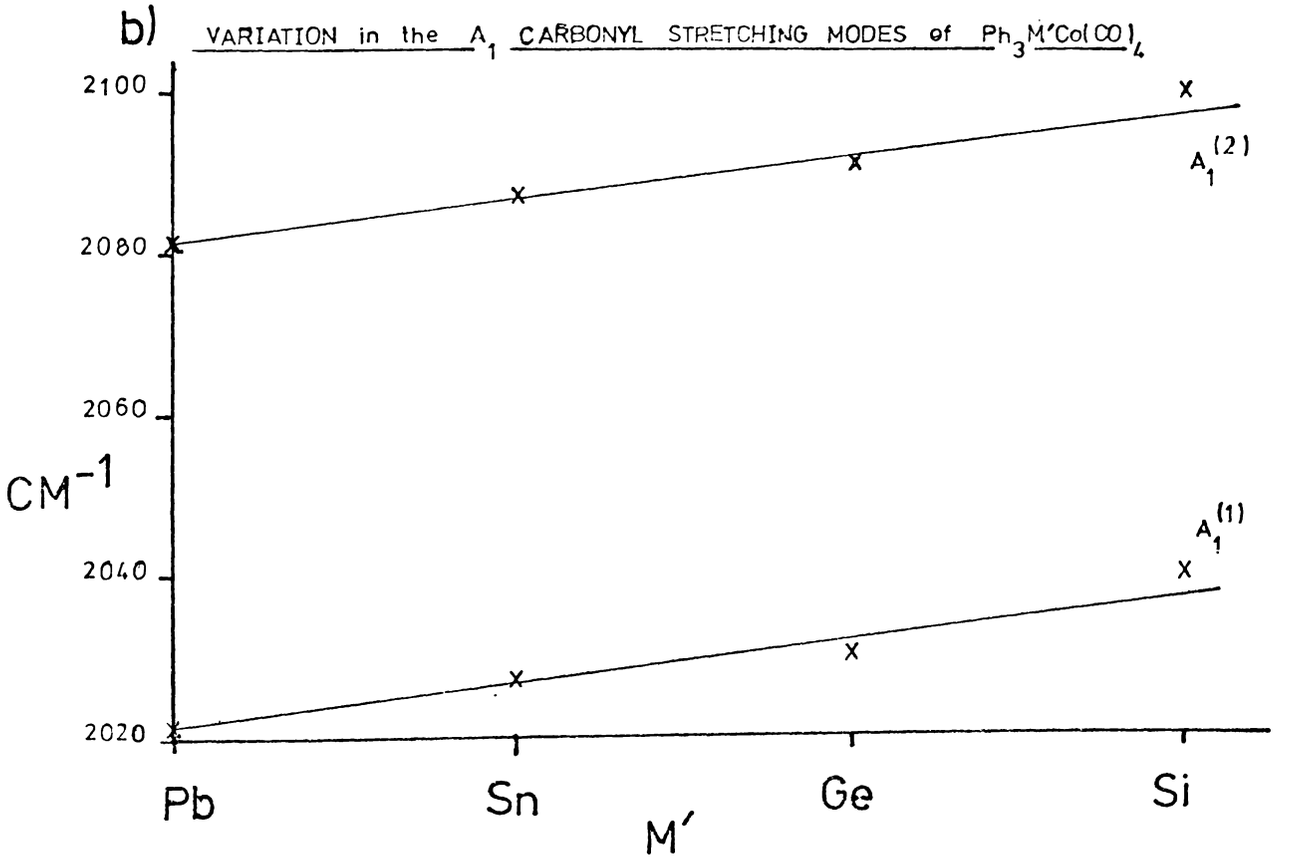


FIGURE 8.8 Contd.

c) VARIATION in the SYMMETRIC CARBONYL STRETCH in $X_3GeCo(CO)_4$, $X_2Ge[Co(CO)_4]_2$, $MeGeX_2Co(CO)_4$ and $MeGeX[Co(CO)_4]_2$

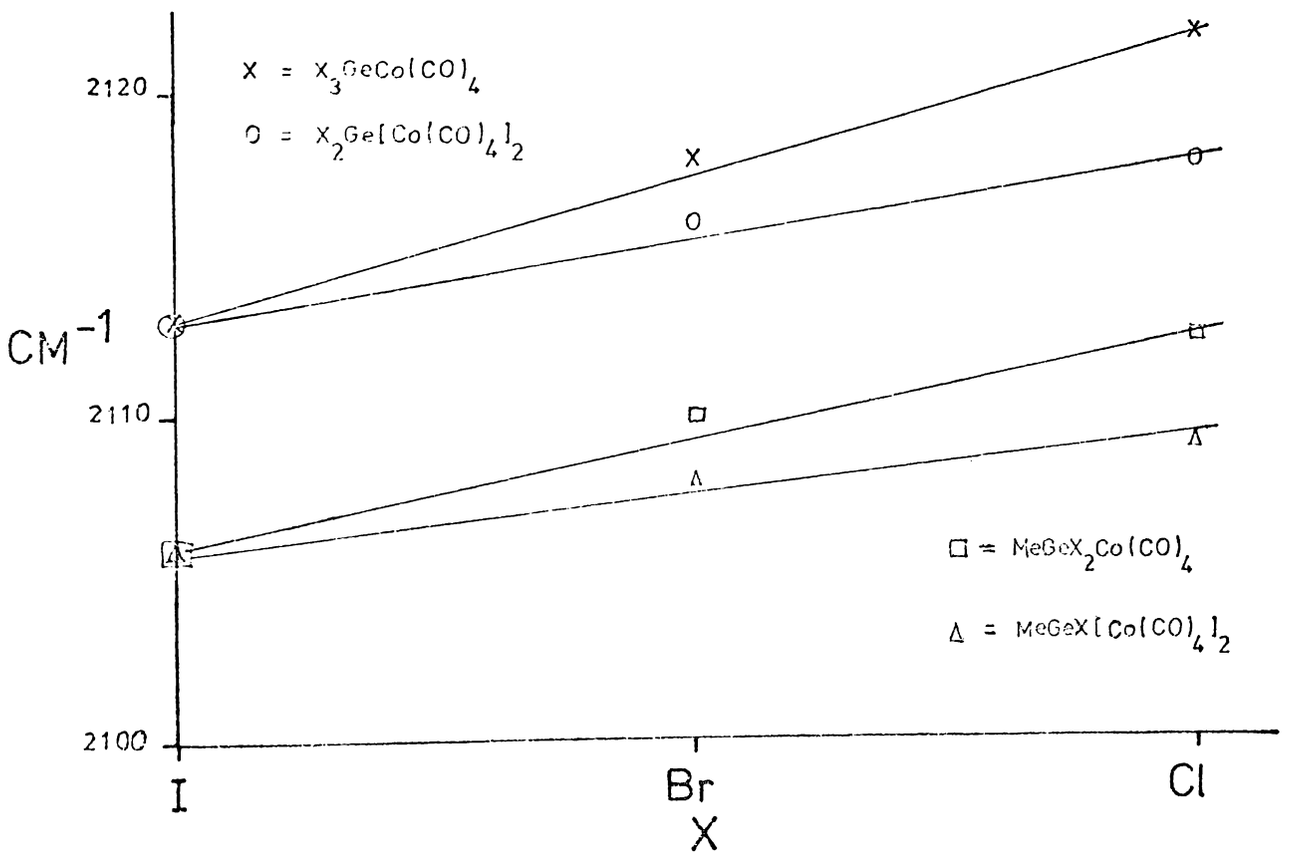


Figure 8.8a shows the variation in the average energy of all carbonyl absorptions (excluding ^{13}C modes) for the series $X_nM'[Co(CO)_4]_{4-n}$. (n = 0 - 3 ; X = Cl ,Br ; M' = Ge , Sn). This shows quite clearly that the effect of increasing the number of halogen substituents on the Group IVB atom (relative to $-Co(CO)_4$) is to increase the average energy of the carbonyl absorptions. This can be understood in terms of the electon withdrawal of the halogens, as discussed in Section 8.3.2. The figure also gives an idea of the relative magnitudes of the substituent effects. i.e. the main effect here is obviously the number of halogens, rather than which halogen or which Group IVB metal. The data for this figure were arrived at by averaging all observed modes. If the E modes in the C_{3v} derivatives are double-weighted, there is a small downward shift for the groups of points for $X_3M'Co(CO)_4$ and $XM'[Co(CO)_4]_3$. $X_3M'Co(CO)_4$ points cover the range 2066-2072 cm^{-1} (compared to 2075-2080 cm^{-1} without E-mode-weighting). In the case of $XM'[Co(CO)_4]_3$ derivatives, the 2051-2054 cm^{-1} range changes to 2046-2053 cm^{-1} upon weighting the E modes. (N.B. Since the lower energy modes for $XM'[Co(CO)_4]_3$ derivatives have not yet been individually assigned, this range represents the upper and lower limits possible for various E mode assignments).

These changes do not affect the trend of the plot. Indeed, they give a better staight line fit, as might be expected for a better representation of the energy average.

The effect of changing the Group IVB atom, for a given set of substituents, is shown in Figure 8.8b. Here, the two A_1 modes of $Ph_3M'Co(CO)_4$ show the same sort of energy change in going from lead to silicon. (N.B. The E mode also shows a similar change). This particular set of derivatives was

chosen as being one of the few to include lead. Several other sets show the same effect for Sn,Ge and Si. The reason for this effect is not completely straight forward. It might be expected that the electronegativity of the Group IVB element itself would be involved in the same way as noted above. However, tabulations of electronegativity values (143) show different changes, depending on their method of calculation. Thus, the Allred Rochow values show the "expected" changes from Ge to Sn to Pb, but silicon does not fit with the experimental data. Values estimated by Pauling's method also show an irregularity for lead. The size of the Group IVB atom (which follows the observed trend) could be related by the effectiveness of π-overlap of the cobalt 3d orbitals with the appropriate M' orbitals. Thus, if the empty 3d orbitals on silicon provide the right overlap with the cobalt 3d orbitals, the larger Ge ,Sn and Pb orbitals would be expected to give successively less electron withdrawal and hence less relative C-O bond strength enhancement.

Figure 8.8c shows the effects of specific changes in the substituents on germanium. The decreasing electronegativity in going from Cl to Br to I can be seen to decrease the energy of the high energy A_1 (or A') mode for $X_3GeCo(CO)_4$, $X_2Ge[Co(CO)_4]_2$, $MeGeX_2Co(CO)_4$ and $MeGeX[Co(CO)_4]_2$. This mode (the symmetric carbonyl stretch in the monocobalt derivatives and the in-phase combination of these in the bis-cobalt ones) was chosen as one of the two assigned modes for the bis-cobalt derivatives. (The other shows a similar trend).

Two other substituent effects are obvious here. Firstly, the difference in energy between the two "pairs" of lines shows the effect of replacement of one halogen with a methyl substituent. i.e. decreasing the total electron

withdrawal capacity decreases the absorption energies as discussed. Similarly, but to a lesser extent (reflected by the separation within the "pairs" of lines), replacement of a halogen with a $-Co(CO)_4$ group has the same effect. This distinction can be seen to decrease from Cl to Br to I. In the latter case, it seems that the electron withdrawal effects of -I and $-Co(CO)_4$ are very much the same.

Thus, the effective electron withdrawal from cobalt in complexes of the type $ABCM'Co(CO)_4$ can be seen from the above data to decrease for $ABCM'$- in the order :

$$X_3M' > X_2M'[Co(CO)_4] > XM'[Co(CO)_4]_2 > M'[Co(CO)_4]_3$$

Within this main order of effects come the sub-orders :

For a given M' :

$$ABC = Cl_3 > Br_3 , Cl_2[Co(CO)_4] > I_3 , I_2[Co(CO)_4] > Cl_2Me > Br_2Me , BrMe[Co(CO)_4] > I_2Me , IMe[Co(CO)_4]$$

For a given ABC :

$$M' = Si > Ge > Sn > Pb$$

The exact positions of the mixed substituents of the type $ABC = Br_3 , Cl_2[Co(CO)_4]$ and $MeBr_2 , MeBr[Co(CO)_4]$ are too close to be distinguished on the basis of the above information.

The above order is a general one only, particularly as applied to changing M'. Thus, the specific bonding requirements of the substituents on M' could change relative positions in this sub-order and hence make small changes in the main order.

APPENDIX ONE

Approaches to Germanium Hydride Derivatives of Rhenium Carbonyl

A1.1 Introduction:

Amongst the relatively few known germanium derivatives of rhenium carbonyl (1,2), the more recent reports of $GeH_3Re(CO)_5$ (146) and $Me_3GeRe(CO)_5$ (147) were of direct interest to work in this laboratory. A few series of derivatives of the type $Me_xGeH_{3-x}M(CO)_n$ (x = 0 - 3 ; M = Mn , n = 5 ; M = Co , n = 4 ; M = Fe/2 , n = 4/2) have been completed here in the past (53,54,148,149,150) and it was of interest to examine the rhenium series for comparative studies with those already known. Further, recent work (54,140) has established a metal exchange series for germanium-bonded transition metal carbonyls : Mn > Fe > Co. The driving force behind this exchange (which involves reaction of e.g. $Mn(CO)_5^-$ with $GeH_3Co(CO)_4$) is thought to be related to the relative nucleophilicities of the metal carbonyl anions. The above series is consistent with reported nucleophilicities (29), which show relative values :

$$Co(CO)_4^- = 1$$

$$Mn(CO)_5^- = 77$$

$$Re(CO)_5^- = 2.5 \times 10^4$$

The rhenium value suggested the ready extension of the metal exchange series.

A1.2 $GeH_3Re(CO)_5$

A1.2.1 Direct Preparation :

The literature preparation of this compound was

repeated. i.e.: GeH_3Cl (152 mg ; 1.4 mmoles) was condensed onto the deep yellow THF solution of $NaRe(CO)_5$ (prepared by Na/Hg reduction of $Re_2(CO)_{10}$ (490 mg ; 0.75 mmoles) over a period of one day's stirring). This was reacted at room temperature for ca. 4 hours while the colour paled and NaCl was deposited. After initial removal of solvent, most of the $GeH_3Re(CO)_5$ was condensed into a U-trap over 18 hours of pumping. More GeH_4 (ca. 30%) was recovered here than reported (ca. 14%). The product was characterised by its infrared.nmr and mass spectra, all of which compared closely with those reported. (146). The residues from the reaction contained $Re_2(CO)_{10}$ and $GeH_2[Re(CO)_5]_2$. The latter was identified by its infrared spectrum only, in agreement with that originally assigned to this product. (146).

A1.2.2 Preparation by Metal Exchange.

$NaRe(CO)_5$, prepared in Et_2O from $Re_2(CO)_{10}$ (284 mg ; 0.44 mmoles) was reacted for ca. 20 minutes at room temperature with $GeH_3Mn(CO)_5$ (260 mg ; 0.96 mmoles) (145). After removal of the immediate volatiles, the reaction vessel was pumped,through a U-trap at - 196°C for one day. The colourless, crystalline, solid product trapped here was identified as $GeH_3Re(CO)_5$ by comparison with the literature, as noted above. The initial volatile components of the system were found to contain both GeH_4 and $GeH_3Mn(CO)_5$.

A1.2.3 Reactions of $GeH_3Re(CO)_5$

i) $GeH_3Re(CO)_5/SnCl_4$:

$GeH_3Re(CO)_5$ (27 mg ; 0.07 mmoles) was reacted with $SnCl_4$ (21 mg ; 0.08 mmoles) in benzene at 10°C in an nmr tube, using TMS in ethyl benzene as external reference. The 6.88 τ signal for $GeH_3Re(CO)_5$ diminished in favour of one at 4.23 τ , which may be assigned to $GeH_2ClRe(CO)_5$. Reaction

appeared to be complete in one hour at ca. 75% monochlorination. (N.B. Interference from the benzene signal made integration impractical.) Benzene extraction of the products from the $SnCl_2$ formed gave a spectrum with better resolution, which also showed a minor singlet at 3.76 τ , probably due to some $GeHCl_2Re(CO)_5$.

ii) $GeH_2ClRe(CO)_5$/MeMgI :

MeMgI was allowed to react in Et_2O with the off-white $GeH_2ClRe(CO)_5$ (prepared as above) for 30 minutes at room temperature. The solution quickly turned pale yellow and no further changes were observed. Pumping the products through a -45°C U-trap gave a very small amount of white solid whose infrared spectrum showed :

2116 m	νCO
2050 m	
2025 s,sh	
2005 ws	
1985 m	
1970 w	$\nu^{13}CO$
600 s	δRe-C-O
585 s	
560 w-m	
395 s	νRe-C

N.B. Assignments of the lower region are made by comparison with the reported spectrum of $GeH_3Re(CO)_5$ (146).

The mass spectrum of this solid was reasonably consistent with that expected for $MeGeH_2Re(CO)_5$, but overlap of higher mass fragments prevented positive identification beyond an envelope intensity pattern corresponding to $GeRe(CO)_x^+$. Even higher mass fragments due to $GeRe_2(CO)_x^+$

were seen in the mass spectrum of the residues. See Figure 1.2 , p.17 for basic $GeRe_x^+$ intensity patterns.

iii) $GeH_2ClRe(CO)_5/NaMn(CO)_5$:

$NaMn(CO)_5$ prepared from $Mn_2(CO)_{10}$ (28 mg ; 0.07 mmoles) was reacted in Et_2O with ca. 0.1 mmoles $GeH_2ClRe(CO)_5$ for 5 hours at room temperature. No volatile product was found after pumping for ca. 1 day through a U-trap at -196°C. A benzene extract of the orange solid residues showed no nmr signals. $Mn_2(CO)_{10}$ was identified as the main carbonyl product, from a hexane solution infrared spectrum. (2045, 2014 , 1983 cm^{-1}). This also showed the following absorptions :

2126 w	νCO
2092 m	
2076 m	
2027 vs	
2005 m-s	
1996 s	
1970 w	$\nu^{13}CO$
640 vs	δRe-C-O
598 s	
460 w-m	νRe-C

The size of sample made further analysis impractical and no assignment could be made to this product.

A1.3 $MeGeH_2Re(CO)_5$

i) Preparation by Metal Exchange :

Several attempts were made to carry out reactions similar to that in A1.2.2 :

i.e.: $MeGeH_2Mn(CO)_5 + NaRe(CO)_5 \longrightarrow MeGeH_2Re(CO)_5 + NaMn(CO)_5$

In each case most of the $MeGeH_2Mn(CO)_5$ was recovered, along with $Re_2(CO)_{10}$ (151).

A similar reaction carried out with $MeGeH_2Co(CO)_4$ again yielded $Re_2(CO)_{10}$, but the cobalt was recovered as $Co_2(CO)_8$, suggesting that reaction had occurred, and the resulting $NaCo(CO)_4$ had decomposed. A hexane extract of the residues also showed a component with the following infrared spectrum:

2102 w	νCO
2075 m	
2048 m	
2018 vs	
2005 s,sh	
1992 s	
680 m-s	δRe-C-O
585 m-s	

This product and the A1.2.3 ii) product are inconsistent with one another as candidates for $MeGeH_2Re(CO)_5$.

ii) Direct Preparation :

Several preparations of the following type were attempted :

$$MeGeH_2Br + NaRe(CO)_5 \longrightarrow MeGeH_2Re(CO)_5 + NaBr$$

These reactions resulted in the production of mixtures which showed very complex infrared spectra. $Re_2(CO)_{10}$ could be identified in each case. Successive sublimations at 40-50°C removed this component, leaving two components as the main products from this system; a volatile component, removed by diffusion pumping of the reaction vessel, and the non-volatile component, cleaned up by sublimation. The hexane solution infrared spectra of these compounds showed:

"Volatile" Component	Sublimate
2128 vw	2135 w
2121 w-m	2108 m
2070 vw	2070 w-m
2053 vw	2050 w-m
2045 m	
2024 S	2022 vvs
2014 vvs	2018 vvs
2001 vs	2004 vs,sh
	1990 vs
1985 w-n	1983 m
1976 w-m	1973 m
1957 vw	1960 m,br
1941 vvw	

The mass spectra of these compounds also indicated that they were mixed products. Highest mass envelopes appeared at m/e = 816 - 824. Methyl and carbonyl losses could be seen over most of the mass range down to m/e = 185 / 187 (Re^+). From the contours of the ion envelopes, the predominant ion species seemed to be those of $GeRe_2^+$ and $GeRe_3^+$ species, though none could be specifically identified.

A1.4 $Me_2GeHRe(CO)_5$

Direct preparations were attempted, as above, i.e.:

$$Me_2GeHBr + NaRe(CO)_5 \longrightarrow Me_2GeHRe(CO)_5 + NaBr$$

After 5 hours of reaction at room temperature the THF was removed and the reaction vessel diffusion-pumped for a day. A small amount of clear solid was removed in this way, leaving further solid apparently sublimed onto the upper

parts of the reaction vessel. These two components gave different infrared spectra (see below), while the residue appeared to be made up of the latter component and $Re_2(CO)_{10}$ (by infrared).

Most Volatile	Least Volatile
2115 s (a)	2130 s
2053 w-m	2115 s
2042 m	2060 s
2015 vvs	2050 s
2008 vvs	2020 vvs
1999 vs	2012 vs
1982 m	1980 w
1973 m	601 s
1956 w-m	595 s

a) This absorption appeared to be shouldered at 2119 , 2111 cm^{-1}.

The mass spectrum of these products showed strong patterns up to ca. m/e = 520 , followed by weaker ones up to ca. m/e = 620. Carbonyl loss and possibly methyl loss was observed. While it was possible that $Me_2GeHRe(CO)_5$ may have been present, its fragmentations would be common to and overlapped by those of the $GeRe_2^+$ species which dominated the spectrum. Again, assignment of the higher mass species could not be made.

A1.5 Discussion

One of the most important features of this system is the preparation of $NaRe(CO)_5$. Many preparations are thought to have failed due to lack of (or minimal) reduction of the $Re_2(CO)_{10}$. Reduction did not appear to be very efficient in

Et_2O and stirring times of one day or more in THF, over Na/Hg were found necessary to produce the deep yellow solution of anion. Even this, when checked in the infrared, still showed the presence of $Re_2(CO)_{10}$. Other workers (152) have found anion preparations to proceed to 40% reduction. They also found it necessary to carry out alkali halide eliminations at lowered temperatures, to inhibit the halogen exchange and subsequent elimination also seen in the manganese system. i.e.:

$$NaRe(CO)_5 + R_3GeX \longrightarrow XRe(CO)_5 + NaGeR_3$$

$$XRe(CO)_5 + NaRe(CO)_5 \longrightarrow Re_2(CO)_{10} + NaX$$

This was tried, but since the results were as poor as others, which were also subject to other "variables", no conclusions could be made on this matter. Similarly, whether the $Re_2(CO)_{10}$ found in reaction products was due to this mechanism or merely incomplete reduction of starting material, is uncertain. One reduction was followed by a sublimation step, which yielded virtually nothing. This, however, is not consistent with a low reduction yield.

The predominance of formation of polyrhenium derivatives in the methyl- and dimethyl systems is strange, and unexplained at this point. Neither "extreme" derivative ($GeH_3Re(CO)_5$ nor $Me_3GeRe(CO)_5$ in this series shows the same results under the same preparative conditions. (146,147). Any mechanism of further substitution of hydride or methyl substituents would be expected to be paralleled in the all-hydride or all-methyl derivatives.

While the single experimental success with $GeH_3Re(CO)_5$ and the observed consumption of $MeGeH_2Co(CO)_4$ are the only results supporting the metal exchange in this system, it seems highly likely that rhenium will take its expected

position in the exchange series. i.e. :

Re > Mn > Fe > Co

These are only preliminary results and more work needs to be done to establish the position clearly.

APPENDIX TWO

Approaches to Germanium Hydride Derivatives of Vanadium Carbonyl

A2.1 Introduction

In 1959 Natta et al.(153) first reported the 17-electron $V(CO)_6$. The great interest in this unusual carbonyl is reflected by the literature that has appeared about it, since that time (154-183). Interest in the more stable 18-electron anion, $V(CO)_6^-$, has been equally high; more so from a synthetic point of view. (184-211). (N.B. These reports are only those limited to the hexacarbonyl systems. Numerous others have been published about other variously - substituted carbonyl derivatives of vanadium). More recent interest has been in the area of seven co-ordinate vanadium hexacarbonyls (and others) (193,196,202), while Ellis and Palazzotto (212) have further extended this to 8-co-ordination with the use of $V(CO)_5^{3-}$. The only Group IVB derivatives so far prepared are $Ph_3SnV(CO)_6$ (196) and $SiH_3V(CO)_6$. (203)

The latter compound was prepared via :

$$SiH_3I + MV(CO)_6 \longrightarrow SiH_3V(CO)_6 + MI \qquad (M = Na,Tl)$$

For M = Na , the diglyme - free salt was required, while for M = Tl , the salt was prepared by reaction of thallium metal with $V(CO)_6$. An unusual feature of this relatively unstable compound is the room temperature decomposition to $(SiH_3)_2O$ and $V(CO)_6$.

The germanium analogue might be expected to be more stable to this mode of decomposition, due to its much lower affinity for oxygen. This could balance the inherent

instability of the seven-co-ordinate vanadium to some extent. For these reasons it was decided to attempt the preparation of $GeH_3V(CO)_6$ as described below.

A2.2 $MV(CO)_6$ Preparations

a) M = Tl : Addition of $TlSO_4$ to aqueous solutions of $Na(diglyme)_2V(CO)_6$ (diglyme = $CH_3O(CH_2CH_2O)_2CH_3$) resulted in minor solid precipitation. This solid gave a broad infrared absorption at ca. 1850 cm^{-1}, similar to that of the diglyme-stabilized sodium salt. However, reactions of germyl halides with this solid returned only starting materials.

b) M = Et_4N : Using the method of Rehder et al.(204), $Et_4NV(CO)_6$ was prepared as a pale yellow solid, showing no change over several days in air. Again, presence of the $V(CO)_6^-$ was monitored by the infrared absorption at ca. 1850 cm^{-1}. The observed stability was further reflected in reaction with GeH_3Br in Et_2O, which returned largely reactants, leaving minor, dark residues which only showed very weak carbonyl absorptions.

c) M = Na : Using the preparation described in reference (164), $V(CO)_6$ was prepared by the acid treatment of aqueous $Na(diglyme)_2V(CO)_6$ and extracted with Et_2O. Extracts and washings were dried with Na_2SO_4 (anhydrous) for a few minutes before removing the ether with a water pump. Gas is evolved in the latter stages of this removal and the yellow solution darkens, to leave a dark yellow/brown residue. The blue/green $V(CO)_6$ so-formed is pumped into a cold trap (-196°C) containing P_2O_5 for final drying. At this point the neutral hexacarbonyl can be identified by a strong infrared absorption at ca. 1980 cm^{-1}. (N.B. The blue/green solid gives yellow ether solutions).

The dry $V(CO)_6$ is condensed (over a period of hours) onto Na/Hg in the reduction vessel described in Chapter Two, along with ca. 5mls of Et_2O. Reduction at room temperature for two or three minutes turns the solution pale green. It is decanted at this point, as before. A check on the anion so-formed can be made by its infrared solution spectrum.

d) M = H : Though unconfirmed, the above preparation is reported to go through $HV(CO)_6$, after theacidification step. (154,164). The evolution of gas on removal of the last of the ether, in forming $V(CO)_6$, is put forward as evidence. Thus, samples were retained for reaction at this point in the above preparations.

A2.3 Coupling Reactions with Germanium

A2.3.1 Reaction of $Na(diglyme)_2V(CO)_6$ with GeH_3Br

At room temperature, without solvent, this reaction resulted in CO evolution. GeH_4 was produced and residues contained no carbonyl. In CH_2Cl_2 solution at -40°C, an orange colouration was observed, but no carbonyl products could be identified with this. Starting materials were largely returned.

A2.3.2 Reactions of "$HV(CO)_6$"

i) With GeH_3Br : In Et_2O, no colour changes were observed at -30°C. After two days at room temperature, a pale yellow solid was covered with pale yellow solution. The latter showed νGeH at ca. 2120 cm^{-1} and a little $V(CO)_6^-$ at ca. 1850 cm^{-1}.(The resultant form of the GeH_3Br was not determined). The solid showed no carbonyl infrared absorptions.

ii) With Ge_2H_6 : Twenty minutes of reaction in Et_2O at room temperature returned only reactants. No GeH_4 was observed, as might be consistent with :

$$Ge_2H_6 + HV(CO)_6 \longrightarrow GeH_3V(CO)_6 + GeH_4$$

A2.3.3 Reactions of $V(CO)_6$

i) With GeH_3Br : Monitored in Et_2O with nmr for ca. 12 hours at temperatures from -40°C to + 10°C, this reaction showed no nmr changes. After 3 weeks at + 15°C, orange solid had formed in the tube. The volatiles no longer contained GeH_3Br and the orange solid contained no carbonyl.

ii) With Ge_2H_6 : Gas evolution was observed with this room temperature reaction. The infrared spectrum of the volatile products showed GeH_4 had been formed. $V(CO)_6$ was the only carbonyl-containing species remaining.

A2.3.4 Reactions of $NaV(CO)_6$ with GeH_3X

The -40°C reaction of $NaV(CO)_6$ with GeH_3Br in diethyl ether gave an orange solution. Volatiles were removed at this temperature after ca. 1.5 hours of reaction time. Residues at -20°C were then pumped through a U-trap at -196°C. The upper fraction showed GeH_4, while the infrared spectrum of the U-trap fraction showed GeH_3Br, along with :

2040 m,sh

2018 s

The gas-sampled mass spectrum of this fraction showed a large CO^+ ion, GeH_3Br fragments and other minor envelopes up to ca. m/e = 340, which could not be assigned. The pale residues darkened upon exposure to glovebox atmosphere at room temperature and gave a positive bromide test.

A similar reaction at -45°C with GeH_3Cl for 30 minutes showed no GeH_4 production. GeH_3Cl was returned in the volatile fraction, leaving a yellow residue, whose hexane solution infrared absorptions were : 2040 m,br,sh

2025 m

1985 vs

The latter mode was similar to that seen for $V(CO)_6$, but no blue/green colouration from this compound was seen.

The reaction of GeH_3I was similar, but both GeH_4 and GeH_3I were returned after 45 minutes reaction at -45°C. The pale red hexane extract of the residues showed weak absorptions at ca. : 2040 sh
2025

A2.4 Coupling Reactions with Silicon

The -45°C reaction of SiH_3I and SiH_3Br with $NaV(CO)_6$ were carried out as reported in the preparation of $SiH_3V(CO)_6$. (203). Removal of volatiles yielded orange solid as reported, followed by much darker deposits which looked like $V(CO)_6$. The head fraction of the volatiles showed a little $(SiH_3)_2O$. A sample of the solid fraction was condensed onto an infrared cold cell window, giving a yellow coating which showed no infrared absorptions at all. Reaction residues gave positive halide tests.

A2.5 Discussion

The results of most preparations indicate that coupling has taken place. i.e. observation of colour formation in solution, positive halide tests, formation of GeH_4, (presumably from decomposition of a Ge-V species rather than from GeH_3Br itself) and the formation of $(SiH_3)_2O$ and $V(CO)_6$, as reported for the silyl system (203). However, the fact that the silyl analogue was not isolated, as reported, indicates that the main problem in all systems was one of technique, rather than compound instability. Certainly it seems that one of the important features of both silyl and germyl systems is that the reaction products be removed from reaction residues as

quickly as possible. This could be seen from the decomposition observed for $SiH_3V(CO)_6$ at lower temperatures than those reported.

The relative consistency in the appearance of the 2040 , 2020 cm^{-1} absorptions from extracted products suggests that these could be the germyl equivalents of the $SiH_3V(CO)_6$ carbonyl absorptions : 2088 m

2026 m

1990 vs

1959 s

From the handling of both unisolated products, it would seem that $GeH_3V(CO)_6$ will probably show similar stability properties to those reported for $SiH_3V(CO)_6$. This would make the decomposition path for the germyl system an interesting one, since abstraction of a carbonyl oxygen to form $(GeH_3)_2O$ would not be expected. N.B. It would seem that whether or not this is the path followed by $(SiH_3)_2O$ is uncertain, since $(SiH_3)_2O$ very readily formed in other apparently non-oxygen-containing systems. e.g. Most preparations of SiH_3X carried out here returned moderate yields of $(SiH_3)_2O$.

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