STUDIES ON
POLYGERMANYL-TRANSITION METAL (CARBONYL) DERIVATIVES

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To

my parents

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ABSTRACT

The compounds $Ge_2H_5Mn(CO)_5$, $Ge_2H_5Co(CO)_4$ $(Ge_2H_5)_2Fe(CO)_4$, $Ge_3H_7Mn(CO)_5$, $[GeH_2Mn(CO)_5]_2$ and $[GeH_2Co(CO)_4]_2$ have been prepared by alkali-halide elimination reactions between the appropriate polygermanyl halides and metal carbonyl anions. The characterisation by infrared, Raman, n.m.r. and mass spectrometry of these compounds is discussed in detail. The physical properties and reactions have also been investigated and compared, in parallel with the parent polygermanes. Reagents used include hydrogen halides, group IV metal halides, mercuric halides and Na/NH_3 solution. Most of the reactions were studied by n.m.r. spectroscopy and the intermediates and products further characterised. Transition metal exchange is shown to be a useful synthetic route to yield the unsymmetric iron compound $Ge_2H_5(GeH_3)Fe(CO)_4$ and possibly $GeH_3(SiH_3)Fe(CO)_4$.

The polygermanyl-transition metal carbonyl derivatives are shown to be more stable than the germyl analogues and reasons, with spectroscopic evidence, are discussed.

CHAPTER 1. INTRODUCTION

1.1 Definitions

This thesis deals with di- and tri-germane derivatives of manganese, iron and cobalt carbonyls e.g. $GeH_3GeH_2Mn(CO)_5$.

It is convenient at this point to introduce a general terminology. The symbol M' is used to denote the group IV elements Si, Ge, Sn or Pb while M is used for a transition metal. R is used specifically to denote an organic group. While tin and lead are clearly metals, germanium and silicon are often termed metalloids: for convenience, the term metal is sometimes used to cover all four elements as in the phrase "group IV metal-transition metal bond".

The group IV hydrides in the series M'_nH_{2n+2} (n = 1,2,3 ...) are normally referred to as mono-, di-, tri-, etc. -silane, -germane, -stannane, and -plumbane. These parent compounds form the basis of a nomenclature system similar to that of methane and its derivatives. As a basic distinction, it should be noted that the "germyl" derivatives refer to compounds of the general form GeH_3X while "digermanyl" compounds are represented by Ge_2H_5X and "trigermanyl" by Ge_3H_7X. "Digermanyl" should not be confused with "digermyl" and "trigermanyl" with "trigermyl" which respectively indicate $(GeH_3)_2X$ and $(GeH_3)_3X$ compounds.

The following common abbreviations will be used in various parts of the text:

Me : CH_3, methyl

Et : C_2H_5, ethyl

Pr^i : $(CH_3)_2CH$, iso-propyl

Bu^i : $(CH_3)_3C$, iso-butyl

Ph : C_6H_5, phenyl

Cp : C_5H_5, cyclopentadienyl

diphos : $(Ph_2PCH_2)_2$

THF : tetrahydrofuran

TMS : tetramethylsilane

nmr : nuclear magnetic resonance

i.r. : infrared

p : polarised

dp : depolarised

v : very

w : weak

m : medium

s : strong

sh : shoulder

br : broad.

1.2 General Introduction

The new class of compounds referred to by the title of this thesis links two different areas of organometallic chemistry – the chain compounds of the group IV elements and the group IV-substituted metal carbonyls. The main interest is in the hydrides so that the first two review sections deal principally with M'_nH_{2n+2} and $H_3M'M(CO)_x$ respectively. The much more numerous organic derivatives are dealt with only briefly with emphasis on those properties which clarify or complement the properties of the hydrides.

The existence of compounds with chains of group IV atoms has been well established for 60 years. Gilman, Atwell and Cartledge (1) covered work on catenated organic compounds of silicon, germanium, tin and lead up to mid 1965. Other reports (2 - 6) on chain compounds appeared and were followed by a review of the physical and chemical properties of the alkylpolysilanes (7) by Kumada and Tamao. Attention then focused on mixed element chains, so that when a thorough review by Mackay and Watt (8) on the chain compounds of group IV metals appeared in 1969, a wide array of mixed chains were known.

Progress in the development of the mixed chains stimulated interest in many other aspects of organometallic chemistry particularly in the field of group IV-transition metal compounds. Reviews by Vyazankin et al. (9), Brooks and Cross (10) and to a lesser extent Glockling and Stobart (11) cover developments of the group IV-transition metal compounds for the period up to 1972. Earlier general reviews have appeared (12, 13, 14) as have others with more specific reference to germanium (15, 16) and to silicon (17, 18) derivatives. Continuing interest in recent years is reflected in Annual Reports (19) and Specialist Periodical Reports (20, 21, 22) of the Chemical Society. Two recent books (23, 24) provide good coverage of both catenated and transition metal compounds of silicon.

1.3 Catenated Hydrides of the Group IV Elements

Group IV elements (M' = Si, Ge, Sn, Pb) with the exception of lead, are capable of forming very stable chains of the same atom or mixed atoms provided the substituents are carefully chosen (1 - 8). Chains of silicon, germanium or tin form fully organo-substituted species $R_{2n+2}M'_n$, probably of unlimited length and including straight and branched configurations. Hydrides of chain lengths up to 10 atoms are well established for silicon and germanium. Disilane, Si_2H_6, the first group IV metal hydride with a M'-M' bond to be discovered, was reported in 1902 by Moissan. Stock (25, 26) became the first to study in detail this and higher hydrides, and demonstrated the reaction with hydrogen halides forming halogen-containing derivatives. In 1924, Dennis, Corey and Moore (27) isolated the first polygermanes Ge_2H_6 and Ge_3H_8. No new hydrides were reported for the next two decades. With improved preparative methods and separation techniques over the following 20 years compounds of silicon and germanium with chain lengths of up to 10 atoms in length were identified mainly by gas-liquid chromatography. The chain hydride of tin is restricted to Sn_2H_6, first reported by Jolly (28, 29) in 1960, SiH_3SnH_3 and GeH_3SnH_3 (30). Any chain compounds of lead are restricted to Pb_2R_6 and $(R_3Pb)_4Pb$. Table 1.1 lists the silicon, germanium and tin hydrides known, including compounds with Si - Ge bonds.

Table 1.1 Catenated Group IV-Metal Hydrides

Hydride	Properties		Preparation
	m.p	b.p (°C)	(See text in 1.3.1)
Silicon			
SiH_4 (26)	-185.0	-111.9	
Si_2H_6	-132.5	- 14.5	1(26,31,32); 2(33,34); 3SD(35,36); 3Py(37); 3P(38,39); 4(40); 5(41)
Si_3H_8	-117.4	52.9	1(26,31,32); 3SD(35,36; 3P(39); 4(40).
Si_4H_{10}(a)	- 84.3	107.4	1(26,42,43); 3SD(36)
iso-Si_4H_{10}	- 99.1	101.4	1(31,32); 3SD(35)
n-Si_4H_{10}	- 89.9	108.1	1(31,32); 3SD(35)
higher fractions (b)			1(26,32,44,45)
Germanium			
GeH_4 (27,46)	-165	- 88.5	
Ge_2H_6	-109	29	1(27,31,44,46). 2(47,48); 3SD(47); 3Py(49); 3P(50); 4(51,52); 5(41,53).
Ge_3H_8	-106	110.5	1(27,44); 2(47,48); 3SD(47,54)
Ge_4H_{10} (a)		117	1(55)
iso-Ge_4H_{10}			1(31); 3(47,54)
n-Ge_4H_{10}		214	1(31); 3(47,54)
Ge_5H_{12} (a)		234	1(55)
neo-Ge_5H_{12}			3(47,53,54)
iso-Ge_5H_{12}			1(31)
n-Ge_5H_{12}			3(45,54)
higher fractions (b)			3(47)

Tin			
Sn_2H_6	Decomposes readily above -112		2(28,48,56)
SiH_3SnH_3) GeH_3SnH_3)	Decompose above -80		2(30)
Silicon-Germanium			
H_3SiGeH_3		7.0	1(29,31,57); 3SD(57,58); 3P(59); 4(60)
$H_5Si_2GeH_3$	-113.4	V39.6(c)	1(31); 3SD(58)
$(H_3Si)_2GeH_2$ (a)			3SD(58)
$H_5Ge_2SiH_3$			3SD(58)
Ge_2SiH_8	-108.5	V19.3(c)	1(29,31)
n-Si_3GeH_{10}	- 87.1	V 4.7(c)	1(31)
n-Si_4GeH_{12}	- 71.5		1(31)
higher fractions (b)			3(31,45)

(a) Isomer mixtures, usually enriched in n-polymer.

(b) Mixtures of compounds 5-9 catenated metal atoms in n-, iso-, or neo-configurations.

(c) V - vapour pressure at 0°.

1.3.1 Syntheses

There are four general preparative routes to the catenated hydrides:

(1) Acid hydrolysis of alloys of M' with an electropositive element (usually Mg or Ca) (26,27,29,33,55)

e.g. $Mg_2Ge + HCl \rightarrow H_2 + GeH_4 + Ge_2H_6 + Ge_3H_8$ ....

16.5% 4.5% 0.2%

(2) Reductions by complex hydrides (47,48,56,61)

e.g. $Ge^{IV} + BH_4^- + H^+ \rightarrow GeH_4 + Ge_2H_6 + Ge_3H_8$ . . . .

The only known polystannane, Sn_2H_6, was made by borohydride reduction of aqueous stannite (56).

(3) Silent-Electric Discharge (SD: 35,36,47,54,57,58); Pyrolysis (Py) and Photolysis (P) (38,39,49,50,59).

(4) Alkali-Halide Elimination (40,51,52,53,60)

e.g. $SiH_3K + Me_3SnCl \rightarrow Me_3SnSiH_3 + KCl$ (62)

(5) Elimination of Hg from $(R_3M')_2$ Hg

e.g. $(Me_3Si)_2Hg \xrightarrow{\Delta} Me_3SiSiMe_3 + Hg$

This route has recently been demonstrated by Ebsworth et al. (41) and is worth more detailed comment since it is relatively new and offers a synthesis which is potentially more specific than 1 – 4. It has been successfully used to synthesise Me_3SiSiH_3, Si_2H_6, Me_3SiGeH_3 and Ge_2H_6. The most commonly used mercury compound is bis(trimethylsilyl)mercury, $(Me_3Si)_2Hg$, and the following sequence of reactions with GeH_3Br was monitored with ^1H and ^{199}Hg nmr.

$GeH_3Br + (Me_3Si)_2Hg \rightarrow GeH_3\text{-}Hg\text{-}SiMe_3 + Me_3SiBr$ . . . (1)

$GeH_3\text{-}Hg\text{-}SiMe_3 + GeH_3Br \rightarrow (GeH_3)_2Hg + Me_3SiBr$ . . . (2)

$GeH_3\text{-}Hg\text{-}SiMe_3 \rightarrow Me_3SiGeH_3 + Hg$ . . . (3)

$(GeH_3)_2Hg \rightarrow Ge_2H_6 + Hg$ . . . (4)

The rate of the above sequence of reactions is temperature controlled and the extent of the reaction is dependent on the ratio of the reactants. Germyl bromide reacts in a 1:1 ratio with $(Me_3Si)_2Hg$ to give GeH_3-Hg-$SiMe_3$ and Me_3SiBr quantitatively. This, on standing, exposure to light, or warming, gives Me_3SiGeH_3 (reaction (3)). Alternatively, with excess of GeH_3Br, the bis-germylmercury compound is formed. This in turn can be decomposed to give digermane (reaction (4)).

Although attempts at the synthesis of methyldigermanes by this method have so far been unsuccessful (53), it is potentially a useful preparative route as it has several advantages over the other methods described earlier. Firstly, yields calculated from nmr sequential reactions are fairly high (70-80%) and secondly, hardly any by-products are observed. The Hg-coupling reaction offers the added potential of synthesising unsymmetric digermanes, e.g. Me_3GeGeH_3, $Me_2GeHGeH_3$ and chains of mixed group IV atoms e.g. GeH_3-$SiMe_3$ by using the appropriate reagents and conditions. Already, this method is proving very useful. Pyrolysis or photolysis of $(Me_3Si)_2Hg$ or $(Me_3Ge)_2Hg$ with organic compounds give a wide variety of products including hexamethyl-substituted disilane, digermane, distannane (63-68) and cyclic compounds (69). The chlorosilyl and chlorogermyl mercurials e.g. $(Cl_3Ge)_2Hg$ and reaction products have also been studied (70,71).

It has recently been found that co-condensation of thermally evaporated germanium vapour with trimethylsilane yields bis-trimethylsilylgermane, $Me_3SiGeH_2SiMe_3$ (72). The first carbon-functional halo-methyldisilane $XCH_2SiH_2SiH_3$ has also been recently reported (73). It was prepared by the reaction of diazomethane with hexachlorodisilane, followed by $LiAlH_4$ reduction of the $ClCH_2Si_2Cl_5$ produced.

1.3.2 Properties of the M'–M' Bond

Although distannane, Sn_2H_6 is the only catenated tin hydride prepared so far and it decomposes rapidly above −112 °C, hexamethylditin Sn_2Me_6 is stable (b.p. ca.62°) and over sixty organo-polystannanes with chains of up to nine tin atoms are known. Similarly no lead hydrides have been characterised although partially substituted monoplumbanes have been reported (74). However, organo-compounds with Pb–Pb bonds do exist. Thus it would appear that the absence of catenated hydrides of tin other than Sn_2H_6 does not arise from the weakness of the M'–M' bond, but is rather related to that of the M'–H bond. In the case of lead, however, the much more limited range of compounds suggests that Pb–Pb bond strength is substantially lower than for the other members of the group. Measurements of M'–M' bond strength by various methods are tabulated in Table 1.2. The bond dissociation energies D obtained by electron impact and kinetic studies (75–80) are rather variable, depending on the method of determination. The thermochemical bond energies E (81–83) derived from combustion of group IV hydrides by explosion with stibine is a more artificial concept than D. It was originally introduced to predict heats of formations but fails to consider a wide range of interactions for these predictions to be valid. The D and E values calculated from appearance potentials in mass spectroscopic studies (84) are probably satisfactory and compare well with some literature values obtained by more conventional methods

(85,86). Electron impact data frequently give high values as it is difficult to be sure that the fragments of the molecule have no excess kinetic energy, and also that the fragment being measured actually arises from the parent ion. However, in the mass spectroscopic studies (84) assumptions that the $Me_3M'+$ ions resulted mainly from M'-M' bond cleavage of the parent ion $Me_6M'_2$ (see Table 1.2(c)) not $Me_{6-n}M'_2$ and that the ions $Me_3M'^+$ formed have little (< 0.1 eV) or no excess energy were supported by metastable peak studies and also by the self consistency of the results. Although there is little comparison between (a), (b) and (c) in the above table, the order of bond strength is clear and is as expected:

$$Si - Si > Si - Ge > Ge - Ge > Sn - Sn > Pb - Pb$$

In addition, neither chain length nor substituent seem to alter these values by any significant extent.

Table 1.2 Energies of M'–M' Bonds (kJ.mole^{-1})

(a) Bond Dissociation Energy, D (X_3M'–$M'X_3$)

Compound	D	Method (*)	Ref.
H_3Si–SiH_3	213.6	K	76
	336.2	EI	77
Me_3Si–$SiMe_3$	280.2	K	78
	359.0	EI	75
Cl_3Si–$SiCl_3$	353.7	EI	87
H_3Ge–GeH_3	140.1	K	79
	315.2	EI	80
H_3Ge–SiH_3	416.7	EI	80

(b) Thermochemical Bond Energy, E

Compound	E	Method (*)	Ref.
Si_2H_6	199.7	Explosion with SbH_3	82
Si_3H_8	201.4	"	81
Ge_2H_6	162.8	"	81
Ge_3H_8	166.3	"	81
H_3SiGeH_3	182.1	"	83
Sn_2H_6	124.3	EI	80

(c) Bond Dissociation, D and Thermochemical, E

Bond Energies by Mass Spectroscopy (84)

Compound	D	E
$Me_3SiSiMe_3$	288.9	283.7
Me_3Si–$GeMe_3$	281.9	264.4
Me_3Ge–$GeMe_3$	280.2	246.9
Me_3Si–$SnMe_3$	285.4	234.6
Me_3Ge–$SnMe_3$	288.9	224.1
Me_3Sn–$SnMe_3$	257.4	154.3
Me_3Pb–$PbMe_3$	227.6	138.3

* EI = Electron Impact, K = kinetics

Usually the most convenient means of demonstrating the presence of a M'–M' bond is by vibrational spectroscopy. Although these low frequency metal–metal stretching absorptions often show only weakly in the infrared, they usually give rise to intense Raman bands. This technique is now commonly used to study metal–metal bonds and some examples of M'–M' stretching frequencies together with the force constants derived from them are shown in Table 1.3.

Table 1.3 M'–M' Stretching Frequencies and Force Constants

Bond	Compound	νM'–M' (cm^{-1})	fM'M'(mdyn.Å^{-1})	Ref
Si–Si	Si_2H_6	435p	1.81	89,90
	Si_2Me_6	404p	1.70	91,91
Si–Ge	H_3SiGeH_3	362p	1.70	58,58
Ge–Ge	Ge_2H_6	268p	1.60	92,90
	Ge_2Me_6	273p	1.54	91,91
	Ge_3H_8	245p, 288dp	1.60	54,58
Sn–Sn	Sn_2H_6		1.33	93
	Sn_2Me_6	192p	1.39	91,91
	Sn_2Ph_6	136p	1.17	91,91
Pb–Pb	Pb_2Me_6	113p	1.01	91,91

Other means have also been used to study the M'–M' bond. Results obtained from gaschromatographic study of compounds of the type $Et_3M'M'Et_3$ gave the following electronic polarizability values: Si–Si, 15.4; Si–Ge, 15.8; Ge–Ge, 16.7; Sn–Sn, 17.0; Ge–Sn, 17.2; Sn–Sn, 20.6 (Å^3) (94). Bond length determinations by crystal studies and by electron diffraction or microwave methods on gases have been reported. The Si-Si bond length is well-established, the determinations on Si_2Cl_6 averaging 2.30Å. There is no marked change in Si-Si by varying the substituents. The Ge-Ge bond length is not well-established and scarcely any values for Sn-Sn or Pb-Pb are available. However, it is worth noting the mean of the M'-M' distances in disilane and digermane is 2.36 Å which matches the experimentally measured value of SiH_3GeH_3 as shown in Table 1.4. Thus it seems, multiple bonding is unlikely, despite earlier suggestions (95).

Table 1.4 M'-M' Bond Lengths

Bond	Compound	M'-M' (Å)	Ref.
Si-Si	Si_2H_6	2.32 ± 0.03	96
	Si_2Me_6	2.34 ± 0.01	97
	Si_2Cl_6	2.29 ± 0.05	98
Si-Ge	H_3SiGeH_3	2.357 ± 0.004	95
Ge-Ge	Ge_2H_6	2.41 ± 0.02	99
	Ge_3H_8	2.41 ± 0.02	99
Sn-Sn	Sn_2Ph_6	2.770 ± 0.004	100
Pb-Pb	Pb_2Me_6	2.88 ± 0.03	101

There has been much work and speculation about the nature of the M'-M' bond and these centre around the possibility of $(p-p)\pi$, $(p-d)\sigma$, $(p-d)\pi$ and $(d-d)\pi$ bonding. Some bonding considerations of silicon have been briefly reviewed by Simpson (102).

Silicon and its congeners in group IV fail to form stable derivatives containing double and triple bonds analogous to those in unsaturated carbon compounds, although (p–p)π bonded intermediates have been postulated in a number of reactions (4, 103). The reasons for this failure range from poor π–overlap of the more diffuse p–orbitals to the inherent strength of the σ–bonds of Si, Ge and Sn. All group IV elements have the same electronic configurations in the outermost filled level. However, all except carbon have a set of five unoccupied d–orbitals. Observed differences between the chemical behaviour of carbon and the heavier elements have been interpreted in terms of the participation of those vacant d–orbitals in bond–formation, example, the existence of the fluoro–anions SiF_6^{2-} and GeF_6^{2-} and a number of adducts formed by halosilanes (104) and halogermanes (105) with various donor molecules. Coordination numbers greater than four are rare with carbon. The ability of silicon and germanium to expand their coordination number, using the unoccupied d–orbitals to form acceptor σ–bonds, has been used as the explanation.

The commonly cited example of (p–d)π bonding in group IV chemistry is that of trisilylamine, $(SiH_3)_3N$. Burg (106) found that $(SiH_3)_3N$ was an unexpectedly weak donor compared with methyl analogues. In contrast to $(CH_3)_3N$ which is pyramidal, its structure was determined by Hedburg (107) to have a planar heavy atom skeleton. This structure was rationalised by assuming the nitrogen atom at the centre of a trigonal plane forming σ–bonds with the three silicon atoms leaving the lone pair of electrons in a pure p–orbital at right angles to this plane. The energy of this p–orbital may be lowered by donating electron density from it into the correct symmetry vacant d-orbitals of the adjacent silicon atom. Thus the weak donor ability of the nitrogen in $(SiH_3)_3N$ observed by Burg. Despite preliminary suggestions from vibrational spectra to the contrary, electron diffraction examination of trigermylamine, $(GeH_3)_3N$ also indicated a planar Ge_3N skeleton (108). $(p-d)\pi$ bonding has been invoked to rationalise any alteration in the bond angle at atoms adjacent to silicon relative to the analogous carbon compound, or any shortening of the Si-X bond compared with the unexpected single bond length. The symmetry requirements for the possibility of significant $(p-d)\pi$ overlap have been discussed by Ebsworth (109) who also pointed out that there may be considerable overlap between a d-orbital on silicon and a lone pair of electrons on an adjacent atom which occupies a tetrahedral site with respect to a central silicon atom, thus drastic structural changes need not necessarily accompany $(p-d)\pi$ bonding. Thus although the angle at phosphorus in $(SiH_3)_3P$ (110) and $(GeH_3)_3P$ (111) is considerably less than the tetrahedral angle, there is still the possibility of π-character involving the silicon d-orbitals as inferred from the poor donor ability of the P atom. Numerous other techniques apart from structural studies have been used to investigate the possibility of $(p-d)\pi$ bonds. The Raman and solid-state i.r. spectra of germyl-isocyanate, GeH_3NCO, seem to confirm a non-linear heavy atom skeleton (112). The inference is taken that $(p-d)\pi$ bonding is not as important here as in the silyl analogue which has a linear skeleton. Ebsworth (109) in a comprehensive review of the role of d-orbitals in group IV chemistry sums up that such a bond is most likely to be important between silicon and the first row elements N, O and F while the position regarding heavier substituent atoms remains uncertain.

The recent expansion of the chemistry of the group IV bond to transition metals has stimulated investigation into the possibility of multiple bond character in the M'–M bond especially (d–d)π interaction. This is more appropriately discussed in section 1.4.2.

1.3.3 Reactions and Derivatives

Reactions of the group IV hydrides are well established and have been given a thorough review by Mackay et al. (8). Few new reactions have since been added. In general, there are two types of reactions:

(a) cleavage (including insertion into M'–M' bond)

and

(b) substitution.

(a) Cleavage reactions.

The metal-metal bonds of disilane (113) or digermane (52,114) are cleaved by KH,

e.g. $Ge_2H_6 + KH \longrightarrow GeH_3K + GeH_4$

with digermane reacting faster than disilane. With excess disilane, Si_2H_5K and Si_3H_7K are also formed probably via $KSiH_3$ or from disilane plus $KSiH_3$. Potassium metal in monoglyme reacts to cleave the Ge–Ge bond and give GeH_4, not GeH_3K (115).

Reaction of polysilanes with sodium amalgam has also been reported; for example Si_4H_{10} gave about 20% SiH_4, 10% Si_2H_6, 20% Si_3H_8, 10% unchanged Si_4H_{10} and 15% higher silanes together with solid hydride when reacted for 48 hours with 1% amalgam (26).

As shown by conductimetric titrations, all the Ge–Ge links in digermane or trigermane are cleaved by sodium in ammonia (116). A limited amount of hydrogen is evolved which probably arises by side reaction between Ge–H and the solvent:

$$Ge_2H_6 + 2Na \xrightarrow{NH_3} 2GeH_3Na$$

$$Ge_3H_8 + 4Na \xrightarrow{NH_3} 2GeH_3Na + GeH_2Na_2$$

Jolly (117) has shown that GeH_4 reacts with liquid ammonia solutions of potassium or potassium amide to form $KGeH_3$, germanium imide ($Ge(NH)_2$: xNH_3) and hydrogen gas. The fraction of GeH_4 converted to germanium imide increases with increasing potassium concentration but remains constant with potassium amide concentration. Amide ion is thus an intermediate in the reaction of germane and very likely, polygermanes with metal–ammonia solutions.

Pyrolysis studies by Ring et al. of Si_2H_5 (118, 119), Si_3H_8 (118), Ge_2H_6 (119) and SiH_3GeH_3 (120) demonstrated M'–M' bond cleavage with a 1,2-hydrogen migration producing silene, SiH_2 and germene, GeH_2 (in the latter case) which inserts into M'–H bonds,

e.g. (119) $Ge_2H_6 \longrightarrow GeH_2 + GeH_4$

$$Ge_2H_6 + GeH_2 \longrightarrow Ge_3H_8$$

There is also evidence to suggest insertion into the M'–M' bond in the pyrolysis of Si_3H_8 from a good yield of i-Si_5H_{12} (121),

$$Si_3H_8 \longrightarrow HSiSiH_3 + SiH_4$$

$$Si_3H_8 + HSiSiH_3 \longrightarrow SiH_3SiH_2SiH(SiH_3)SiH_3$$

Phillips (45) obtained a wide range of both high molecular weight and branched chain silicon-germanium hydrides in electrical discharges of monogermane with monosilane and disilane.

In a solvent, iodine cleaves digermane to give germyl iodide as the main product (122,123),

$$Ge_2H_6 + I_2 \xrightarrow{\text{solvent}} 2GeH_3I$$

(b) Substitution reactions.

Stock showed that silanes were readily halogenated when treated by hydrogen halides or organic halogen compounds in presence of $AlCl_3$ (26),

e.g. $Si_2H_6 + HCl \xrightarrow{AlCl_3} Si_2H_5Cl + H_2$

while trisilane gave $Si_3H_4Cl_4$ and $Si_3H_3Cl_5$.

MacDiarmid et al. (124-127) improved on Stock's technique and found that the action of HX/AlX_3 converted Si_2H_6 to Si_2H_5X (X = Cl, Br, I) and that the disilanyl halides were stable when carefully freed from traces of aluminium halides. They also found that Si_2H_5X gave halide exchange with heavy metal salts (124),

e.g. $Si_2H_5Br + AgCl \longrightarrow Si_2H_5Cl + AgBr$.

Si_2H_5CN was prepared by this method (124).

Disilane also substitutes with boron halides (127-130),

e.g. $Si_2H_6 + BX_3 \longrightarrow Si_2H_{6-x}X_x$ (X = Cl, Br)

The reaction of BCl_3 with Si_3H_8 reported by Drake et al. (129,131) gave $(SiH_3)_2SiHCl$, the first characterised derivative of trisilane, and also 1,3-dichlorotrisilane,

$$Si_3H_8 + BCl_3 \longrightarrow \underset{62\%}{(SiH_3)_2SiHCl} + \underset{38\%}{(SiH_2Cl)_2SiH_2}$$

Reaction with BBr_3 resulted in the 1- and 2-bromosubstituted isomers. Subsequent passage of the chlorocompounds over antimony fluoride at 25 °C yielded $SiH_3SiH_2SiH_2F$ from $(SiH_3)_2SiHCl$ and $SiH_3SiH_2SiHF_2$ from $(SiH_2Cl)_2SiH_2$.

Digermane decomposes rapidly in the presence of aluminium halides (122). However, substitution occurs over heated AgX (122),

$$Ge_2H_6 + AgX \xrightarrow{250\ ^{o}C} \underset{25-40\%}{Ge_2H_5X} + Ag + \tfrac{1}{2}H_2 \quad (X = Cl, Br)$$

and as for the disilanyl halides, the digermanyl halides are capable of halide exchange with AgX,

$$Ge_2H_5I + AgX \longrightarrow \underset{20-70\%}{Ge_2H_5X} + AgI \quad (X = Cl, Br)$$

Bromine substitutes digermane to yield some Ge_2H_5Br (122) but the product is usually contaminated with GeH_2Br_2 pointing to a further attack with cleavage by Br_2 once Ge_2H_5Br is formed. Separation of Ge_2H_5Br and GeH_2Br_2 is very difficult. Although I_2 in the presence of a solvent attacks both the Ge-Ge and Ge-H bonds (122), the direct reaction of iodine with Ge_2H_6 at low temperatures (132) is still the best method for preparing pure Ge_2H_5I in high yields,

$$Ge_2H_6 + I_2 \xrightarrow{-63\ ^{o}C} Ge_2H_5I + HI.$$

Although Ge_2H_5I is an unstable liquid at room temperature, it can be handled in a vacuum system (132) and used in reactions, for example in the halide exchange reactions above (122) at low temperatures. Many digermanyl derivatives have been prepared in situ using Ge_2H_5I as the starting material. With $LiAlD_4$, Ge_2H_5D was obtained (133). RGe_2H_5 (R = Me, Et) have been prepared by the reaction (134,146) of Ge_2H_5I with RMgI and using a similar procedure, $Ge_2H_5Mn(CO)_5$ (135) was obtained with $NaMn(CO)_5$.

Trigermane reacts similarly with iodine (136,137),

$$Ge_3H_8 + I_2 \xrightarrow{-63\ ^oC} Ge_3H_7I + HI$$

and like the digermanyl iodide, Ge_3H_7I is too unstable to be characterised. It was converted <u>in situ</u> to Ge_3H_7D (136) and $MeGe_3H_7$ (137) using $LiAlD_4$ and MeMgI respectively,

$$\begin{aligned} Ge_3H_7I + MeMgI \xrightarrow{-63\ ^oC} & \ 2\text{-}MeGe_3H_7 \quad (86\%) \\ & + 1\text{-}MeGe_3H_7 \quad (14\%) \\ & + Mg^{2+} + I^- \end{aligned}$$

The product mixture showed that substitution was mainly on the central germanium atom. In the elemental iodination of trisilane, the preferred monoiodoisomer is 1-iodotrisilane which is favoured to the extent of 4:1 over 2-iodotrisilane (138).

Another important route to the halides is reaction with $SnCl_4$ (139). In equimolar proportions,

$$\begin{aligned} Ge_2H_6 + SnCl_4 \longrightarrow & \ Ge_2H_5Cl \quad (80\%) \\ & + 1,2\text{-}Ge_2H_4Cl_2 \quad (20\%) \\ & + SnCl_2 + HCl \end{aligned}$$

Presumably,

$$SnHCl_3 \longrightarrow SnCl_2 + HCl.$$

Reaction is rapid at room temperature. With excess digermane, the only product is the monochloride. HCl is not involved in further substitutions from the absence of H_2. Disilane, in equimolar proportions yields a 50:50 mixture of disilanyl chloride, Si_2H_5Cl

and the 1,2-dichloride (140). Ge_2H_6 reacts very slowly with $SiCl_4$ to give Ge_2H_5Cl (141). A preliminary study (142) of the $SnCl_4$ reaction with trigermane at -23 °C gave, upon methylation, a mixture of mono- and di-methyltrigermane.

The stabilities and handling properties of some polygermanyl halides are listed below:

Ge_2H_5I - distils at ca. 0 °C with ca. 10% decomposition

$Ge_2H_4I_2$)
) - decomposes before distillation.
Ge_3H_7I)

Ge_2H_5Cl - distils at 0 °C with little loss: decomposes at room temperature at about 10% in 2 hours in the gas phase, faster as liquid, accessible only via Ge_2H_5I or in presence of HCl and $SnCl_2$.

$Ge_2H_4Cl_2$) - more stable than iodides:
)
Ge_3H_7Cl) little loss on distillation; decomposition and disproportionation at ca.10-20% in 1 hour.

The I_2 (143) and $SnCl_4$ (53) substitution of Ge_2H_6 and $MeGe_2H_5$ have been compared, with the digermanes in slight excess. The iodides produced were converted to the methyl derivatives.

$$\begin{aligned} Ge_2H_6 \xrightarrow[-63^{\circ}C\ to\ -45^{\circ}C]{I_2/MeMgI}\ & MeGe_2H_5 \quad (40\text{–}70\%) \\ & +\ 1,1\text{-}Me_2Ge_2H_4 \quad (0\text{–}2\%) \\ & +\ 1,2\text{-}Me_2Ge_2H_4 \quad (4\text{–}17\%) \\ & +\ 1,1,2\text{-}Me_3Ge_2H_3 \quad (0\text{–}1\%) \end{aligned}$$

$$Ge_2H_6 \xrightarrow[R.T.]{SnCl_4/MeMgI} MeGe_2H_5 \quad (80\text{–}100\%)$$

$$+ \quad 1,2\text{-}Me_2Ge_2H_4 \quad (0\text{–}20\%)$$

$$MeGe_2H_5 \xrightarrow[-45\ ^{o}C]{I_2/MeMgI} 1,1\text{-}Me_2Ge_2H_4 \quad (38\text{–}44\%)$$

$$+ \quad 1,2\text{-}Me_2Ge_2H_4 \quad (14\text{–}18\%)$$

$$+ \quad 1,1,2\text{-}Me_3Ge_2H_3 \quad (12\text{–}19\%)$$

$$MeGe_2H_5 \xrightarrow[R.T.]{SnCl_4/MeMgI} 1,1\text{-}Me_2Ge_2H_4 \quad (73\%)$$

$$+ \quad 1,2\text{-}Me_2Ge_2H_4 \quad (14\%)$$

$$+ \quad 1,1,2\text{-}Me_3Ge_2H_3 \quad (14\%)$$

$$1,1\text{-}Me_2Ge_2H_4 \xrightarrow[R.T.]{SnCl_4/MeMgI} 1,1,1\text{-}Me_3Ge_2H_3 \quad (100\%)$$

The results showed that $SnCl_4$ substituted more specifically. The HI produced in the iodination step was found to be reactive and was involved in secondary iodinations with H_2 evolved. The results also show the methyl group as activating the α -germanium to a greater extent than the β -germanium towards further substitution.

Alkyl derivatives of digermane are also obtained by the addition of Ge-H to olefinic bonds (144),

$$Ge_2H_6 + C_2H_4 \xrightarrow[5\text{–}10\ atm.]{120\text{–}160\ ^{o}C} EtGe_2H_5$$

However, at these temperatures, redistribution and rearrangement occur quite readily giving complex mixtures of alkyl mono-, di-, and tri-germanes. Khandelwal and Pinson have found that the irradiation of a 0.6:1 mixture of digermane and ethylene with cobalt-60 gamma rays produced only ethylmonogermane and ethyldigermane (145).

The reactions of digermane and trigermane are summarised in Fig. 1.1 and Fig. 1.2.

Fig. 1.1 The Reactions of Digermane

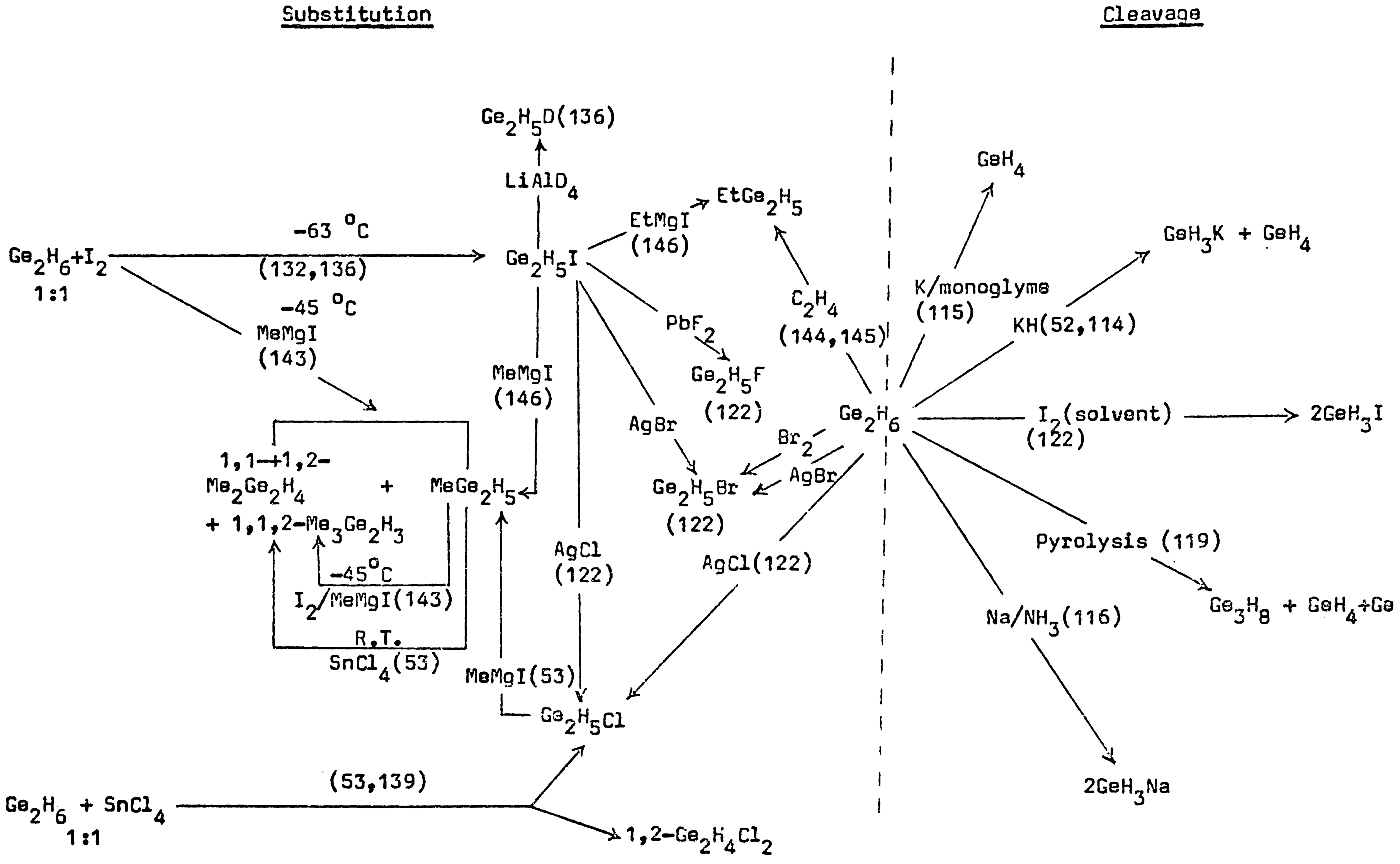
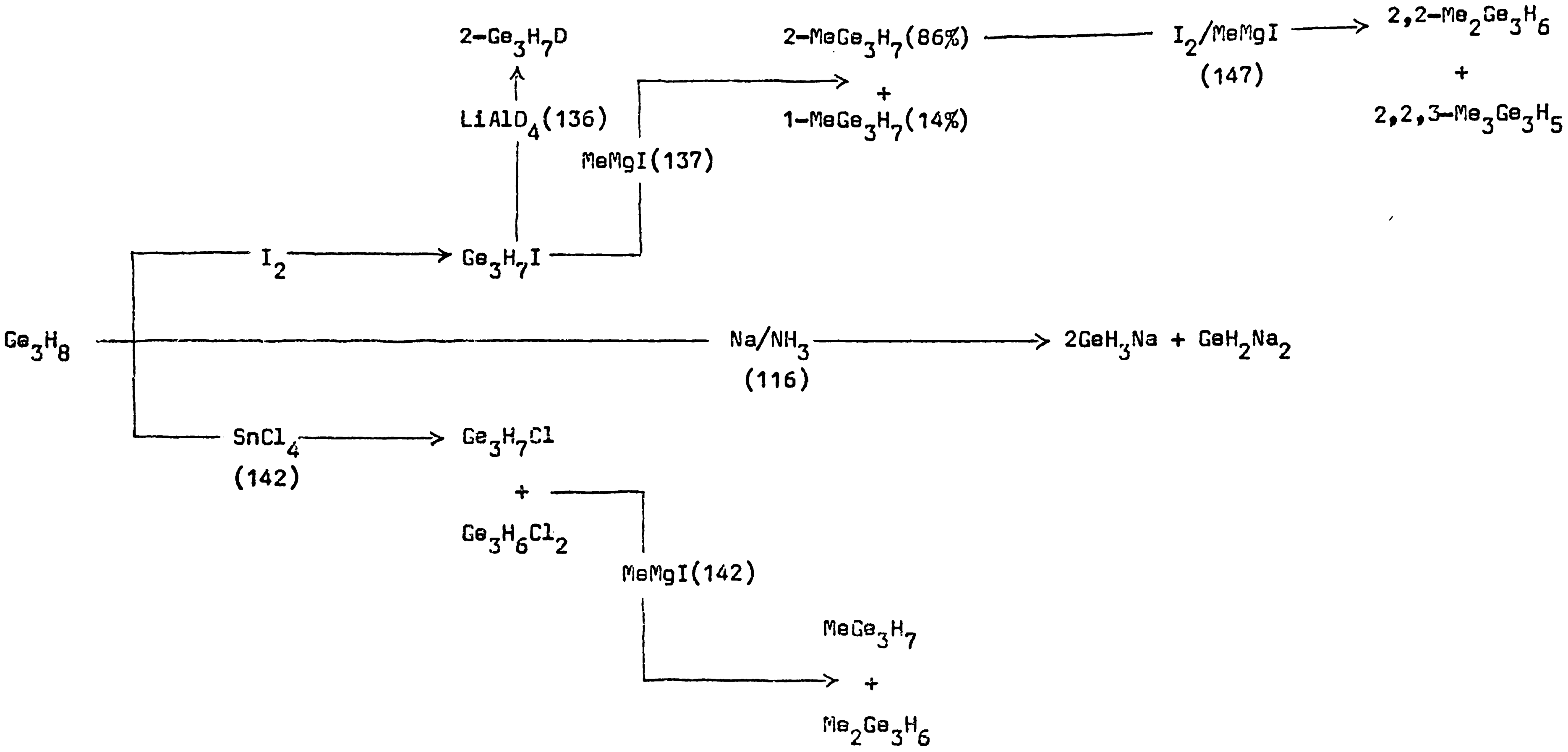


Fig. 1.2 The Reactions of Trigermane



1.4 Group IV (Hydride) Derivatives of Transition Metals

The first group IV transition metal compounds made were alkyl lead derivatives of iron carbonyl reported in 1941 by Hein and Pobloth (148). Since then, especially over the past 20 years, the field of group IV transition metal bonded compounds has grown to one of considerable proportions (9-22,24). The latest review (149) is on the group IVB derivatives of the iron triad carbonyls. The range of hydride derivatives is much less extensive but the number is growing steadily. Table 1.5 lists the group IV (hydride)-transition metal complexes reported to date. Most of these complexes contain Mn, Fe or Co, and the number decreases towards the left, right and down the transition elements in the periodic table. To the left the 18-electron rule would require high coordination numbers, which may mean a decrease in stability. Although group IV transition metal complexes of Re, Ru, Os and Ir are more stable than the first row congeners, fewer compounds are known probably because the heavier metal compounds are less readily available and more expensive. Some of the more common substituents on the transition metal are CO, PR_3 (where R = halogen or organic group), halogen and organic π-ligands such as C_5H_5. The main substituents accompanying hydrogen on the group IV metals are alkyls (Me, Et, Pr, Bu), the halogens and Ph. There are many times more non-hydride containing group IV transition metal complexes, $R_3M'ML_x$, than those listed in Table 1.5 and most of these are listed in the literature already mentioned. The more limited range of hydrides probably reflects primarily the M'-H stability and secondarily their handling properties. The small number of

Table 1.5 Group IV (Hydride) Derivatives of Transition Metals

	Method of preparation (see text in 1.4.1)	References
Titanium		
$[H_2SiTiCp_2]_2$	1.2	150
Vanadium		
$H_3SiV(CO)_6$	1.1	151
Chromium, Molybdenum or Tungsten		
$H_3SiM(CO)_3Cp$ M = Cr, Mo, W	1.1	152
$(Me_2SiH)M(CO)_3Cp$ M = Cr, W	1.1	153
$(MeSiHCl)M(CO)_3Cp$ M = Mo, W	1.1	154
Manganese and Rhenium		
$H_3SiMn(CO)_5$	1.1(b)	155–158
$H_2Si\ [Mn(CO)_5]_2$	1.1	159,160
$H_2SiClMn(CO)_5$	1.1	160
$HSiCl\ [Mn(CO)_5]\ [Co(CO)_4]$	2	160
$H_3GeMn(CO)_5$	1.1(b,d)	161,162
$H_2Ge\ [Mn(CO)_5]_2$	2,but using $HMn(CO)_5$	159
$MeGeH_2Mn(CO)_5$	1.1(b,d)	141
$Me_2GeHMn(CO)_5$	1.1	163
$Ph_2GeHMn(CO)_5$	1.1(c)	164
$Ph_2SnHMn(CO)_5$	1.1(c)	164

$H_2Sn\ [Mn(CO)_5]_2$	1.1(c)	164
$HSn\ [Mn(CO)_5]_3$	1.1(c)	164
$H_3SiRe(CO)_5$	1.1	165
$H_3GeRe(CO)_5$	1.1	165–167
$Ph_2GeHRe(CO)_5$	1.1(c)	164
$H_2Ge\ [Re(CO)_5]_2$	1.1	165–167
$Ph_2SnHRe(CO)_5$	1.1(c)	164
$H_2Sn\ [Re(CO)_5]_2$	1.1(c)	164

Iron and Osmium

$(H_3Si)_2Fe(CO)_4$	1.1	168,169
$H_3Si(H)Fe(CO)_4$	1.1	168,169
$H_3SiFe(CO)_2Cp$	1.2	170
$Me_2SiHFe(CO)_2Cp$	1.1	171
$(H_3Ge)_2Fe(CO)_4$	1.1(a,b)	172–174
$H_3Ge(H)Fe(CO)_4$	1.1	172–174
$[H_2GeFe(CO)_4]_2$	4	174,175
$[XHGeFe(CO)_4]_2$ $X = Cl,Br$	4	174
$(MeGeH_2)_2Fe(CO)_4$	1.1(a,b)	176,177
$MeGeH_2(H)Fe(CO)_4$	1.1	176
$[(MeGeX)(MeGeY)Fe(CO)_4]_2$ $X = Y = H$ or $X = H,\ Y = Cl,Br$	4	176,177
$(Me_2GeH)_2Fe(CO)_4$	1.1(a)	178
$Me_2GeH(H)Fe(CO)_4$	1.1	178
$H_3GeFe(CO)_2Cp$	1.1	173
$(Ph_2Ge)(PhGeH)Fe_2(CO)_6$	2	179
$H_2Ge\ [Fe(CO)_2Cp]_2$	5(c)	180
$(H_3Ge)_2Os(CO)_4$	1.1	181
$H_3Ge(H)Os(CO)_4$	1.1	181

Cobalt and Iridium		
$H_3SiCo(CO)_4$	1.1	155,156,158,199,200
$MeSiH_2Co(CO)_4$	2	201
$Me_2SiHCo(CO)_4$	1.1	160
$Ph_2SiHCo(CO)_4$	2(e)	202,203
$Cl_2SiHCo(CO)_4$	1.1,2	160
$H_2Si\ [Co(CO)_4]_2$	1.1	160
$H_3GeCo(CO)_4$	1.1	182,183
$MeGeH_2Co(CO)_4$	1.1	184
$Me_2GeHCo(CO)_4$	1.1	163
$MeGeH\ [Co(CO)_4]_2$	2	185
$HSn\ [Co(CO)_3(PBu^n{}_3)]_3$	5	186
$(CO)(PPh_3)_2Ir(X)(Cl)M'H_3$ (X = H,Cl,Br,I; M' = Si,Ge)	3.1	187
$(PPh_3)_2(CO)Ir(H)_2SiH_2Cl$	3.1	187
Platinum		
trans-$(SiH_2NMe_2)Pt$- $(PEt_3)_2Cl$	3.2	198
$(SiH_2X)_2Pt(Et_3P)_2HI_2$	3.1	188,189
$(Ph_2SiH)_2Pt$(diphos)	3.2	190
$(Ph_2SiH)(H)Pt(PEt_3)_2$	3.2	191
$(Me_2SiH)(H)Pt(PEt_3)_2$	3.2	191
trans- $[PtX(PEt_3)_2(Y)]$ (X = Cl,Br,I; Y = $H_2M'ZM'H_3$, $ZM'H_3$, $M'ClH_2$, $M'H_2ZH$, $M'ClH_2$; Z = O,S,Se; M' = Si,Ge)	3.2	192
trans-$PtI(PEt_2)_2Y$ (Y = $H_2SiN(SiH_3)_2$, SiH_3 $H_2SiP(SiH_3)_2$)	3.2	193

trans-$XPt(PEt_3)_2M'H_{3-x}X_x$ (M' = Si, Ge; X = Cl, Br, I; x = 0-3)	3.2	194-196
$HPt(PEt_3)_2(GeH_2Cl)_x(GeHCl_2)_{3-x}$ (x = 1-3)	3.2	194,195,197

<u>Notes</u>:

(a) These compounds are capable of self-condensation to form cyclised 4-centred compounds.

(b) Reaction studies with Br_2, $M'Cl_4$ (M'= C, Si, Ge, Sn) or HgX_2 (X = Cl, I) have been carried out to produce a range of halo-substituted intermediates, many of them still containing M'-H bonds.

(c) In these cases, group IV-hydrogen bonds were formed after reaction of halide derivatives with a reducing agent such as $NaBH_4$, $(Bu^i)_2AlH$ or $LiAlH_4$.

(d) These compounds have also resulted from metal-metal exchange reactions (198):

e.g. $GeH_3Co(CO)_4 + NaMn(CO)_5 \longrightarrow GeH_3Mn(CO)_5 + NaCo(CO)_4$

(e) Not isolated, seen as intermediate in (202).

derivatives and lack of lead-hydride species follows from the weakness of the M'-H bonds. On the other hand, the high reactivity of Si-H to oxygen, water and bases means that only species volatile enough to handle in a vacuum line are readily manipulated.

1.4.1 Syntheses

There are five general preparative routes to the complexes listed in Table 1.5.

(1) Alkali-Halide Elimination

1.1 Reaction between a group IV halide with a transition metal anion,

e.g. (157) $SiH_3I + NaMn(CO)_5 \xrightarrow{\text{ether}} SiH_3Mn(CO)_5 + NaI$

This is by far the most commonly used and probably the most well established route, differences arising for individual compounds only in the manner of preparation of the group IV halide, and the transition metal anion and the conditions for the reaction. Most anions of Mn and Co are prepared by an alkali metal amalgam reduction of the metal carbonyls, but $Fe(CO)_4^{2-}$ is most conveniently prepared using metal-ammonia solution.

1.2 Reaction of the transition metal halide with the group IV anion :

e.g. (170) $H_3SiK + BrFe(CO)_2Cp \longrightarrow H_3SiFe(CO)_2Cp + KBr$

Elimination of this sort is rare.

(2) Reaction of a Group IV Hydride with a Metal Carbonyl:

e.g. (179,204) $Ph_2GeH_2 + Co_2(CO)_8 \longrightarrow Ph_3GeCo_2(CO)_7 + CO + H_2$

In many instances, although (2) is an alternative route to (1), the yields obtained are usually lower and these reactions often produce polynuclear complexes (205). This reaction can be specific: for example, in the synthesis of the first known Ge-Mn bonded species between GeH_4 and $HMn(CO)_5$, the only product was $H_2Ge\,[Mn(CO)_5]_2$ with no mono- or tri-substituted derivatives formed (159).

(3) Oxidative Reactions:

3.1 Oxidative addition reactions

e.g. (188) $H_3M'X + trans\text{-}(Et_3P)_2PtI_2 \longrightarrow (M'H_2X)(H)PtI_2(PEt_3)_2$

(M' = Si, Ge; X = Cl, I)

In these reactions, it is usually the transition metal that is oxidised. Oxidative reactions are often followed by elimination (3.2) and are commonly found for group VII and VIII transition metals.

3.2 Oxidative addition with elimination

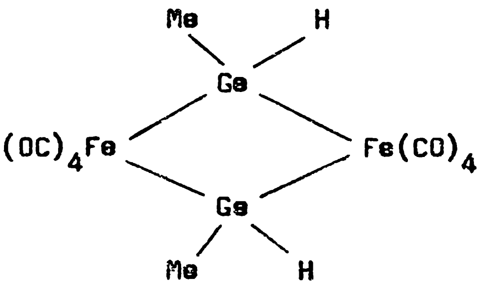
e.g. (196) $H_3M'X + trans\text{-}XPt(PEt_3)_2H \longrightarrow trans\text{-}XPt(PEt_3)_2\text{-}M'H_2X + H_2$

(M' = Si, Ge;

X = F, Cl, Br, I)

(4) Self-Reaction or Condensation (176,177):

e.g. $2(MeGeH_2)_2Fe(CO)_4 \longrightarrow$



$+ 2\ MeGeH_3$

Some compounds, particularly those of iron, tend to self-condense, forming thermodynamically more stable cyclic compounds. This tendency seems to increase with the number of methyl groups on the parent molecule, and is always accompanied by an elimination process. Condensation of $(Me_3Sn)_2Fe(CO)_4$ with elimination of Me_4Sn has also been reported (94,205).

(5) Insertion of Divalent Germanium or Tin Compounds

e.g. (180) $GeI_2 + [Fe(CO)_2Cp]_2 \longrightarrow I_2Ge\ [Fe(CO)_2Cp]_2$

This type of reaction proceeds more readily in metal carbonyls with bridging CO's. The halide produced can then be reduced to the hydrides. $Cl_2Sn\ [Fe(CO)_2Cp]_2$ (206) and $Cl_2Sn\ [Co(CO)_4]_2$ (207) have also been produced in the same manner.

1.4.2 The Nature of the M'-M Bond

Like the M'-M' bond, this metal-metal bond has also been the subject of a great deal of work and speculation, but its true nature still remains unclear. Attempts mainly by physical and spectroscopic methods have been made to correlate bond length, bond strength, force constants and the substituent effects on both the group IV metal and also on the transition metal, but results by different workers have often been contradictory.

X-ray studies (208) often show a reduction from the calculated M'-M bond lengths, obtained as a sum of the radii of the two metals, but such predictions fail to consider many uncertainties. For example, the observed Sn-Mn bond length in $R_3SnMn(CO)_5$ (R = Me,Ph) (209,210) is 2.67 Å whereas the sum of the metallic radii of tetrahedral tin and octahedral manganese is 2.77 Å. There is as yet no one set of values for the radii of the transition metals that is generally accepted so caution must be exercised when interpreting this reduction in bond length. Table 1.6 shows the metal-metal bond lengths of a section of compounds.

Substitution on M with a good π - acceptor ligand has been observed to shorten the M'-M bond. Replacement of a CO in $R_3SnMn(CO)_5$ by PPh_3 shortens the Sn-Mn bond by about 2%. Substitution on M' with a strongly electronegative ligand causes shortening of the Si-Co bond in the order $H_3SiCo(CO)_4$ (225), $Cl_3SiCo(CO)_4$ (226) to $F_3SiCo(CO)_4$ (227) showing σ -contribution effects (see Table 1.6). Thus the metal-metal bond has been discussed in the literature in terms of:

a) a σ-component and

b) a π-donation component from the transition metal to the group IV metal, and

c) an electrostatic component (i.e. the effects of changes in M'-M bond polarity.

π-donation is thought to derive from overlap of the filled d-orbitals of the transition metal with the vacant d-orbital of the group IV metal. Evidence (228) has also been proposed in favour of an "across-space" $(p \longrightarrow d)\pi$ interaction between equatorial CO groups and the group IV element in $X_3SiCo(CO)_4$ (X = F,Cl). This intramolecular interaction gained some support from the fact that the equatorial carbonyl groups are in fact bent towards the silicon substituents (226,227).

Table 1.6 Examples of M'–M Bond Lengths

Compound	Observed length (Å)	Reference
$Ph_3SiZr(Cl)Cp_2$	2.81	211
$Me_3SiMn(CO)_5$	2.50	212
$Me_3GeMn(CO)_5$	2.60	213
$Ph_3GeMn(CO)_5$	2.54	214
$Br_3GeMn(CO)_5$	2.44	215
$Me_3SnMn(CO)_5$	2.67	209
$Ph_3SnMn(CO)_5$	2.67	210
$Ph_2Sn\ [Mn(CO)_5]_2$	2.70	216
$Ph_3SnMn(CO)_5(Ph_3P)$	2.62	217
$ClSn\ [Mn(CO)_5]_3$	2.74	218
$Cl_3SnMn(CO)_5$	2.67	219
$Me_3GeRe(CO)_5$	2.69	213
$Me_3SnRe(CO)_5$	2.74	213
$(Cl_3Si)_2Fe(H)(CO)Cp$	2.25	220
$Cl_2Ge\ [Fe(CO)_2Cp]_2$	2.36	221
$Ph_3SnFe(CO)_2Cp$	2.54	222
$Cl_3SnFe(CO)_2Cp$	2.47	223
$Me_2Sn\ [Fe(CO)_2Cp]_2$	2.60	218
$Cl_2Sn\ [Fe(CO)_2Cp]_2$	2.49	224
$Sn\ [Fe(CO)_4]_4$	2.54	205
$H_3SiCo(CO)_4$	2.38	225
$Cl_3SiCo(CO)_4$	2.25	226
$F_3SiCo(CO)_4$	2.23	227

Vibrational spectroscopy has been commonly used to study the M'–M bond. Table 1.7(a) shows the observed metal–metal stretching frequencies for a selection of compounds together with the force constants obtained assuming simple models. The M'–Co bond in $X_3M'Co(CO)_4$ (M' = Si, Ge, Sn; X = F, Cl, Br, I) has been subjected to rigorous investigations by Risen (229,230,231) and Van den Berg (232,233) using valence force field calculations (see Table 1.7(b)), but still there is considerable discrepancy between results obtained. Van den Berg interprets the bonding forces in terms of a bonding scheme in which the metal–ligand backbonding proves to be the most important contributor. The metal–metal force constant decreases in the series F >Cl >Br = H,D> I for a particular metal. For a specific ligand X, the sequence is Ge > Si > Sn.

Attempts have also been made to use carbonyl modes to derive information about M'–M bonding, by adopting the Cotton–Kraihansel approximation (239). For systems where there is likelihood of 'π-bonding contributions from ligands other than carbon monoxide in substituted systems, Graham (240) has introduced $\Delta\sigma$ and $\Delta\pi$ parameters, derived from carbonyl stretching force constants which indicate the relative σ - donor/ π-acceptor capacities of ligands on the transition metal other than CO.

Surprisingly, very little work has been reported on M'–M bonding energies. However, recently mass spectroscopy is increasingly being used to probe the metal–metal bond strength. Lappert (241), Stobart (234,242,243) and Spalding (244) have derived bond dissociation energies from appearance potentials obtained by

Table 1.7 Metal-Metal Stretching Frequencies (cm^{-1}) and Force Constants (mdyn. $\mathring{A}^{-1}$)

a) Simple Model Calculations

Compound	ν obs.M'–M	$f_{M'M}$(DA)(a)	$f_{M'M}$(PDA)(b)	Ref.
$Me_3SiMn(CO)_5$	297	0.97	3.24	234
$H_3GeMn(CO)_5$	219	0.88	1.54	235
$MeGeH_2Mn(CO)_5$	220	0.9	1.7	163
$Me_2GeHMn(CO)_5$	200	0.7	1.6	163
$Me_3GeMn(CO)_5$	194	0.69	1.63	234
$Cl_3SnMn(CO)_5$	198		1.09	236
$Me_3GeRe(CO)_5$	165		0.68	236
$Me_3SnRe(CO)_5$	147		0.85	236
$H_3Ge(H)Fe(CO)_4$	226	0.95	1.57	235
$H_3GeCo(CO)_4$	228	1.0	1.6	163
$Me_3GeCo(CO)_4$	192	0.71	1.51	237
$Et_3GeCo(CO)_4$	188	0.69	1.71	237
$Cl_3GeCo(CO)_4$	243	1.1	3.0	163
$Br_3GeCo(CO)_4$	200	0.8	2.6	163
$I_3GeCo(CO)_4$	160	0.5	1.9	163
$Me_3SnCo(CO)_4$	177	0.73	1.54	237
$(Me)_2ClSnCo(CO)_4$	185	0.78	1.77	238
$MeCl_2SnCo(CO)_4$	197	0.89	2.11	238
$Cl_3SnCo(CO)_4$	203	0.94	2.34	238

Notes: (a) Assumes a diatomic (DA) model taking into account only masses of the two metal atoms.

(b) Assumes the so-called pseudodiatomic (PDA) model, uses for the effective mass of each pseudoatom the sum of that of the metal atom plus those of the attached ligands.

b) Valence Force Field Calculations

Compound	ν exp.	νcalc.	$f_{M'M}$	Ref.
$Cl_3SiFe(CO)_4^-$	307	312	1.35	233
$H_3SiCo(CO)_4$	315	310	1.50	233
$F_3SiCo(CO)_4$	245	234	2.00	233
$Cl_3SiCo(CO)_4$	309	310	1.32	230
$Cl_3SiCo(CO)_4$	308	309	1.45	232
$Cl_3GeFe(CO)_4^-$	254	254	1.29	229
$Cl_3GeCo(CO)_4$	240	240	1.05	230
$Br_3GeCo(CO)_4$	200	200	0.96	231
$I_3GeCo(CO)_4$	161	161	0.52	231
$H_3GeCo(CO)_4$	223	222	1.30	232
$F_3GeCo(CO)_4$	222	218	1.70	232
$Cl_3GeCo(CO)_4$	242	244	1.52	232
$Br_3GeCo(CO)_4$	199	203	1.30	232
$I_3GeCo(CO)_4$	161	161	0.85	232
$Cl_3SnFe(CO)_4^-$	211	211	1.36	229
$Br_3SnFe(CO)_4^-$	185	185	1.10	229
$Cl_3SnCo(CO)_4$	204	205	1.23	230
$Br_3SnCo(CO)_4$	182	182	1.05	231
$I_3SnCo(CO)_4$	156	156	0.64	231
$Cl_3SnCo(CO)_4$	205	201	1.30	232
$Br_3SnCo(CO)_4$	186	188	1.20	232
$I_3SnCo(CO)_4$	158	158	0.85	232

mass spectrometry and a sample of these values is given in Table 1.8. It is quickly noticed that studies have mainly been on $X_3M'ML_x$ compounds. This is because the appearance potentials of $M'X_3^+$ ions, on which the dissociation energies are based, are more easily obtained than any other ion types in mass spectroscopic fragmentation. Attempts were also made to correlate these bond dissociation energies to the ion abundances of species with the M'–M bond still intact, and to the bond lengths. Although in many instances the ion-abundances offer good supporting evidence for conclusions reached for the dissociation energies, the correlations are not good enough (234,241,243). However, good comparisons (244) were observed between bond dissociation energies obtained for Sn–Mn and Sn–Fe bonded compounds and previously determined metal–metal bond lengths (see Tables 1.8 and 1.6).

Mossbauer Studies (245,246) on tin and iron compounds, ^{55}Mn nmr (247) and ^{59}Co nqr (248) have all been carried out, and the results were interpreted as indicating some π-bonding in these compounds. Photoelectron spectral studies on silyl and germyl derivatives of Mn, Re and Co (249) provide evidence for the absence of any π-interaction between the transition-metal d-orbitals and group IV ligands.

Spectroscopic and chemical techniques continue to be used to probe the M'–M bond as many points about its nature remain unresolved. More recent workers, however, have chosen to explain the metal–metal bond more in terms of a σ-bond with perhaps a small π-component. It is most generally accepted at present, however, that π-bonding is relatively weak.

Table 1.8 M'–M Bond Dissociation Energies and Ion Abundance of M'–M Bonded Species from Mass Spectrometry

Compound	D(M'–M) (eV)	Ion Abundance, M'–M Bonded Species. (%)	Ref.
$Me_3GeCr(CO)_3Cp$	2.03	16	241
$Me_3GeMo(CO)_3Cp$	2.60	34	241
$Me_3GeW(CO)_3Cp$	2.81	57	241
$Me_3SnCr(CO)_3Cp$	2.32	22	241
$Me_3SnMo(CO)_3Cp$	3.08	53	241
$Me_3SnW(CO)_3Cp$	3.28	80	241
$Me_3SiMn(CO)_5$	2.64	37	234
$Me_3GeMn(CO)_5$	2.40	52	234
$Me_3SnMn(CO)_5$	2.51	59	234
$Me_3SnMn(CO)_5$	2.04	-	244
$Ph_3SnMn(CO)_5$	2.09	-	244
$Me_2SnClMn(CO)_5$	2.24	-	244
$Me_3SiRe(CO)_5$	3.1	76	243
$Me_3GeRe(CO)_5$	3.2	97	243
$Me_3SnRe(CO)_5$	3.7	95	243
$Me_3SiFe(CO)_2Cp$	1.97	-	244
$Me_3SiFe(CO)(PPh_3)Cp$	2.23	-	244
$Me_3SnFe(CO)_2Cp$	2.30	-	244
$Ph_3SnFe(CO)_2Cp$	2.58	-	244
$Cl_3SnFe(CO)_2Cp$	3.06	-	244
$Me_3SiCo(CO)_4$	2.4	50	243
$Me_3GeCo(CO)_4$	3.2	66	243
$Me_3SnCo(CO)_4$	2.8	66	243

1.4.3 Reactions

Whereas group IV–cobalt compounds are seen to undergo mainly metal-metal cleavage reactions and group IV–manganese compounds mainly substitution reactions, most reactions of the iron complexes usually involve both cleavage and substitution, followed by a self-reaction.

a) Cleavage reactions.

The metal-metal bonds in $SiH_3Co(CO)_4$ (200) and $GeH_3Co(CO)_4$ (183) are susceptible to scission by both hydrogen halides, HX (X = F, Cl, Br) and mercuric halides HgX_2 (X = Cl, Br, I):

e.g. $GeH_3Co(CO)_4 + HCl \longrightarrow GeH_3Cl + HCo(CO)_4$ (183)

and $2SiH_3Co(CO)_4 + HgX_2 \longrightarrow 2SiH_3X$ (X = Cl, Br, I)

$+ Hg\,[Co(CO)_4]_2$ (200)

The intermediate $XHg\,[Co(CO)_4]$ was also found.

Bromine cleaves the Si–Co bond in $SiH_3Co(CO)_4$ (199,200) but with $MeGeH_2Mn(CO)_5$ both cleavage and substitution are seen (141),

$MeGeH_2Mn(CO)_5 + Br_2 \longrightarrow MeGeBr_3 + MeGeBr_2Mn(CO)_5$

HCl has also been reported to cleave the Si–V bond in $SiH_3V(CO)_6$ (151),

$SiH_3V(CO)_6 + HCl \longrightarrow SiH_3Cl + V(CO)_6 + \frac{1}{2}H_2$.

Ammonia cleaves the Si–metal bond (156). In the manganese case, the products are clear cut,

$2SiH_3Mn(CO)_5 + NH_3 \longrightarrow 2HMn(CO)_5 + (SiH_3)_2NH$

CO does not insert into either Si–Mn or Si–Co bonds in $SiH_3Mn(CO)_5$ (157) and $SiH_3Co(CO)_4$ (200). SO_2, however, is seen to attack the Si–M (M = Mn, Co) bonds (157,200) to give evidence of Si–O–Si species while insertion (141) of SO_2 into $GeH_3Mn(CO)_5$ has been indicated,

$$GeH_3Mn(CO)_5 + SO_2 \longrightarrow GeH_3.SO_2.Mn(CO)_5$$

b) Substitution reactions

Silyl–manganese (157) and germyl–manganese (162) compounds undergo substitution with the hydrogen halides to give a mixture of halo–substituted products:

$$M'H_3Mn(CO)_5 + xHCl \xrightarrow{\Delta} M'H_{3-x}Cl_xMn(CO)_5 + xH_2$$

$MeGeH_2Mn(CO)_5$ (141) yielded only $MeGeCl_2Mn(CO)_5$.

With mercuric halides (141) similar results were obtained with $GeH_3Mn(CO)_5$ and $MeGeH_2Mn(CO)_5$,

$$GeH_3Mn(CO)_5 + HgI_2 \longrightarrow GeH_{3-x}I_xMn(CO)_5$$

while $MeGeH_2Mn(CO)_5$ gave only $MeGeCl_2Mn(CO)_5$ with $HgCl_2$. It is interesting to note that the $MeGeH_2Mn(CO)_5$ tends to give the fully substituted product with hydrogen and mercuric halides, suggesting an activating effect of the methyl group.

Substitution reactions with group IV–tetrahalides as reagents have been extensively studied with the group IV(hydride)–transition metal compounds.

$SiCl_4$ has been found to be inert to $(Me_xGeH_{3-x})Mn(CO)_5$, $x = 0, 1$ (141).

$GeCl_4$ reacts with $GeH_3Mn(CO)_5$ (250) to give an equilibrium mixture of the halo–substituted products.

$$GeH_3Mn(CO)_5 + GeCl_4 \longrightarrow GeH_{3-x}Cl_xMn(CO)_5 + GeHCl_3$$

With $MeGeH_2Mn(CO)_5$ (141) under similar conditions there was complete conversion to $MeGeCl_2Mn(CO)_5$.

$SnCl_4$ is more reactive. Although no reaction with group IV(hydride) manganese derivatives has been studied, reactions with other silyl (139,140) and germyl (53,139) derivatives show $SnCl_4$ to be a fast and specific chlorinating reagent.

CCl_4 reacts with $MeGeH_2Mn(CO)_5$ to yield an equilibrium mixture of $MeGeHClMn(CO)_5$ and $MeGeCl_2Mn(CO)_5$, with the latter dominating. $CHCl_3$ and CH_2Cl_2 are also observed (141).

The overall reactions of the group IV-tetrahalides follow the order:

$$C \gg Si < Ge \lll Sn$$

The reversal in reactivity of $M'Cl_4$ when $M' = C$ may possibly be attributable to a different mechanism. Thus, for example, the CCl_4 reactions may proceed <u>via</u> free radical intermediates. The order of reactivities of the other tetrahalides can be rationalised in terms of the relative M'-X bond strengths of the respective halides. These reaction studies are usually complicated by the involvement of the hydride products e.g. $CHCl_3$ and $GeHCl_3$ in further substitutions.

Other reagents used in substitution studies are PX_3 (X = F, Cl) and their reactions with $MeGeH_2Mn(CO)_5$ proceed stepwise to give a mixture of products, $MeGeH_{2-x}X_xMn(CO)_5$ (141), including in the case of PF_3, products from substitution on Mn with CO displacement.

No substitution reactions of Si-H or Ge-H in cobalt derivatives have yet been observed. However, CO substitution of $SiH_3Co(CO)_4$ (200) and $GeH_3Co(CO)_4$ (183) by PPh_3 have been observed, e.g. $SiH_3Co(CO)_4 + PPh_3 \longrightarrow SiH_3Co(CO)_3PPh_3 + CO$

c) Reactions of Fe compounds.

The reactions of group IV(hydride)-iron derivatives are more complicated, as both cleavage and substitution may occur, usually followed by self-reaction.

$(SiH_3)_2Fe(CO)_4$ reacts with HCl with cleavage of the Si-Fe bonds (169),

$$(SiH_3)_2Fe(CO)_4 + 2HCl \longrightarrow 2SiH_3Cl + H_2Fe(CO)_4.$$

However, a similar reaction of $(GeH_3)_2Fe(CO)_4$ with HCl (173,174) or $HgCl_2$ (173) also produced GeH_4. Reaction studies by Mackay and Bonny (174,177) show the reaction to proceed <u>via</u> the routes:

$$(GeH_3)_2Fe(CO)_4 + HCl \longrightarrow H_2 + (GeH_3)(GeH_2Cl)Fe(CO)_4 \quad \ldots (1)$$

$$(GeH_3)(GeH_2Cl)Fe(CO)_4 + HCl \longrightarrow GeH_3Cl + [Fe(CO)_4(H)(GeH_2Cl)] \quad \ldots (2)$$

Also,

$$(GeH_3)(GeH_2Cl)Fe(CO)_4 \longrightarrow GeH_4 + [(GeHCl)Fe(CO)_4]_2 \quad \ldots (3)$$

The reactions of $(MeGeH_2)Fe(CO)_4$ (177) with HX (X = Cl, Br) and $HgCl_2$ were even more complicated with substitution and cleavage occurring stepwise, with elimination of methylchlorogermanes. Condensation products were also observed.

$(GeH_3)_2Fe(CO)_4$ undergoes substitution with both $SiCl_4$ and $SnCl_4$ (174), very slowly with the former:

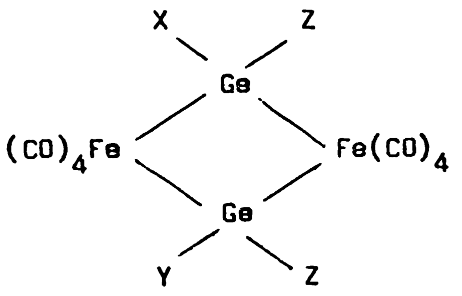
$$(GeH_3)_2Fe(CO)_4 + SiCl_4 \longrightarrow GeH_3(GeH_2Cl)Fe(CO)_4 + SiHCl_3$$

There is also simple polychlorination with $SnCl_4$:

$$(GeH_3)_2Fe(CO)_4 + 2SnCl_4 \longrightarrow (GeH_2Cl)_2Fe(CO)_4 + 2SnCl_2 + 2HCl.$$

Reaction with $SnCl_4$ is complicated by the HCl produced by initial substitution, as seen earlier. Self-reaction from the chloro-substituted products results in the formation of cyclised products,

e.g. $2(GeHYZ)_2Fe(CO)_4 \longrightarrow$ I



I

X = H, Y = H, Z = Cl

X = H, Y = Cl, Z = Cl

X = Cl, Y = Cl, Z = Cl

Reactions of $(MeGeH_2)_2Fe(CO)_4$ with CCl_4, SiX_4 (X = Cl, Br) and $SnCl_4$ have also been studied (177). Polysubstitutions are even more extensive than in $(GeH_3)_2Fe(CO)_4$. The reactions of $(GeH_3)_2Fe(CO)_4$ are summarised in Fig. 1.3.

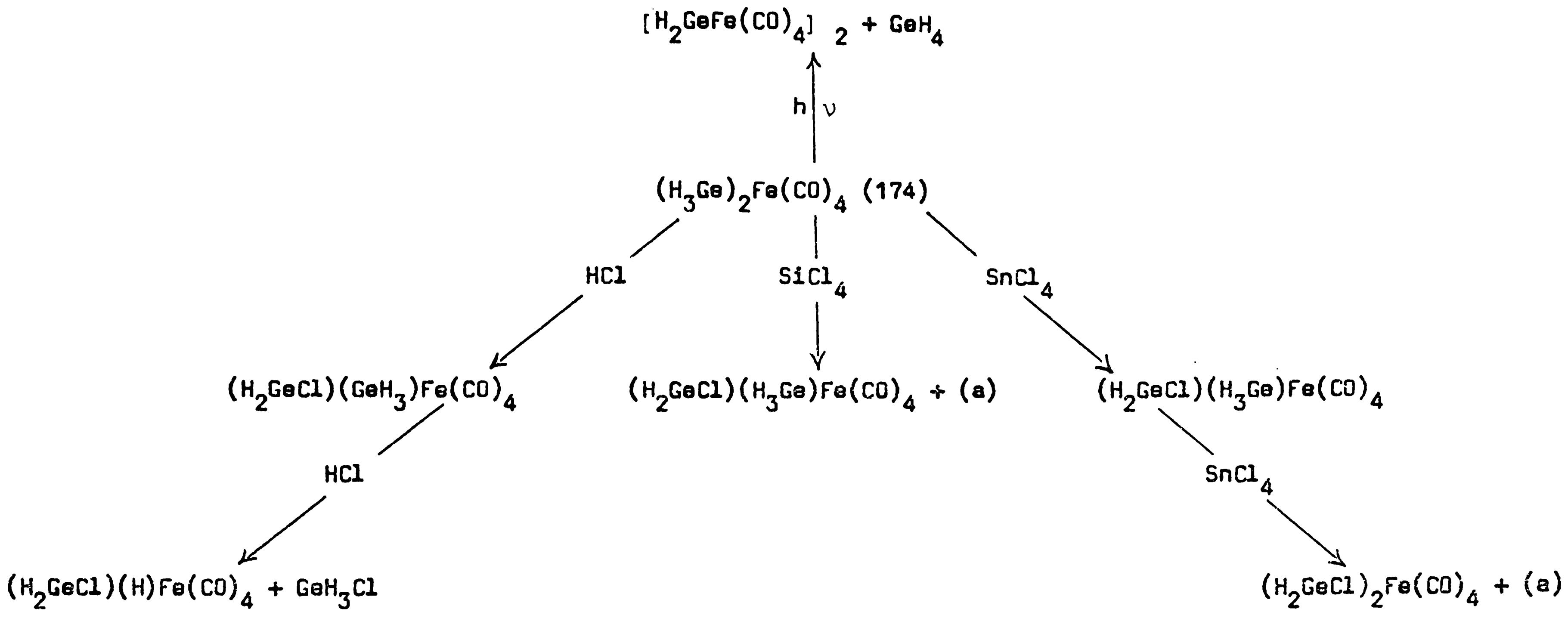
d) Adduct formation

$M'H_3M(CO)_x$ (M' = Si, Ge; M = Mn, Co) have all been observed to form adducts with R_3N (R = Me, Et) in a 1:2 ratio,

e.g. $SiH_3Co(CO)_4 + 2NMe_3 \longrightarrow SiH_3Co(CO)_4.2NMe_3$ (158)

$(SiH_3)_2Fe(CO)_4$ also forms an adduct with NMe_3 in a 1:2 ratio, not 1:4. Cleavage reaction with HCl shows the adduct complex to be the symmetrical one, $(SiH_3.NMe_3)_2Fe(CO)_4$.

Fig. 1.3 Reactions of $(GeH_3)_2Fe(CO)_4$



(a) Higher molecular weight compounds, $[(XZGe)(YZGe)Fe(CO)_4]_2$

X = H, Y = H, Z = Cl

X = H, Y = Cl, Z = Cl

X = Cl, Y = Cl, Z = Cl

e) Transition-metal exchange.

It has recently been established by Mackay et al. (198) that one metal carbonyl anion is capable of displacing another on a germane in the order

$$Co \longrightarrow Fe \longrightarrow Mn$$

Thus, using equimolar quantities,

$$CH_3GeH_2Co(CO)_4 + Mn(CO)_5^- \longrightarrow CH_3GeH_2Mn(CO)_5 + Co(CO)_4^-$$

and

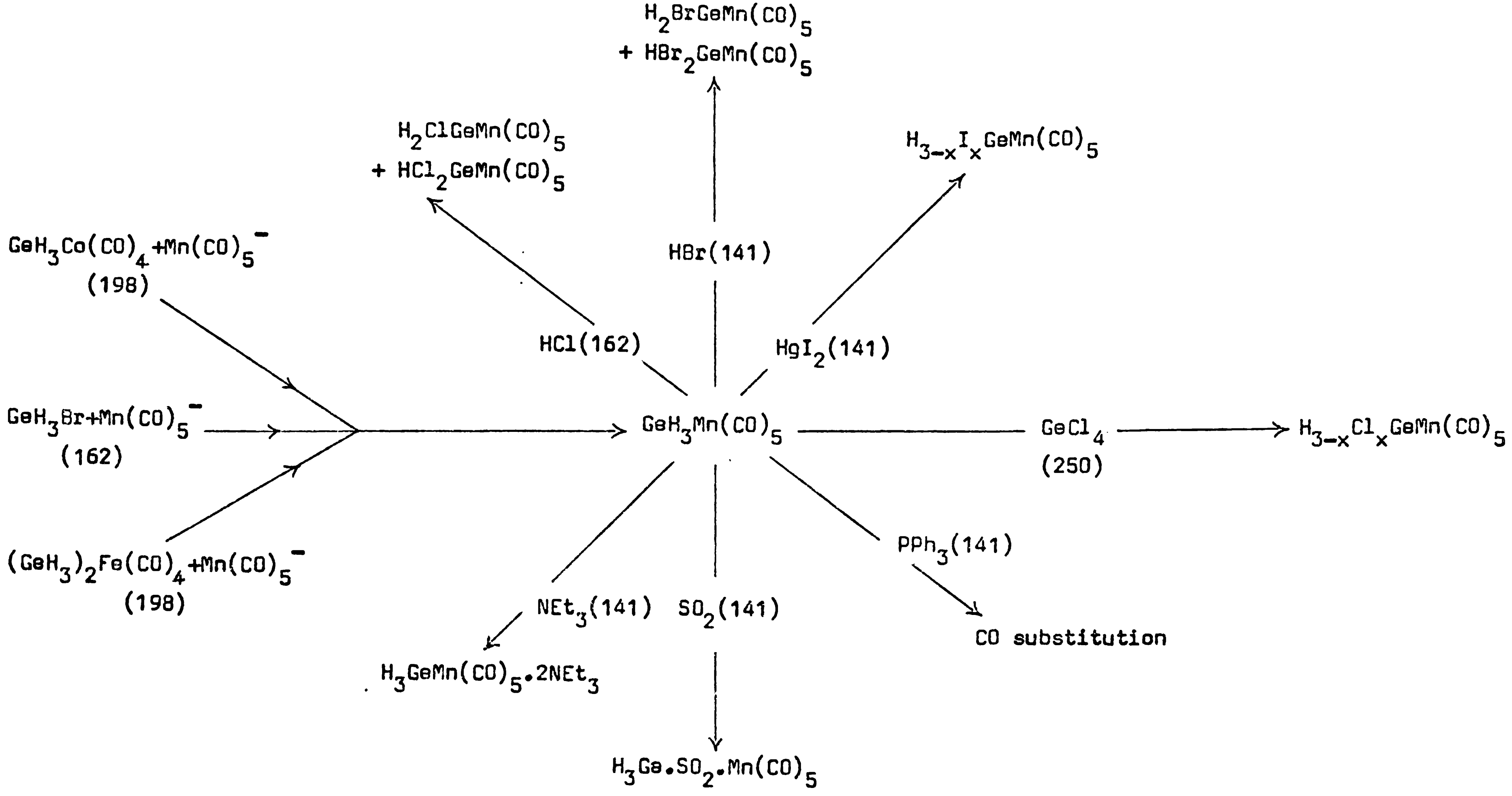
$$Mn(CO)_5^- + (GeH_3)_2Fe(CO)_4 \longrightarrow GeH_3Mn(CO)_5 + GeH_3Fe(CO)_4^-$$

Addition of HCl to the residue in the latter case yielded some $HMn(CO)_5$ together with $(GeH_3)HFe(CO)_4$ but little $H_2Fe(CO)_4$.

Preliminary studies indicate $GeH_3Co(CO)_4$ exchanges with $Fe(CO)_4^{2-}$ to yield $(GeH_3)_2Fe(CO)_4$.

Fig. 1.4 summarises the reactions of $GeH_3Mn(CO)_5$

Fig. 1.4 The Reactions of $GeH_3Mn(CO)_5$



1.5 The Catenated Group IV-Transition Metal Compounds

The first attempt at preparing a transition metal complex containing a catenated group IV ligand was by MacDiarmid (251,252, quoted in Ref.171) in 1969 who found no stable product from the reaction between Me_5Si_2H and $Co_2(CO)_8$. This was attributed to the weakness of the Si-Si bond. However, the manganese complex, $Me_5Si_2Mn(CO)_5$ and its rhenium analogue were isolated from a similar reaction with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (252). Since then, especially in the last few years, a number of such compounds containing a group IV-group IV metal bond have been prepared thus establishing a class of its own. These compounds are listed in Table 1.9. Before work on this thesis began, all but three were fully substituted with organic groups. The only hydrides reported were $Ge_2H_5Mn(CO)_5$ (135) and the classic $H_2Sn_2[Mn(CO)_5]_4$ (253,254). The partially methylated $GeH_3Me_2GeMn(CO)_5$ has also been prepared as part of the characterisation of $Me_2GeClGeH_3$ (53). Contradicting predictions (251,252) about the low stability of such bulky compounds, particularly the hydrides, these compounds show little tendency to decompose. The synthesis of the three hydride type complexes stimulated the author's interest into the field and has led to the preparation and characterisation of a series of polygermanium (hydride)-transition metal carbonyls.

The methods of preparation of the catenated group IV-transition metal compounds are essentially those of the mono-group IV-transition metal derivatives described earlier in section 1.4.1.

Table 1.9 Catenated Group IV-Transition Metal Compounds

	Preparation(a)	Characterisation(d)	Ref.
$Me_3SiMe_2SiM(CO)_3Cp$ M = Cr, Mo, W	1.1	IR,NMR,MS,EA,MW,Rx	255,256
$XSiMe_2SiMe_2M(CO)_3Cp$ M = Cr, Mo, W; X = F, Cl, Br	1.1	IR,'H NMR, ^{19}F NMR, MS,EA,MW,Rx	255,256
$Me_3SiMe_2SiMn(CO)_5$	2	IR, NMR	252
$(Me_3Si)_nMe_{3-n}SiMn(CO)_5$ n = 1,2,3	1.1,2	IR,NMR,MS,EA	257,258
$(Me_3Si)_nMe_{3-n}SiMn(CO)_4PPh,$ n = 1,2,3	1.1,2	IR,NMR,MS,EA	257,258
$Me_3SiMe_2SiRe(CO)_5$	2	IR,NMR	252
$Me_3Si(Me_2Si)_nFe(CO)_2Cp$ n = 1,2,3	1.1	IR,NMR,MS,EA	171
$(Me_2Si)_n\ [Fe(CO)_2Cp]_2$ n = 2,3	1.1	IR,NMR,MS,EA	171
$(Me_3Si)_nMe_{3-n}SiFe(CO)_2Cp$ n = 1,2,3	1.1	IR,NMR,MS,EA	257
$XSiMe_2SiMe_2Fe(CO)_2Cp$ X = F, Cl, Br	1.1	IR,'H NMR, ^{19}F NMR, MS,EA,MW,Rx	255,256
$[(C_6H_5)_3P]_2\overline{Pt\ [Si(C_6H_5)_2]_3Si}(C_6H_5)_2$	3.2	IR,UV,EA,MW,Rx	259
$1,2\text{-}Ph_2Ge_2\ [Mn(CO)_5]_4$	1.1	EA	260
$1,2\text{-}Ge_2Cl_4\ [Mn(CO)_5]_2$	1.1	EA	260
$[(GeMe_2)_2Fe(CO)_4]_2$	1.1	IR,NMR,MS,EA,Rx	261
$Me_2Ge\ [Me_2GeFe(CO)_4]_2$	1.1	IR,NMR,MS,EA,Rx	261
$Ph_3Sn(Ph_2Ge)Mn(CO)_5$	(b)	IR,NMR,EA,MW	164
$Sn_2\ [Re(CO)_5]_6$	1.1	EA	262
$Me_9Sn_4\ [P(OPh_3]_2FeCp$	1.2	IR,'H NMR,^{13}C NMR, Rx.	263

Table 1.9 (cont.)

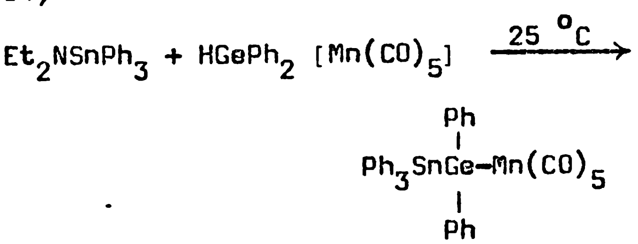
	Preparation(a)	Characterisation(d)	Ref.
Hydrides			
$GeH_3GeH_2Mn(CO)_5$	1.1	IR,R,NMR,MS,Rx	135,53 this work
$GeH_3GeMe_2Mn(CO)_5$	1.1	IR,R,NMR,MS	53
$(GeH_3)_2GeHMn(CO)_5$	1.1	IR,R,NMR,MS,Rx	this work
$[GeH_2Mn(CO)_5]_2$	1.1	IR,NMR,MS	this work
$GeH_3GeH_2(GeH_3)Fe(CO)_4$	(c)	IR,R,NMR,MS,Rx	this work
$(GeH_3GeH_2)_2Fe(CO)_4$	1.1	IR,R,NMR,MS,Rx	this work
$GeH_3GeH_2Co(CO)_4$	1.1(c)	IR,R,NMR,MS,Rx	this work 264
$[GeH_2Co(CO)_4]_2$	1.1	IR,NMR,MS,Rx	this work
$H_2Sn_2[Mn(CO)_5]_4$	5	IR,MS,XD,EA,MW,Rx	253,254

Notes:

(a) The numbers refer to the various preparative methods described in section 1.4.1

(b) Coupling of a tin amido derivative to a group IV (hydride)-transition metal complex,

e.g. (164)



$$Et_2NSnPh_3 + HGePh_2[Mn(CO)_5] \xrightarrow{25\ ^{o}C} Ph_3Sn\overset{Ph}{\underset{Ph}{Ge}}{-}Mn(CO)_5$$

The tin is coupled to the group IV metal with the elimination of hydrogen. The above example provided the only known mixed group IV metal chain derivative of a transition metal.

Table 1.9 (cont.)

(c) Specific preparative routes found in this work (see text, 264)

(d) IR = Infrared
R = Raman
NMR = Nuclear Magnetic Resonance
MS = Mass Spectroscopy
ME = Mossbauer Effect Studies
XD = X-ray Diffraction studies
UV = Ultra-Violet
EA = Elemental Analysis
MW = Molecular Weight determinations.
Rx = Reaction studies.

1.5.1 The M'–M'–M System

It is evident from Table 1.9 that previous workers preferred the use of the fully organo-substituted catenated group IV metals with a single M'–X (X = halogen), M'–H or M'–other functional group to couple to the transition metals. This is probably because the organic substituents are unreactive and the products formed stable. This will also avoid complications leading to cyclised compounds (see 1.4.3(c)). However, the three hydride-derivatives reported showed remarkable stabilities. The attempted synthesis of Sn $[Mn(CO)_5]_2$ by Noltes (253,254) turned out to give $H_2Sn_2[Mn(CO)_5]_4$ instead, with stable Sn–H and Sn–Sn bonds. In the i.r. spectrum the absorption at 1725 cm^{-1}, is assigned to the Sn–H frequency. The low value of ν(Sn–H), in fact the lowest value so far reported for a tin hydride (265) was interpreted as probably due to the enhanced p-character of the Sn–H bond in the transition metal-tin hydride. The bond length between the two tin atoms (2.89Å) is somewhat greater than that in the cyclic hexamer of diphenyltin (Sn–Sn = 2.78Å) (267) and that in hexaphenyl tin (Sn–Sn = 2.77Å) (100). The tin-manganese distances (2.67 and 2.73Å) are not considerably different from those in $Me_3SnMn(CO)_5$ (Sn–Mn = 2.67Å) (268) and in $Ph_3SnMn(CO)_5$ (Sn–Mn = 2.67Å) (269).

Stobart (135) reported that $Ge_2H_5Mn(CO)_5$ showed no tendency to decompose at room temperature in vacuo or under nitrogen, and in air it reacted only slowly. This behaviour is in marked contrast to that of ethylmanganese carbonyl, $C_2H_5Mn(CO)_5$ (270), which is sensitive to oxidation and decomposes under vacuum even at −10 °C. Methylmanganese carbonyl, $CH_3Mn(CO)_5$ (271), is relatively stable (m.p. 95 ^{o}C). This is easily explained by the β-elimination mechanism (272) in $C_2H_5Mn(CO)_5$ with displacement of ethylene, C_2H_4, which is not available to other group IV elements. In fact, Braterman and Cross (273) have suggested that metal-carbon bonds are in no way qualitatively different from metal-hydrogen, metal-metal, or metal-nitrogen bonds. The vibrational spectrum of $Ge_2H_5Mn(CO)_5$ showed general features similar to those observed for $GeH_3Mn(CO)_5$ (161,162), but two Raman bands were observed in the metal-metal stretching region. These bands were assigned to ν Ge-Ge at 273 cm^{-1} and to ν Ge-Mn at 205 cm^{-1}. In digermane νGe-Ge was found at 268 cm^{-1} and νGe-Mn at 219 cm^{-1} in $GeH_3Mn(CO)_5$ (161,162). The differences in these frequencies and those found for $Ge_2H_5Mn(CO)_5$ were suggested as indicating some interaction between these two modes, thus more accurately described as the symmetric and asymmetric Ge-Ge-Mn stretches.

Interest in the polysilanyl compounds was derived from two sources. The nature of the Si-M bond in transition metal systems has been the subject of continued speculation, particularly with respect to the involvement of d-orbitals on silicon in (d-d)π interactions and also the possibility of bonding interactions between carbonyl ligands and the metal bound silicon atom (208). There is evidence from other organosilicon systems to suggest that electron delocalisation can then occur through the d-orbitals of catenated silicon atoms (274,276) and such a process could enhance (d-d)π bonding in polysilanyl metal systems. Furthermore, the steric requirements of the bulky ligands could markedly affect both the geometry and the bonding in Si-M systems. However, King and Malisch found no correlation between the permethylsilanyl chain length and the ν(CO) stretching frequencies, even when a highly electronegative element e.g. F, Cl or Br were substituted on the β-Si, thus showing there to be very little ligand effect on the electron distribution of the metal carbonyl group. Using the Graham $\Delta\sigma$ and $\Delta\pi$ parameters (240), derived from the carbonyl stretching force constants, Nicholson and Simpson (257) found the trends with the series $(Me_3Si)_nMe_{3-n}SiMn(CO)_5$ were consistent with the supposition of two conflicting effects. Starting from the Me_3Si derivative, they found that there is an initial increase in σ-donor/π-acceptor ability with the first β-silicon substitution ($n = 1$). They explained this effect in terms of electron release by the Me_3Si group and d-orbital availability for delocalised π-bonding. Further substitution ($n = 2,3$), however, reverses this trend as the steric requirements of the polysilyl ligand increase and non-bonded interactions lengthen the Si-Mn bond. The Si-Mn bond in $(Me_3Si)_3SiMn(CO)_5$ has been shown (258) to be significantly longer than that in $Me_3SiMn(CO)_5$.

1.5.2 Reactions

The reactions of this type of compound are less predictable than the previous two classes already discussed. Both the M'-M' and M'-M bonds are available for cleavage. There are also two types of hydrogens available for substitution, those on the α-group IV metal and those on the other group IV atoms.

a) Cleavage reactions

No cleavage reactions of catenated group IV (hydride)-transition metal compounds have yet been reported. However, iodine cleaves the Sn-Sn bond in $CpFe\,[P(OPh)_3]_2Sn\,(SnMe_3)_3$ (277),

$$CpFe\,[P(OPh)_3]_2Sn(SnMe_3)_3 + 3I_2 \longrightarrow CpFe\,[P(OPh)_3]_2SnI_3 + 3Me_3SnI$$

b) Substitution reactions.

Preliminary reaction studies (53) of $GeH_3GeH_2Mn(CO)_5$ with $SnCl_4$ and I_2 have previously been carried out by the author. Reaction with $SnCl_4$ showed substitution mainly on the α-germanium atom,

$$\begin{aligned} GeH_3GeH_2Mn(CO)_5 + SnCl_4 \longrightarrow\ & GeH_3GeHClMn(CO)_5 \quad (78\%) \\ & + GeH_2ClGeHClMn(CO)_5 \quad (14\%) \\ & + GeH_2ClGeH_2Mn(CO)_5 \quad (6\%) \\ & + SnCl_2 + HCl \end{aligned}$$

There was no evidence for the HCl produced in the reaction being reactive. It is interesting to note that no $GeH_3GeCl_2Mn(CO)_5$ was found.

$GeH_3GeH_2Mn(CO)_5$ has also been observed to substitute with I_2,

$$GeH_3GeH_2Mn(CO)_5 + I_2 \longrightarrow GeH_2GeHIMn(CO)_5 + HI$$

Substitution was also at the α-germanium atom, but the HI produced was reactive. Although the exact interpretation of the metal-metal bond cleavage by HI was unclear, two possible schemes were proposed:

i) Ge–Mn and Ge–Ge bond cleavages

$$GeH_3GeHIMn(CO)_5 + HI \xrightarrow{\text{Ge–Mn cleavage}} GeH_3GeHI_2 + HMn(CO)_5$$

and

$$GeH_3GeHIMn(CO)_5 + HI \xrightarrow{\text{Ge–Ge cleavage}} GeH_2IMn(CO)_5 + GeH_3I$$

or

ii) formation of an equilibrium mixture

$$GeH_3GeHIMn(CO)_5 + HI \xrightleftharpoons{\text{Ge–Ge cleavage}} GeH_2IMn(CO)_5 + GeH_3I$$

The presence of Sn–H bonds in $H_2Sn_2\ [Mn(CO)_5]_4$ (253,254) was chemically confirmed by the reactions with CCl_4 and CBr_4,

e.g. $HSn\ [Mn(CO)_5]_2 — [Mn(CO)_5]_2\ SnH + CBr_4$

$$\longrightarrow BrSn\ [Mn(CO)_5]_2 — [Mn(CO)_5]_2\ SnBr$$

The aims of our studies with the polygermanyl (hydride) derivatives are four-fold:

(i) to see if the digermanyl derivatives of Fe and Co were stable enough to be isolated,

(ii) to study the trends and differences in the physical, spectroscopic and reaction properties of the series by varying the transition metal,

(iii) to find whether these properties showed any changes by adding more germyl groups to the α-germanium atom, or, as in the M–M'–M'–M system by the addition of more metal carbonyl groups and

(iv) to see which metal-metal bonds, M'–M' or M'–M are susceptible to cleavage and also which hydrogens – the α-germanium hydrogens or the ones on the GeH_3 group are susceptible to substitution.

CHAPTER 2. GENERAL EXPERIMENTAL DETAILS

2.1 General

Since many of the compounds mentioned in this thesis are volatile and most of them are air-sensitive, they are handled in a conventional multi-purpose vacuum frame fitted with storage bulbs and mercury manometers. The vacuum obtained with a rotary oil pump was usually sufficient for normal manipulations, but if a lower pressure was required, especially for manipulations of the less volatile polygermanyl metal carbonyl derivatives, a mercury diffusion pump was available. Normal greased taps were employed, but teflon taps were used when compounds e.g. the germanes and the germyl-metal carbonyls, appeared to be soluble in the tap grease or when there was a possibility of "streaking" of the greased taps due to the presence of, say, an ether solvent.

Fractional distillation was employed to separate the components of a volatile mixture. The constant low temperatures required for fractional distillations, and in some cases for reactions, were obtained by partially freezing a suitable compound using liquid nitrogen to form a fluid slush; the temperature at the melting point of the compound being maintained as long as solid remained. Some of the more convenient compounds and their melting points are given below:

ice/water/salt	0 °C ⟶ -20 °C
carbon tetrachloride	-22.6 °C
chlorobenzene	-45.2 °C
chloroform	-63.5 °C
ethyl acetate	-82.4 °C
toluene	-95.0 °C
n-propanol	-127 °C

Manipulations with air-sensitive solids or liquids were made in a glove box flushed rigorously with nitrogen. Phosphorus pentoxide was used to dry the atmosphere in the glove box and sodium was used to remove O_2.

2.2 Spectroscopic Techniques

a) Infrared Spectroscopy

Routine spectra were obtained on either a Shimadzu 1R-27G (range 4000 cm^{-1} - 400 cm^{-1}) or a Beckmann 1R-20A (range 4000 cm^{-1} - 250 cm^{-1}), but definitive spectra of new compounds or intermediates were recorded on a high resolution Perkin-Elmer 180 (range 4000 cm^{-1} - 50 cm^{-1}). Gas samples were recorded using 10 cm gas cells or in cases of compounds with low vapour pressures e.g. $Ge_2H_5Co(CO)_4$, a gas cell of 20 cm path length was used. These cells are fitted with 5 cm diameter KBr windows. A similar empty cell was usually placed in the reference beam to balance atmospheric and KBr absorptions. As the vapour pressure of most polygermanyl-transition metal derivatives are too low at room temperature to give a satisfactory spectrum in the gas phase, a solid-film and a solution spectrum were usually recorded instead. A cold cell was used to run a spectrum of a solid-film, frozen on to a KBr window cooled by liquid nitrogen, while a solution cell was used to obtain the solution spectrum, usually using cyclohexane as solvent. Again, similar empty balance cells, in the case of solution cell containing solvent only, were used. Attempts at recording spectra from 400 cm^{-1} - 50 cm^{-1} using high density polythene windows were not satisfactory as metal-metal stretching bands appear only weakly in the far infrared. Strong bands were obtained with Raman spectroscopy.

DCl or polystyrene bands were used to calibrate spectra (278).

b) Raman Spectroscopy

Raman spectra were recorded at the University of Auckland on a J.A.S.C.O. R300 spectrometer using the green line (4880 Å) of an Argon Ion 'Control' Laser operating at 21 mW. The samples were contained in a sealed tube shown in Fig. 2.1 (C) and sampled as described for nmr below. This was very convenient for recording the nmr spectrum of a small amount of the neat sample and then recording the Raman spectrum. This also allowed for an easy check for decomposition after a Raman spectrum had been recorded by repeating the nmr spectrum.

All samples were scanned only in the region of greatest interest i.e. the metal-metal stretching region from 0 cm^{-1} to 500 cm^{-1}. This was because of fairly rapid decomposition, especially of the cobalt compounds in the laser beam, and the strong brown colour of the decomposition product absorbs a considerable amount of energy so that the spectrum obtained deteriorated with time. The 1800 cm^{-1} - 2300 cm^{-1} region of trigermanylpentacarbonylmanganese was also recorded.

The strong plasma absorption at 352 cm^{-1} was used for calibration. It is probably worth making a note here that fluorescent lighting of the room produces a strong absorption at 2178 cm^{-1}, close to the main νCO and νGeH modes between 2000 cm^{-1} to 2100 cm^{-1}.

c) Nuclear Magnetic Resonance Spectroscopy

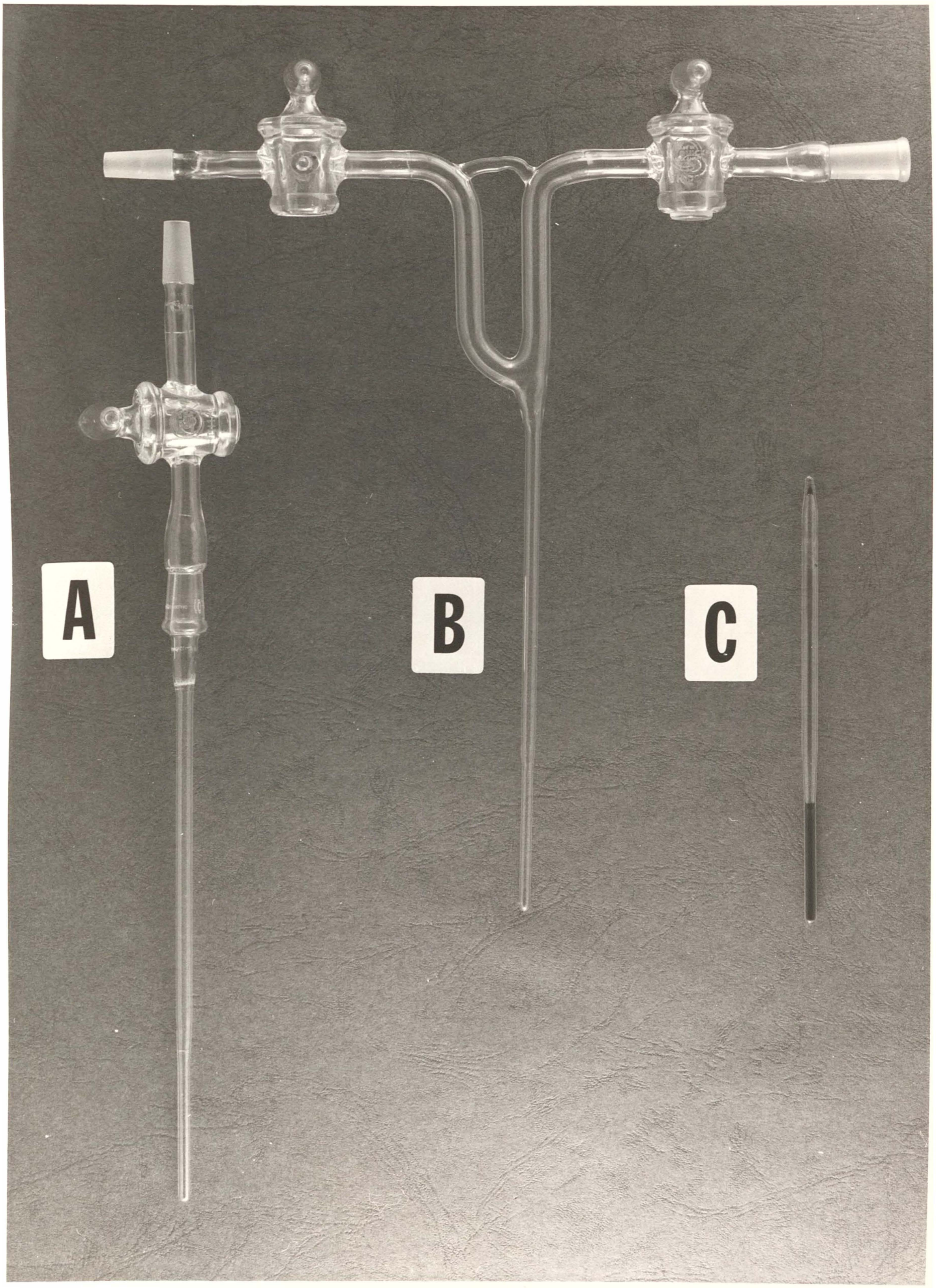
All samples were run in sealed tubes (Fig. 2.1(C)) on a 60 MHz J.E.O.L. C60HL High Resolution nmr instrument. These nmr tubes were usually modified (53) to have a 4 cm taper of smaller bore tubing than the normal nmr tubes. This allowed the spectra of small amounts of samples to be recorded. The normal upper length of the nmr tube allows faster condensation of sample into the tube, but this was usually not good enough with the polygermanyl-metal derivatives. Fig. 2.1(B) shows the type of trap (279) used to condense high molecular weight complexes, which may be opened to the pump to facilitate "dragging". This piece of glassware was also often used for weighing the high molecular weight compounds. The adaptor (Fig. 2.1(A) was used to check the purity of starting intermediates (e.g. GeH_3Br, Ge_2H_5Cl).

As all the derivatives studied in this work are closely related, all samples were recorded as 5-10% solutions in benzene, although in several reactions, deuterobenzene or silicon tetrachloride were used instead to allow examination of signals occurring close to that of benzene. The following benzene chemical shifts (53) were used as the basis for assigning the chemical shifts of samples recorded:

Figure 2.1

Modified Glassware for NMR

(see text for details)


A
B
C

5% TMS in C_6H_6 = 2.883τ

5% C_6H_6 in TMS = 2.830τ

5% TMS + 5% C_6H_6 in CCl_4 = 2.77 τ

Chemical shifts of some starting materials e.g. GeH_4, Ge_2H_6 (280), Ge_3H_8 (54) previously reported in some other solvents were recorded in benzene to provide a basis for comparison. The solvent effect for similar concentrations relative to benzene was measured for several solvents:

C_6H_{12}	- 0.08 ppm
$CDCl_3$	+ 0.06 ppm
$SiCl_4$	+ 0.07

A few measurements of varying concentrations of SiH_3Cl were made to demonstrate concentration effects, relative to external TMS and internal benzene:

5%	5.98τ
70%	5.58τ
100%	5.30τ

Samples used for recording Raman spectra and also materials from nmr reaction tubes were recovered using the apparatus shown in Fig. 2.2 where a description of its operation is also given.

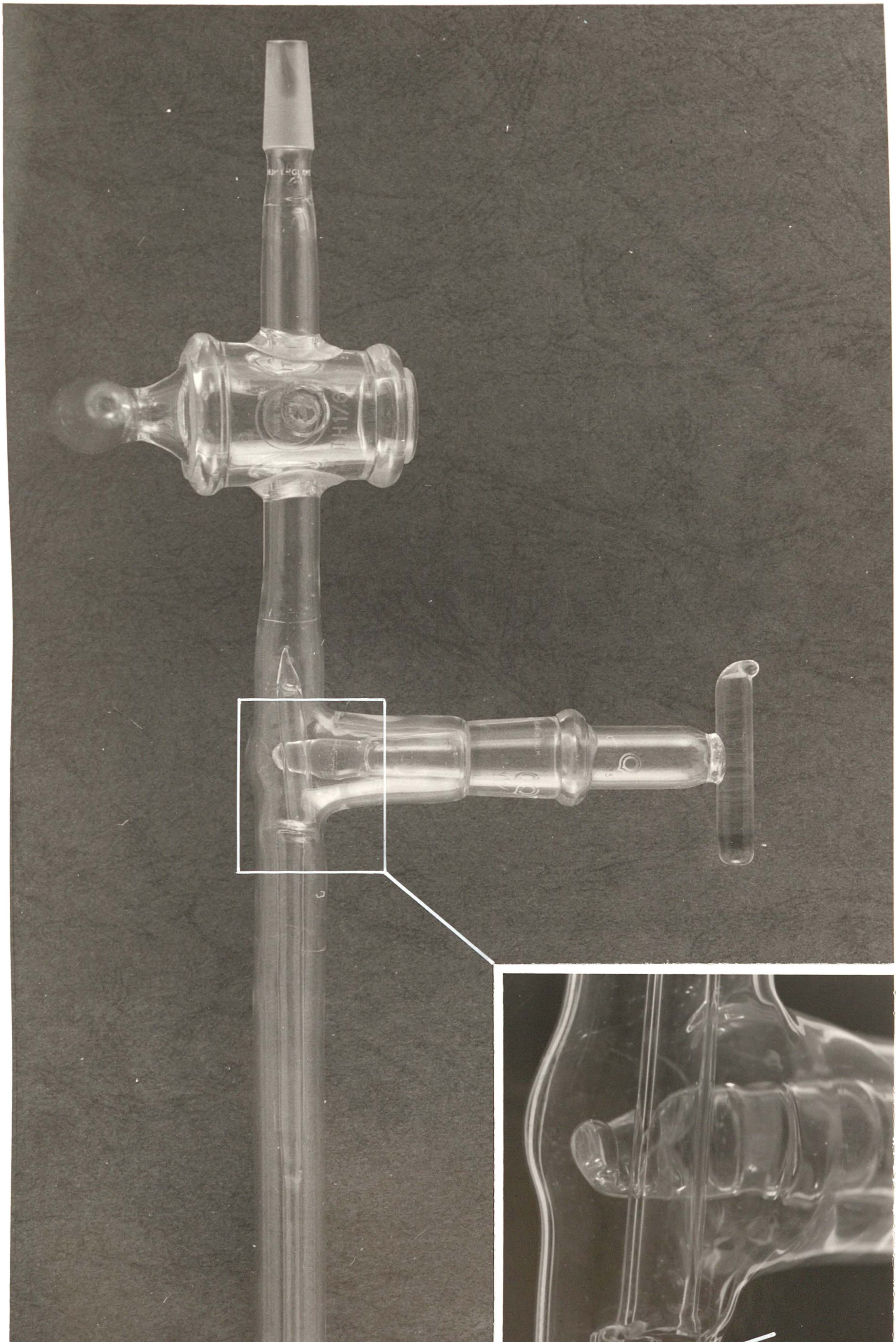


Figure 2.2

Apparatus for Recovery of Materials from NMR Tubes

Inset shows in greater detail the T-junction.

A fine scratch is first made with a glass-knife at about the point of the tube which matches the indentation (arrowed, see figure). The tube was then inserted into the apparatus with point of scratch facing away from the indentation and the system evacuated on the vacuum line. The main tap was then closed and the tube easily broken at point of scratch by turning the second tap which applies a force at top end of tube, a second equal force at bottom end of tube being supplied by the wall of the apparatus about the pivot, which is the indentation. If the tube contains very volatile material or solvent, "splashing" on opening of tube can be avoided by first cooling the material with liquid nitrogen before snapping it open. This was very useful for efficient recovery of the less volatile fraction e.g. the polygermanyl derivatives or decomposition residues which remain in the nmr tube upon removal of solvent or more volatile fraction.

d) Mass Spectroscopy

The spectra were recorded at Ruakura Agricultural Research Centre on a Varian CH5 Spectrometer using conventional gas sampling techniques or the solid insertion probe. As most of the compounds in this work are air-sensitive, solutions or solids were introduced on to the gold cup of the spectrometer probe under the protection provided by an argon-flushed plastic bag which was fitted with plastic gloves for manipulations (279).

The presence of five naturally occurring isotopes of germanium produces characteristic intensity patterns in the mass spectra of compounds containing this element. Glockling et al. (281) have calculated the mass and abundance combinations for the Ge_2, Ge_3 and Ge_4 cases. During these studies further calculations were made using the abundances (282) of Cl, Fe and Si isotopes and the calculated envelopes for a variety of envelopes are reproduced in Fig. 2.3. These mass spectral patterns provided valuable support for parent ion as well as fragment assignments. The intensity patterns seen in Fig. 2.3 are "open" structures. However, in the germanium containing series fragmentation by loss of H gives overlapping patterns so that the envelopes usually appear as "closed" structures. Thus although there are only small differences in the mass spectral patterns of envelopes of species containing the same number of Ge atoms they are a useful aid in identification and calculation of hydrogen ratios.

e) Elemental Analysis

Analyses were carried out by the microanalysis service at the University of Otago.

Figure 2.3

Calculated Mass Spectral Envelope Patterns

Natural abundances (291), %:

Germanium

^{70}Ge	20.52
^{72}Ge	27.43
^{73}Ge	7.76
^{74}Ge	36.54
^{76}Ge	7.76

Chlorine

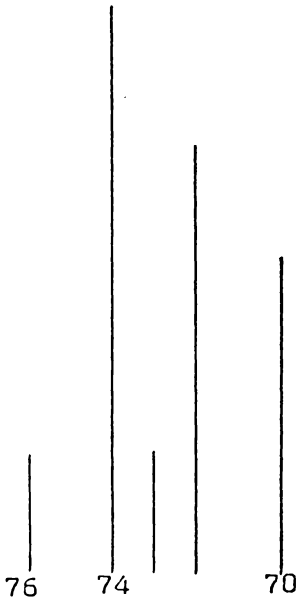
^{35}Cl	75.53
^{37}Cl	24.47

Iron

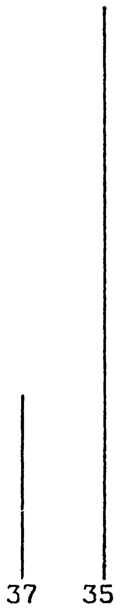
^{54}Fe	5.82
^{56}Fe	91.66
^{57}Fe	2.91
^{58}Fe	0.33

Silicon

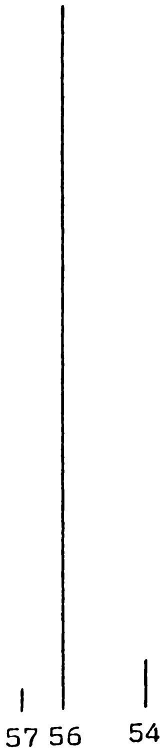
^{28}Si	92.21
^{29}Si	4.70
^{30}Si	3.09



Ge_1

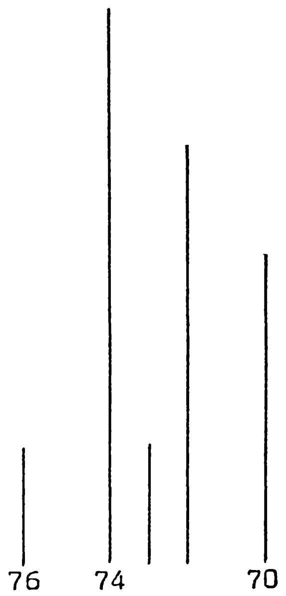


Cl

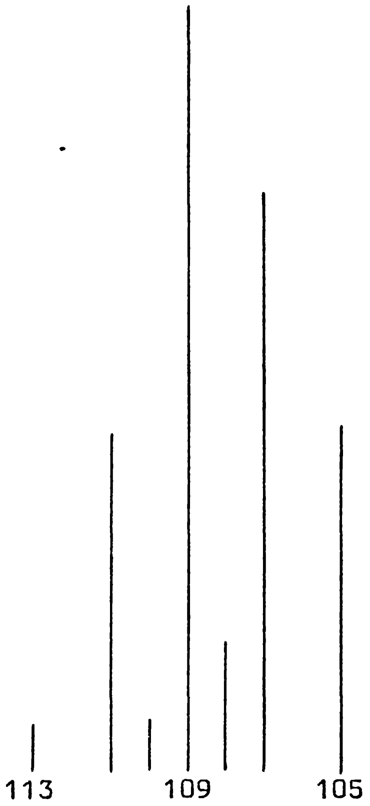


Fe

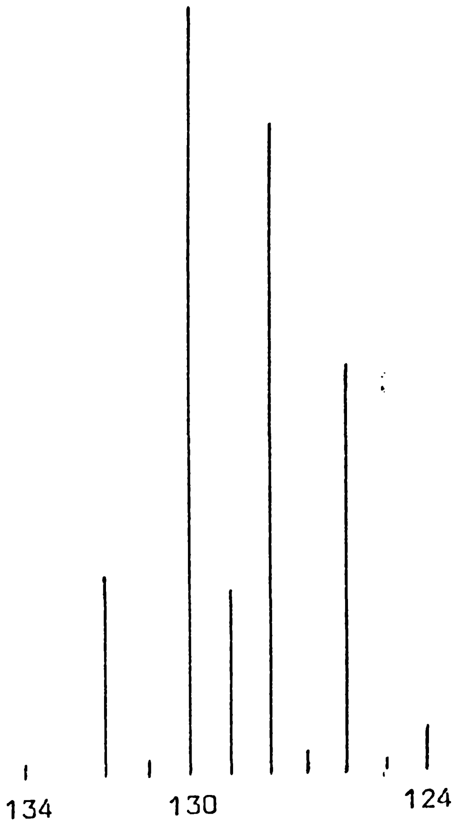
Si



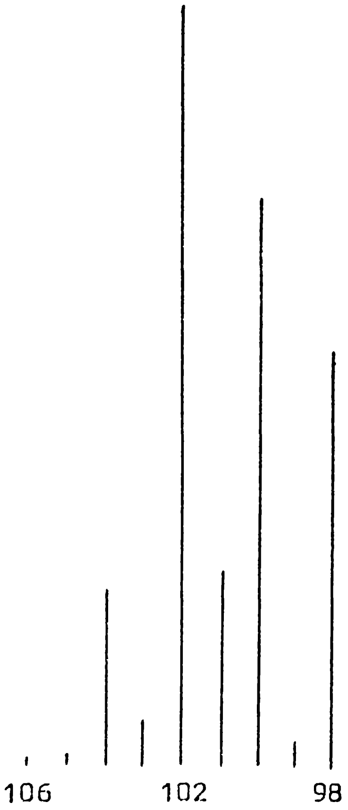
Ge



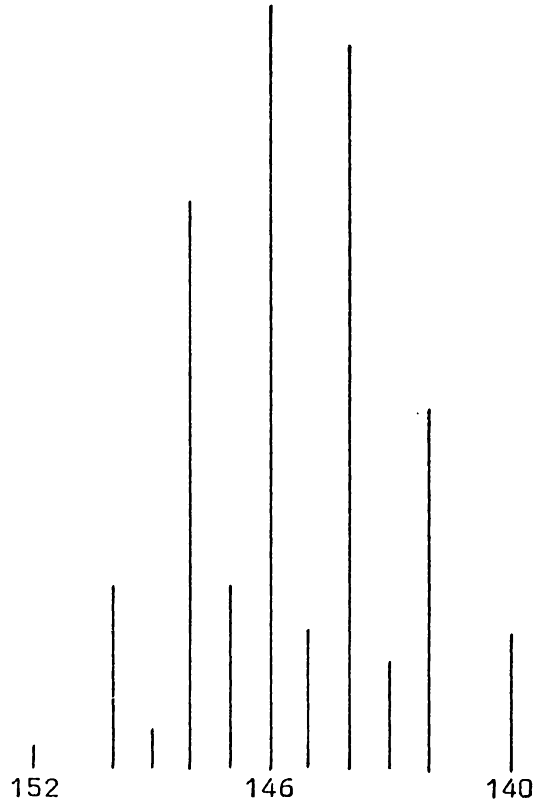
GeCl



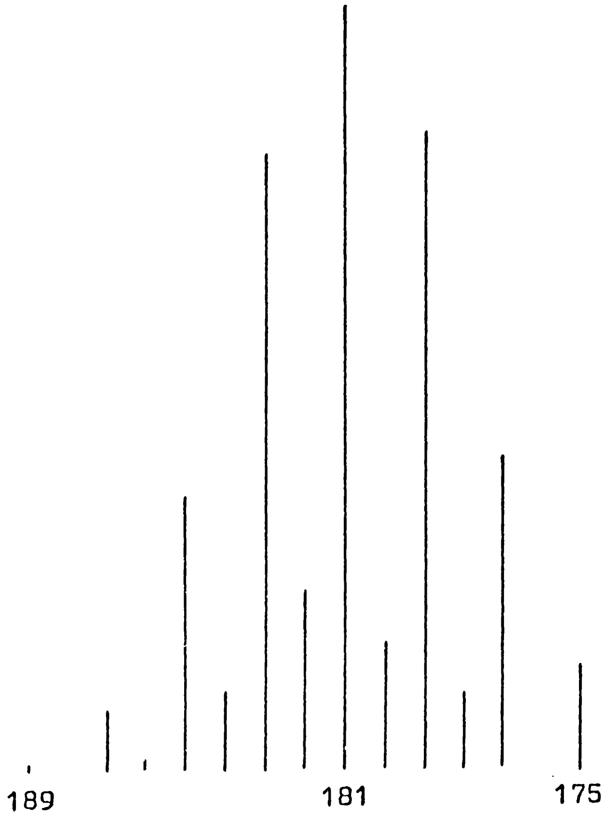
GeFe



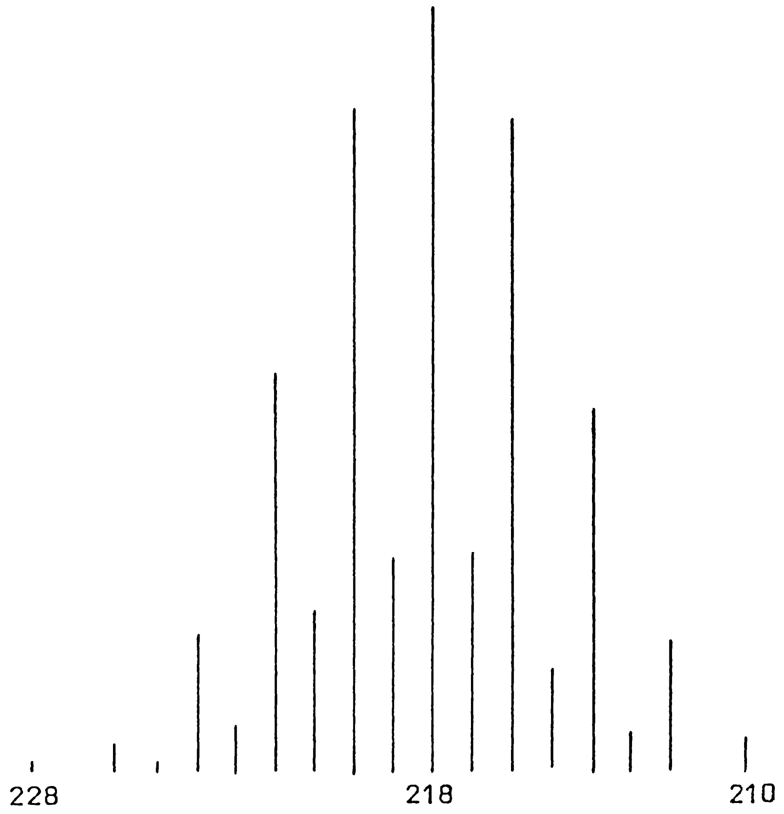
GeSi



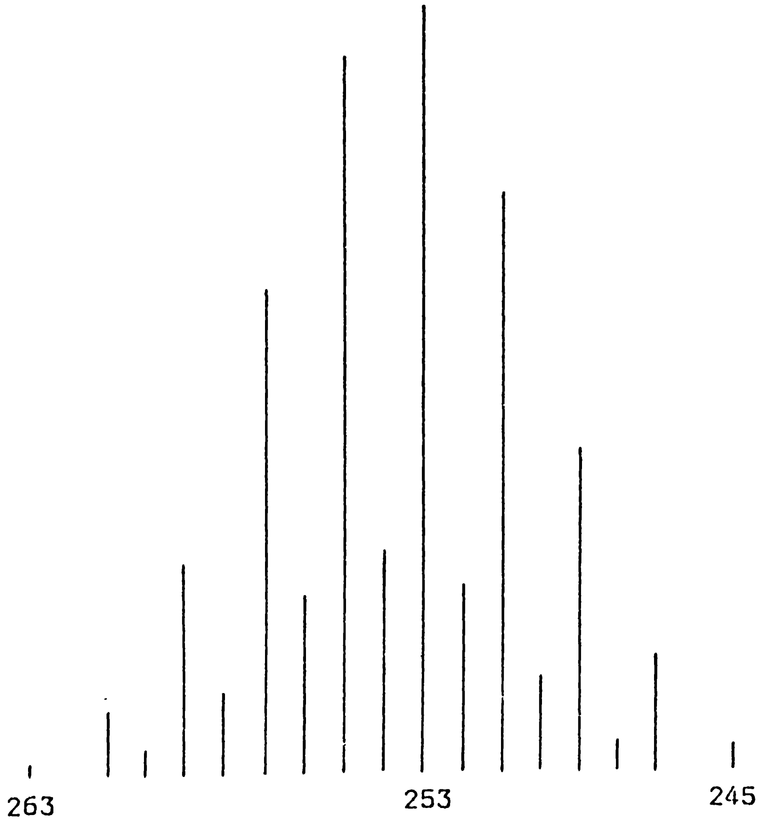
Ge_2



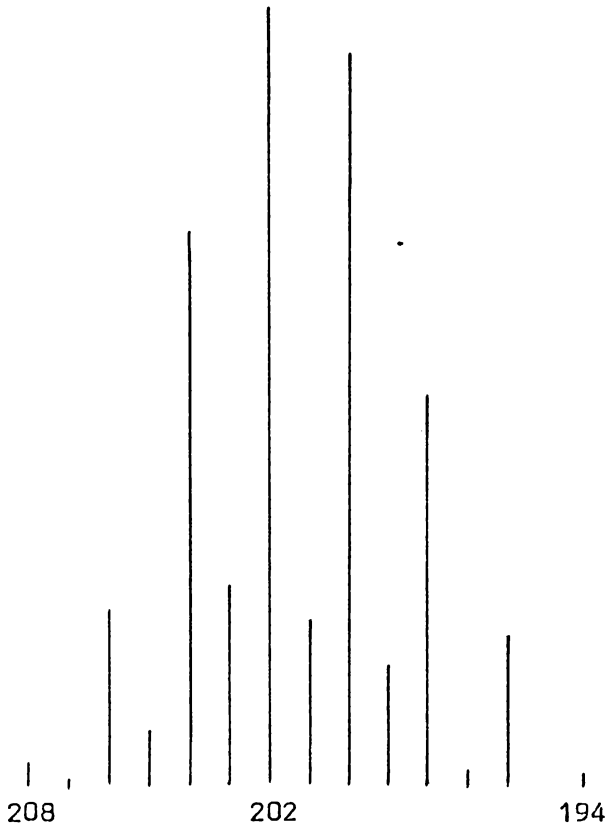
Ge_2Cl



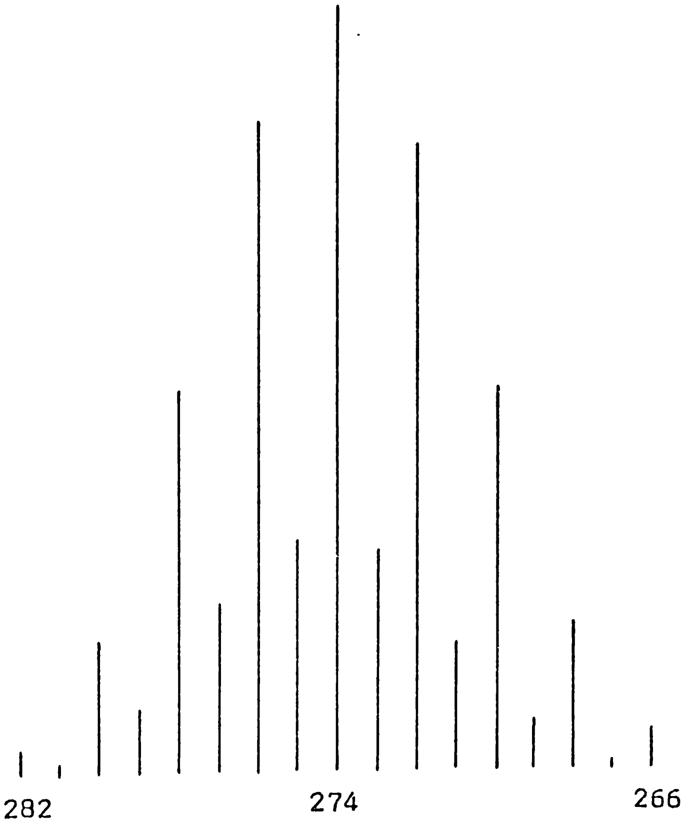
Ge_3



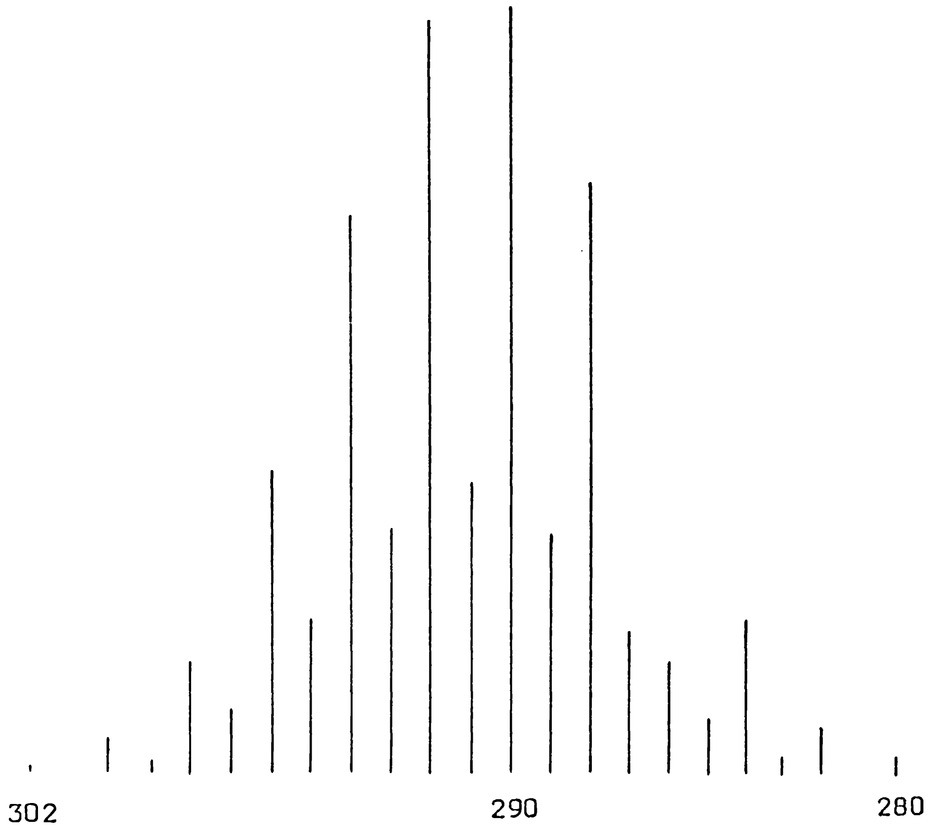
Ge_3Cl



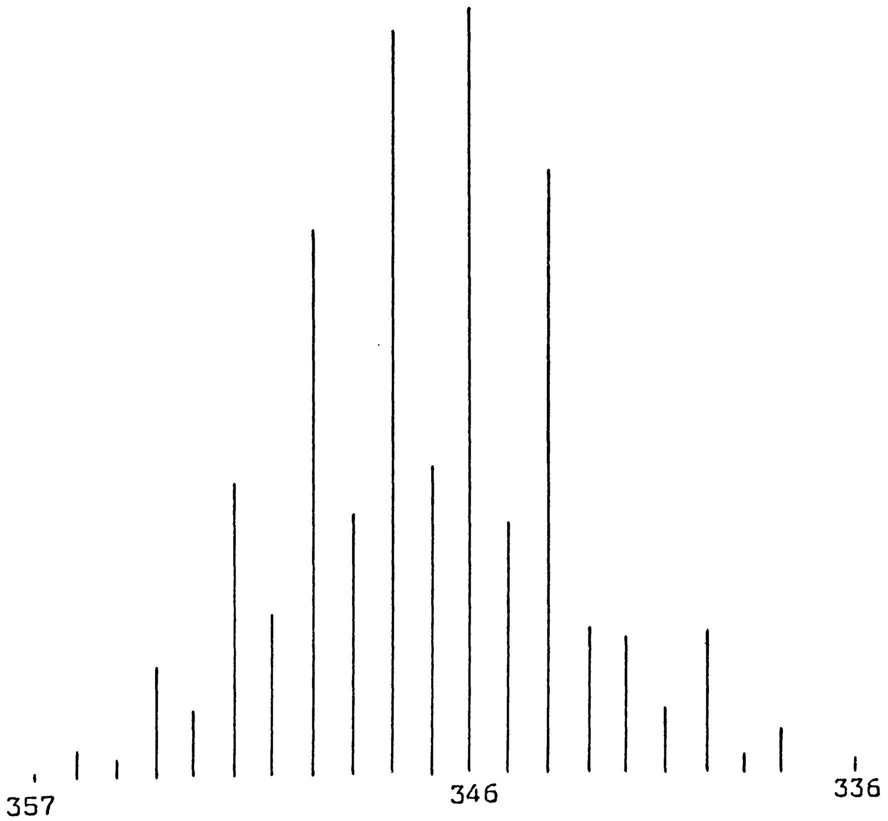
Ge$_2$Fe



Ge$_3$Fe



Ge_4



Ge_4Fe

2.3 Starting Materials

a) Germanium Hydrides

Monogermane was prepared by the acid hydrolysis of an aqueous germanate with sodium borohydride as described by Drake and Jolly (48). Although digermane, Ge_2H_6 and trigermane, Ge_3H_8 were also obtained, the yields were insufficient for the experiments described here. Monogermane was converted to the higher hydrides by the action of a silent-electric discharge (47).

b) Germanium Halide Derivatives; GeH_3Br, Ge_2H_5Cl, $Ge_2H_4Cl_2$

Germyl bromide, GeH_3Br was prepared by the method of Geisler et al. (283) by direct bromination of GeH_4 at low temperatures (-127 ^oC).

Digermanyl chloride, Ge_2H_5Cl and digermanyl dichloride, 1,2-$Ge_2H_4Cl_2$ were prepared by the action of $SnCl_4$ on Ge_2H_6 described by Ebsworth (139). The yield of the dichloride improved with excess $SnCl_4$.

c) Solvents and other materials

Diethyl ether was used as the solvent in the preparations of the manganese and cobalt carbonyl derivatives while n-pentane and n-hexane were used for the iron carbonyl derivatives. These solvents were stored over sodium wire and distilled off lithium aluminium hydride before use. A continuous reflux-still using sodium/benzophenone as the drying agent was also available for drying the ether.

Solvents used for spectroscopy (vibrational and nmr) were benzene, deuterobenzene, and cyclohexane. All were of spectroscopic grade, as was the carbon tetrachloride used in some reactions. The other commonly used reagents, silicon tetrachloride and germanium tetrachloride were distilled on the vacuum line before use with particular care being taken to remove HCl. Iodine was resublimed. These reagents were B.D.H. laboratory grade.

Manganese carbonyl, $Mn_2(CO)_{10}$ and cobalt carbonyl were supplied by Pressure Chemicals and iron carbonyl $Fe(CO)_5$ by Merck-Schuchardt. The manganese and iron compounds were used without any further treatment, but the cobalt compound was normally resublimed before use, except when taken from a freshly-opened bottle. $Fe(CO)_5$ was stored in the dark to avoid decomposition.

The sodium used for preparing sodium amalgam and sodium-ammonia solutions was repurified by melting and then separating the melt from the oxide.

All other reagents were used as supplied, although volatile compounds were usually given a crude fractionation on the vacuum line before use.

2.4 Preparative Aspects

As the anion preparation and metal-metal coupling step *via* alkali-halide elimination are common in the syntheses of the metal carbonyl derivatives in this work, it is convenient at this stage to describe the general procedure.

a) Anion preparations

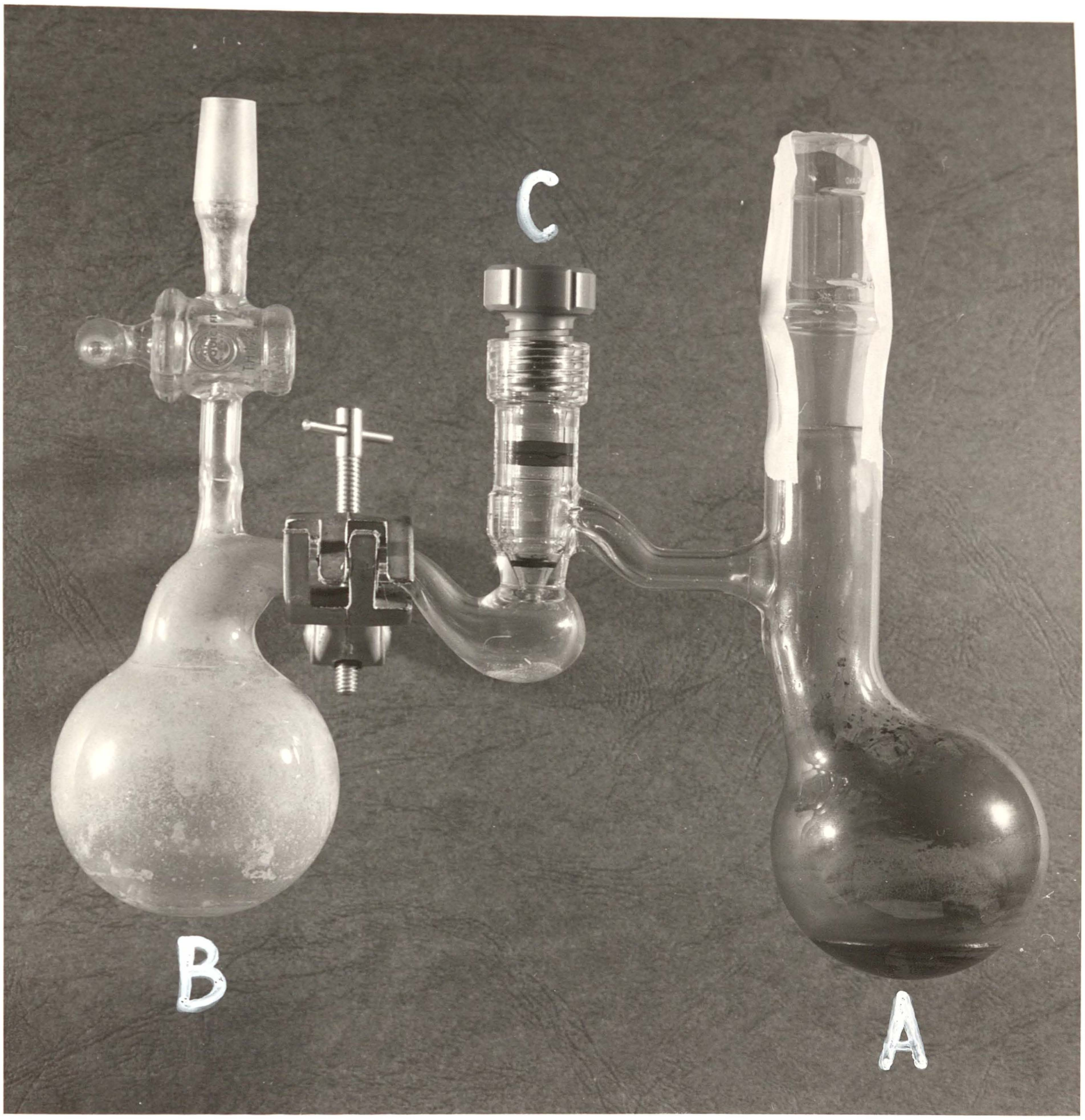
In a typical preparation of the manganese or cobalt carbonyl anion, diethyl ether (*ca.* 50 ml) was distilled off $LiAlH_4$ into bulb A of the reaction vessel (see Fig. 2.4) via bulb B and tap C on the vacuum line. Tap C was then closed. $Mn_2(CO)_{10}$ or $CO_2(CO)_8$ was then introduced into A in a glove box and dissolved in the ether. This was followed by a 1% sodium-amalgam (usually an excess) and the reaction vessel restoppered. The stopper was held in place with some tape as the vigorous shaking to follow of the reaction mixture to accelerate reduction causes an increase in ether pressure which is liable to blow the stopper off. A completely reduced anion solution is usually achieved after 20 minutes, and is colourless. The amalgam residues were allowed to settle before the ethereal solution of the anion was poured into the previously evacuated bulb B <u>via</u> tap C which was again closed to isolate the amalgam from further reaction.

The volume of ether was reduced to leave a 5 ml slurry of the sodium salt in ether. The sodium salt prepared in this manner has always been observed to come down as oily droplets, light-green for manganese and light-pink for cobalt, as the volume of ether is reduced to form a two-phase system. This was used for coupling with the polygermanyl halide. Anions prepared in this manner have always given yields in the region of 80%.

In a typical preparation of the iron carbonyl dianion $Fe(CO)_4^{2-}$, a slight excess of $Fe(CO)_5$ was condensed into a sodium-ammonia solution (usually kept to a low concentration, <u>ca</u>. 0.3 M) at -63 °C. Reaction is much faster if the $Fe(CO)_5$ is condensed on or close to the sodium-ammonia surface as $Fe(CO)_5$ is a solid at -63 °C and will not react if condensed too high up the reaction vessel. Completion of reaction was shown by the discharge of the blue colour in the Na/NH_3 solution to give an orange-brown suspension.

Figure 2.4

Reaction Vessel for Anion Preparation


C
B
A

All ammonia was removed by distillation at -63 °C followed by pumping at room temperature through a trap at -63 °C into one at -196 °C to leave a buff-coloured $Na_2Fe(CO)_4$ in the reaction vessel. Ammonia was recovered in the trap held at liquid nitrogen temperature and unreacted $Fe(CO)_5$ at -63 °C.

N-pentane or n-hexane was usually introduced as solvent for the dianion which was then ready for coupling with the polygermanyl halide.

We have evolved the reaction vessel (see Fig. 2.4) which is essentially a modified Schlenck tube to improve product yields. Previous attempts at preparing the anions gave 35-45% yields of the product (184), compared to about 80% here. This is probably due to the sensitive nature of the anions, especially Co, to both air and oxygen. The use of this reaction vessel allows preparation, separation and reaction of the anion in a closed system without it ever getting exposed to the surroundings. This apparatus consists of two reaction bulbs joined together by a teflon tap.

The sodium was first repurified. It has been found (184) that basic compounds like sodium hydroxide, ethoxide or basic organic compounds in the presence of ether promote the decomposition of $GeH_3Mn(CO)_5$ with the production of GeH_4 and Ge_2H_6, thus leading to a low yield of $GeH_3Mn(CO)_5$. A sodium-ammonia solution and not sodium amalgam was used to reduce $Fe(CO)_5$ as use of the latter leads to rather complex polynuclear anions.

b) Metal-metal coupling and recovery of products.

The polygermanyl halide, e.g. Ge_2H_5Cl, was then condensed into the anionic solution prepared above and the mixture shaken for 15 minutes usually at room temperature during which time sodium halide was observed to be deposited. The volatiles were then fractionated through traps held at −23 °C, −45 °C, −127 °C into one held at −196 °C. Solvents (ether, pentane or hexane) were recovered at −127 °C and the polygermanyl-transition metal carbonyl derivatives at −23 °C. Unreacted halide and other products were stopped in the other traps. Where products, e.g. $[GeH_2Mn(CO)_5]_2$ and $[GeH_2Co(CO)_4]_2$ are non-volatile, they were extracted with cyclohexane from the reaction bulb B with a long pipette.

The metal carbonyl derivatives have strong characteristic odours. This was noticed on the grease of ground glass joints of vacuum line equipment during manipulations.

c) NMR reaction studies.

As the polygermanyl derivatives are of low volatility, introduction of samples into nmr tubes for reaction studies is facilitated by the trap (see Fig. 2.1(B)) which also allows easy weighing. This was followed by a solvent, usually benzene, and the reagent. The tube was then sealed and reaction followed under subdued lighting by monitoring changes in the nmr signals. As most of the reactions studied in this work were slow, the tubes were stored in an empty vacuum flask with a screw-top between observations.

d) General lighting conditions.

All work in this thesis was carried out in an enclosed laboratory with only fluorescent lighting, which did not seem in any way to affect the metal carbonyl derivatives. These compounds are sensitive to white light or sunlight. Thus, exposure to light in this work means exposure to sunlight.

CHAPTER 3. PREPARATION, CHARACTERISATION AND REACTIONS OF DIGERMANYLPENTACARBONYLMANGANESE, $GeH_3GeH_2Mn(CO)_5$

Although $Ge_2H_5Mn(CO)_5$ (135) is a known compound, its characterisation has been reported only briefly. Here, the full properties and characterisation are given so that comparisons with other compounds may be made. The chemistry of the polygermanes has been explored to some extent (53,132,133,134,143). Further investigations have been made and as the chemistry of these parent hydrides in many ways resembles that of $Ge_2H_5Mn(CO)_5$, particularly in terms of substitution reaction patterns, it was found convenient to include most of the studies in this chapter. The discussions to follow in the latter part of this chapter, as in Chapters 4, 5 and 6 are in much the same general categories in which the experiments are considered in the earlier part.

3.1 Preparation of $Ge_2H_5Mn(CO)_5$

The method used for the preparation was essentially that used by Mackay et al. for $GeH_3Mn(CO)_5$ (162) and by Stobart for $Ge_2H_5Mn(CO)_5$ (135) except that Ge_2H_5Cl (139) instead of Ge_2H_5I (132) was used.

$$Ge_2H_5Cl + NaMn(CO)_5 \longrightarrow Ge_2H_5Mn(CO)_5 + NaCl$$

This compound was prepared at various stages of the work, but a typical preparation is as follows:

Digermanyl chloride (427.0 mg, 2.303 mmol) prepared by the action (139) of $SnCl_4$ on digermane, was condensed into $NaMn(CO)_5$ prepared from $Mn_2(CO)_{10}$ (800 mg, 4.10 mmol) as described earlier (see section 2.4). The mixture was shaken for 15 minutes at room temperature, in which time the originally light-green colour disappeared and insoluble white sodium chloride deposited. The volatiles were fractionated. Ether was recovered in the traps at $-196\ ^oC$ and $-127\ ^oC$, traces of Ge_2H_5Cl at $-45\ ^oC$ and $Ge_2H_5Mn(CO)_5$ (579.8 mg, 1.676 mmol, 73.0% based on initial Ge_2H_5Cl) at $-23\ ^oC$, which was purified by passing through a trap held at ice temperature. Traces of unreacted $Mn_2(CO)_{10}$ were removed this way. The compound was identified as <u>digermanylpentacarbonylmanganese</u>, by the mass of the parent ions in the mass spectrum ($m/e = 352$ to 336 : ${}^{12}C_5{}^1H_5{}^{16}O_5{}^{55}Mn{}^nGe_2$ requires 352 for $n = 76$ to 340 for $n = 70$ with $P-H = 50\%P$, $P - 2H = 20\%\ P$, $P - 3H = 10\%\ P$ and $P - 4H = 5\%\ P$). The ^1H nmr spectrum shows an A_3B_2 pattern which analysed to give $\tau GeH_3 = 6.53$, $\tau GeH_2 = 6.85$ and $J = 4.4$ Hz (c.f. 6.56 τ and 6.91τ in $CDCl_3$ (135)).

$Ge_2H_5Mn(CO)_5$ is a colourless liquid with a vapour pressure of *ca.* 0.5 mm at 20 °C. The compound showed the stability reported previously (135) i.e. no tendency to decompose at room temperature, *in vacuo* or under nitrogen, and in air decomposed slowly, leaving yellow involatile residues. In fact physical observations show this catenated group IV complex to be at least as stable if not more stable than either Ge_2H_6 or $GeH_3Mn(CO)_5$. $Ge_2H_5Mn(CO)_5$ has a strong odour, similar to that of digermane.

The mass and vibrational spectra are reported and discussed in some detail in the latter part of this chapter.

3.2 Reactions of Polygermanes and $Ge_2H_5Mn(CO)_5$

3.2.1 Halogenation of Ge_2H_6, Ge_3H_8 and $MeGe_2H_5$ with CCl_4 and $GeCl_4$

a) $Ge_2H_6 + CCl_4$

Ge_2H_6 (28.4 mg, 0.187 mmol) and CCl_4 (26.2 mg, 0.170 mmol) were sealed with benzene in a nmr tube and the reaction followed by ^1H nmr at room temperature. Reaction was slow and the first sign of reaction was a triplet at 6.71τ after 20 hours. Reaction was stopped after 75 hours as the product Ge_2H_5Cl decomposes (122) slowly at room temperature (see page 20). At this stage 10% of the Ge_2H_6 had been consumed. The final reaction mixture consisted of C_6H_6 (2.88τ), Ge_2H_6 (6.92τ c.f. 6.72τ in C_6H_{12} (280)), Ge_2H_5Cl (triplet 6.71τ, quartet 4.78τ, J = 4.2 Hz; c.f. 6.37τ, 4.61τ, J = 4.1 Hz in cyclohexane (122)) and CH_2Cl_2 (3.71τ). The presence of $CHCl_3$ was uncertain due to the strong signal of C_6H_6.

b) $Ge_2H_6 + GeCl_4$

Ge_2H_6 (38.2 mg, 0.251 mmol) and $GeCl_4$ (51.8 mg, 0.240 mmol) were sealed with benzene in a nmr tube. The nmr spectrum observed over 3 days at room temperature showed no change. However, a weak signal at 6.71τ, presumably the triplet signal attributable to Ge_2H_5Cl, started to show after a week.

c) Ge_3H_8 in CCl_4

A sample of Ge_3H_8 in CCl_4 with TMS as internal reference was observed at room temperature. The signals due to Ge_3H_8 (τ GeH_3 = 6.79, τ GeH_2 = 6.95, J = 4.0 Hz c.f. 6.68τ, 6.88τ, J = 4.0 Hz (54)) disappeared slowly over 2 days with a large amount of $CHCl_3$ (2.8τ) recorded suggesting polychloro-substitution.

The polysubstituted compound was not soluble in CCl_4. A chloride micro-analysis showed the precipitate to contain 60% Cl, which is in excess of four chlorine atoms per molecule.

d) $Ge_3H_8 + CCl_4$

Ge_3H_8 (49.0 mg, 0.22 mmol) was reacted with CCl_4 (28.0 mg, 0.18 mmol) at room temperature in C_6D_6. The first sign of reaction was seen after 32 hours, with a small doublet at 6.53τ and a septet at 4.65τ , $J = 4.0$ Hz, assigned to $(GeH_3)_2GeHCl$. An equilibrium was reached after about 40 hours when 10% of the Ge_3H_8 had been consumed, with no sign of the reaction proceeding any further for the next 26 hours.

e) $Ge_3H_8 + GeCl_4$

A sample of Ge_3H_8 (65.3 mg, 0.290 mmol) and $GeCl_4$ (49.5 mg, 0.230 mmol) in C_6D_6 were combined at room temperature. No reaction was recorded even after 66 hours.

f) $CH_3Ge_2H_5 + CCl_4$

A 20% (<u>ca.</u> 0.2 mmol) $CH_3Ge_2H_5$ solution in Ge_2H_6 with a trace of benzene as reference was reacted with CCl_4 (0.2 mmol). Although no new signals were seen in the nmr as the reaction proceeded, the signals due to $CH_3Ge_2H_5$ (τ CH_3 = 9.61, τ GeH_3 = 6.73, τGeH_2 = 6.48, J(HGeCH) = 4.5 Hz, J (HGeGeH) = 4.0 Hz; c.f. 9.79 τ, 6.79τ , 6.42τ , J(HGeCH) = 4.3 Hz, J (HGeGeH) = 3.9 Hz in C_6H_6 (134) slowly weakened over 74 hours. First sign of reaction noticed at 6½ hours when traces of white deposits were observed. This was, presumably, a chloro-digermane and is insoluble in Ge_2H_6.

3.2.2 Halogenation of $Ge_2H_5Mn(CO)_5$ with CCl_4 and $GeCl_4$.

a) $Ge_2H_5Mn(CO)_5 + CCl_4$

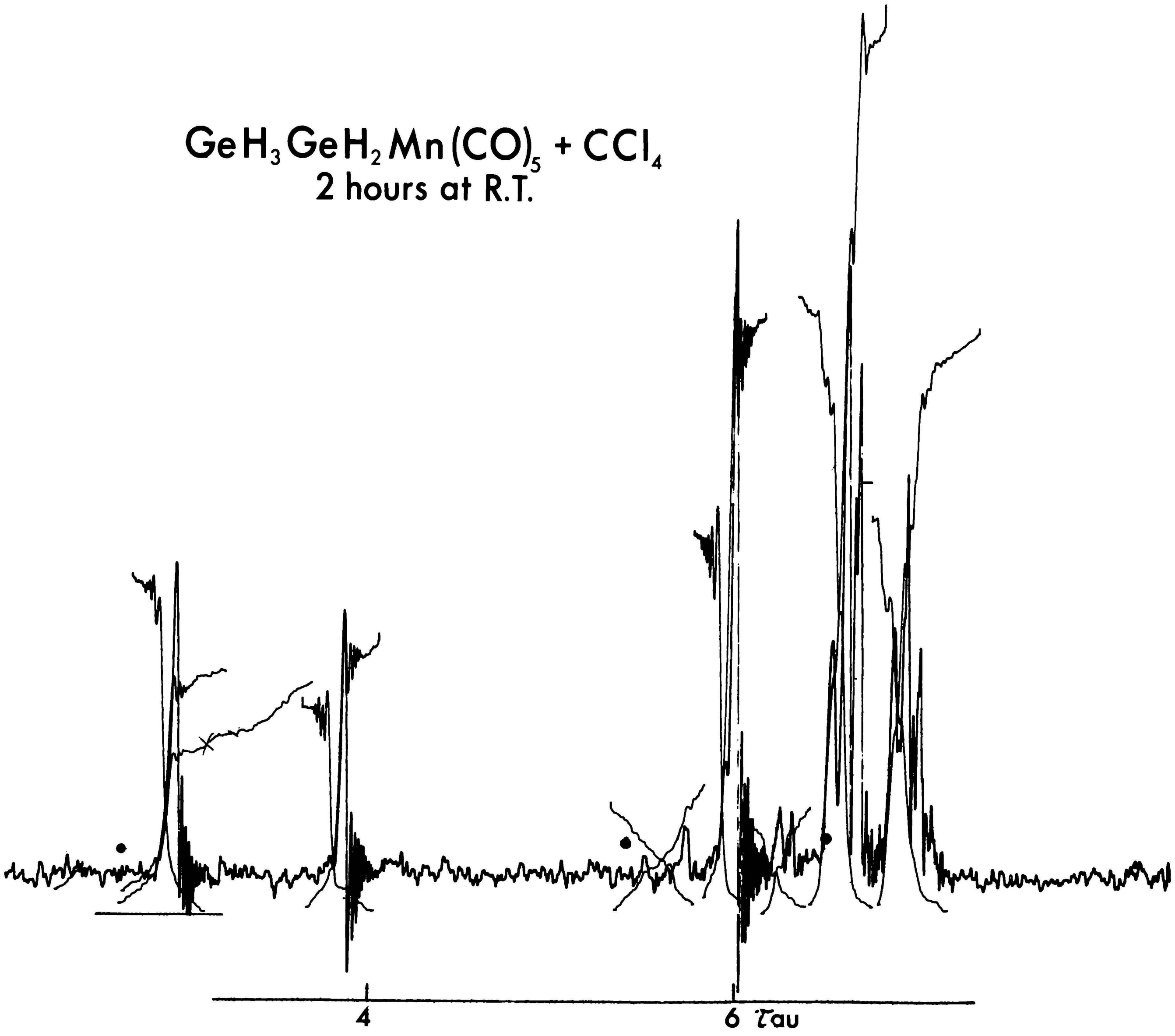
$Ge_2H_5Mn(CO)_5$ (36.30 mg, 0.1049 mmol) and CCl_4 (16.00 mg, 0.1039 mmol) were combined in deuterobenzene and the reaction followed by ^1H nmr at room temperature. Product signals were detected almost immediately. A weak doublet at 6.18τ, assigned to the GeH_3 signal of $GeH_3GeHClMn(CO)_5$ and a singlet at 5.96τ, assigned to $GeH_3GeCl_2Mn(CO)_5$ appeared. The doublet signal remained weak right through the reaction while the singlet grew steadily for 20 minutes when equilibrium was reached. The spectrum of the equilibrium mixture (quantities calculated from relative intensities by integration) consisted of $GeH_3GeH_2Mn(CO)_5$ ($\tau\, GeH_3 = 6.58$, $\tau GeH_2 = 6.91$, $J = 4.8$ Hz; 53.3%), signals attributable to $GeH_3GeHClMn(CO)_5$ ($\tau\, GeH_3 = 6.18$, $\tau GeH_2 = 4.08$, $J = 4.0$ Hz; 6.67%) and $GeH_3GeCl_2Mn(CO)_5$ ($\tau\, GeH_3 = 5.96$; 40%). $CHCl_3$ (2.8τ) and CH_2Cl_2 (3.8 τ) were present in the ratio of 1:6. No further changes were observed for the next six hours and the signals attributable to the chloro-compounds did not show any weakening. Fig. 3.1 shows the nmr spectrum recorded at equilibrium.

The tube was opened and all the volatiles were removed leaving a colourless least volatile liquid (<u>ca</u>. 0.5 mm Hg at 23 °C) which turns slightly yellow during normal handling. An infrared spectrum of this liquid in cyclohexane was recorded and showed absorptions assignable to a mixture of $GeH_3GeH_2Mn(CO)_5$, $GeH_3GeHClMn(CO)_5$ and $GeH_3GeCl_2Mn(CO)_5$. The infrared spectrum is reported and discussed later on in this chapter.

Figure 3.1

NMR Spectrum of $Ge_2H_5Mn(CO)_5$ + CCl_4
Reaction Mixture at Equilibrium after
2 hours.

$GeH_3GeH_2Mn(CO)_5 + CCl_4$
2 hours at R.T.



b) $Ge_2H_5Mn(CO)_5$ + $GeCl_4$

The reaction between $Ge_2H_5Mn(CO)_5$ (23.9 mg, 0.069 mmol) and $GeCl_4$ (14.3 mg, 0.067 mmol) at room temperature in deuterobenzene was slow. Product signals after 24 hours included a doublet at 6.21 τ assigned to the GeH_3 resonance of $GeH_3GeHClMn(CO)_5$, about half the intensity of the triplet GeH_3 signal of the unreacted $GeH_3GeH_2Mn(CO)_5$ and a weak singlet at 5.93 τ assigned to $GeH_3GeCl_2Mn(CO)_5$ which was about an eighth the intensity of the doublet. A second singlet to lower field at 2.85 τ was assigned to $GeHCl_3$ (c.f. 2.50 τ in $GeCl_4$ (141)). These signals continued to grow to reach an equilibrium at 50 hours when the doublet was of about the same intensity as the triplet. A recognisable quartet also appeared at 4.08τ. The ratio of the singlet 5.93τ signal to the doublet remained the same throughout the reaction period. The reaction mixture at equilibrium (from relative intensities by integration) consisted of $GeH_3GeH_2Mn(CO)_5$ (6.71τ, 6.00τ, J = 4.8 Hz; 42.4%), $GeH_3GeHClMn(CO)_5$ (6.21τ, 4.08τ, J = 4.0 Hz; 51.5%), $GeH_3GeCl_2Mn(CO)_5$ (5.93 τ; 6.06%) and $GeHCl_3$ (2.85 τ). No signals assignable to GeH_2Cl_2 or GeH_3Cl were observed. A spectrum of the reaction mixture recorded after a further 30 hours showed no change or weakening of the product signals. Fig. 3.2 shows the nmr spectrum at 80 hours.

The nmr tube was opened and the more volatile fraction removed, to leave a colourless lower fraction. An infrared solution spectrum in cyclohexane showed it to be a mixture of the starting material, $Ge_2H_5Mn(CO)_5$ together with the mono- and di-chlorosubstituted products as obtained in (a) above. The reaction and infrared

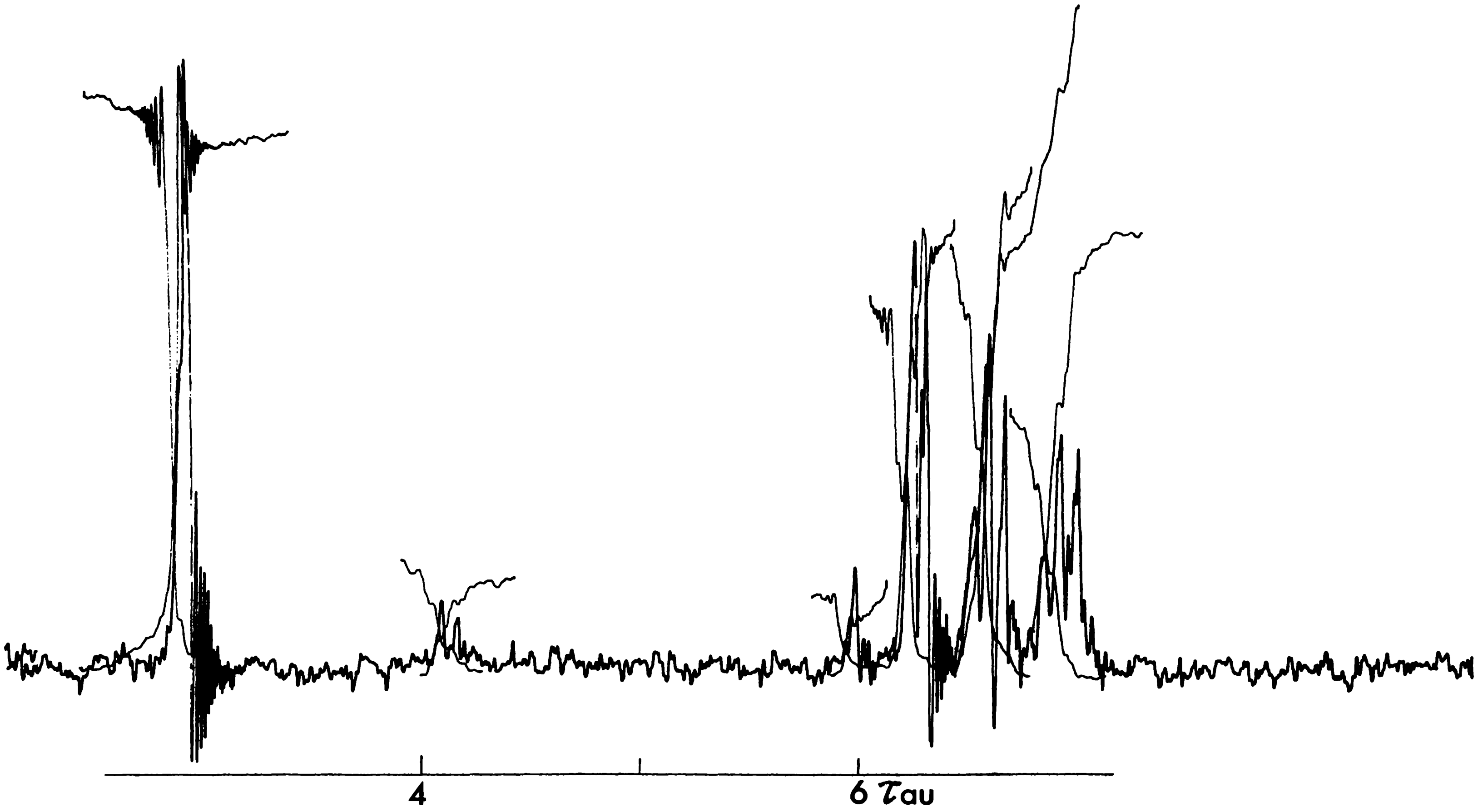
Figure 3.2

NMR Spectrum of $Ge_2H_5Mn(CO)_5$ + $GeCl_4$

Reaction Mixture at Equilibrium after

80 hours

$GeH_3GeH_2Mn(CO)_5 + GeCl_4$
80 hours at R.T.



spectrum of the product mixture are compared with (a) and discussed together towards the end of the chapter.

3.2.3 Reaction of $Ge_2H_5Mn(CO)_5$ and Ge_3H_8 with Sodium-Ammonia Solutions

a) $GeH_3GeH_2Mn(CO)_5$ + Na/NH_3

$Ge_2H_5Mn(CO)_5$ was titrated, by accurate weight measurements, against an approximately 0.24 M Na/NH_3 solution (2.0 mmol Na in 9 ml NH_3) in a reaction tube. $Ge_2H_5Mn(CO)_5$ was condensed in portions into the Na/NH_3 solution at liquid N_2 temperature and reaction carried out at -63 °C, with shaking. Incondensibles were recorded and removed before addition of next lot of $Ge_2H_5Mn(CO)_5$. The end-point was recorded when the blue Na/NH_3 solution turned brown and this occurred after a total of 0.470 mmol of $Ge_2H_5Mn(CO)_5$ had been added, approximately a 4 Na: 1 $Ge_2H_5Mn(CO)_5$ ratio. A total of 0.026 mmol of hydrogen was produced. The titration figures are shown below:

$Ge_2H_5Mn(CO)_5$ (m.moles)		H_2 (mm Hg in 140 ml)	H_2 (m.moles)
0.1587		0.5	0.0038
0.1399		1.0	0.0076
0.1714		2.0	0.015
0.470	End-point	3.5	0.026
0.2147		0.2	0.0015

A further 0.2147 m.moles of $Ge_2H_5Mn(CO)_5$ was added after end-point had been reached. No colour change was observed but a further small amount of hydrogen was evolved although this showed a considerable drop over earlier additions.

With the reaction mixture kept at −63 °C, most of the NH_3 was removed. CH_3I (280.8 mg, 1.976 mmol) was then condensed into the reaction vessel and the reaction mixture shaken for 30 minutes at −63 °C and then 10 minutes at room temperature. The colour changed from brown to red. The volatiles were fractionated through traps held at −23 °C, −83 °C, −127 °C into one held at −196 °C. The −196 °C fraction contained CH_3GeH_3 and traces of ammonia. NH_3 was completely removed by drawing the gaseous mixture through a tube of $CaCl_2$ and then further leaving it over $CaCl_2$ for several minutes. I.r. and nmr spectra showed the remaining fraction to be CH_3GeH_3 (41.6 mg, 0.45 mmol., 96.2% of $Ge_2H_5Mn(CO)_5$ at neutralisation) (τ CH_3 = 9.98, τ GeH_3 = 6.59, J = 4.2 Hz; c.f. 9.71τ , 6.55τ , J = 4.22 Hz in CS_2 (284).

I.r. spectra of the −127 °C and −83 °C fractions showed both to contain ammonia, $(CH_3)_2GeH_2$ and some $GeNH_x$ containing material. The two fractions were combined and the ammonia removed by warming in portions into a vessel containing 20% H_2SO_4. The resulting gaseous mixture was dried over $CaCl_2$ which removed water as well as the $GeNH_x$ by-product component present in trace amounts, the remaining fraction was confirmed by nmr to be $(CH_3)_2GeH_2$ (8.5 mg, 0.08 mmol., <u>ca.</u> 20%) (τ CH_3 = 9.78, τ GeH_3 = 6.49, J = 4.2 Hz; c.f. 9.71τ , 6.27τ , J = 3.95 Hz in CCl_4 (285)).

The trap held at −23 °C contained small amounts of white crystalline material of low vapour pressure (<u>ca.</u> 2 mm). I.r. and nmr spectra showed the white crystals to be $CH_3Mn(CO)_5$ (9.50τ , <u>ca.</u> 2%; c.f. 9.95τ (271)).

b) $GeH_3GeH_2GeH_3$ + Na/NH_3

The titration procedure was similar to that in (a) above. Ge_3H_8 was titrated against a 0.24 M Na/NH_3 solution (3.738 mmol Na in 18 ml NH_3) at −63 °C. Several portions of Ge_3H_8 was used and the blue-colour of the Na/NH_3 solution was discharged upon adding between 0.9 and 0.94 mmoles of Ge_3H_8. A total of about 0.15 mmoles of incondensible gas (most probably hydrogen) was recorded.

Most of the ammonia was then removed, and CH_3I (567.4 mg, 3.996 mmol) added. The volatiles were fractionated and the infrared spectra showed Ge–H and C–H containing products and traces of ammonia in the −196 °C trap, and ammonia in the −83 °C trap. The −196 °C fraction was purified and ammonia scrubbed out in the same manner as in (a) above. The nmr spectrum of the remainder of the fraction in benzene showed CH_3GeH_3 (τ CH_3 = 9.98, τ GeH_3 = 6.56, J = 4.0 Hz) and $(CH_3)_2GeH_2$ (τ CH_3 = 9.91, τ GeH_3 = 6.26, J = 3.8 Hz). Integration showed the ratio of the components in the mixture in the ratio of 1.7:1.

3.3 Discussion

3.3.1 The Mass Spectrum of Digermanylpentacarbonylmanganese

The mass spectrum of a gas sample showed no real differences from that of a liquid sample and is listed in Table 3.1. Assignments of the envelopes due to the fragment families and the hydrogen ratios were obtained with the aid of calculated Ge, and Ge_2 mass spectral envelope patterns worked out in Fig. 2.3. In $GeH_3Mn(CO)_5$ (162) there is a strong tendency by fragments containing both metal atoms to retain all three hydrogen atoms, thus suggesting

Table 3.1 Mass Spectrum of $GeH_3GeH_2Mn(CO)_5$

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogens(b) n = 5	4	3	2	1	0
336–352	$H_xGe_2Mn(CO)_5^+$	10.4	10.0	5.0	2.0	1.0	0.5	
309–324	$H_xGe_2Mn(CO)_4^+$	9.20	0.5	0.5	10.0	0.5		
279–296	$H_xGe_2Mn(CO)_3^+$	10.9	0.5	1.0	10.0	1.0	0.5	0.3
252–266	$H_xGe_2Mn(CO)_2^+$	8.05			10.0	1.0	0.8	
225–238	$H_xGe_2Mn(CO)^+$	27.0			10.0	1.0		
196–210	$H_xGe_2Mn^+$	100			10.0	1.0	0.5	
265–274	$H_xGeMn(CO)_5^+$	67.3			0.5	1.0	10.0	1.0
237–246	$H_xGeMn(CO)_4^+$	54.0			0.5	1.0	10.0	1.0
208–217	$H_xGeMn(CO_3^+$	21.6				1.0	10.0	2.0
181–190	$H_xGeMn(CO)_2^+$	6.61			2.0	2.0	10.0	2.0
153–162	$H_xGeMn(CO)^+$	11.5			3.0	3.0	10.0	2.0
125–134	H_xGeMn^+	42.3			2.0	1.0	10.0	1.0
141–155	$H_xGe_2^+$	15.2			1.0	10.0	1.0	
70–79	H_xGe^+	4.48			2.0	2.0	2.0	10.0
196	$HMn(CO)_5^+$	1.72						
195	$Mn(CO)_5^+$	1.15						
168	$HMn(CO)_4^+$	0.43						
167	$Mn(CO)_4^+$	0.43						
140	$HMn(CO)_3^+$	1.15						
139	$Mn(CO)_3^+$	2.01						
112	$HMn(CO)_2^+$	0.86						
111	$Mn(CO)_2^+$	4.60						
84	$HMn(CO)^+$	1.72						
83	$Mn(CO)^+$	5.75						

Table 3.1 (cont.)

56	HMn^+	2.01
55	Mn^+	10.6
28	CO^+	(c)

Footnotes:

(a) Summed over x = 5, 4, 3, 2, 1, 0 and over Ge isotopes where appropriate. Manganese is monoisotopic.

(b) Strongest component of family arbitrarily assigned 10, with other components relative to this.

(c) Strong peak, includes N_2^+.

the major process to be the stepwise loss of CO, which is confirmed by metastable peaks. CO loss and hydrogen retention is also found for $Ge_2H_5Mn(CO)_5$ but no metastables were observed. In fact, in all the spectra recorded of $Ge_2H_5Mn(CO)_5$, the parent ions retained the full stoichiometric number of hydrogens i.e. five. The retention of hydrogen by the manganese derivatives is in contrast to digermane and other polygermanes where hydrogen loss occurs readily (47,54). Another major process seems to be GeH_2 elimination (286). In the $H_xGeMn(CO)_4{}^+$ families, the relative intensities for different values of x approximately parallel those of the $H_{x+2}Ge_2Mn(CO)_y{}^+$ ions for each value of y (especially in the case x = 1 for y = 4,3,2 and 0). This suggests that GeH_2 loss is a major process from $Ge_2H_xMn(CO)_y{}^+$ ions.

The strongest envelope in the spectrum is that of $H_xGe_2Mn^+$ i.e. $[P-(CO)_y]^+$ where P is the parent ion and y the full number of carbonyls. It now appears that this feature is common for all hydrido- and methyl-silyl (157,169,200), germyl (162,173,187) and polygermanyl-transition metal derivatives, although in some methyl containing germanium-iron compounds (176) this does not hold. The total intensity of the $[P-(CO)_y]^+$ family has usually been used as the composite base peak, and such a base peak has very useful implications as we shall see in Chapter 6 as part of the identification of $Ge_2H_5(GeH_3)Fe(CO)_4$.

Rearrangement ions $HMn(CO)_n{}^+$ (n = 5 to 0) were observed. Overall, the spectrum shows the domination by even-electron ions emphasised by Glockling (287).

Fragments retaining Ge_2Mn and GeMn carry 39.3% and 48.3% respectively of the ion current, adding up to 87.6% the proportion of ion current carried by ions retaining the Ge–Mn bond, showing an increase over $GeH_3Mn(CO)_5$ at 79.7% (162).

3.3.2 The Vibrational Spectrum of Digermanylpentacarbonylmanganese

The vibrational spectrum of $GeH_3GeH_2Mn(CO)_5$ is listed in Table 3.2. The assignments were made by comparison with Ge_2H_5X compounds (X = Me (134,143), X = Cl (133)) and $GeH_3Mn(CO)_5$ (162). $Ge_2H_5Mn(CO)_5$ has, at best, C_s symmetry with 48 fundamental modes of vibration. Only about a half of these are observed so that a complete assignment is not possible. The two strong CO_{eq} a_1 and e bands and a weaker CO_{ax} a_1 band shows the metal carbonyl moiety to reflect the local C_{4v} symmetry, in which three infrared active ($2a_1$+e) and one Raman active (b_1) carbonyl stretching modes are expected, rather than the true C_s one. These bands are in positions close to those found for $GeH_3Mn(CO)_5$ (162), $SiH_3Mn(CO)_5$ (157) and $HMn(CO)_5$ (288).

As in most compounds containing the GeH_3 group, the asymmetric and symmetric GeH_3 deformations are found around 870 cm^{-1} and 790 cm^{-1} respectively. The medium – weak band at 683 cm^{-1} in the solution spectrum corresponding to the 684 cm^{-1} absorption in the solid spectrum was assigned to the GeH_2 wag.

The two metal-metal stretches at 273 cm^{-1} and 205 cm^{-1} have been compared by Stobart (135) to the Ge–Ge stretch at 268 cm^{-1} in digermane (92,289) and Ge–Mn stretch at 219 cm^{-1} in $GeH_3Mn(CO)_5$ (160) (see page 52). Differences between the respective

Table 3.2 Vibrational Spectrum of $GeH_3GeH_2Mn(CO)_5$ (cm^{-1})

Solution(a)	Solid	Tentative assignment
2103 mw	2105 mw	νCO, a_1
2098 vw,sh	2099 vw,sh	
2086 vw,sh	2080 w,sh	$\nu^{13}CO$
2067 w,sh	2060 mw	νGeH
2056 mw		
2044 vw,sh		
2038 vw,sh		
2032 vw,sh		
2028 w,sh		
2010 vvs,sh	1998 s,sh	νCO, a_1
2006 vvs	1982 vvs	νCO, e
1974 w	1970 w,sh	$\nu^{13}CO$
1966 vw		
870 w	885 w	δasym. GeH_3, a' + a"
	869 w	δGeH_2, a'
792 mw	790 mw	δsym. GeH_3, a'
683 mw	684 w	GeH_2 wag
675 w	673 w	GeH_2 twist?
667 mw	668 w	δMnCO, a'
655 s	646 s	
648 mw,sh		
635 s	624 s	
	605 vw	
470 w	471 w	GeH_3 rocks

Table 3.2 (cont.)

(b)	409 vs,p	ν MnC
(b)	273 s,p	ν asym. GeGeMn, a'
(b)	205 vs,p	ν sym. GeGeMn, a'
(b)	105 vs	skeletal bending

Footnotes:

(a) Infrared solution spectrum in cyclohexane

(b) Raman spectrum from ref. (135).

vibrational frequencies were interpreted as interaction between these two metal-metal stretching modes in $GeH_3GeH_2Mn(CO)_5$. Thus the description of the two observed bands as the asymmetric and symmetric Ge-Ge-Mn stretches.

3.3.3 Substitution Reactions

a) Polygermanes

As previously mentioned in the introductory chapter (see pages 19 and 20), equimolar proportions of Ge_2H_6 and $SnCl_4$ (53,139) yields a 4:1 mixture of Ge_2H_5Cl and the disubstituted 1,2-$Ge_2H_4Cl_2$. This reaction was rapid at room temperature and the HCl produced was non-reactive. $SiCl_4$ has been reported (141) to monosubstitute Ge_2H_6 extremely slowly with initial reaction observed after 2 weeks. In this work we show the intermediate reactivities of CCl_4 and $GeCl_4$ showing initial reactions after 20 hours and 1 week respectively. As the reactions were slow and Ge_2H_5Cl decomposes at a relatively faster rate, there was little possibility of studying polychlorosubstitution. The appearance of CH_2Cl_2 also suggests the involvement of $CHCl_3$ produced in the initial reaction in substitution of Ge_2H_6,

$$Ge_2H_6 + CCl_4 \longrightarrow Ge_2H_5Cl + CHCl_3$$

$$Ge_2H_6 + CHCl_3 \longrightarrow Ge_2H_5Cl + CH_2Cl_2$$

Trigermane reacts very slowly with CCl_4 showing initial reaction after 32 hours.

$$Ge_3H_8 + CCl_4 \longrightarrow (GeH_3)_2GeHCl + CHCl_3$$

Substitution as expected was on the central germanium (137) (see page 19), but reaction only consumed about 10% of the initial Ge_3H_8. In CCl_4, polychlorosubstitution was extensive, suggesting that even the hydrogens on the GeH_3 groups are attacked under rigorous conditions. However, no reaction was recorded with $GeCl_4$. Compared with similar reactions of digermane above, it would appear that the slow rate and less extensive substitution in trigermane is due to steric hindrance brought on by the introduction of an extra GeH_3 group. The rate of substitution by $GeCl_4$ was intermediate between CCl_4 and $SiCl_4$. The overall reactivity order is thus

$$\mathrm{C} \gg \mathrm{Si} < \mathrm{Ge} <\!<\!< \mathrm{Sn}$$

with substitution by $SnCl_4$ being the fastest. This probably reflects the relative weakness of the Sn–Cl bond.

The reaction of $CH_3Ge_2H_5$ with CCl_4 was more rapid than that of Ge_2H_6, indicated by the precipitation of white solids after 6½ hours. Since I_2 (147) and $SnCl_4$ (53) have been shown to preferentially substitute the α -hydrogen, it is likely that the initial product here is $CH_3GeHClGeH_3$, though no characterisation of the white solid was obtained. $CHCl_3$ reacts as well as CCl_4.

b) $Ge_2H_5Mn(CO)_5$

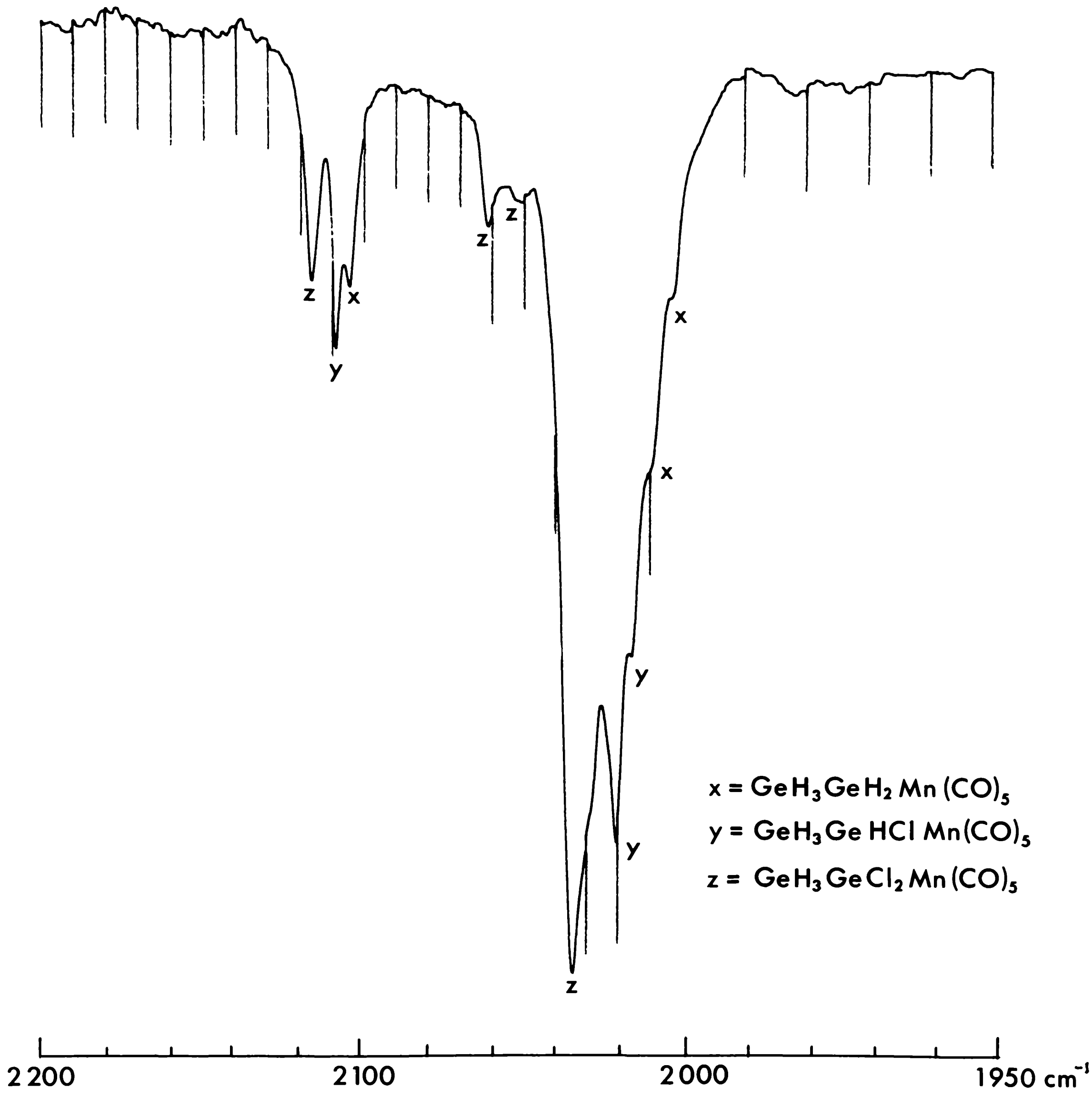
The substitution chemistry of $Ge_2H_5Mn(CO)_5$ has been subject to some limited study and this has been reviewed in pages 54 and 55. Reactions with $SnCl_4$ and I_2 have shown substitution mainly on the α -germanium atom (53). Also mentioned was the complete substitution in $[Mn(CO)_5]_2SnHSnH[Mn(CO)_5]_2$ (253,254) by CCl_4 or CBr_4 in which the single hydrogen on each tin atom was replaced.

The infrared spectrum of the less volatile fraction of the product mixtures resulting from reaction with CCl_4 and with $GeCl_4$ were recorded and the 1950 cm^{-1} to 2200 cm^{-1} region reproduced in Figs. 3.3, and 3.4 respectively. By comparing the i.r. spectrum of pure $Ge_2H_5Mn(CO)_5$, part of which is shown in Fig. 3.5, with those obtained for the product mixtures, it was found that unreacted $Ge_2H_5Mn(CO)_5$ was a component in both cases. A comparison of the spectra of the two product mixtures showed them to contain different proportions of two other components. The relative intensities of the absorption bands of each component in each reaction mixture yielded approximately the same ratios as observed in the nmr where these two product components were assigned to $GeH_3GeHClMn(CO)_5$ and $GeH_3GeCl_2Mn(CO)_5$. The comparison of the infrared spectra allowed the sorting out of 2 sets of bands and these are listed in Tables 3.3 and 3.4. The absorption bands are those expected of a compound containing a GeH_3 and a $Mn(CO)_5$ group, and a GeCl bond, thus supporting the earlier assignments of $GeH_3GeHClMn(CO)_5$ and $GeH_3GeCl_2Mn(CO)_5$. It is generally observed that the νCO stretching frequencies increase with the number of substituted halides as in $X_3SiCo(CO)_4$ (208,232) and $RnCl_{m-n}Sn\ [Co(CO)_4]_{4-m}$ (238,290) ($R = Me, Et, Pr^n, Bu^n, Ph$; $X = Cl, Br, I$). This is the effect of electron withdrawal by the halide substituent thus decreasing back donation into the carbonyl π^*-orbitals. Thus in this case, the set of vibrations with the higher carbonyl frequencies are assigned to $GeH_3GeCl_2Mn(CO)_5$.

The spectra show all the features observed for $GeH_3GeH_2Mn(CO)_5$.

Figure 3.3

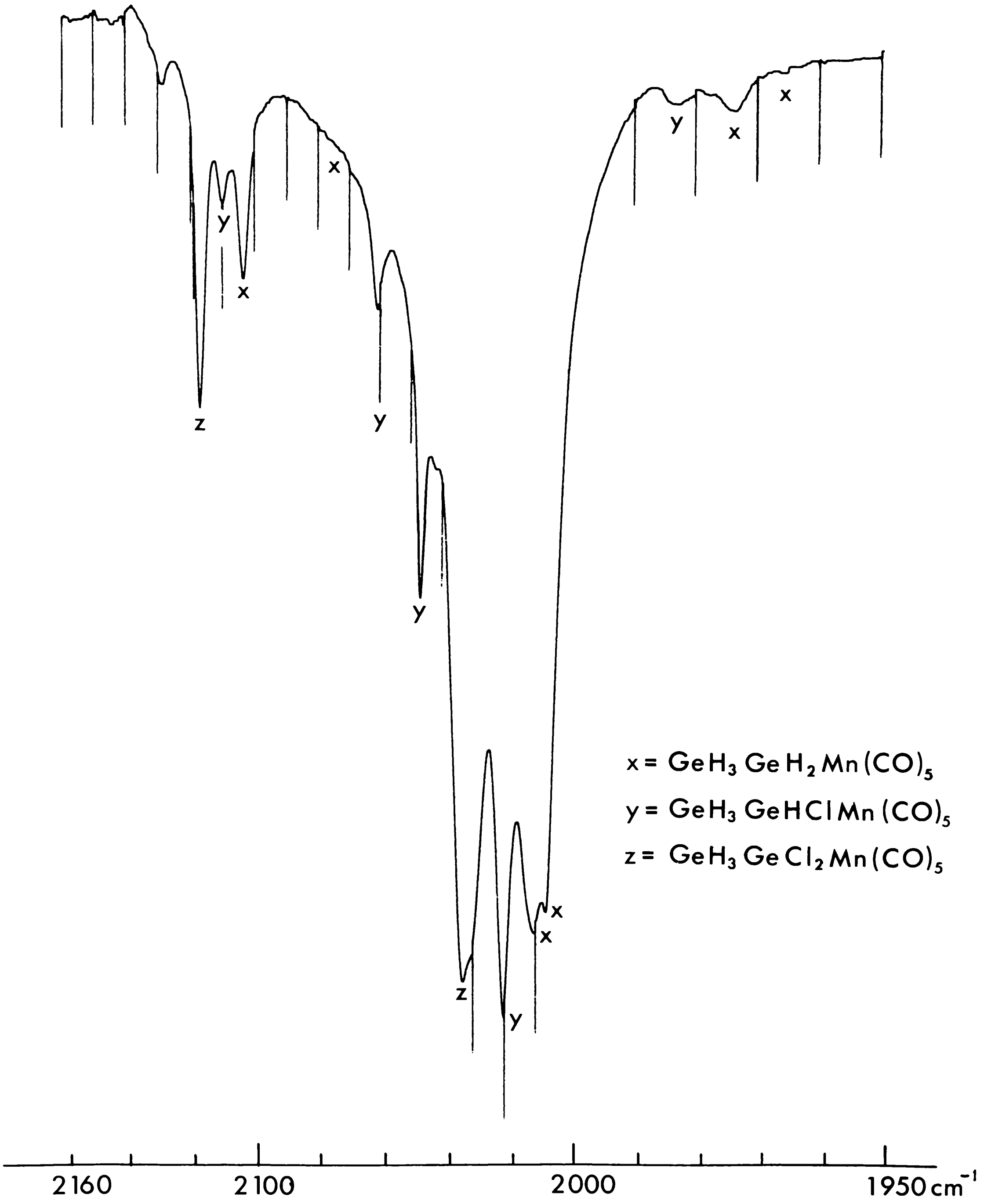
I.r. Spectrum of 1950 cm^{-1} to 2200 cm^{-1} Region of Product Mixture from $Ge_2H_5Mn(CO)_5 + CCl_4$ Reaction



$GeH_3GeH_2Mn(CO)_5 + CCl_4$

Figure 3.4

I.r. Spectrum of 1950 cm^{-1} to 2160 cm^{-1} Region of Product Mixture from $Ge_2H_5Mn(CO)_5 + GeCl_4$ Reaction



$GeH_3GeH_2Mn(CO)_5 + GeCl_4$

Figure 3.5

I.r. Spectrum of 1950 cm^{-1} to 2160 cm^{-1}

Region of $Ge_2H_5Mn(CO)_5$

$GeH_3GeH_2Mn(CO)_5$

Table 3.3 Infrared Spectrum of $GeH_3GeHClMn(CO)_5$ (cm^{-1})(a)

	Assignment
2110 w	νCO, a_1
2061 w	νGeH
2047 m	
2020 vs	νCO, e
2015 w,sh	νCO, a_1
1982 vw	$\nu {}^{13}CO$
858 vw	δasym. GeH_3
780 w	δsym. GeH_3
668 w	δGeH
655 m	$\delta MnCO$
463 w	GeH_3 rock
372 w	νMnC
351 w	$\nu GeCl$

(a) Infrared solution spectrum in cyclohexane.

Table 3.4 Infrared Spectrum of $GeH_3GeCl_2Mn(CO)_5$ (cm^{-1})(a)

	Assignment
2117 w	νCO, a_1
2061 w 2052 w	νGeH
2035 vs	νCO, e
2029 w,sh	νCO, a_1
1984 vw	ν^{13}CO
835 vw	δasym. GeH_3
780 vw 758 w 722 vw	δsym. GeH_3
646 m	δMnCO
460 w	GeH_3 rock
372 w	νMnC
351 w	νGeCl

(a) Infrared solution spectrum in cyclohexane.

A comparison shows interaction of both the asymmetric and symmetric GeH_3 deformation modes with the $\nu GeCl$ mode as the deformation frequencies decrease with increase of number of substituted chlorine atoms. The 668 cm^{-1} absorption in $GeH_3GeHClMn(CO)_5$ is assigned to the deformation of the lone Ge–H bond. No absorption band was observed in this GeH_x deformation region for $GeH_3GeCl_2Mn(CO)_5$. Only one band was observed in the spectra of the resulting product mixtures from the two reactions in the region where GeCl stretches usually occur. Analysis showed the intensity of the 351 cm^{-1} band in the spectrum from the CCl_4 reaction to that from the $GeCl_4$ reaction to be approximately 1.4:1 relative to the other observed bands. As the concentration of the solutions used to run the spectra is close to being the same the ratio seems to reflect the chloride content of the mixtures as deduced from the proportions of the chloro-compounds observed in the nmr spectra thus suggesting overlap of the $\nu GeCl$ mode of the two chloro-compounds.

The composition of the product mixtures suggests polychloro-substitution to different extent in the two reactions. Substitution by CCl_4 proceeds in 2 steps:

$$GeH_3GeH_2Mn(CO)_5 + CCl_4 \xrightarrow{\text{fast}} GeH_3GeHCl - Mn(CO)_5 + CHCl_3$$

$$GeH_3GeHClMn(CO)_5 + CCl_4/CHCl_3 \xrightarrow{\text{very fast}} GeH_3GeCl_2Mn(CO)_5 + CHCl_3/CH_2Cl_2$$

The second substitution step was so rapid that only a trace of the mono-substituted $GeH_3GeHClMn(CO)_5$ was observed at any instant of the reaction process. Only approximately half the CCl_4 was consumed and the $CHCl_3$ produced in the first substitution step was used in the even faster second substitution step to form the dichlorosubstituted compound, $GeH_3GeCl_2Mn(CO)_5$.

The substitution between $Ge_2H_5Mn(CO)_5$ and $GeCl_4$ was much slower, more ordered, and less extensive. As only $GeHCl_3$ and no GeH_2Cl_2 or $GeHCl_3$ were observed, the trace of polychlorosubstitution was probably also due to $GeCl_4$:

$$Ge_2H_5Mn(CO)_5 + GeCl_4 \xrightarrow{\text{slow}} GeH_3GeHClMn(CO)_5 + GeHCl_3$$

$$GeH_3GeHClMn(CO)_5 + GeCl_4 \xrightarrow{\text{very slow}} GeH_3GeCl_2Mn(CO)_5 + GeHCl_3$$

Substitution by $SnCl_4$ (53) yielded 78% $GeH_3GeHClMn(CO)_5$, 14% $GeH_2ClGeHClMn(CO)_5$ and 6% $GeH_2ClGeH_2Mn(CO)_5$ (see page 54). No $GeH_3GeCl_2Mn(CO)_5$ was observed. Thus it seems substitution is dependent on the size of the substituting reagent. Steric hindrance at the α-germanium probably does not allow the approach of another $SnCl_4$ molecule to substitute the lone hydrogen on the α-germanium in $GeH_3GeHClMn(CO)_5$, but CCl_4 and/or $CHCl_3$ manages easily, and $GeCl_4$ with some difficulty. This is also seen with Ge_2H_6 and $CH_3Ge_2H_5$. These compounds react with $SnCl_4$ (see pages 19 and 21) to yield only the 1- and 1,2-chlorosubstituted derivatives.

The substitution chemistry of $Ge_2H_5Mn(CO)_5$ resembles that of $CH_3Ge_2H_5$ (53,143). Initial reaction of CCl_4 was observed almost immediately with $Ge_2H_5Mn(CO)_5$ and after 6½ hours with $CH_3Ge_2H_5$; reaction between the former and $GeCl_4$ was observed after 24 hours. This corresponds to 20 hours and a week in Ge_2H_6 with CCl_4 and $GeCl_4$ respectively. The results clearly support earlier conclusions (see pages 21 and 54) that the $Mn(CO)_5$ and CH_3 groups not only activate the molecule towards substitution but also directs the substitution mainly to the hydrogens on the α-germanium.

The overall reactivities of the group IV tetrahalides observed in the substitution of the polygermanes and $GeH_3Mn(CO)_5$ (141) is maintained with the catenated group IV derivatives, i.e.

$$C \gg Si < Ge \lll Sn.$$

Another striking feature noted in the substitution reactions of $Ge_2H_5Mn(CO)_5$ is the relative stability of the chloro-substituted products, $GeH_3GeHClMn(CO)_5$ and $GeH_3GeCl_2Mn(CO)_5$, demonstrated by the little tendency of these compounds to decompose at room temperature through the long periods, at times up to 80 hours, required for the reaction studies. This is in marked contrast to GeH_3GeH_2Cl (122) which shows complete decomposition in 6½ hours (see page 20). The stability of the chloro-digermanylmanganese derivatives is very likely due to the earlier mentioned electron withdrawal by the halide substituent leading to an increase in the ν CO stretching frequencies. An effect of this is probably to strengthen the Ge-Cl bond, hence the higher stability of such compounds. Further evidence is drawn from compounds of the type $Cl_{4-n}Ge\ [Co(CO)_4]_n$ (291). These compounds show high stabilities and with no decomposition even when handled in the open.

3.3.4 Cleavage of Ge–Ge and Ge–Mn Bonds by Na/NH_3 Solutions

The cleavage of the Ge–Ge bonds in $GeH_3GeH_2GeH_3$ is really a repeat of the conductimetric titrations by Emeleus and Mackay (116) where it was found that the end-point occurred at the hydride:sodium ratio of 0.25, meaning 4 parts of Na were required to titrate 1 part of Ge_3H_8. This hydride:Na ratio at end-point was maintained in this work, thus the main reaction was clearly represented by the equation:

$$Ge_3H_8 + 4Na \longrightarrow 2GeH_3Na + GeH_2Na_2$$

This was confirmed by the isolation of the methylated products CH_3GeH_3 and $(CH_3)_2GeH_2$ in approximately the stoichiometric ratio of 2:1.

$$2GeH_3Na + GeH_2Na_2 + 4CH_3I \longrightarrow 2CH_3GeH_3 + (CH_3)_2GeH_2 + 4NaI$$

A similar reaction of sodium in ammonia was found with $GeH_3GeH_2Mn(CO)_5$. The 4:1 $Ge_2H_5Mn(CO)_5$:Na ratio clearly indicates the cleavage of each metal–metal bond:

$$GeH_3GeH_2Mn(CO)_5 + 4Na \longrightarrow GeH_3Na + GeH_2Na_2 + NaMn(CO)_5$$

This was followed by methylation with CH_3I:

$$GeH_3Na + GeH_2Na_2 + NaMn(CO)_5 + 4CH_3I \longrightarrow$$

$$CH_3GeH_3 + (CH_3)_2GeH_2 + CH_3Mn(CO)_5 + 4NaI$$

An almost quantitative yield was obtained for CH_3GeH_3, but yields for $(CH_3)_2GeH_2$ (17%) and $CH_3Mn(CO)_5$ (2%) were relatively low. This is probably representative of the relative stabilities of the respective anions under the reaction conditions in the presence of ammonia.

In both the experiments conducted, hydrogen was evolved during the titrations. The $H_2:Ge_3H_8$ and $H_2:Ge_2H_5Mn(CO)_5$ ratios at end point were 0.16:1 and 0.06:1 respectively. These are significantly lower than the 0.4:1 ratio obtained in the reported conductimetric titration of Ge_3H_8 (116) in which a 2.8M sodium-ammonia solution was used. The considerably higher production of hydrogen in the reported work is almost certainly due to the high concentration of the sodium-ammonia solution used. Rustad and Jolly (117) have proposed the following mechanism to explain the low yield of $KGeH_3$ and high production of hydrogen in the reaction of GeH_4 and potassium-ammonia solution:

$$e^- + GeH_4 \longrightarrow GeH_3^- + H \ldots \qquad (1)$$

$$H + e^- \longrightarrow H^- \ldots \qquad (2)$$

$$H^- + NH_3 \longrightarrow NH_2^- + H_2 \ldots \qquad (3)$$

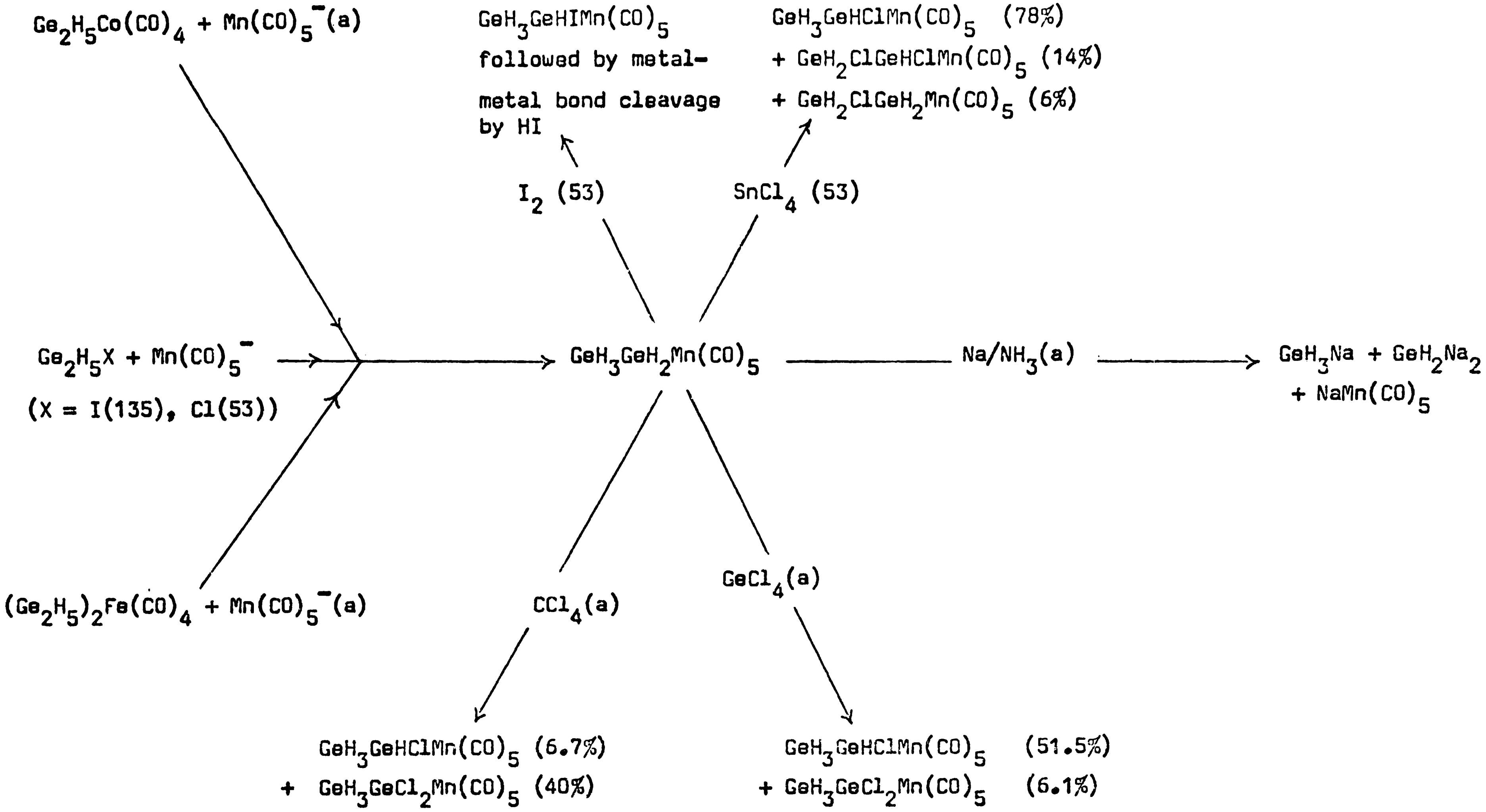
$$2H \longrightarrow H_2 \ldots \qquad (4)$$

$$GeH_4 + NH_2^- \longrightarrow GeH_3^- + NH_3 \ldots \qquad (5)$$

$$GeH_4 + NH_2^- \longrightarrow GeH_3NH_2 + H^- \ldots \qquad (6)$$

GeH_3NH_2 undergoes rapid ammonolysis to give an imide. Production of the imide is thus catalysed by high metal concentrations leading to excess hydrogen formed. This mechanism probably accounted for some of the hydrogen in the titrations of Ge_3H_8 and $Ge_2H_5Mn(CO)_5$. This explains why the initial sodium concentration was kept to a low 0.24M. However, the reported conductimetric experiment showed a slight increase in specific conductivity after end-point had been reached on further addition of Ge_3H_8. Taken with the negligible amount of hydrogen observed when another portion of $Ge_2H_5Mn(CO)_5$ was added to the reaction mixture after the end-point had been reached also suggests H_2 to arise by reaction of one or more anions with either Ge_3H_8 or $Ge_2H_5Mn(CO)_5$. This side reaction may in part account for the deficit of Me_2GeH_2.

The reactions of $GeH_3GeH_2Mn(CO)_5$ are summarised in Fig. 3.6.


$Ge_2H_5Co(CO)_4 + Mn(CO)_5^-$(a)
$Ge_2H_5X + Mn(CO)_5^-$
(X = I(135), Cl(53))
$(Ge_2H_5)_2Fe(CO)_4 + Mn(CO)_5^-$(a)
$GeH_3GeH_2Mn(CO)_5$
$GeH_3GeHIMn(CO)_5$
followed by metal-metal bond cleavage by HI
I_2 (53)
$GeH_3GeHClMn(CO)_5$ (78%)
+ $GeH_2ClGeHClMn(CO)_5$ (14%)
+ $GeH_2ClGeH_2Mn(CO)_5$ (6%)
$SnCl_4$ (53)
Na/NH_3(a)
$GeH_3Na + GeH_2Na_2$
+ $NaMn(CO)_5$
CCl_4(a)
$GeH_3GeHClMn(CO)_5$ (6.7%)
+ $GeH_3GeCl_2Mn(CO)_5$ (40%)
$GeCl_4$(a)
$GeH_3GeHClMn(CO)_5$ (51.5%)
+ $GeH_3GeCl_2Mn(CO)_5$ (6.1%)

(a) This work.

CHAPTER 4. PREPARATION, CHARACTERISATION AND REACTIONS OF DIGERMANYLTETRACARBONYL COBALT, $GeH_3GeH_2Co(CO)_4$

Since digermanylpentacarbonylmanganese does not decompose as expected from its sterically strained structure - in fact physical handling points to even higher stability than $GeH_3Mn(CO)_5$ - it seemed likely that the cobalt analogue can also be prepared. This proved to be the case. An earlier attempt at its synthesis was unsuccessful (292).

4.1 Preparation of $Ge_2H_5Co(CO)_4$

The method used for the preparation of $Ge_2H_5Co(CO)_4$ was that successfully used for preparing $Ge_2H_5Mn(CO)_5$,

i.e. $Ge_2H_5Cl + NaCo(CO)_4 \longrightarrow Ge_2H_5Co(CO)_4 + NaCl$

Digermanyl chloride (394.3 mg, 2.12 mmol) was condensed into $NaCo(CO)_4$, prepared from dicobalt octacarbonyl (1.063 g, 3.11 mmol) as described earlier in section 2.4. The reaction mixture was shaken for 15 minutes at room temperature. The reaction vessel was wrapped with aluminium foil to minimise light. The volatiles were then fractionated to give ether at -127 °C, traces of Ge_2H_5Cl and $HCo(CO)_4$ at -45 °C (identified by i.r.), and $Ge_2H_5Co(CO)_4$ (576.4 mg, 1.79 mmol, 84.4% based on the Ge_2H_5Cl added) at -23 °C. The compound was identified as digermanyltetracarbonylcobalt, by the mass of the parent ions in the mass spectrum (m/e = 328 to 315: ${}^{12}C_4{}^{1}H_5{}^{16}O_4{}^{59}Co{}^{n}Ge_2$ requires 328 for n = 76 to 316 for n = 70 with P-H = 3% P.) Further characterisation is provided by the fragmentation pattern, the vibrational spectrum, by the chemical reactions reported below, and by the ^1H nmr spectrum. This shows an A_3B_2 pattern with τ GeH_3 = 6.51, τ GeH_2 = 6.25, and J = 4.2 Hz. The mass and vibrational spectra are reported and discussed in the latter part of this chapter.

$Ge_2H_5Co(CO)_4$ is a colourless liquid which turns orange-brown then dark brown in daylight with slow evolution of digermane (identified by i.r.) and CO. These changes are very slow in the dark, a liquid sample showing only slight browning after a week. It is just volatile in the vacuum line with a vapour pressure about 0.3-0.4 mm at 20 °C : 1 to 2 mmoles may be transferred in ½ hour at diffusion pump pressures. It has a strong odour, similar to that of digermane.

4.2 Reactions

a) Ge_2H_5Cl and $GeH_3Co(CO)_4$

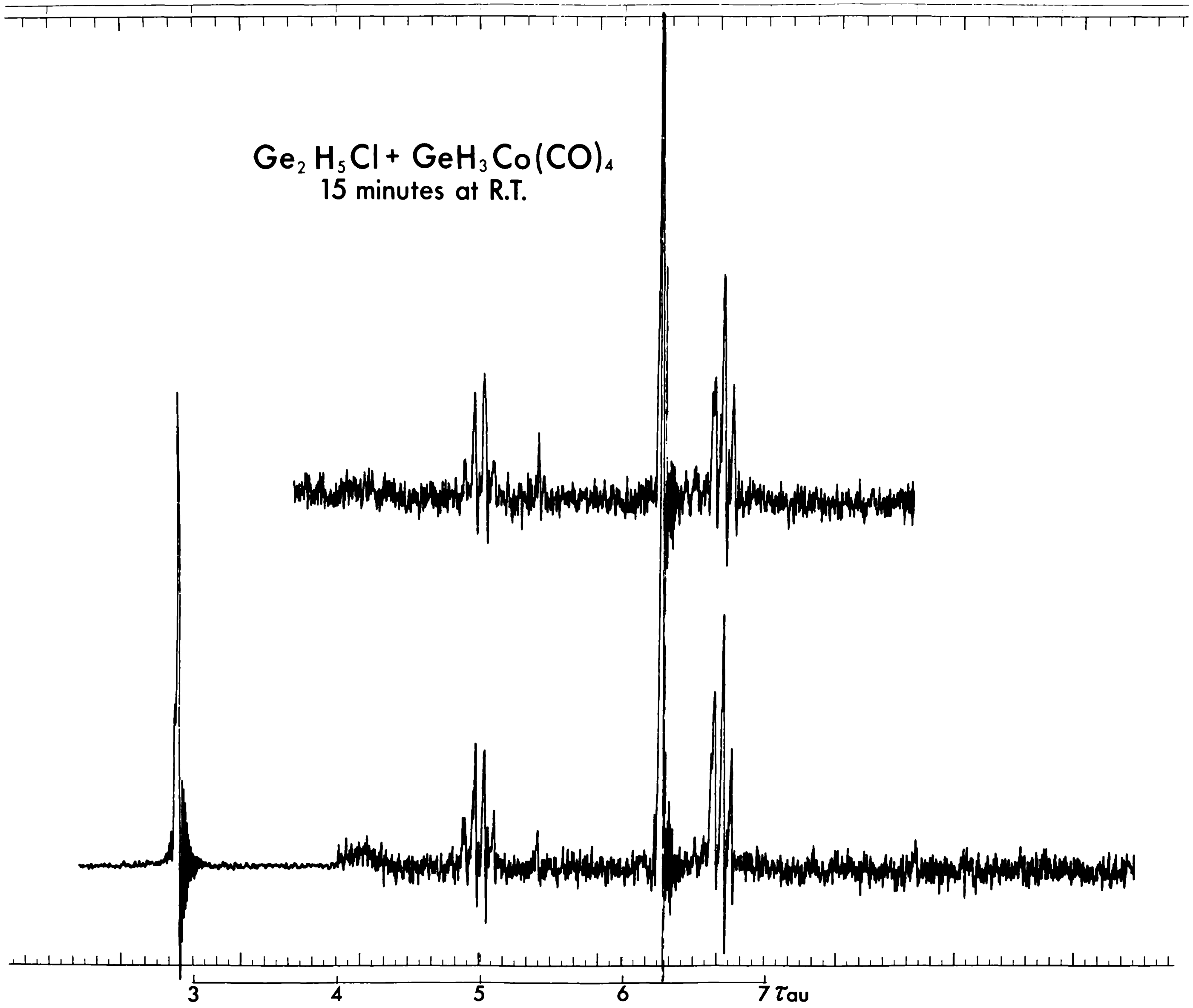
Ge_2H_5Cl (22.5 mg, 0.121 mmol) and $GeH_3Co(CO)_4$ (38.4 mg, 0.155 mmol) were combined in deuterobenzene and the reaction followed by ^1H nmr at room temperature. Product signals were detected after 15 minutes and changes ceased after 7 hours when the reaction mixture (from relative intensities by integration) consisted of Ge_2H_5Cl (τ GeH_3 = 6.71, τ GeH_2 = 4.98, J = 4.1 Hz, 10%), $GeH_3Co(CO)_4$ (6.27τ , 31%), $Ge_2H_5Co(CO)_4$ (τ GeH_3 = 6.51, τ GeH_2 = 6.25, J = 4.2 Hz, 31%) and GeH_3Cl (5.38 τ , 29%) (c.f. Ge_2H_5Cl = 6.37 τ , 4.61 τ , J = 4.1 Hz; GeH_3Cl = 4.89 τ in cyclohexane solutions (122)). Figs. 4.1 and 4.2 show the nmr spectra recorded at the beginning and towards the end of the reaction.

Figure 4.1

NMR Spectrum of

Ge_2H_5Cl + $GeH_3Co(CO)_4$ Reaction

at 15 minutes.



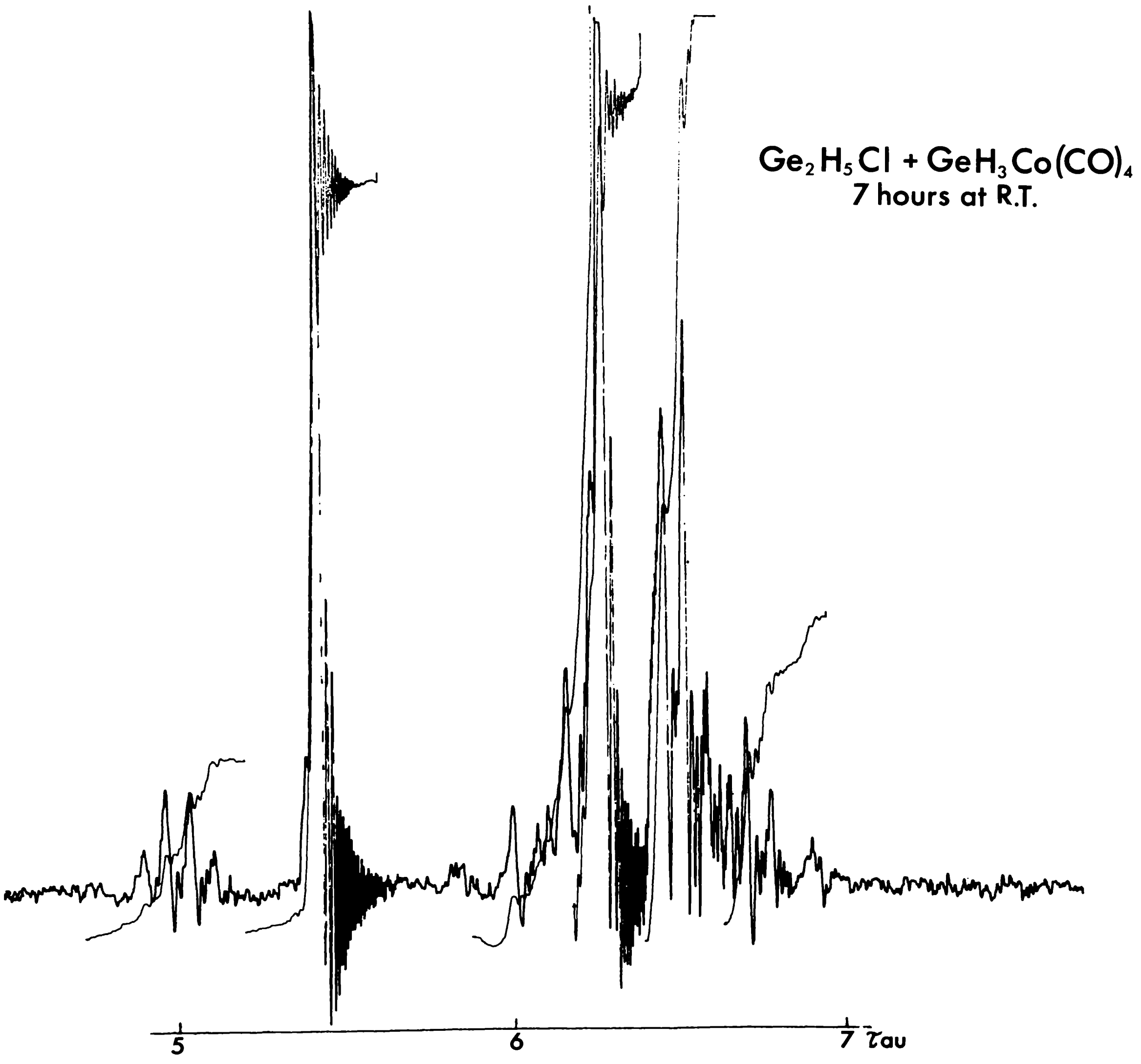
Ge$_2$H$_5$Cl + GeH$_3$Co(CO)$_4$
15 minutes at R.T.

Figure 4.2

NMR Spectrum of

$Ge_2H_5Cl + GeH_3Co(CO)_4$

Reaction at 7 hours.


$Ge_2H_5Cl + GeH_3Co(CO)_4$
7 hours at R.T.
5
6
7
τau

The tube was opened and fractionation yielded $Ge_2H_5Co(CO)_4$ (29.75 mg, 0.092 mmol, 76% of initial Ge_2H_5Cl).

b) $Ge_2H_5Co(CO)_4$ and CCl_4 or $GeCl_4$

$Ge_2H_5Co(CO)_4$ (0.14 mmol) and CCl_4 (0.10 mmol) were sealed with deuterobenzene in an nmr tube. No change, apart from slight yellowing, was observed over 7 days.

In a similar experiment, $Ge_2H_5Co(CO)_4$ (0.13 mmol) was mixed with $GeCl_4$ (0.12 mmol). No change was observed.

The above experiments were repeated with $GeH_3Co(CO)_4$. Similar negative results were obtained.

c) $Ge_2H_5Co(CO)_4$ and $HgCl_2$

$Ge_2H_5Co(CO)_4$ (65.2 mg, 0.203 mmol) was drawn through a tube packed with $HgCl_2$ and the products collected at -196 °C. Fractionation yielded digermane with a trace of chlorogermane at -120 °C (1.5 mg, <u>ca.</u> 4%), Ge_2H_5Cl (33.0 mg, 0.18 mmol, 91% of initial $Ge_2H_5Co(CO)_4$) at -45 °C, and unreacted $Ge_2H_5Co(CO)_4$ (2.6 mg, <u>ca.</u> 4%) at -23 °C. All product components were identified by their i.r. spectra. A yellow layer, probably $Hg[Co(CO)_4]_2$, was left on the $HgCl_2$.

d) $Ge_2H_5Co(CO)_4$ and $Mn(CO)_5^-$

$Ge_2H_5Co(CO)_4$ (337.7 mg, 1.049 mmol) was condensed on to 5 ml of ether solution of $NaMn(CO)_5$ prepared using $Mn_2(CO)_{10}$ (585.0 mg, 1.5 mmol) in the usual manner. The reaction mixture was shaken for 15 minutes at room temperature and the volatiles removed. $Ge_2H_5Mn(CO)_5$ (340.7 mg, 0.985 mmol, 93%) identified by i.r. and nmr spectra was found to be the only volatile product. All the $Ge_2H_5Co(CO)_4$ was consumed. A slightly yellow solid was left in the reaction vessel. When exposed to air this solid turned purple, characteristic of the reaction of $NaCo(CO)_4$.

4.3 Discussion

4.3.1 General

Although $Ge_2H_5Co(CO)_4$ is light-sensitive, decomposition is slower and less extensive than in $GeH_3Co(CO)_4$. In the dark, the digermanyl compound showed only slight decomposition after 1 week indicated by a light brown colour, whereas a parallel reaction with the germyl analogue gave an intense dark brown colour. This is probably good evidence that the digermanyl derivative is more stable than the germyl one, reversing earlier predictions. Previous studies (183,184) showed that the brown colour in the decomposition of $GeH_3Co(CO)_4$ is due to the decomposition product and that this decomposition product is intensely coloured so that a small amount can cause a strong colouration, although actual decomposition may be minimal. This was observed to be the case with $Ge_2H_5Co(CO)_4$ as more than 90% was recovered from a coloured sample that had been in the laser beam of a Raman spectrometer for several hours during recording of the Raman spectrum.

4.3.2 The Mass Spectrum of Digermanyltetracarbonylcobalt

All the mass spectra run were dominated by very strong $H_xGe_2^+$ and H_xGe^+ envelopes, which varied in intensity relative to the other ions observed, and were especially dominant with gas sampling. These ions thus arise mainly from decomposition possibly with Ge_2H_6 as a major decomposition product. This decomposition is probably accelerated by contact with metal surfaces e.g. the probe of the spectrometer. The intensity pattern of the remaining ion envelopes remained consistent for gas-sampled and liquid-sampled spectra. Thus the main features of the spectrum can be determined and this is shown in Table 4.1.

The assignments of families and hydrogen ratios were made with the aid of the calculated Ge_2 and Ge_1 envelope patterns given in Fig. 2.2. The pattern of CO loss, hydrogen retention and GeH_2 elimination is broadly similar to those observed for $GeH_3Co(CO)_4$ (183) and $Ge_2H_5Mn(CO)_5$ (see section 3.3.1). There is a systematic CO loss from $H_xGe_2Co(CO)_n^+$ and $H_xGeCo(CO)_n^+$ ions (n = 4,3,2,1). Hydrogen loss becomes significant only after two carbonyls are lost. By comparing the relative intensities and the hydrogen ratio pattern of $H_xGe_2Co(CO)_n^+$ and $H_xGeCo(CO)_n^+$ families, it is quickly noticed that the latter family arises by GeH_2 elimination of the former, thus

$$H_xGe_2Co(CO)_n \longrightarrow H_{x-2}GeCo(CO)_n + GeH_2$$

Rearrangement ions e.g. $HCo(CO)_4^+$ are also observed.

As there is a close similarity between this spectrum and those of $Ge_2H_5Mn(CO)_5$, $GeH_3Mn(CO)_5$ (162) and $GeH_3Co(CO)_4$ (183) it was found possible to approximate the relative intensities of the $H_xGe_2^+$ and H_xGe^+ families. In $Ge_2H_5Mn(CO)_5$, the relative intensities of these families (see section 3.3.1) are 15.2 and 4.48 respectively, while the relative intensities of the H_xGe^+ family in $GeH_3Mn(CO)_5$ (162) and $GeH_3Co(CO)_4$ (183) are 7.2 and 23.6 respectively.

Table 4.1 Mass Spectrum of $GeH_3GeH_2Co(CO)_4$

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogens(b)					
			x=5	4	3	2	1	0
315–328	$H_xGe_2Co(CO)_4^+$	2.09	10.0	0.3				
285–300	$H_xGe_2Co(CO)_3^+$	55.4	10.0	1.0	0.5	0.3		
258–272	$H_xGe_2Co(CO)_2^+$	89.6	4.2	2.0	10.0			
227–241	$H_xGe_2Co(CO)^+$	71.3				1.1	10.0	2.6
199–213	$H_xGe_2Co^+$	100				0.3	10.0	8.2
243–250	$H_xGeCo(CO)_4^+$	26.1			10.0	0.7		
213–222	$H_xGeCo(CO)_3^+$	69.6			10.0	0.4	0.8	0.6
185–194	$H_xGeCo(CO)_2^+$	92.2			4.5	1.0	10.0	1.4
157–166	$H_xGeCo(CO)^+$	85.2			0.5	0.6	10.0	2.5
129–138	H_xGeCo^+	79.1			1.0	1.5	10.0	8.2
140–155	$H_xGe_2^+$	25(c)						10.0
70–79	H_xGe^+	15(c)						10.0
172	$HCo(CO)_4^+$	2.61						
171	$Co(CO)_4^+$	9.57						
143	$Co(CO)_3^+$	1.74						
116	$HCo(CO)_2^+$	0.87						
115	$Co(CO)_2^+$	21.7						
88	$HCo(CO)^+$	0.87						
87	$Co(CO)^+$	20.0						
60	HCo^+	0.87						
59	Co^+	10.4						
28	CO^+	(d)						

Table 4.1 (cont.)

Footnotes:

(a) Summed over $x = 5, 4, 3, 2, 1, 0$ and over Ge isotopes where appropriate. Cobalt is monoisotopic.

(b) Strongest component of family arbitrarily assigned 10, with other components relative to this.

(c) These are calculated values. See text for details.

(d) Strong peak, includes N_2^+.

Thus it is reasonable to assign the relative intensities of 25 for $H_xGe_2^+$ and 15 for H_xGe^+ families in the mass spectrum of $Ge_2H_5Co(CO)_4$.

Characteristic of most high molecular weight cobalt compounds e.g. $Br_2Ge\,[Co(CO)_4]_2$ (291), the parent ion is relatively weak but all other $H_xGe_2Co(CO)_n^+$ and $H_xGeCo(CO)_n^+$ ions are strong accounting for (apart from $H_xGe_2^+$ and H_xGe^+ arising from fragmentation) 40.9% and 45.2% of the total ion current, which is similar to the ratio obtained for $Ge_2H_5Mn(CO)_5$. Thus the proportion of ion current carried by ions retaining Ge-Co bond would add up to 86% if the estimates for $Ge_2H_x^+$ and GeH_x^+ are valid, which is significantly higher than in $GeH_3Co(CO)_4$ where the ion abundance of such species is 77.5%.

4.3.3 The Vibrational Spectrum of Digermanyltetracarbonylcobalt

The vibrational spectrum of $GeH_3GeH_2Co(CO)_4$ is listed in Table 4.2. The assignment of modes due to the digermanyl fragment was made with reference to Ge_2H_5X compounds (133,134,143) and also to $Ge_2H_5Mn(CO)_5$. The solid-film spectrum shows 37 bands. Forty-two fundamental vibrations are expected of its C_s symmetry. As with most compounds containing the $Co(CO)_4$ moiety, $Ge_2H_5Co(CO)_4$ exhibits a local C_{3v} symmetry. Three strong carbonyl modes are seen in the gas and solution spectra in positions close to those found for $GeH_3Co(CO)_4$ (183) so the spectrum is reflecting the local C_{3v} symmetry rather than the true C_s one. The phase shift is more marked than for $GeH_3Co(CO)_4$ and the lowest band splits into two strong components in the solid, perhaps corresponding to the a' and a"

Table 4.2 Vibrational Spectrum of $GeH_3GeH_2Co(CO)_4$ (cm^{-1})

Gas	Solution(a)	Solid	Tentative assignment
2104 ms	2097 s	2097 s)	ν CO, a'
		2089 m)	
2085 mw	2077 m	2078 m)	ν^{13}CO, a'
		2069 mw)	
2074 sh	2064 m	2038 m)	νGeH
2072 m		2032 m)	
2044 s	2035 s	2020 w	νCO, a'
		2000 s)	
2020 vs	2008 vvs	1989 vs)	νCO, a' + a"
		1982 vvs)	
2007 w			
1990 vs)			
1983 w)	1971 w	1970 w)	
		1965 vw)	ν^{13}CO
		1960 w)	
		1959 w)	
		1953 w)	
		920 vvw,br	
		877 m,sh)	
876 vw,br	872 w	873 m)	δasym.GeH_3, a' + a"
		868 w)	
864 w,br		858 m)	
		852 m)	GeH_2 bend, a'

Table 4.2 (cont.)

815 vvw			
		799 vvw	
791 m	784 m	784 s	δ sym. GeH_3, a'
		778 s	
762 vw			
749 vw			
		669 m	GeH_2 wag.
673 m,br	667 m	667 s	
		658 m	GeH_2 twist? rock?
		649 m	
556 ms	551 m	560 m,sh	δ CoCO, a'
		549 s	
		512 vw	GeH_2 twist?
500 vw,br	528 w	508 w	
		500 vw	
		487 w	GeH_3 rocks
478 vw,br	474 w	475 m	
		459 w	
	(b)415 s,p	418 w	ν CoC, a'
	(b)269 s,p		ν asym. GeGeCo, a'
	(b)205 vs,p		ν sym. GeGeCo, a'

Footnotes:

(a) Infrared solution spectrum in cyclohexane.

(b) Raman spectrum of neat liquid.

equatorial stretches deriving from the C_{3v} e mode. However, the solid spectrum shows a much larger number of bands than the gas or solution spectra so the splitting may arise from crystal effects. Two clear bands in the deformation region are assigned as the prominent (133,134) GeH_3 symmetric deformation near 800 cm^{-1} and the strong GeH_2 wag below 700 cm^{-1}. The other deformations are clear in the solid state spectrum. The polarised Co–C stretch at 415 cm^{-1} matches the very strong mode found (183) at 420 cm^{-1} for $GeH_3Co(CO)_4$. The metal-metal stretches are both polarised and occur at 269 and 205 cm^{-1}, compared with 268 cm^{-1} for digermane (92,289), 228 cm^{-1} for $GeH_3Co(CO)_4$ (183) and values for $Ge_2H_5Mn(CO)_5$ of 273 and 205 cm^{-1}. It is interesting that very similar frequencies are observed for both the cobalt and manganese compounds, with the asymmetric stretch near νGeGe of the polygermanes and the symmetric stretch at 10–15 cm^{-1} below the Ge–metal mode of the germyl compounds. As the compound is light sensitive and darkened rapidly in the laser beam, only the low frequency region was observed in the Raman. This problem can perhaps be overcome by using a 'cold-cell' type sampling method or a rotating cell.

4.3.4 Halide-Transition Metal Exchange

A 5:4 mixture of $GeH_3Co(CO)_4$ and GeH_2H_5Cl comes to equilibrium after a few hours with the balance

$$GeH_3Co(CO)_4 + Ge_2H_5Cl = Ge_2H_5Co(CO)_4 + GeH_3Cl$$

lying well in favour of the digermanyl cobalt species. This is the first observed halide-transition metal exchange where both functional groups are attached to a group IV metal. Alternatively, this reaction can also be described as a group IV-group IV exchange. The reaction clearly demonstrates $Ge_2H_5Co(CO)_4$ and GeH_3Cl to be thermodynamically favoured over $GeH_3Co(CO)_4$ and Ge_2H_5Cl thus lending support to physical observations that the polygermanyl transition metal compounds are more stable than their germyl analogues and conversely the germyl halides more stable than the digermanyl ones. The feasibility of such a reaction is probably dependent on the nett bond-breaking and bond-making energy changes. Although the possible useful applications of this new reaction is still speculative, it is likely to be restricted to reactants with relatively weak M'-X bonds (X = halides, Co, Fe).

4.3.5 Substitution and Cleavage Reactions of $Ge_2H_5Co(CO)_4$

No reaction was observed between $Ge_2H_5Co(CO)_4$ or $GeH_3Co(CO)_4$ and CCl_4 or $GeCl_4$ under similar conditions to those where substitutions of Mn and Ge_2 compounds were found (see section 1.4.3(b)). In fact, no substitution at M' has yet been reported of a cobalt derivative. The only substitution observed so far is displacement of CO by PPh_3 in $SiH_3Co(CO)_4$ (156,199,200) and in $GeH_3Co(CO)_4$ (141).

The more commonly observed reactions of group IV-cobalt compounds involve cleavage of the M'-Co bond (see section 1.4.3(a)). HgX_2 (X = Cl,Br,I) quantitatively cleaves the Si-Co or Ge-Co bonds in $SiH_3Co(CO)_4$ (200), $GeH_3Co(CO)_4$ (183), $MeGeH_2Co(CO)_4$ (184) and $Me_2GeHCo(CO)_4$ (163). Such a reaction with the catenated group IV (hydride)-transition metal compounds involves an extra element -

the presence of the M'–M' bond. However, this work demonstrates that only the Ge–Co bond in $Ge_2H_5Co(CO)_4$ is cleaved in the reaction with $HgCl_2$

$$2Ge_2H_5Co(CO)_4 + HgCl_2 \longrightarrow 2Ge_2H_5Cl + Hg\,[Co(CO)_4]_2$$

and the reaction is essentially quantitative, being accompanied by a little Ge_2H_6 probably arising from Ge_2H_5Cl. A trace of GeH_3Cl could indicate a minor amount of Ge–Ge cleavage.

4.3.6 Metal–Metal Exchange

It has been shown (198) that a transition metal anion is capable of displacing another bonded to a GeH_3 or $MeGeH_2$ group in the order:

$$Co \longrightarrow Ge \longrightarrow Mn$$

This work shows the metal carbonyl exchange in the polygermanyl-transition metal carbonyls follows the same course. The digermanyl group is exchanged

$$Ge_2H_5Co(CO)_4 + Mn(CO)_5^- \longrightarrow Ge_2H_5Mn(CO)_5 + Co(CO)_4^-$$

with no evidence of Ge–Ge cleavage and with a somewhat higher recovery of the manganese compound, again possibly reflecting the better method of anion preparation.

CHAPTER 5. PREPARATION AND CHARACTERISATION OF 2-TRIGERMANYLPENTACARBONYLMANGANESE $(GeH_3)_2GeHMn(CO)_5$, 1,2-BIS(PENTACARBONYLMANGANIO)-DIGERMANE $[GeH_2Mn(CO)_5]_2$, AND 1,2-BIS(TETRACARBONYLCOBALTO)-DIGERMANE $[GeH_2Co(CO)_4]_2$.

The reaction chemistry of digermane and trigermane have been reviewed in Chapter 1 (1.3.3). An equimolar mixture of Ge_2H_6 and $SnCl_4$ (139,140) affords a 4:1 product mixture of Ge_2H_5Cl and 1,2-GeH_4Cl_2. Iodine reacts similarly with Ge_2H_6 (132,136) and has been shown to substitute mainly on the central atom of trigermane (137) at -63 °C, yielding on methylation of the iodotrigermane, a mixture of 2-methyltrigermane (80%) and the 1-substituted isomer (12%).

As the syntheses of the manganese and cobalt derivatives of digermane had been successful, with few complications, using the well-established alkali-halide elimination, it was decided to extend the transition metal carbonyl studies to the disubstituted digermane system and also into the trigermane system using the above known substitution routes as access to these compounds.

5.1 Preparation

5.1.1 Preparation of $Ge_3H_7Mn(CO)_5$

Trigermane (639.2 mg, 2.83 mmol) was condensed on to resublimed iodine (685.3 mg, 2.70 mmol) in a vessel with a side-arm and allowed to warm to -63 °C. Reaction took place over 7 hours to leave a pale-violet liquid. The volatiles at -63 °C were fractionated to give H_2 (0.10 mmol), Ge_3H_8 (trace) at -83 °C and HI (283.2 mg, 2.10 mmol) at -196 °C. An ethereal solution of excess $NaMn(CO)_5$, prepared from $Mn_2(CO)_{10}$ (117 mg, 3.5 mmol) was added under nitrogen to the frozen Ge_3H_7I via a side-arm in the reaction tube. The reaction mixture was shaken for 30 minutes at room temperature after which the volatiles were fractionated to give ether at -196 °C and $Ge_3H_7Mn(CO)_5$ with a trace of $Ge_2H_5Mn(CO)_5$ (identified by i.r. and nmr) at -23 °C. Removal of the head fraction (ca. 2%) left a pure sample of $Ge_3H_7Mn(CO)_5$ (665.3 mg, 1.584 mmol, 72% based on HI formed). The compound was identified as 2-trigermanylpentacarbonylmanganese by the ^1H nmr spectrum which shows a doublet signal at 6.36 τ, a septet at 7.09 τ, and J = 4.4 Hz, integration giving their relative intensities at approximately 6:1. These signals are assignable to $(GeH_3)_2$ and GeH of $(GeH_3)_2GeHMn(CO)_5$ respectively. There was no evidence for the presence of the 1-isomer. The parent ions in the mass spectrum are found at m/e = 409 to 430 ($^{12}C_5{}^1H_7{}^{16}O_5{}^{55}Mn^nGe_3$ requires 430 for n = 76 to 412 for n = 70 with P - H = 80% P, P - 2H = 30% P and P - 3H = 20% P). Further characterisation was provided by the fragmentation pattern, the vibrational spectrum and by the reaction with CCl_4. These are reported and discussed in later sections of this chapter.

$(GeH_3)_2GeHMn(CO)_5$ is a colourless liquid of extremely low vapour pressure ($<$ 0.1 mm at 23 °C) and several hours were required to move 1.5 mmol at diffusion pump pressures. The compound showed no tendency to decompose in light at room temperature and showed remarkable thermal stability. A sample of the compound and another of Ge_3H_8 in sealed tubes were heated to 80 °C for 30 minutes. Nmr and i.r. spectra showed no signs of decomposition in either case.

5.1.2 Preparation of $Mn(CO)_5GeH_2GeH_2Mn(CO)_5$

Digermanyl dichloride, $ClGeH_2GeH_2Cl$ (150.8 mg, 0.6855 mmol) was condensed into $NaMn(CO)_5$ prepared in the usual manner by the reduction of $Mn_2(CO)_{10}$ (424.2 mg, 1.088 mmol). The mixture was shaken for 15 minutes at room temperature after which all volatiles were removed, leaving a non-volatile colourless liquid amongst solid residues (NaCl and excess $NaMn(CO)_5$) in the reaction vessel. This was extracted with cyclohexane. The compound was identified as <u>1,2-bis(pentacarbonylmanganio)digermane</u> (yield estimated at 70%) by the singlet resonance at 6.03τ in the nmr spectrum taken with the mass of the parent ions in the mass spectrum (m/e = 533–546: $^{12}C_{10}\,^{1}H_4\,^{16}O_{10}\,^{55}Mn_2\,^{n}Ge_2$ requires 546 for n = 76 to 534 for n = 70 with P – H = 5% P). Further characterisation was obtained by the mass spectral fragmentation pattern and by the infrared spectrum. Attempts at recording the Raman spectrum of a solution sample in cyclohexane were unsuccessful due to strong fluorescence.

$[GeH_2Mn(CO)_5]_2$ is a non-volatile, colourless oil. The compound showed no tendency to decompose at room temperature *in vacuo*, under nitrogen atmosphere, or in light and has the characteristic strong digermane odour.

5.1.3 Preparation of $Co(CO)_4GeH_2GeH_2Co(CO)_4$

The procedure was similar to that for $[GeH_2Mn(CO)_5]_2$. Digermanyl dichloride, $ClGeH_2GeH_2Cl$ (163.1 mg, 0.7380 mmol) was condensed into $NaCo(CO)_4$ prepared using $Co_2(CO)_8$ (455.0 mg, 1.331 mmol). The product was extracted in a similar manner, using cyclohexane to yield 1,2-bis(tetracarbonylcobalto)-digermane (estimated yield 80%). $[GeH_2Co(CO)_4]_2$ lacks the parent ion in the mass spectrum, but the singlet resonance at 5.69τ taken with the mass spectral fragmentation pattern, the infrared spectrum, and its reaction with $HgCl_2$ all support the above formulation for the compound. These are reported and discussed later in this chapter.

$[GeH_2Co(CO)_4]_2$ forms non-volatile colourless crystals, but rapidly gains a dark brown colour when exposed to light. Decomposition is slow in the dark yielding a brown solution with no evidence for production of Ge_2H_6. As with most digermanyl derivatives, the compound has the typical strong odour characteristic of digermane.

5.2 Reactions

5.2.1 $(GeH_3)_2GeHMn(CO)_5$ and CCl_4

a) $(GeH_3)_2GeHMn(CO)_5$ in CCl_4

Changes in the ^1H nmr spectrum of a sample of $(GeH_3)_2GeHMn(CO)_5$ in CCl_4 with internal TMS as reference, were observed at room temperature. Reaction was rapid and complete in ½ hour, the parent signals disappearing leaving a yellow precipitate. A large amount of $CHCl_3$ (2.80 τ) was observed with no evidence for CH_2Cl_2.

Integration showed the $CHCl_3$ signal to be slightly less intense than the original doublet signal of $(GeH_3)_2GeHMn(CO)_5$. A chloride microanalysis showed the precipitate to contain 36% Cl corresponding to in excess of 3 chlorine atoms per molecule.

b) $(GeH_3)_2GeHMn(CO)_5 + CCl_4$

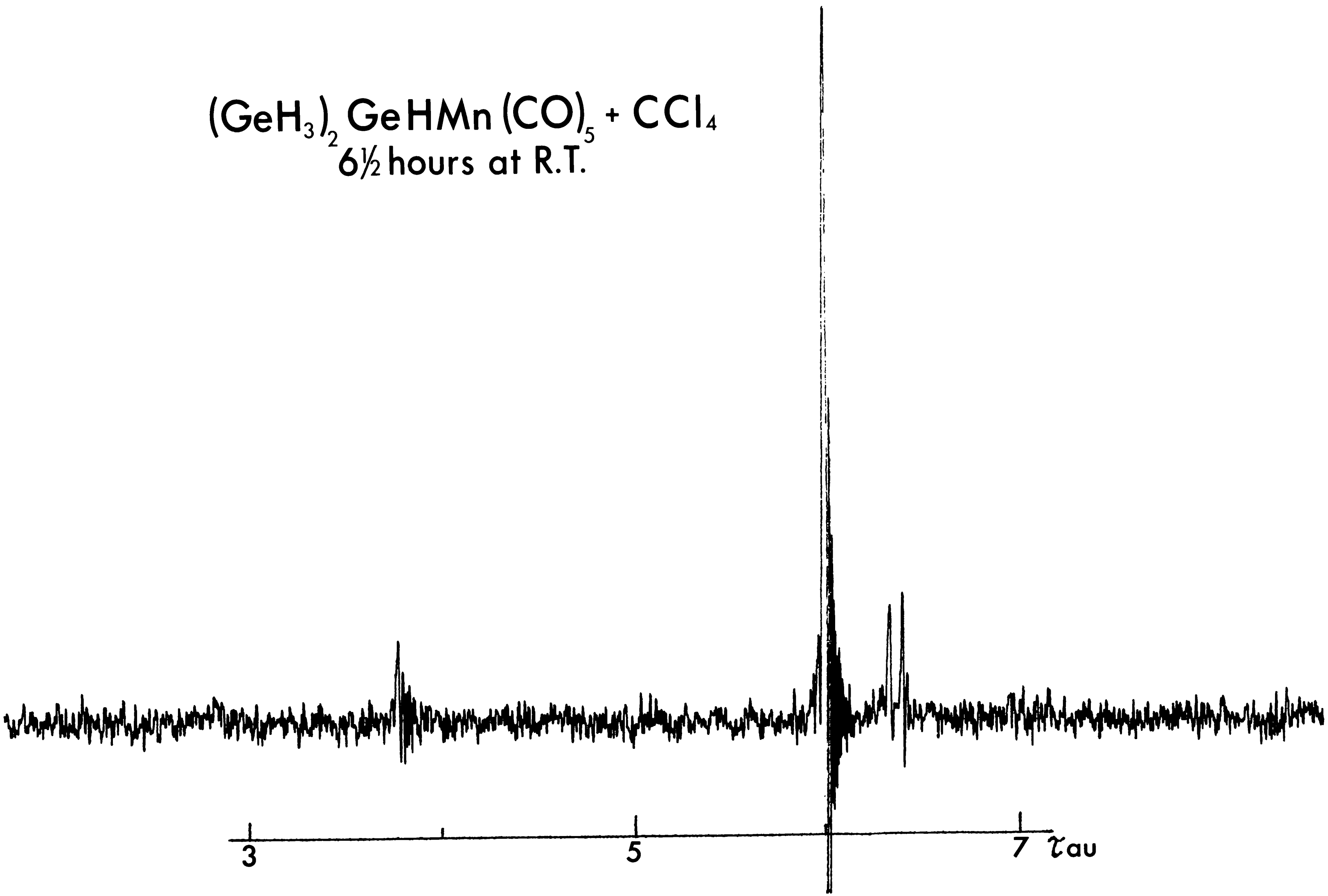
$(GeH_3)_2GeHMn(CO)_5$ (23.2 mg, 0.055 mmol) and CCl_4 (7.3 mg, 0.047 mmol) were combined with deuterobenzene in a nmr tube. No reaction was observed at +5 ^{o}C for 20 minutes. Reaction, however, was rapid at room temperature with immediate changes observed. A singlet signal at 6.05 τ assigned to $(GeH_3)_2GeClMn(CO)_5$ together with a weaker singlet at 3.81 τ assigned to CH_2Cl_2 appeared and increased over the reaction period although not proportionally. At no instant was the $CHCl_3$ signal at 2.8 τ much stronger than the weak overlapping deuterobenzene resonance. These changes ceased after 4 hours and integration showed the assigned chloro-compound and excess starting material, $(GeH_3)_2GeHMn(CO)_5$, to be present in the ratio of 5.5:1 in the reaction mixture. The sum of the intensities of the weak $CHCl_3$ and CH_2Cl_2 signals was approximately a sixth the intensity of the strong singlet due to $(GeH_3)_2GeClMn(CO)_5$. No further changes were observed for the next 2½ hours and the signal assigned to the chlorosubstituted product did not show any sign of weakening. The nmr spectrum recorded at 6½ hours is shown in Fig. 5.1. The reaction tube was opened. The solvent and excess $(GeH_3)_2GeHMn(CO)_5$ were removed on the vacuum line to leave a near to involatile, colourless liquid which slowly gained a light-orange tint during manipulations.

Figure 5.1

Nmr Spectrum of

$(GeH_3)_2GeHMn(CO)_5 + CCl_4$

Reaction at 6½ hours



$(GeH_3)_2GeHMn(CO)_5 + CCl_4$
6½ hours at R.T.

An i.r. spectrum of a cyclohexane solution and the mass spectrum were recorded of this liquid and confirmed the earlier assignment of $(GeH_3)_2GeClMn(CO)_5$. These spectroscopic details are discussed later on.

5.2.2 $Co(CO)_4GeH_2GeH_2Co(CO)_4$ and $HgCl_2$

$[GeH_2Co(CO)_4]_2$ (ca. 0.13 mmol) and $HgCl_2$ (13.6 mg, 0.05 mmol) were combined in benzene and reaction followed by ^1H nmr at room temperature. Changes were detected almost immediately. As the singlet resonance at 5.69τ due to $[GeH_2Co(CO)_4]_2$ weakened, a new singlet at 5.09 τ (same value as ref. 139) was observed, attributed to $(GeH_2Cl)_2$. Two weak triplet signals of equal intensities were also observed towards the end of the reaction and these were assigned to the intermediate $Co(CO)_4GeH_2GeH_2Cl$. These occurred at $\tau GeH_2Co = 5.97$, $\tau GeH_2Cl = 4.75$ and $J = 4.24$ Hz). Changes ceased after 30 minutes with the product mixture composed largely of $(GeH_2Cl)_2$ and excess $[GeH_2Co(CO)_4]_2$ with $Co(CO)_4GeH_2GeH_2Cl$ as a minor product. A brown-grey deposit, probably $ClHgCo(CO)_4$ or $Hg[Co(CO)_4]_2$ was observed, but with no free Hg. After prolonged standing at room temperature the product resonance at 5.09τ weakened relative to the singlet of the excess $[GeH_2Co(CO)_4]_2$ to give rise to weak signals at 6.70τ and 4.93τ assigned to the GeH_3 and GeH_2 signals of Ge_2H_5Cl.

The tube was opened and volatiles fractionated through traps held at −23 °C into one held at −196 °C. I.r. spectra of gas samples showed the contents in the liquid nitrogen trap to be the solvent benzene together with a trace of Ge_2H_5Cl (133), and the material stopped at -23 °C to be 1,2-$Ge_2H_4Cl_2$ also contaminated with Ge_2H_5Cl. As the infrared spectrum of 1,2-$Ge_2H_4Cl_2$ has not been reported, the spectrum of a pure sample used as the starting material in the preparation of $[GeH_2Co(CO)_4]_2$ was recorded and the spectrum obtained for the above chlorocompound compared well with this. 1,2-Ge_2H_4Cl showed decomposition to Ge_2H_5Cl while the i.r. spectrum was being recorded. The spectrum is reported together with the discussion of the reaction towards the end of this chapter.

5.3 Discussion

5.3.1 General

The reaction of iodine with trigermane at -63 °C followed by manganese carbonyl coupling yielded only 2-$Ge_3H_7Mn(CO)_5$ and no 1-$Ge_3H_7Mn(CO)_5$ was detected,

$$Ge_3H_8 + I_2 \xrightarrow{-63\ ^{o}C} Ge_3H_7I + HI$$

$$Ge_3H_7I + NaMn(CO)_5 \longrightarrow (GeH_3)_2GeHMn(CO)_5 + NaI$$

In contrast to the similar iodine substitution followed by methylation of trigermane (137) which produced a 7:1 mixture of 2-$MeGe_3H_7$ and 1-$MeGe_3H_7$. This can be attributed to the fact that a slight deficit of iodine was used for the reaction in this work whereas an equimolar reactant mixture was used in the earlier study. Reaction time is probably not a factor as the iodination process in this work was allowed 7 hours compared with 2 hours in the previous case. The 2.1 mmoles of HI resulted from I_2 substitution of Ge_3H_8 to give monoiodotrigermane and the 0.1 mmoles of H_2 is evolved by HI substitution of Ge_3H_8 or Ge_3H_7I to further give traces of monoiodotrigermane or polyiodotrigermane. This leaves 0.5 of the total 2.7 mmoles of I_2, probably consumed in Ge-Ge bond cleavage of 0.5 mmoles of Ge_3H_8 resulting in the small amount of $Ge_2H_5Mn(CO)_5$ formed on coupling. The rest of the trigermane (2.3 mmoles) was consumed in substitution which corresponds to the total amount of HI and H_2 obtained. Thus the HI suggests a 78% conversion of trigermane to monoiodotrigermane. The 72% yield of the manganese compound based on HI is therefore quite reasonable as monoiodination forms HI. Any polymanganese compound, if formed, from the traces of polyiodotrigermane would not be volatile and would have remained in the reaction vessel. The reactivity of HI (143) has been observed elsewhere (see pages 21,22) with digermane. No transition metal derivative of trigermane has yet been reported. 2-trigermanylpetacarbonylmanganese is thus the first transition metal derivative of a group IV metal (hydride) with a catenation of three group IV metal atoms.

The reactions between 1,2-digermanyldichloride and excess metal carbonyl anions yield single compounds:

$$ClGeH_2GeH_2Cl + 2M(CO)_x^- \longrightarrow M(CO)_xGeH_2GeH_2M(CO)_x + 2Cl^-$$

$$(M = Mn,\ x = 5;\quad M = Co,\ x = 4)$$

This shows complete halide elimination to give near quantitative yields of the products. As the digermanyl di-transition metal compounds are non-volatile, they had to be extracted from the reaction vessel with a solvent involving some loss, thus the approximate yields. The first example of a M-M'-M'-M system was a disilanyl di-iron compound by King _et al._ (171):

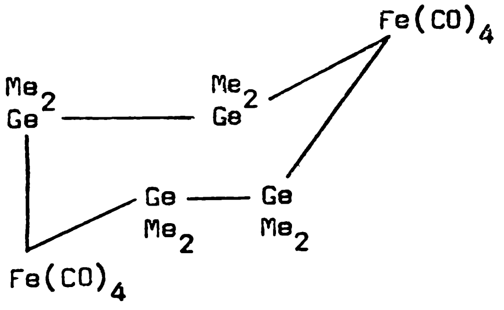
$$ClSiMe_2SiMe_2Cl + 2NaFe(CO)_2Cp \longrightarrow CpFe(CO)_2SiMe_2SiMe_2Fe(CO)_2Cp + 2NaCl$$

Malisch (255) expanded this system to include the chromium, molybdenum and tungsten analogues and also demonstrated the quantitative nature of the reaction by isolating the partially substituted compounds:

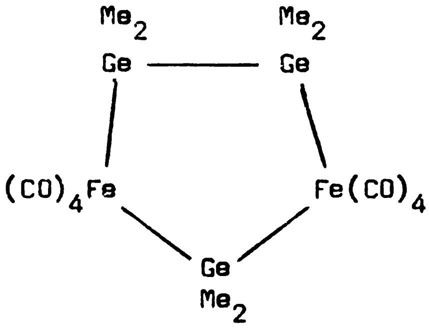
$$XSiMe_2SiMe_2X + NaM(CO)_nCp \longrightarrow Cp(CO)_nMSiMe_2SiMe_2X$$

$$(M = Cr,\ Mo,\ W,\ Fe;\quad n = 3,2;\quad X = F,\ Cl,\ Br)$$

Working with the dianion system, Triplett and Curtis (261) isolated the novel heterocyclic compounds, cyclo - 1,4-bis(tetracarbonyliron) - 2,3,5,6 - tetrakis (dimethylgermanium) and cyclo - 1,3 - bis(tetracarbonyliron) - 2,4,5 - tris - (dimethylgermanium), I and II, respectively.



I



II

$$ClMe_2GeGeMe_2Cl + Na_2Fe(CO)_4 \longrightarrow I + II + 2NaCl$$

The three-membered ring $Me_2GeGeMe_2Fe(CO)_4$ is not formed. This is perhaps due to the angle strain as such a structure requires the acute trimetallic angle of 60^o compared with the normal tetrahedral angle of germanium. No attempt was made at the reaction between $ClGeH_2GeH_2Cl$ and $Na_2Fe(CO)_4$ in this work as it is likely to lead to complex structures observed for $ClMe_2GeGeMe_2Cl$ above.

The increase in steric crowding by the introduction of another GeH_3 group in $(GeH_3)_2GeHMn(CO)_5$ does not seem to make it any less stable than $GeH_3GeH_2Mn(CO)_5$. It is thermally just as stable as trigermane to the experimentally conducted temperature of 80 °C, but is considerably more stable than $GeH_3Mn(CO)_5$ (162) which begins to show decomposition at 60.5 °C. Thus there is increasing evidence to suggest the catenated germanium derivatives are more stable than their germyl analogues.

Model studies reveal considerable steric crowding in the M–M'–M'–M systems. In fact these compounds containing the four metal chain are restricted to the trans-configuration as free rotation is not possible. Yet these compounds show stabilities at least comparable to the M'–M'–M systems. Thus it would seem that both the manganese and cobalt carbonyl groups confer a certain degree of stability to the molecule containing it, enough to overcome the strain imposed by steric crowding.

5.3.2 The Mass Spectra of Trigermanylpentacarbonylmanganese, Bis(pentacarbonylmanganio)-digermane and Bis(tetracarbonylcobalto)-digermane.

The mass spectrum of trigermanylpentacarbonylmanganese was obtained by gas-sampling and is listed in Table 5.1 along with the assignments and relative ion intensities of the various families which were made with the aid of the calculated mass spectral envelopes for Ge_3, Ge_2 and Ge_1 given in Fig. 2.3.

The fragmentation pattern of $(GeH_3)_2GeHMn(CO)_5$ largely resembles those of $GeH_3Mn(CO)_5$ (162), $GeH_3GeH_2Mn(CO)_5$ (see section 3.3.1) and $GeH_3GeH_2Co(CO)_4$ (see section 4.3.2). The major processes are CO loss and Ge-Ge bond cleavage by either GeH_2 or GeH_4 elimination. The $H_xGe_2Mn(CO)_n^+$ ions are formed mainly by GeH_2 elimination of the $H_xGe_3Mn(CO)_n^+$ species and the $H_xGeMn(CO)_n^+$ ions in turn formed from the $H_xGe_2Mn(CO)_n^+$ fragment ions by a similar process. However, there is evidence also for GeH_4 loss e.g.

$$H_7Ge_3Mn(CO)_5^+ \longrightarrow H_3Ge_2Mn(CO)_5^+ + GeH_4$$

Hydrogen loss in the $H_xGe_3Mn(CO)_n^+$ families becomes significant only after loss of one carbonyl with the base peak $H_xGe_3Mn^+$ largely containing three hydrogens. The $H_xGe_2Mn(CO)_n^+$ and $H_xGeMn(CO)_n^+$ families tend to retain three and one hydrogen respectively.

Rearrangement ions e.g. $HMn(CO)_5^+$ are also seen. The ion currents carried by Ge_3Mn, Ge_2Mn and GeMn containing species are 20%, 46% and 22% respectively. These species retaining the Ge-Mn bond account for 88% of the total ion current, which is almost exactly the same as that for $Ge_2H_5Mn(CO)_5$ at 87.6% but both significantly higher than the 79.7% obtained for $GeH_3Mn(CO)_5$ (162).

Table 5.1 Mass Spectrum of $(GeH_3)_2GeHMn(CO)_5$

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogen(b) x=7	6	5	4	3	2	1	0
409–430	$H_xGe_3Mn(CO)_5^+$	3.2	10	8	3	2				
380–402	$H_xGe_3Mn(CO)_4^+$	4.5	10	3	3	2	1			
351–372	$H_xGe_3Mn(CO)_3^+$	8.9	3	5	10	3	?	?		
324–344	$H_xGe_3Mn(CO)_2^+$	4.9		?	10	?	?			
296–316	$H_xGe_3Mn(CO)^+$	10.2			10	?	?			
274–288	$H_xGe_3Mn^+$	100			?	?	10	?	?	
335–352	$H_xGe_2Mn(CO)_5^+$	75.4			1	1	10	1	1	1
309–323	$H_xGe_2Mn(CO)_4^+$	62.9				1	10	0.5		
281–295	$H_xGe_2Mn(CO)_3^+$	62.1				2	10	?		
253–267	$H_xGe_2Mn(CO)_2^+$	12.5				?	10	1	1	
225–239	$H_xGe_2Mn(CO)^+$	25.0				?	10	?		
198–210	$H_xGe_2Mn^+$	73.9					10			
265–272	$H_xGeMn(CO)_5^+$	52.3							10	1
237–244	$H_xGeMn(CO)_4^+$	37.9							10	2
209–216	$H_xGeMn(CO)_3^+$	12.9							10	?
181–189	$H_xGeMn(CO)_2^+$	5.7						1	10	3
153–161(c)	$H_xGeMn(CO)^+$	8.5						1	10	3
125–133(c)	H_xGeMn^+	29.2						1	10	5
212–230	$H_xGe_3^+$	8.5				?	?	10	?	
143–154	$H_xGe_2^+$	17.0						10	5	
70–77	H_xGe^+	5.7							6	10
196	$HMn(CO)_5^+$	1.7								
195	$Mn(CO)_5^+$	1.5								
168	$HMn(CO)_4^+$	0.2								
167	$Mn(CO)_4^+$	0.4								

Table 5.1 (cont.)

140	$HMn(CO)_3^+$	0.4
139	$Mn(CO)_3^+$	1.7
112	$HMn(CO)_2^+$	0.4
111	$Mn(CO)_2^+$	3.2
84	$HMn(CO)^+$	(d)
83	$Mn(CO)^+$	4.2
56	HMn^+	5.3
55	Mn^+	36.0
28	CO^+	(e)

Footnote:

(a) Summed over x = 1 - 7 and Ge isotopes where appropriate.

(b) Relative to strongest component of the family = 10.0

(c) Metastable peaks observed.

(d) Strong peak, includes trace of hydrocarbon in background.

(e) Strong peak, includes N_2^+.

The mass spectra of $[GeH_2Mn(CO)_5]_2$ and $[GeH_2Co(CO)_4]_2$ were obtained using the solid insertion probe and are summarised in Tables 5.2 and 5.3. A noticeable feature in the mass spectrum of the latter compound is the weak peaks due to $H_xGe_2^+$ and H_xGe^+. These peaks were dominant in the spectra of $Ge_2H_5Co(CO)_4$. This seems to support earlier suspicions that those strong peaks were due to Ge_2H_6, a product of decomposition of $Ge_2H_5Co(CO)_4$. Earlier observations have shown that decomposition of $[GeH_2Co(CO)_4]_2$ does not give rise to Ge_2H_6. Another feature of the spectrum of $[GeH_2Co(CO)_4]_2$ is the lack of the parent ions $H_xGe_2Co_2(CO)_8^+$. The parent ions appeared quite strongly in $GeH_3Co(CO)_4$ (183), as a weak envelope in $Ge_2H_5Co(CO)_4$, and are absent in $X_{4-n}Ge[Co(CO)_4]_n$ (X = Cl, Br) (291). Thus there are strong indications to suggest weakening of the parent ions of a cobalt derivative as it becomes more complex. Only seven carbonyl loss envelopes from $H_xGe_2Co_2(CO)_n^+$ are seen, but ten in $H_xGe_2Mn_2(CO)_n^+$.

The fragmentation patterns of $[GeH_2Mn(CO)_5]_2$ and $[GeH_2Co(CO)_4]_2$ are very similar. There is complete loss of hydrogens after loss of two or three carbonyls from the parent ions. There is little tendency for direct Ge–Ge bond cleavage as only weak $H_xGeMn(CO)_n^+$ peaks were observed. Surprisingly, strong peaks due to $H_xGeCo_2(CO)_n^+$ ion were observed instead, suggesting Ge–Ge bond cleavage to be accompanied by a 1,2-metal carbonyl group rearrangement. In the spectra of $Ge_2H_5Co(CO)_4$ (see Table 4.1) and $Ge_3H_7Mn(CO)_5$ (see Table 5.1) rearrangement ions of the type $HM(CO)_x^+$ are observed as in other reported cases (162,183).

Table 5.2 The Mass Spectrum of $[GeH_2Mn(CO)_5]_2$

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogen(b)				
			x=4	3	2	1	0
533–546	$H_xGe_2Mn_2(CO)_{10}^+$	25.0	10	0.5			
503–517	$H_xGe_2Mn_2(CO)_9^+$	2.4		9	10	8	
475–488	$H_xGe_2Mn_2(CO)_8^+$	2.3			10	5	
446–460	$H_xGe_2Mn_2(CO)_7^+$	4.3			2	3	10
418–429	$H_xGe_2Mn_2(CO)_6^+$	3.3				5	10
390–402	$H_xGe_2Mn_2(CO)_5^+$(c)	20.0					10
362–374	$H_xGe_2Mn_2(CO)_4^+$(c)	47.1					10
334–346	$H_xGe_2Mn_2(CO)_3^+$(c)	46.6					10
306–318	$H_xGe_2Mn_2(CO)_2^+$(c)	14.6					10
279–291	$H_xGe_2Mn_2(CO)^+$(c)	17.1					10
250–263	$H_xGe_2Mn_2^+$	100				4	10
	$H_xGe_2Mn(CO)_5^+$(d)	trace					
	$H_xGe_2Mn(CO)_4^+$(d)	trace					
	$H_xGe_2Mn(CO)_3^+$(d)	trace					
	$H_xGe_2Mn(CO)_2^+$(d)	trace					
225–238	$H_xGe_2Mn(CO)^+$	2.2		6	10	6	
195–208	H_xGeMn^+	31.2				3	10
460–469	$H_xGeMn_2(CO)_{10}^+$	2.9			1	5	10
432–439	$H_xGeMn_2(CO)_9^+$	56.1				1	10
404–411	$H_xGeMn_2(CO)_8^+$	16.8				2	10
376–383	$H_xGeMn_2(CO)_7^+$	5.9				3	10
348–355	$H_xGeMn_2(CO)_6^+$	3.4				2	10
320–327	$H_xGeMn_2(CO)_5^+$	14.0				2	10
292–300	$H_xGeMn_2(CO)_4^+$	7.7			2	2	10

Table 5.2 (cont.)

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogen(b)				
			x = 4	3	2	1	0
264–272	$H_xGeMn_2(CO)_3^+$	22.5			2	2	10
236–243	$H_xGeMn_2(CO)_2^+$	3.1				6	10
208–215	$H_xGeMn_2(CO)^+$	2.3				5	10
180–187	$H_xGeMn_2^+$	15.1				4	10
267–274	$H_xGeMn(CO)_5^+$(c)	1.6		6	10		
238–245	$H_xGeMn(CO)_4^+$(c)	4.6			2	10	
210–217	$H_xGeMn(CO)_3^+$(c)	5.0		1	2	10	
182–189	$H_xGeMn(CO)_2^+$(c)	8.1			1	10	
153–161	$H_xGeMn(CO)^+$	6.6			5	10	1
125–132	H_xGeMn^+	18.3				8	10
140–153	$H_xGe_2^+$	2.9				8	10
72–79	H_xGe^+	1.2		8	10		
390	$Mn_2(CO)_{10}^+$	0.5					
362	$Mn_2(CO)_9^+$	0.2					
344	$Mn_2(CO)_8^+$	0.1					
306	$Mn_2(CO)_7^+$	0.1					
278	$Mn_2(CO)_6^+$	0.0					
250	$Mn_2(CO)_5^+$	0.0					
222	$Mn_2(CO)_4^+$	1.3					
194	$Mn_2(CO)_3^+$?	0.1					
166	$Mn_2(CO)_2^+$	0.4					
138	$Mn_2(CO)^+$	0.1					
110	Mn_2^+	3.7					

Table 5.2 (Cont.)

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogen(b)				
			x =4	3	2	1	0
196	$HMn(CO)_5^+$	1.8					
195	$Mn(CO)_5^+$	5.5					
168	$HMn(CO)_4^+$	0.9					
167	$Mn(CO)_4^+$	0.5					
140	$HMn(CO)_3^+$	1.8					
139	$Mn(CO)_3^+$	1.7					
112	$HMn(CO)_2^+$	1.0					
111	$Mn(CO)_2^+$	3.7					
84	$HMn(CO)^+$	8.5					
83	$Mn(CO)^+$	4.6					
56	HMn^+	9.8					
55	Mn^+	19.5					
28	CO^+	(e)					

Footnotes:

(a) Summed over x = 0-4 and Ge isotopes where appropriate.

(b) Relative to strongest component of the family = 10.0

(c) Overlapping with envelopes due to $H_xGeMn_2(CO)_n^+$

(d) Traces of these fragment ions identified by slight irregular shape of strong overlapping envelopes of $H_xGe_2Mn_2(CO)_n^+$

(e) Strong peak, includes N_2^+.

Table 5.3 The Mass Spectrum of $[GeH_2Co(CO)_4]_2$

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogen(b)				
			x = 4	3	2	1	0
	$H_xGe_2Co_2(CO)_8^+$	0					
457–470	$H_xGe_2Co_2(CO)_7^+$	18.3	10	0.5			
428–442	$H_xGe_2Co_2(CO)_6^+$	37.7	10	1	1		
399–414	$H_xGe_2Co_2(CO)_5^+$	66.3	0.5	0.5	10	0.5	
370–383	$H_xGe_2Co_2(CO)_4^+$	21.1				0.5	10
342–355	$H_xGe_2Co_2(CO)_3^+$	64.0				0.5	10
314–327	$H_xGe_2Co_2(CO)_2^+$	51.4				1	10
286–299	$H_xGe_2Co_2(CO)^+$	45.1				1	10
258–271	$H_xGe_2Co_2^+$	100				5	10
	$H_xGe_2Co(CO)_4^+$(c)						
	$H_xGe_2Co(CO)_3^+$(c)						
	$H_xGe_2Co(CO)_2^+$(c)						
229–243	$H_xGe_2Co(CO)^+$	3.5	2	10	1		
199–212	$H_xGe_2Co^+$	25.7				3	10
	$H_xGeCo_2(CO)_8^+$	0					
384–391	$H_xGeCo_2(CO)_7^+$	4.7				1	10
354–363	$H_xGeCo_2(CO)_6^+$	5.5				1	10
328–335	$H_xGeCo_2(CO)_5^+$	3.8				3	10
302–307	$H_xGeCo_2(CO)_4^+$	7.0				1	10
272–279	$H_xGeCo_2(CO)_3^+$	6.5				1	10
244–251	$H_xGeCo_2(CO)_2^+$	0.7				2	10
216–223	$H_xGeCo_2(CO)^+$	1.0				2	10
188–195	$H_xGeCo_2^+$	5.6				5	10

Table 5.3 (Cont.)

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogen(b)				
			x = 4	3	2	1	0
240–246	$H_xGeCo(CO)_4^+$(d)	1.0				10	
212–218	$H_xGeCo(CO)_3^+$(d)	0.7				10	
184–190	$H_xGeCo(CO)_2^+$(d)	1.5				10	
156–162	$H_xGeCo(CO)^+$(d)	4.0				10	
127–133	H_xGeCo^+(d)	11.4					10
140–153	$H_xGe_2^+$(d)	4.0				5	10
71–77	H_xGe^+(d)	0.7				10	3
342	$Co_2(CO)_8^+$(d)	0.6					
314	$Co_2(CO)_7^+$(d)	0.6					
286	$Co_2(CO)_6^+$(d)	0.6					
258	$Co_2(CO)_5^+$(d)	0.6					
230	$Co_2(CO)_4^+$	0.3					
202	$Co_2(CO)_3^+$?						
174	$Co_2(CO)_2^+$(d)	0.2					
146	$Co_2(CO)^+$(d)	0.9					
118	Co_2^+(d)	0.9					
171	$Co(CO)_4^+$(d)	0.6					
143	$Co(CO)_3^+$?						
115	$Co(CO)_2^+$	1.7					
87	$Co(CO)^+$	8.6					
59	Co^+	1.7					
28	CO^+	(e)					

Table 5.3 (Cont.)

Footnotes:

(a) Summed over x = 0–4 and Ge isotopes where appropriate

(b) Relative to strongest component of the family = 10

(c) Overlapped by strong envelopes due to $Ge_2Co_2(CO)_n^+$, but presumably weak.

(d) Weak peaks and where overlap occurs identified by irregular shape of overlapping envelope

(e) Strong peak, includes N_2^+.

The earlier mentioned examples $X_{4-n}Ge\ [Co(CO)_4]_n$ (291) also show metal carbonyl rearrangement as relatively strong peaks due to $Co_2(CO)_n^+$ are present. Such ions are again observed here. The spectra of both $[GeH_2Mn(CO)_5]_2$ and $[GeH_2Co(CO)_4]_2$ are dominated by species retaining the Ge-Ge bond compared to $Ge_2H_5Mn(CO)_5$ or $Ge_2H_5Co(CO)_4$:

	Sum of Ge_2M_2 and Ge_2M (%)	Sum of GeM_2 and GeM (%)
$Mn(CO)_5GeH_2GeH_2Mn(CO)_5$	55	33
$Co(CO)_4GeH_2GeH_2Co(CO)_4$	85	11
$GeH_3GeH_2Mn(CO)_5$	39	48
$GeH_3GeH_2Co(CO)_4$	41	45

This seems to indicate a reluctance of the Ge-Ge bonds to cleave in the complex M-M'-M'-M system containing two metal carbonyls. The total ion currents carried by Ge-Mn and Ge-Co retaining fragments in $[GeH_2Mn(CO)_5]_2$ and $[GeH_2Co(CO)_4]_2$ are 88% and 96% respectively.

5.3.3 The Vibrational Spectra of 2-Trigermanylpentacarbonylmanganese, 1,2-Bis(pentacarbonylmanganio)-digermane, and 1,2-Bis(tetracarbonylcobalto)-digermane

The vibrational spectrum of $(GeH_3)_2GeHMn(CO)_5$ is listed in Table 5.4. Only about a half of the expected 57 absorptions are observed, at best. The vibrations due to the manganese carbonyl moiety show good comparison with those of $Ge_2H_5Mn(CO)_5$ and $GeH_3Mn(CO)_5$ (162), again reflecting the local C_{4v} symmetry instead of

Table 5.4 Vibrational Spectra of $(GeH_3)_2GeHMn(CO)_5(cm^{-1})$

I.r.(solution)(a)	I.R.(solid)	Raman(liquid)(b)	Assignment
	2104 vw		
2102 s	2099 vw	2101 s,p	νCO,a_1
2096 w,sh	2098 vw		ν^{13}CO
2068 m,sh	2063 w	2070 w(p?)	νGeH
2060 s	2054 w	2063 m,dp	
	2044 vw		
2050 s	2035 w	2052 s,p	νCO, a_1
2035 vw,sh	2009 m,sh	2040 m,dp	νCO, b_1
2030 vw,sh	2000 w,sh		
2028 w,sh			
	1994 s,sh	2005 vw,dp	νCO, e
2014 s,sh	1990 s,sh		
2007 vvs	1983 vs		
1982 vvw			
1975 w	1969 w,sh		ν^{13}CO
	1965 w,sh		
1965 vw	1959 w,sh		
	1956 w,sh		
1954 vvw	1921 w		
1941 w	1914 w		
	870 vw		δasym.GeH$_3$, a' + a"
	864 vw		

Table 5.4 (Cont.)

I.r.(solution)(a)	I.r.(solid)	Raman(liquid)(b)	Assignment
800 s	783 mw		δ sym.GeH_3 a' + a"
774 s	765 m		
679 w	673 vw		δ GeH
670 vvw			
668 vvw	657 w		δ MnCO, a'
654 vs	648 s		
652 w,sh	635 vw		
639 s,sh	624 m		
588 w,br			
469 w	472 w		GeH_3 rock
		408 s,p	ν Mn-C, a'
		274 m,dp	ν asym. Ge-Ge, a"
		254 m,p	νsym. Ge-Ge, a'
		191 vw,p	νGe-Mn, a'
		155 w	
		105 s	skeletal deformation a"
		75 w,br	Ge-Ge-Ge bend, a'

Footnotes:

(a) I.r. solution spectrum in cyclohexane

(b) Raman spectrum of a neat liquid. Region between 1900 cm^{-1} - 700 cm^{-1} not scanned.

the overall C_s with bands assignable to $2a_1 + b_1 + e$ modes, supported by Raman studies. Vibrations due to the $(GeH_3)_2GeH$- fragment show interesting features. Weak bands in the 850 cm^{-1} region are assigned to the asymmetric GeH_3 deformations. However, there are two clear strong absorptions between 800 cm^{-1} and 750 cm^{-1}. Only one such band is observed in the spectrum of $GeH_3GeH_2Mn(CO)_5$, $GeH_3GeH_2Co(CO)_4$ and GeH_3GeH_2Cl (133). These bands have been assigned to the in-phase and out-of-phase symmetric deformations of the two GeH_3 groups thus lending support to the formulation of the compound with two GeH_3 groups with the $Mn(CO)_5$ group attached to the central germanium atom. The weak band near 675 cm^{-1} is assigned to the deformation due to the lone Ge-H bond, matching the GeH_x deformation in the other manganese derivatives mentioned earlier.

The strong polarised Mn-C stretch at 408 cm^{-1} matches the very strong mode found at 409 cm^{-1} for $GeH_3Mn(CO)_5$ (162). The Raman spectrum of the metal-metal stretching region is shown in Fig. 5.2. The spectra of the same region for Ge_3H_8 (54) and 2-$MeGe_3H_7$ (137) are given in Fig. 5.3 for comparison. The very strong polarised band at 191 cm^{-1} in the spectrum of $(GeH_3)_2GeHMn(CO)_5$ is assigned to the Ge-Mn stretch. This band shows a consistent drop of 14 cm^{-1} from $GeH_3Mn(CO)_5$ at 219 cm^{-1} and $GeH_3GeH_2Mn(CO)_5$ at 205 cm^{-1}. Two medium bands, depolarised at 274 cm^{-1} and polarised at 254 cm^{-1} are assigned to the asymmetric and symmetric Ge-Ge stretches. These bands occur between those found for Ge_3H_8 (288, 245 cm^{-1}) and 2-$MeGe_3H_7$ (287, 241 cm^{-1}). It has been shown (54,58) for a three-metal chain system that there is always

Figure 5.2

Raman Spectrum of $(GeH_3)_2GeHMn(CO)_5$
$(0 - 300\ cm^{-1})$

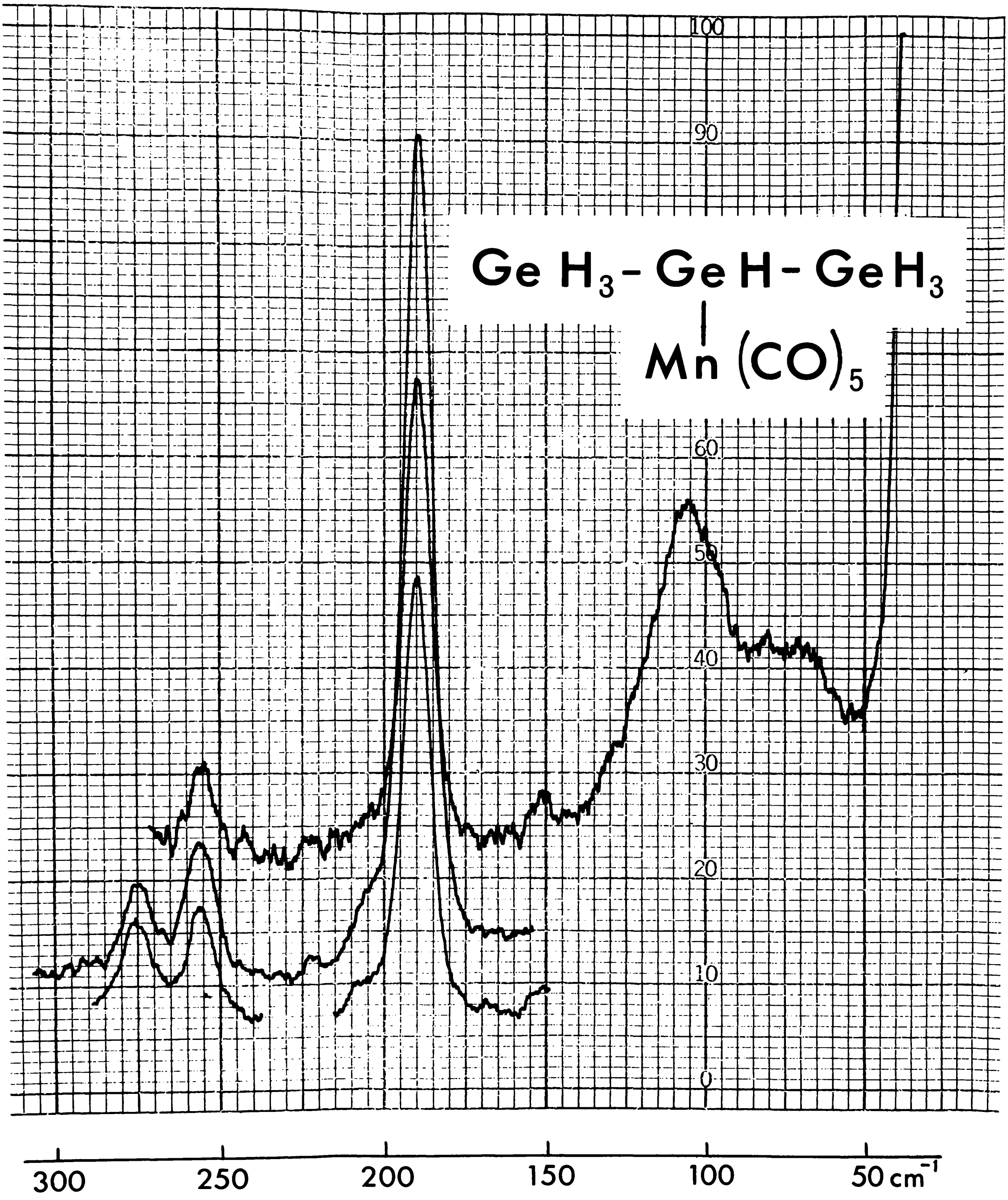
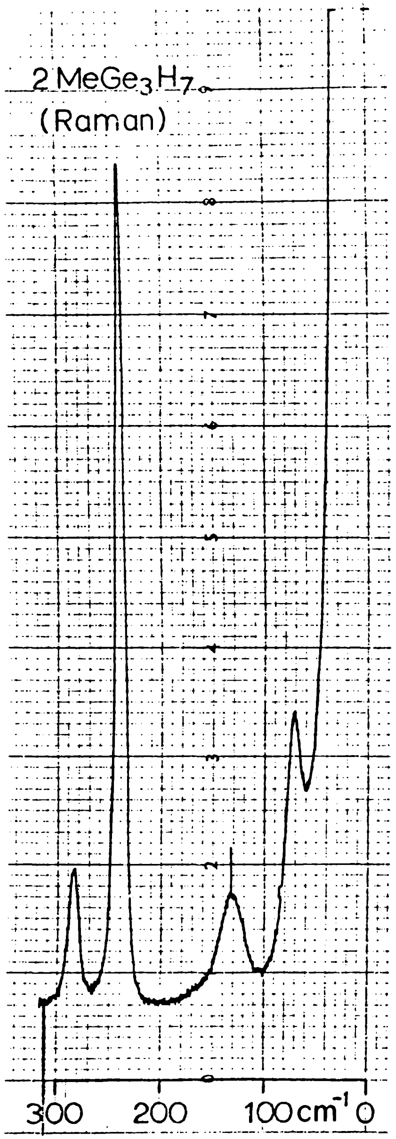
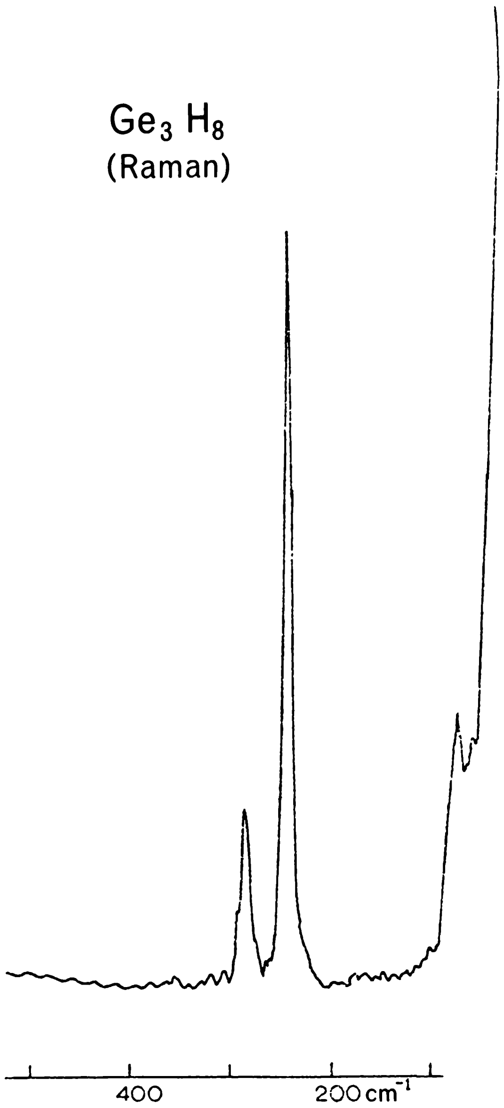

Ge H$_3$ - Ge H - Ge H$_3$
Mn (CO)$_5$
100
90
60
50
40
30
20
10
0
300
250
200
150
100
50 cm^{-1}

Figure 5.3

Raman Spectrum of Ge_3H_8 and 2-$MeGe_3H_7$

(0 - 300 cm^{-1})


2 MeGe$_3$H$_7$
(Raman)
300
200
100 cm^{-1}
0


Ge$_3$ H$_8$
(Raman)
400
200 cm^{-1}

interaction between the two intermetallic bonds, and this has been used to describe the Ge-Ge and GeMn bonds in $GeH_3GeH_2Mn(CO)_5$ (135). Thus, it is probably more appropriate to ascribe the metal-metal stretches in $(GeH_3)_2GeHMn(CO)_5$ as Ge-Ge-Mn stretches.

The infrared spectra of $[GeH_2Mn(CO)_5]_2$ and $[GeH_2Co(CO)_4]_2$ are summarised in Tables 5.5 and 5.6. The spectra are consistent with compounds containing either a $Mn(CO)_5$ or $Co(CO)_4$ moiety together with a GeH_x fragment. The vibrational frequencies do not show any drastic changes from those observed for $Ge_2H_5Mn(CO)_5$ or $Ge_2H_5Co(CO)_4$ or their germyl analogues.

The vibrational spectrum of $(GeH_2Cl)_2$ (see Table 5.9) shows two GeH_2 deformation regions around 850 cm^{-1} and 685 cm^{-1}. The spectra of the transition metal derivatives also show bands in these regions but extra bands seen between 700 cm^{-1} and 750 cm^{-1} in the spectrum of $[GeH_2Mn(CO)_5]_2$ are probably due to traces of impurities or decomposition products.

While these infrared spectra are consistent with the formulations for the di-substituted digermanes, they are by no means definite proofs of them.

5.3.4 Substitution of $(GeH_3)_2GeHMn(CO)_5$

The product of the reaction between $(GeH_3)_2GeHMn(CO)_5$ and CCl_4 earlier assigned as $(GeH_3)_2GeClMn(CO)_5$ is confirmed by the mass spectrum (Table 5.7) and i.r. spectrum (Table 5.8). The natural occurrence of two chlorine isotopes (^{35}Cl = 75.53%, ^{37}Cl = 24.47%) hardly altered the combinational Ge isotopic patterns (see Fig. 2.3). However, the presence of chlorine makes

Table 5.5 The Infrared Spectrum of $[GeH_2Mn(CO)_5]_2$ (cm^{-1})

I.r. (solution)(a)	Assignment
2129 w	
2117 s	νCO, a_1
2098 mw	$\nu\ {}^{13}CO$
2078 vw	νGeH
2068 w	
2060 m	
2047 ms,sh	νCO, a_1
2032 vvs	νCO, e
2021 ms,sh	
2000 mw	
1982 w	$\nu'\ {}^{13}CO$
1942 vw	
860 vw	GeH_2 bend
832 vw	
778 vw	?
758 w	?
668 vw	GeH_2 wag
653 m,sh	$\delta MnCO$
645 s	
459 w	νMnC_{ax}

(a) I.r. solution spectrum in cyclohexane.

Table 5.6 The Infrared Spectrum of $[GeH_2Co(CO)_4]_2$ (cm^{-1})

I.r. (solution)(a)	Assignment
2101 vw	
2091 ms	νCO, a'
2056 w,sh	νGeH
2049 w,sh	
2035 mw	νCO, a'
2010 vvs	νCO, a' + a"
1992 w,sh	ν^{13}CO
1973 w	
850 w	GeH_2 bend
672 w	GeH_2 (wag, twist, rocks?)
665 w	
626 ms	
605 vw	
545 ms	δCoCO
526 mw,sh	
497 w,sh	νCoC + δCoCO
481 mw	
410 w	νCoC

(a) I.r. solution spectrum in cyclohexane

Table 5.7 The Mass Spectrum of $(GeH_3)_2GeClMn(CO)_5$(a)

m/e	Assignment	Relative Intensity(b)	Strongest x
446–466	$H_xGe_3Mn(CO)_5Cl^+$	4.0	6
416–436	$H_xGe_3Mn(CO)_4Cl^+$	6.6	4
386–406	$H_xGe_3Mn(CO)_3Cl^+$	4.2	2
356–376	$H_xGe_3Mn(CO)_2Cl^+$	5.3	0
328–348	$H_xGe_3Mn(CO)Cl^+$	2.9	0
300–320	$H_xGe_3MnCl^+$	28.6	0
413–431	$H_xGe_3Mn(CO)_5{}^+$	3.9	6
384–402	$H_xGe_3Mn(CO)_4{}^+$	3.3	5
354–372	$H_xGe_3Mn(CO)_3{}^+$	6.7	3
344–326	$H_xGe_3Mn(CO)_2{}^+$	2.1	3
300–318	$H_xGe_3Mn(CO)^+$	20.9	5
270–288	$H_xGe_3Mn^+$	100	3
373–387	$H_xGe_2Mn(CO)_5Cl^+$	22.6	3
345–359	$H_xGe_2Mn(CO)_4Cl^+$	22.9	3
316–330	$H_xGe_2Mn(CO)_3Cl^+$	5.3	2
288–302	$H_xGe_2Mn(CO)_2Cl^+$	2.4	2
261–275	$H_xGe_2Mn(CO)Cl^+$	5.9	3
233–247	$H_xGe_2MnCl^+$	36.2	2
338–350	$H_xGe_2Mn(CO)_5{}^+$	95.2	3
310–322	$H_xGe_2Mn(CO)_4{}^+$	71.4	3
280–392	$H_xGe_2Mn(CO)_3{}^+$	47.6	1
254–266	$H_xGe_2Mn(CO)_2{}^+$	7.6	3
226–238	$H_xGe_2Mn(CO)^+$	7.6	3
196–208	$H_xGe_2Mn^+$	51.4	1

Table 5.7 (Cont.)

m/e	Assignment	Relative Intensity(b)	Strongest x
300–308	$H_xGeMn(CO)_5Cl^+$	4.8	0
	$H_xGeMn(CO)_4Cl^+$?		
	$H_xGeMn(CO)_3Cl^+$?		
	$H_xGeMn(CO)_2Cl^+$?		
188–196	$H_xGeMn(CO)Cl^+$	0.4	0
	$H_xGeMnCl^+$?		
265–271	$H_xGeMn(CO)_5^+$	3.8	0
	$H_xGeMn(CO)_4^+$?		
	$H_xGeMn(CO)_3^+$?		
169–187	$H_xGeMn(CO)_2^+$	1.3	0
153–159	$H_xGeMn(CO)^+$	1.0	0
125–131	H_xGeMn^+	7.6	0
249–269	$H_xGe_3Cl^+$	3.1	4
177–191	$H_xGe_2Cl^+$	1.2	2
105–113	H_xGeCl^+	1.2	0
214–230	$H_xGe_3^+$	15.8	2
142–154	$H_xGe_2^+$	6.8	2
70–76	H_xGe^+	3.8	0
196	$HMn(CO)_5^+$	0.9	
195	$Mn(CO)_5^+$	0.9	
168	$HMn(CO)_4^+$	0.1	
167	$Mn(CO)_4^+$	0.3	
140	$HMn(CO)_3^+$	0.2	
139	$Mn(CO)_3^+$	0.7	

Table 5.7 (Cont.)

m/e	Assignment	Relative Intensity(b)	Strongest x
112	$HMn(CO)_2^+$	0.3	
111	$Mn(CO)_2^+$	1.7	
84	$HMn(CO)^+$	0.5	
83	$Mn(CO)^+$	2.4	
56	HMn^+	1.1	
55	Mn^+	28.6	
37	Cl^+	0.1	
35	Cl^+	0.3	
28	CO^+	(c)	

Footnotes:

(a) Assignment of fragments and their relative intensities are rather tentative as the presence of Cl leads to considerable overlap of envelopes, e.g. of $H_xGe_3Mn(CO)Cl^+$ and $H_xGe_3Mn(CO)_2^+$ fragments. ? indicates fragments that are totally unidentifiable because of these overlaps.

(b) Summed over x = 0–6 and germanium-chlorine abundance combinations where appropriate.

(c) Strong peak, but includes N_2^+

Table 5.8 The Infrared Spectrum of $(GeH_3)_2GeClMn(CO)_5$ (cm^{-1})

I.r. (solution)	Assignment
2102 vw,sh	
2098 mw	νCO, a_1
2066 w	νGeH
2059 mw	
2049 mw	
2032 w	νCO, a_1
2021 s	νCO, e + b_1
2015 vs	
2011 vvs	
1988 vw	$\nu\,^{13}$CO
1976 vw	
1941 vw	
785 mw	δsym. GeH_3, a' + a''
751 mw	
674 vw	δMnCO, a'
667 vvw	
654 s	
649 m	
640 w	
466 w	GeH_3 rock
350 vw	νGeCl, a'

Footnote:

I.r. solution spectrum in cyclohexane

assignments more difficult due to the closeness of the CO(m/e = 28) and Cl(m/e = 35,37) masses leading to considerable overlapping of envelopes thus making the fragment assignments and relative intensities of some species given in Table 5.7 more tentative than others. However, the unambiguous presence of $H_xGe_3Mn(CO)_5Cl^+$, $H_xGe_2Mn(CO)_5Cl^+$, $H_xGeMn(CO)_5Cl^+$, $H_xGe_3Cl^+$, $H_xGe_2Cl^+$ and H_xGeCl^+ clearly indicates the parent compound to have the Ge_3Cl skeleton. Overall, the fragmentation pattern, including CO loss, H_2 loss and GeH_2 elimination, matches that observed for $(GeH_3)_2GeHMn(CO)_5$ (see Table 5.1). In addition, Cl loss seems a relatively easy process as the ion abundance of GeCl retaining fragments is relatively low compared to the high total ion current carried by the $H_xGe_3Mn(CO)_n{}^+$ and $H_xGe_2Mn(CO)_n{}^+$ species. Even the most abundant ions are $H_xGe_3Mn^+$ and not $H_xGe_3MnCl^+$, thus deviating from previous general observations with earlier compounds that the most abundant ion is always $[P-(CO)_n]^+$ (n = total number of carbonyls). The ion abundance of Ge-Mn bonded species is <u>ca</u>. 92%.

The i.r. spectrum bears close resemblance to that obtained for $(GeH_3)_2GeHMn(CO)_5$. However, there are several prominent features. The CO stretch e mode is slightly higher while the GeH_3 symmetric in-phase and out-of-phase deformations are slightly lower than in $(GeH_3)_2GeHMn(CO)_5$. Similar observations were earlier made for $GeH_3GeH_xCl_{2-x}Mn(CO)_5$. The increased CO vibrational frequency is due to the chloride inductive effect and the lower GeH_3 deformation is due to interaction between the GeH_3 and GeCl vibrational modes. The GeCl stretch is observed at 350 cm^{-1}.

The evidence available confirms the reaction product to be $(GeH_3)_2GeClMn(CO)_5$. Substitution was as expected on the lone hydrogen on the central germanium and the presence of CH_2Cl_2 and lack of $CHCl_3$ suggests the involvement of $CHCl_3$ in a rapid second step:

$$(GeH_3)_2GeHMn(CO)_5 + CCl_4 \xrightarrow{\text{fast}} (GeH_3)_2GeClMn(CO)_5 + CHCl_3$$

$$(GeH_3)_2GeHMn(CO)_5 + CHCl_3 \xrightarrow{\text{very fast}} (GeH_3)_2GeClMn(CO)_5 + CH_2Cl_2$$

However, under more rigorous conditions, polychlorosubstitution occurs, including substitution of hydrogens on the GeH_3 groups as shown by the 36% chloride content in the product obtained for the sample reacted with excess CCl_4.

The near equimolar reaction took 4 hours, compared with 20 minutes for the similar reaction of $GeH_3GeH_2Mn(CO)_5$ under similar conditions. Thus, addition of a GeH_3 group introduces considerable steric hindrance to attack on the hydrogen on the α-germanium. Again, as with the chloro-products obtained in the chlorosubstitution reactions of $Ge_2H_5Mn(CO)_5$, $(GeH_3)_2GeClMn(CO)_5$ exhibits considerable stability.

5.3.5 Ge-Co Cleavage in $[GeH_2Co(CO)_4]_2$ by $HgCl_2$

The i.r. spectrum (Table 5.9) confirms the reaction product resulting from the reaction between $[GeH_2Co(CO)_4]_2$ and $HgCl_2$ to be $ClGeH_2GeH_2Cl$. A similar spectrum was obtained for $ClGeH_2GeH_2Cl$ prepared separately by action of $SnCl_4$ (139) on Ge_2H_6. Decomposition of the dichloride is rapid to give rise to peaks assignable to GeH_3GeH_2Cl (133).

Table 5.9 The Infrared Spectrum of $ClGeH_2GeH_2Cl$ (cm^{-1})

gas	Assignment
2098 s	νGeH
2089 s	
856 m	GeH_2 bend
848 m	
830 w	
700 m	in- and out-of-phase GeH_2 wags
684 ms	
675 w	GeH_2 twist?
408 ms	νGeCl

The fact that the intermediate $Co(CO)_4GeH_2GeH_2Cl$ was also observed shows the cleavage reaction to occur stepwise:

$$Co(CO)_4GeH_2GeH_2Co(CO)_4 + HgCl_2 \longrightarrow Co(CO)_4GeH_2GeH_2Cl + ClHgCo(CO)_4$$

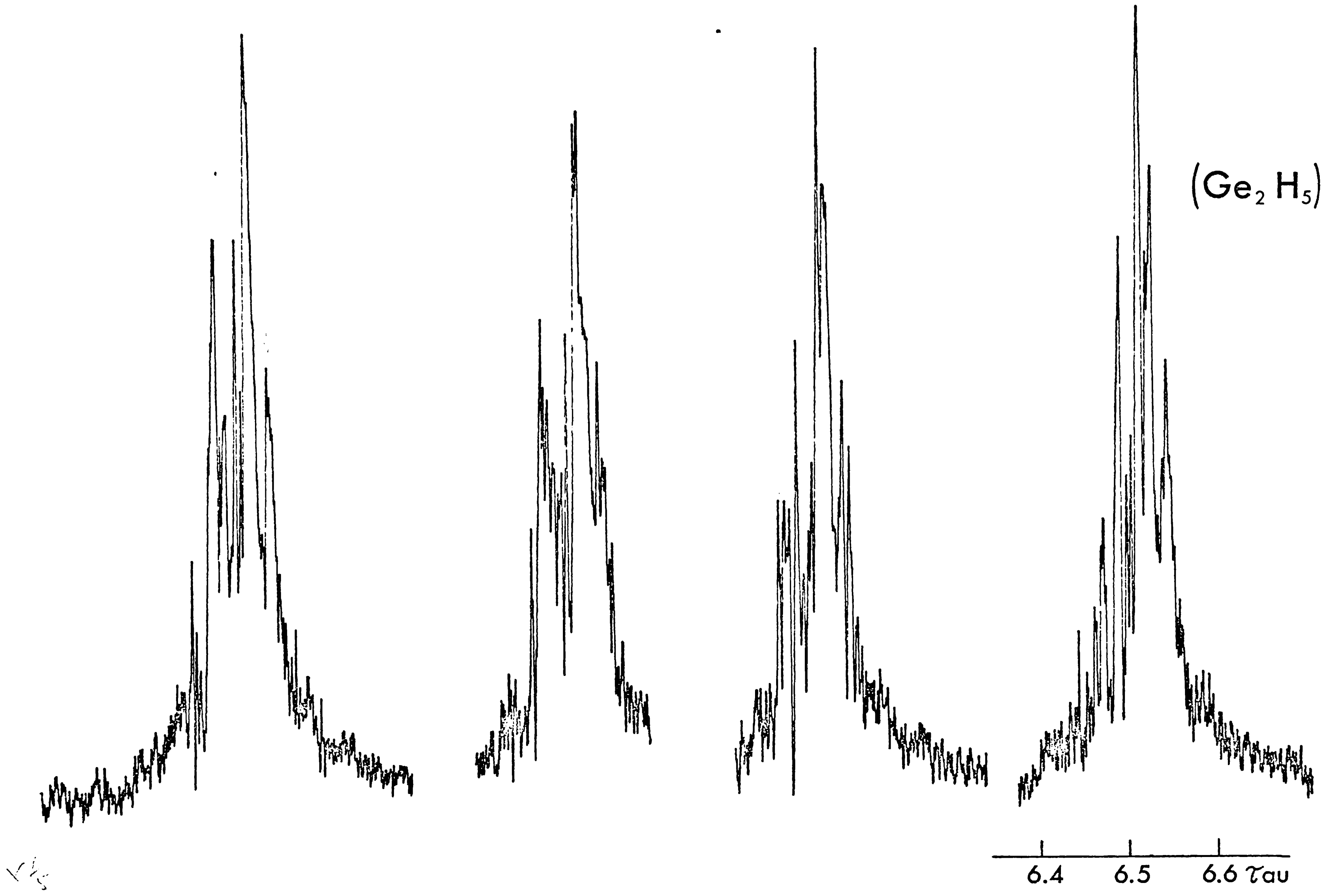
$$Co(CO)_4GeH_2GeH_2Cl + ClHgCo(CO)_4/HgCl_2$$

$$\longrightarrow ClGeH_2GeH_2Cl$$

$$+ Hg[Co(CO)_4]_2/ClHgCo(CO)_4$$

As with the $HgCl_2$ cleavage reaction of $GeH_3GeH_2Co(CO)_4$ there is no evidence for any products resulting from Ge-Ge bond cleavage. Thus it seems, the $HgCl_2$ reaction is specific and cleaves only the Ge-Co bond and not the Ge-Ge bond.

77/241
21/6/77
$(Ge_2H_5)_2Fe(CO)_4$
x $\frac{1}{5}$



$(Ge_2H_5)_2\ Fe(CO)_4$

CHAPTER 6. PREPARATION, CHARACTERISATION AND REACTIONS OF BIS(DIGERMANYL)TETRACARBONYLIRON, $(GeH_3GeH_2)_2Fe(CO)_4$

The bis(germanyl)iron compound $(GeH_3)_2Fe(CO)_4$ (173,175), and methyl derivatives, $(MeGeH_2)_2Fe(CO)_4$ (176) and $(Me_2GeH)_2Fe(CO)_4$ (178) are known. The stability of the compounds in this series decreases with the increase in the number of methyl groups, $(Me_2GeH)_2Fe(CO)_4$ self-reacting rapidly to form the cyclised structure $\{Me_2GeFe(CO)_4\}_2$ (149) (see pages 30,31). The substitution and Ge-Fe bond cleavage chemistry (174,177) of these compounds have also been explored to some extent (see pages 42,43,44). $(GeH_3)_2Fe(CO)_4$ (173) is of intermediate stability between the related germyl-manganese (162) and germyl-cobalt (183) compounds. Following the preparation of the surprisingly stable digermanyl-cobalt compound (Chapter 4) it was thought that unless the addition of a GeH_3 group catalyses cyclisation, the bis(digermanyl)iron complex should also be stable enough to be isolated. This proved to be the case.

6.1 Preparation of $(Ge_2H_5)_2Fe(CO)_4$

The method used was essentially that of Aylett et al., for the preparation of $(SiH_3)_2Fe(CO)_4$ (169):

$$2Ge_2H_5Cl + Na_2Fe(CO)_4 \longrightarrow (Ge_2H_5)_2Fe(CO)_4 + 2NaCl$$

Digermanyl chloride (0.5674 g, 3.051 mmol) was condensed into $Na_2Fe(CO)_4$ in n-pentane (ca. 6 ml) prepared as described previously on page 68, by treating $Fe(CO)_5$ (0.3502 g, 1.787 mmol) with a 0.3 M sodium-ammonia solution (2.704 mmol repurified Na in 10 ml NH_3). The mixture was allowed to react for 15 minutes at room temperature, with shaking and all volatiles then fractionated. Pentane and traces of digermane (92) (identified by i.r.) were recovered at −196 °C. Attempts at separating the digermane from the pentane by fractionation as well as chemically by treating with some $SnCl_4$ were unsuccessful. With $SnCl_4$, a thin film of $SnCl_2$ was deposited but no recoverable Ge_2H_5Cl was achieved. However, by pressure-volume investigation, the amount of digermane was approximately 0.1 mmol. Unreacted Ge_2H_5Cl (133) and traces of $H_2Fe(CO)_4$ (173) (identified by i.r.) were collected at −63 °C, more Ge_2H_5Cl at −45 °C (total recovery of Ge_2H_5Cl = 0.1343 g, ca. 0.72 mmol, includes traces of $H_2Fe(CO)_4$) and traces of a very involatile material at −23 °C. As this material was extremely involatile and was taking a long time to come over, it was decided to change the −23 °C bath to one at liquid nitrogen temperature and the trap opened to a mercury diffusion pump. This "dragging" process was to continue for 2 days as this material was still distilling over this period of time. An observation made here was that the material does not move unless opened to the mercury diffusion pump directly, and even then moves at a very slow rate. This compound was identified as bis(digermanyl)tetracarbonyliron, (0.2815 g, 0.599 mmol, 51.4% based on Ge_2H_5Cl consumed) by the mass of the parent ions in the mass spectrum (m/e = 478 to 458 : ${}^{12}C_4{}^{1}H_{10}{}^{16}O_4{}^{56}Fe{}^{n}Ge_4$ requires 484 for n = 76 to 456 for n = 70) together with the fragmentation pattern, the vibrational spectrum, by the chemical reactions reported below, and by the ${}^{1}H$ nmr spectrum. This shows the closely overlapping signals of an A_3B_2 pattern analysed to give τGeH_3 = 6.53, τ GeH_2 = 6.48 and J = 4.3 Hz. On low resolution only a broad singlet with fine structures was observed. The mass and vibrational spectra are reported and discussed in the latter part of this chapter. Traces of some high molecular weight compound (m/e > 800) was left as a brown deposit in the reaction vessel.

$(Ge_2H_5)_2Fe(CO)_4$ is a colourless liquid with a vapour pressure too low to measure at room temperature. This compound shows little tendency to decompose. A sample in the laser beam of a Raman spectrometer or a cyclohexane solution in an i.r. solution cell exposed to strong daylight for several hours, both showed no colour change, although the i.r. spectrum showed a trace of digermane. It decomposes slowly in air and has a very strong odour, more of the iron carbonyl smell than of digermane.

6.2 Reactions

a) $(Ge_2H_5)_2Fe(CO)_4$ and CCl_4

An approximately 1:2 mixture of $(Ge_2H_5)_2Fe(CO)_4$ and CCl_4 in benzene was observed with the nmr between −20 °C and −5 °C and later at room temperature. Reaction was slow. The first sign of reaction at 16 hours was a singlet at 6.8 τ assigned to GeH_4 and one at 3.8 τ due to CH_2Cl_2. Any $CHCl_3$ signal was masked by the strong benzene resonance. These signals increased in intensity as those of $(Ge_2H_5)_2Fe(CO)_4$ (τ GeH_3 = 6.55, τ GeH_2 = 6.48, J = 4.3 Hz) weakened and finally disappeared after 6 days. No signals assignable to chlorosubstituted products were seen. A white deposit precipitated as the reaction progressed and the two singlets were of near equal intensities right through the reaction. The tube was opened after 6 days and the volatiles fractionated. GeH_4 (0.03 mmol, identified by i.r.) was collected at -196 °C, $CHCl_3$ and CH_2Cl_2 at -120 °C and traces of $CHCl_3$ at -83 °C, leaving a solid yellow residue. No Ge_2H_6 was detected. Insufficient residue was recovered for a proper recording of the mass spectrum. However, an attempt showed m/e greater than 400.

b) $(Ge_2H_5)_2Fe(CO)_4$ in $SiCl_4$

A sample of $(Ge_2H_5)_2Fe(CO)_4$ was dissolved in $SiCl_4$ in an nmr tube with a trace of TMS as internal reference. No change was recorded until after 1½ months. A weak doublet along with a quartet of intensity ratio 3:1 were observed at 6.0 τ and 4.3 τ respectively, J = 4.0 Hz. These signals were assigned to either $GeH_3GeH_2(GeH_3GeHCl)Fe(CO)_4$ or $(GeH_3GeHCl)_2Fe(CO)_4$. Only about 10% of the $(Ge_2H_5)_2Fe(CO)_4$ had reacted at this stage. The nmr spectrum was observed periodically over the next 4½ months, but showed no further changes. The mixture was still a clear solution, showing no decomposition or precipitation.

c) $(Ge_2H_5)Fe(CO)_4$ and $Mn(CO)_5^-$ followed by GeH_3Br

$(Ge_2H_5)_2Fe(CO)_4$ (165.5 mg, 0.349 mmol) was condensed into the specialised trap (see Fig. 2.1B) and material drawn to the tapered end of the attached nmr tube with liquid nitrogen. The tapered end containing the $(Ge_2H_5)_2Fe(CO)_4$ was then detached and inserted into bulb B of the apparatus (see Fig. 2.4) containing an ethereal solution of $NaMn(CO)_5$ in bulb A prepared using $Mn_2(CO)_{10}$ (71.80 mg, 0.1841 mmol). The apparatus was swirled to force the material out of the tapered end and a small volume of ether was condensed into the bulb to ensure most of the material was washed out into the reaction bulb. The solution of $NaMn(CO)_5$ (ca. 50 ml) was then poured over from bulb A into bulb B which was held at liquid nitrogen temperature. The reaction mixture was warmed to $-23\ ^{\circ}C$ for 30 minutes and then to room temperature for a further 30 minutes, with constant swirling. The volatiles were then removed. $Ge_2H_5Mn(CO)_5$ (96.20 mg, 0.2788 mmol, 79.9% based on initial $(Ge_2H_5)_2Fe(CO)_4$) identified (135) by i.r. and nmr, was found to be the only product. All $(Ge_2H_5)_2Fe(CO)_4$ was consumed. No $H_2Fe(CO)_4$ (173) was detected. The residue left in the reaction vessel was a light-yellow solid.

Ether (ca. 3 ml) followed by germyl bromide, GeH_3Br (94.6 mg, 0.6025 mmol) were condensed on to the residue and warmed to room temperature for 30 minutes with shaking. On fractionation some ether was recovered at $-196\ ^{\circ}C$, ether and excess GeH_3Br at $-127\ ^{\circ}C$ and $Ge_2H_5(GeH_3)Fe(CO)_5$ at $-23\ ^{\circ}C$. This compound was identified as digermanyl(germyl)tetracarbonyliron, $Ge_2H_5(GeH_3)Fe(CO)_4$, by the mass of the parent ions in the mass spectrum ($m/e = 404 - 385$: ${}^{12}C_4{}^{1}H_8{}^{16}O_4{}^{56}Fe{}^{n}Ge_3$ requires 408 for $n = 76$ to 386 for $n = 70$ with $P-H = 20\%\ P$), together with the fragmentation pattern, the vibrational spectrum, by the reaction with $SiCl_4$ reported below, and by the ${}^{1}H$ nmr spectrum. This shows an A_3B_2 pattern with a superimposed strong singlet analysed to give $\tau GeH_3 = 6.60$, $\tau\ GeH_2 = 6.55$ and $J = 4.0$ Hz for the Ge_2H_5 fragment, and 6.52τ for the GeH_3 fragment. The reaction and spectroscopic data are further discussed later on.

$(Ge_2H_5)(GeH_3)Fe(CO)_4$ is a colourless liquid of vapour pressure and rate of transfer in the vacuum line intermediate between those of $(GeH_3)_2Fe(CO)_4$ and $(Ge_2H_5)_2Fe(CO)_4$. The liquid shows no decomposition in the dark, but slowly gave a light-yellow colour in the laser beam over 3 hours during the recording of the Raman spectrum. A cyclohexane solution of the sample in an i.r. solution cell showed complete decomposition after 45 minutes in strong daylight. The compound has the characteristic iron carbonyl odour.

d) $Ge_2H_5(GeH_3)Fe(CO)_4$ in $SiCl_4$

$Ge_2H_5(GeH_3)Fe(CO)_4$ (17.73 mg, 0.045 mmol) in $SiCl_4$ was sealed in a nmr tube with TMS as internal reference. Reaction was allowed to proceed at room temperature and changes in the ^1H spectrum were observed at intervals. Reaction was slow - a singlet at 4.93 τ appeared after a week. This was assigned to the GeH_2Cl signal of $Ge_2H_5(GeH_2Cl)Fe(CO)_4$ (c.f. $\tau GeH_3 = 6.52$, $\tau GeH_2Cl = 4.48$ for $GeH_3(GeH_2Cl)Fe(CO)_4$ in CS_2 (174). Resonances due to the Ge_2H_5 group of the product were not distinguishable from the strong signals of the $Ge_2H_5(GeH_3)Fe(CO)_4$. The singlet increased in intensity over 4 weeks when about 10% of the $Ge_2H_5(GeH_3)Fe(CO)_4$ had been consumed. After another 2 weeks, this singlet completely disappeared to give rise to two new singlets at 4.60 τ (of about half the intensity of the original singlet) and at 6.95 τ (of intensity 5-6 times the original singlet). At this stage the solution mixture appeared slightly yellow. The weaker singlet was assigned to $[GeHClFe(CO)_4]_2$ (c.f. 4.80τ for the same compound in CS_2 (174), while Ge_2H_6 was assigned to the singlet at 6.95 τ (compares well with Ge_2H_6 chemical shift elsewhere in this thesis). No Fe–H signal was detected in the 20τ region.

The tube was opened and the volatiles were fractionated to yield Ge_2H_6 and TMS at −127 °C (identified by i.r.) and unreacted $Ge_2H_5(GeH_3)Fe(CO)_4$ at −23 °C. No GeH_4 was detected. A mass spectrum recorded of the light-yellow non-volatile residue left in the reaction tube showed parent ions at m/e 540–562 attributable to $H_2Ge_2Cl_2Fe_2(CO)_8{}^+$ (279) together with eight CO loss envelopes with the strongest envelope at m/e 322–338 assigned to $[P-8(CO)]^+$. These were all moderate to strong envelopes. Ge^+ species were conspicuously weak, but Cl^+ peaks were clearly seen.

6.3 Discussion

6.3.1 General

Although $(GeH_3)_2Fe(CO)_4$ (173), $Ge_2H_5(GeH_3)Fe(CO)_4$ and $(Ge_2H_5)_2Fe(CO)_4$ are all stable in the dark, these three iron derivatives show varying degrees of decomposition in light. $(GeH_3)_2Fe(CO)_4$ (173) becomes yellow within 5 minutes of exposure to light whereas the unsymmetric derivative shows a similar colour change only after 2-3 hours. $(Ge_2H_5)_2Fe(CO)_4$ shows no such colour change but a trace of digermane was detected in an i.r. solution cell after several hours in strong sunlight. The vapour pressure and rate of transfer is inversely proportional to the number of germanium atoms. All three compounds are just manipulable in a high vacuum system, but $(Ge_2H_5)_2Fe(CO)_4$ is the limit. Unlike the digermanyl derivatives of manganese or cobalt which have the characteristic digermane smell, the iron carbonyl smell seems to be the more prevalent with the iron derivatives. Surprisingly, $(Ge_2H_5)_2Fe(CO)_4$ and $Ge_2H_5(GeH_3)Fe(CO)_4$ are liquids as $(GeH_3)_2Fe(CO)_4$ is in the form of white crystals at room temperature. Mass spectrum of the germyl compound shows it to be a monomer. The difference is presumably due to packing difficulties in the crystal.

6.3.2 The Mass Spectrum of Bis(digermanyl)tetracarbonyliron

The mass spectrum of $(Ge_2H_5)_2Fe(CO)_4$ was obtained *via* liquid-sampling and is tabulated in Table 6.1. The assignments have been made using the calculated GeFe combinational isotopic patterns given in Fig. 2.3. Inclusion of Fe makes very little difference to the corresponding Ge isotopic patterns. Like $(GeH_3)_2Fe(CO)_4$ (173), $(Ge_2H_5)_2Fe(CO)_4$ shows a very weak parent ion family in contrast to the comparatively high parent ion abundances observed for the manganese and cobalt derivatives of mono- and di-germane. In common with these complexes, however, decomposition *via* successive elimination of CO is indicated, with a high proportion of the ion current carried by polymetallic fragments. Hydrogen loss becomes significant after loss of one carbonyl or after Ge-Ge bond scission. The low abundances of $H_xGe_3Fe(CO)_4^+$ and $H_xGe_2Fe(CO)_4^+$ ions compared with the high abundances of $H_xGe_3Fe(CO)_n^+$ and $H_xGe_2Fe(CO)_n^+$ ($n = 3$–0) ions suggest CO loss to occur more readily than Ge-Ge bond cleavage. There is little evidence to indicate GeH_2 elimination and it appears that the $H_xGe_3Fe(CO)_4^+$ and $H_xGe_2Fe(CO)_4^+$ originate from $H_xGe_4Fe(CO)_4^+$ by Ge-Ge bond cleavage with elimination of GeH_4 or Ge_2H_6 followed by CO loss. Metastable peaks are

Table 6.1 The Mass Spectrum of $(GeH_3GeH_2)_2Fe(CO)_4$

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogens(b)										
			x=10	9	8	7	6	5	4	3	2	1	0
458–478	$H_xGe_4Fe(CO)_4^+$	0.88	10										
426–449	$H_xGe_4Fe(CO)_3^+$	45.7		1	10	2	2						
398–421	$H_xGe_4Fe(CO)_2^+$	61.8		1	10	2	1						
369–391	$H_xGe_4Fe(CO)^+$	55.6				?	10	2					
338–359	$H_xGe_4Fe^+$	100								2	10		
384–400	$H_xGe_3Fe(CO)_4^+$	9.9					10						
351–369	$H_xGe_3Fe(CO)_3^+$	31.5								2	10	?	
323–342	$H_xGe_3Fe(CO)_2^+$	13.7									10	3	
296–313	$H_xGe_3Fe(CO)^+$	14.1										1	10
266–285	$H_xGe_3Fe^+$	80.2										1	10
317–324	$H_xGe_2Fe(CO)_4^+$	9.5							2	10	5		
282–295	$H_xGe_2Fe(CO)_3^+$	17.6								?	10	3	
252–265	$H_xGe_2Fe(CO)_2^+$	8.8										2	10
224–237	$H_xGe_2Fe(CO)^+$	21.5										1	10
196–209	$H_xGe_2Fe^+$	20.4										?	10
238–245	$H_xGeFe(CO)_4^+$	3.7										3	10
210–217	$H_xGeFe(CO)_3^+$	24.4										1	10
182–189	$H_xGeFe(CO)_2^+$	21.8										3	10
154–161	$H_xGeFe(CO)^+$	5.1										5	10
126–133	H_xGeFe^+	10.6										3	10
284–308	$H_xGe_4^+$(c)	15.6						?	10	?			
212–230	$H_xGe_3^+$(c)	6.2								?	10	?	
141–155	$H_xGe_2^+$	15(d)								3	10	4	
70–77	H_xGe^+	30(d)										8	10

Table 6.1 (Cont.)

m/e	Assignment	Relative Intensity
169	$HFe(CO)_4^+$	1.1
168	$Fe(CO)_4^+$	1.9
141	$HFe(CO)_3^+$	0.6
140	$Fe(CO)_3^+$	1.7
113	$HFe(CO)_2^+$	0.6
112	$Fe(CO)_2^+$	1.3
85	$HFe(CO)^+$	1.0
84	$Fe(CO)^+$	4.8
57	HFe^+	4.4
56	Fe^+	4.4
28	CO^+	(e)

Footnotes:

(a) Summed over x = 10 - 0 and over GeFe combinational isotopes where appropriate.

(b) Strongest component of family assigned 10, with other components relative to this.

(c) Presence of these species identified by irregular shape of overlapping envelopes due to $H_xGe_2Fe(CO)_3^+$ and $H_xGeFe(CO)_3^+$.

(d) Calculated intensities, see text.

(e) Strong peak, but includes N_2^+.

? Indicates presence, but due to overlap with stronger envelopes, does not permit meaningful separation.

noticeably absent. It is therefore difficult to establish some of the fragmentation routes, for example, if the $H_xGeFe(CO)_n^+$ families arose by H_xGe loss from $H_xGe_2Fe(CO)_n^+$ families or by H_xGe_2 loss from $H_xGe_3Fe(CO)_n^+$ families. The ion currents carried by fragments retaining Ge_4Fe, Ge_3Fe, Ge_2Fe and GeFe are 41%, 23%, 12% and 10% of the total ion current, in that order. Clearly the higher polymetallic structures account for the larger part of the total ion current, in contrast to $GeH_3GeH_2Mn(CO)_5$ or $GeH_3GeH_2Co(CO)_4$ (see Tables 3.1 and 4.1) where the ions retaining GeM are more abundant than those containing GeGeM. However, the total abundance of species containing the Ge-Fe bond adds up to 86% matching the Ge-M retaining families of $Ge_2H_5Mn(CO)_5$ and $Ge_2H_5Co(CO)_4$ at 88% and 86% respectively, and all three significantly higher than the germyl derivatives.

All the spectra for $(Ge_2H_5)_2Fe(CO)_4$ obtained by liquid-sampling showed fairly strong $H_xGe_2^+$ and H_xGe^+ envelopes and different runs showed considerable variability in the intensities of these species. The spectrum obtained by gas-sampling showed only these species. Thus resembling $Ge_2H_5Co(CO)_4$ there is decomposition possibly giving rise to Ge_2H_6, hence the strong observed hydride ions. Again, this decomposition may be accelerated by contact with metal surfaces, like the gold cup of the spectrometer insertion probe. All the spectra obtained for $(GeH_3)_2Fe(CO)_4$ by gas or liquid-sampling were swamped by H_xGe^+ ions. However, a spectrum by gas-sampling of $Ge_2H_5(GeH_3)Fe(CO)_4$ (see Table 6.4 in section 6.3.4) showed medium intensity envelopes due to $H_xGe_2^+$ and H_xGe^+ and are presumably genuine i.e. derived from fragmentation of the parent ion. $Ge_2H_5(GeH_3)Fe(CO)_4$ is considerably more stable than $(GeH_3)_2Fe(CO)_4$ so does not decompose as easily.

Furthermore the compound, although observed to be slightly less stable than $(Ge_2H_5)_2Fe(CO)_4$ is considerably more volatile thus allowing it to show in a gas-sampled spectrum without risking decomposition on the spectrometer probe. By comparing the spectra obtained for $(Ge_2H_5)_2Fe(CO)_4$ and $Ge_2H_5(GeH_3)Fe(CO)_4$, it is reasonable to assign relative intensities of 15 and 30 to the $H_xGe_2^+$ and H_xGe^+ families in the spectrum for the former compound.

6.3.3 The Vibrational Spectrum of Bis(digermanyl)tetracarbonyliron

The metal carbonyl stretches and the metal-metal stretches show $(Ge_2H_5)_2Fe(CO)_4$ to have a cis-octahedral configuration similar to $(GeH_3)_2Fe(CO)_4$, thus a C_{2v} symmetry. Under C_{2v} selection rules, the four carbonyl stretching vibrations are expected to be of species $2a_1 + b_1 + b_2$ all of which are allowed both in the i.r. and in the Raman; the two Ge-Fe and two Ge-Ge stretching modes, of symmetry species $a_1 + b_1$, should both appear in the Raman spectrum. All these vibration modes have been assigned to observed vibrations in Table 6.2. A trans-arrangement is a C_{2h} system, in which only two carbonyl stretching modes a_u and b_u of $2a_g + a_u + b_u$ will be i.r. active and likewise only the a_g Ge-Fe stretch and a_g Ge-Ge stretch would be Raman active, the b_u mode being allowed only in the i.r. These are clearly contradicted by the observed absorptions seen for $(Ge_2H_5)_2Fe(CO)_4$, thus favouring the cis-configuration. Only about a third of the 63 fundamental vibrations are observed.

Absorptions due to the two Ge_2H_5 moieties are quite complex, reflecting characteristics of the digermanyl manganese and cobalt complexes and also the GeH_3 deformations of $(GeH_3)_2Fe(CO)_4$ and

Table 6.2 Vibrational Spectrum of $(GeH_3GeH_2)_2Fe(CO)_4$ (cm^{-1})

I.r.(solution)(a)	I.r.(solid)(b)	Assignment
2088 s	2091 ms	νCO, a_1
2080 w,sh		
2070 mw	2064 mw	νGeH
2063 mw	2052 mw	
2024 vvs	2026 vs	νCO, $a_1 + b_1$
2006 vs	1998 vvs	νCO, b_2
1984 vw		ν^{13} CO
1972 vw		
875 w	871 mw	$\delta_{asym.}GeH_3$, a_1
860 w	857 w	
	810 m	$\delta_{sym.}GeH_3$, a_1
789 m	787 m	
692 w	675 m	GeH_2 wag (in-phase and out-of-phase)
662 mw		
	628 w,sh	GeH_2 twist, rock?
609 m	609 s	δFeCO, a_1
464 vw	438 w	GeH_3 rocks

Table 6.2 (Cont.)

(c) 433 s,p	417 vw	νFeC, a_1
(c) 268 m,p		νGeGe,a_1(+ b_1?)
(c) 211 vs,p		νGeFe, a_1
(c) 198 m,dp		νGeFe, b_1
(c) 102 s,dp		Skeletal deformations, b_1

Footnotes:

(a) Infrared solution spectrum in cyclohexane

(b) Sample took 45 minutes to condense on cooled window to form a thin solid film.

(c) Raman spectrum of neat liquid.

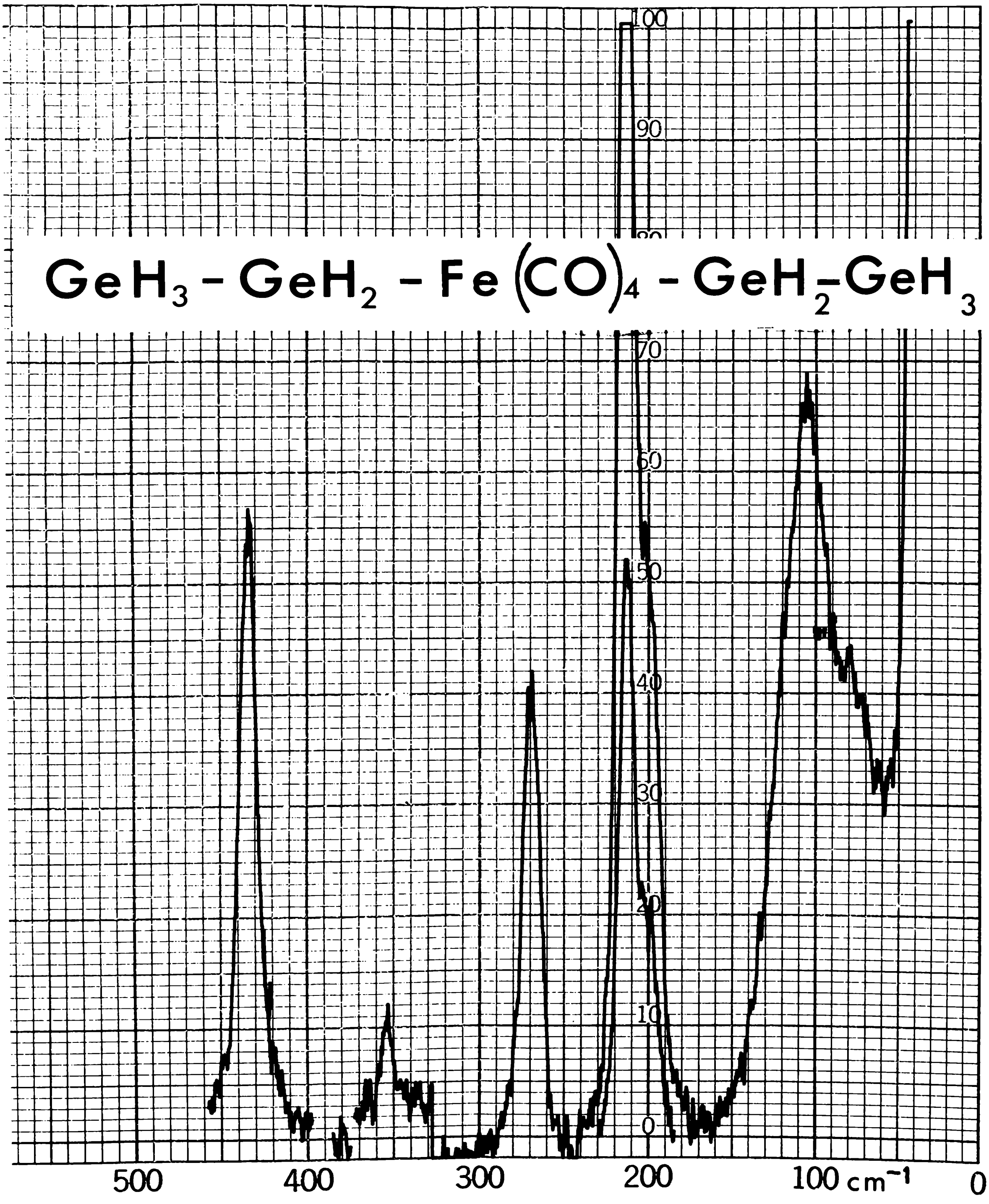
$(GeH_3)_2GeHMn(CO)_5$. Two clear bands in the deformation region are assigned as the prominent GeH_3 symmetric deformation near 800 cm^{-1} and the strong GeH_2 wag below 700 cm^{-1}. The in-phase and out-of-phase symmetric GeH_3 deformations are distinguishable in the solid spectrum while the two well separated bands at 692 cm^{-1} and 662 cm^{-1} in the solution spectrum have been assigned to the in-phase and out-of-phase symmetric wags of the two GeH_2 groups present.

The Raman spectrum of the metal-metal stretching region is given in Fig. 6.1. Only one Raman band is observed in the Ge-Ge region and is assigned to the a_1 mode because it is polarised. The b_1 mode may coincide with this as suggested by a comparison of the relative intensities of various bands to those of $GeH_3GeH_2(GeH_3)Fe(CO)_4$ (see Fig. 6.4) and also by the degree of polarisation of the peaks as shown in Table 6.3. The b_1 mode, if present at all, can be expected to be weak as interaction between the two Ge-Ge bands requires participation of the rigid GeFeGe structure which has an angle of near 90° compared with the GeGeM angles of the manganese and cobalt systems with a near tetrahedral angle, possibly allowing easier "sausage-like" motion of the Ge-Ge-M system. However, the symmetric and asymmetric Ge-Fe stretches are both 18 cm^{-1} below those found at 229 cm^{-1} and 216 cm^{-1} for $(GeH_3)_2Fe(CO)_4$ (155) perhaps due to interaction between the Ge-Ge and Ge-Fe bonds.

Figure 6.1

Raman Spectrum (0 - 500 cm^{-1})

of $(GeH_3GeH_2)_2Fe(CO)_4$



$GeH_3 - GeH_2 - Fe(CO)_4 - GeH_2 - GeH_3$

Table 6.3 Relative Intensities of the Metal-Metal Stretches of $(Ge_2H_5)_2Fe(CO)_4$ and $Ge_2H_5(GeH_3)Fe(CO)_4$

	$(GeH_3GeH_2)_2Fe(CO)_4$			$GeH_3GeH_2(GeH_3)Fe(CO)_4$		
	ν_{M-M}	Relative Intensities		ν_{M-M}	Relative Intensities	
		F(a)	NF(b)		F(a)	NF(b)
νFe-C	433p(a_1)	2.7	10.0	434p(a')	1.2	12
νGe-Ge	268p(a_1+b_1?)	7.5	7.6	268p(a')	3	5
$\nu_{sym.}$Ge-Fe	211p(a_1)	7.5	20	233p(a')	4.5	20
$\nu_{asym.}$Ge-Fe	198dp(b_1)	10	10	202p(a')	6.5	13
δGe_2FeGe_n (n = 1,2)	102dp(b_1)	30	12.3	104dp(a")	9	9

Footnote

(a) With filter, (b) without filter for polarisation studies.

6.3.4 Synthesis of $Ge_2H_5(GeH_3)Fe(CO)_4$

Manganese carbonyl exchange followed by coupling of the residues with GeH_3Br yielded a single product which has been analysed to be the first unsymmetric germanium-iron complex, $Ge_2H_5(GeH_3)Fe(CO)_4$. An earlier study with $(GeH_3)_2Fe(CO)_4$ (198) gave $GeH_3(H)Fe(CO)_4$ on treating residues left after manganese exchange with HCl. No $H_2Fe(CO)_4$ was found. The fact that no $(GeH_3)_2Fe(CO)_4$ was found in this work shows that manganese exchange in an approximately 1:1 ratio is selective and displaces only one Ge_2H_5 from $(Ge_2H_5)_2Fe(CO)_4$ and that the anion so formed is stable under the reaction conditions:

$$(Ge_2H_5)_2Fe(CO)_4 + NaMn(CO)_5 \longrightarrow Ge_2H_5Fe(CO)_4Na + Ge_2H_5Mn(CO)_5$$

$$Ge_2H_5Fe(CO)_4Na + GeH_3Br \longrightarrow Ge_2H_5Fe(CO)_4GeH_3 + NaBr$$

This is potentially a very useful route as it allows access to a wide range of unsymmetric compounds, including those of mixed group IV metals.

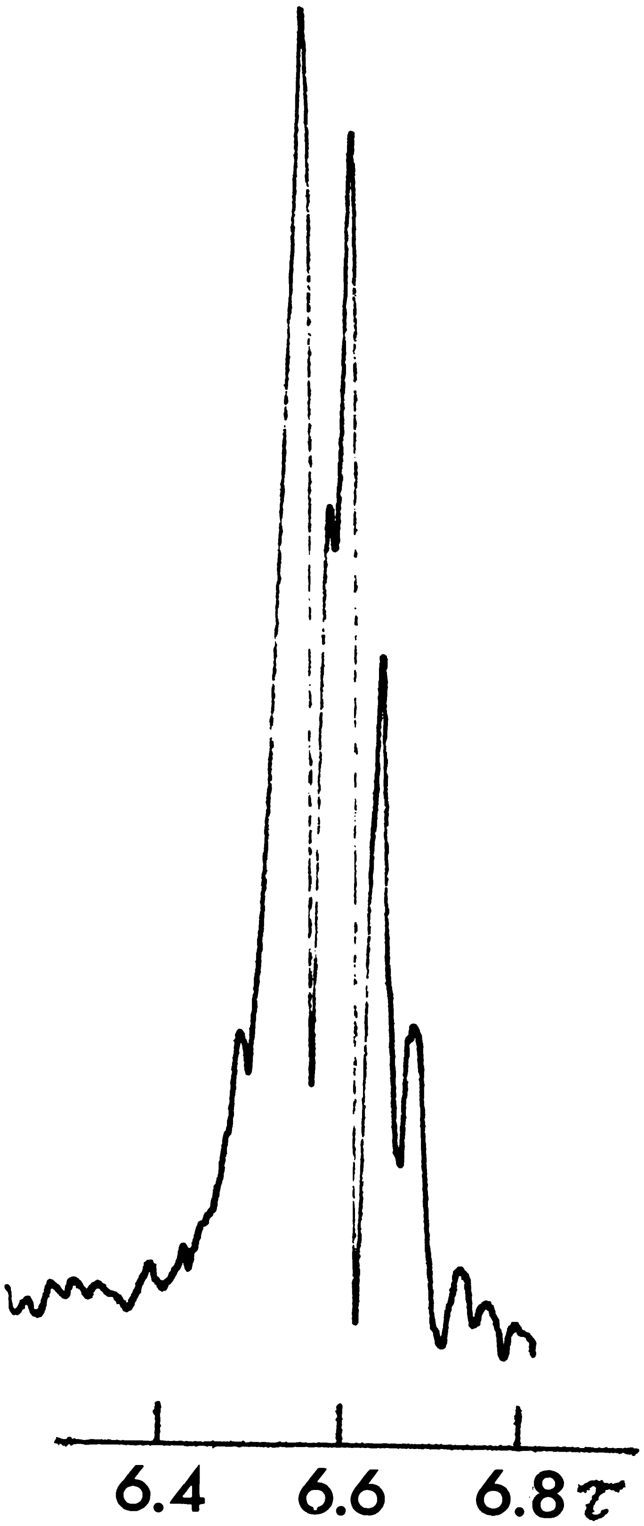
The nmr spectrum of $GeH_3GeH_2(GeH_3)Fe(CO)_4$ is given in Fig. 6.2. It consists of a complex of three overlapping signals, the triplet and quartet ($\tau GeH_3 = 6.60$, $\tau GeH_2 = 6.55$, $J = 4.0$ Hz) due to the GeH_3GeH_2Fe fragment and the singlet (τ $GeH_3 = 6.52$) due to the GeH_3Fe fragment, the GeH_3 signals integrating to give near equal intensities. It is plausible that a similar spectrum may also be obtained from an equimolar mixture of $(GeH_3)_2Fe(CO)_4$ and $(GeH_3GeH_2)_2Fe(CO)_4$. Recalling that in all the mass spectra of the polygermanyl-transition metal derivatives (and the germyl analogues) discussed so far, the strongest envelope used as the

Figure 6.2

NMR Spectrum of

$GeH_3GeH_2(GeH_3)Fe(CO)_4$

$Ge_2H_5(GeH_3)Fe(CO)_4$



base peak has always been the $[P-(CO)_n]^+$ family where n is the total number of carbonyls. The mass spectrum of an equimolar mixture of $(GeH_3)_2Fe(CO)_4$ and $(GeH_3GeH_2)_2Fe(CO)_4$ would have given two base peaks, $H_xGe_2Fe^+$ and $H_xGe_4Fe^+$. The mass spectrum of $Ge_2H_5(GeH_3)Fe(CO)_4^+$ showed the base peak to be due to $H_xGe_3Fe^+$, thus confirming the product to be a single compound and not a mixture of the higher and lower relatives. Fig. 6.3 shows these features in the mass spectra of the three compounds. Although this observation is not very useful here as such a mixture can easily be separated by distillation because of the vast difference in the vapour pressures of the two compounds, it may find useful application in cases where the two are very closely related.

Table 6.4 lists the mass spectrum of $Ge_2H_5(GeH_3)Fe(CO)_4$. It shows all the basic features observed for $(Ge_2H_5)_2Fe(CO)_4$, including CO loss, H_2 loss, Ge–Ge bond cleavage with elimination of GeH_2 or GeH_4. Again, the parent ions are weak, and the relatively weak $H_xGe_2Fe(CO)_4^+$ family as compared to the strong $H_xGe_3Fe(CO)_3^+$ one suggests CO loss to occur more readily than Ge–Ge or Ge–Fe bond scission. This is in contrast to the digermanylmanganese and digermanylcobalt compounds where the reverse is true. The ion currents carried by ions retaining Ge_3Fe, Ge_2Fe and GeFe are 36%, 32% and 19% respectively, of the total ion current, adding up to 87% matching that for $(Ge_2H_5)_2Fe(CO)_4$ at 86%.

The vibrational spectrum of $Ge_2H_5(GeH_3)Fe(CO)_4$ is listed in Table 6.5.

Figure 6.3

Mass Spectrum of Higher Mass

Regions of:

A) $(GeH_3)_2Fe(CO)_4$

B) $GeH_3GeH_2(GeH_3)Fe(CO)_4$

C) $(GeH_3GeH_2)_2Fe(CO)_4$

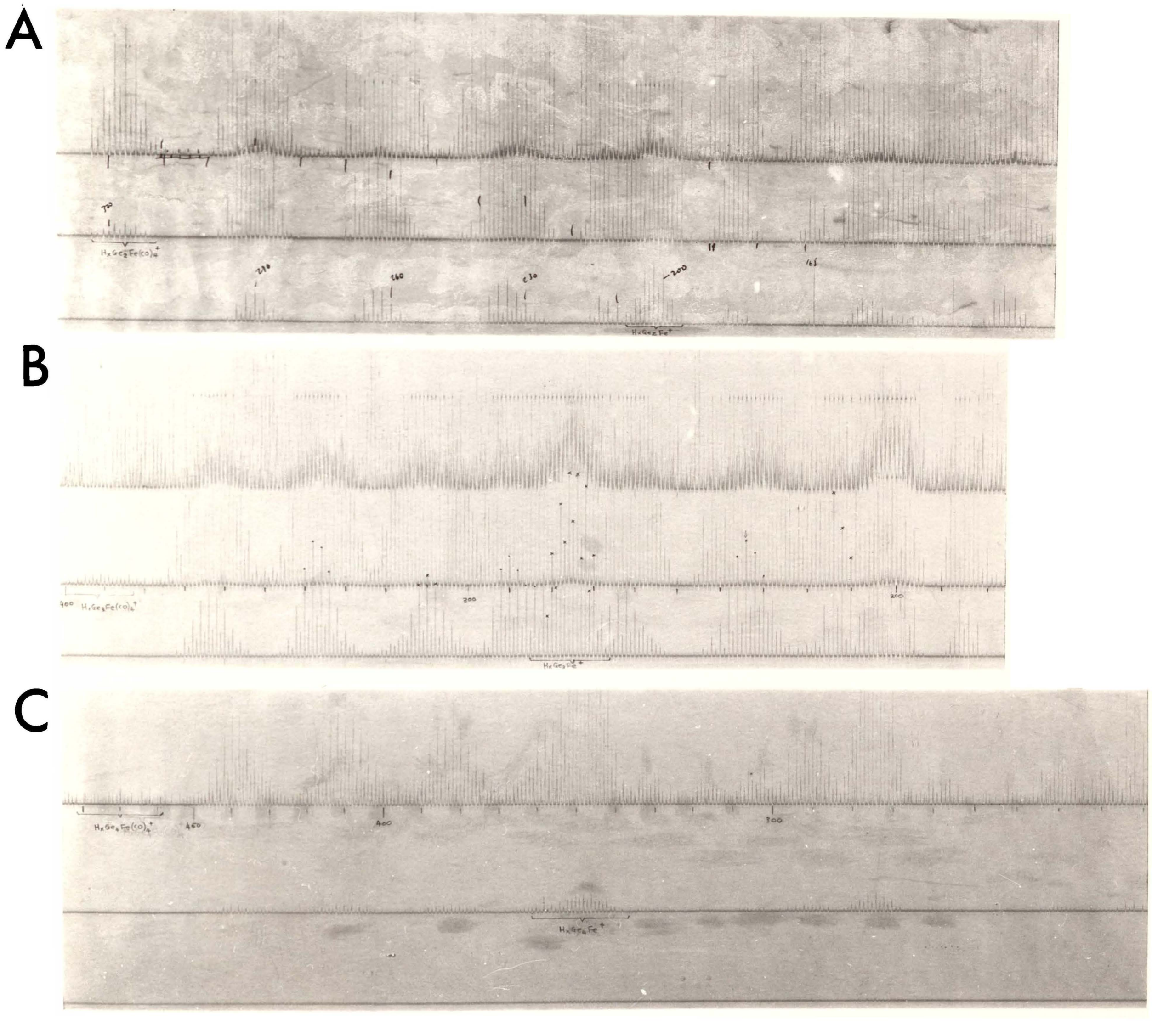

A
300
$H_xGe_2Fe(CO)_4^+$
280
260
230
200
165
$H_xGe_2Fe^+$
B
400
$H_xGe_3Fe(CO)_4^+$
300
200
$H_xGe_3Fe^+$
C
$H_xGe_4Fe(CO)_4^+$
450
400
300
$H_xGe_4Fe^+$

Table 6.4 The Mass Spectrum of $GeH_3GeH_2(GeH_3)Fe(CO)_4$

m/e	Assignment	Relative Intensity(a)	Ratio of hydrogen(b)								
			x=8	7	6	5	4	3	2	1	0
385–404	$H_xGe_3Fe(CO)_4^+$	0.7	10	2							
354–376	$H_xGe_3Fe(CO)_3^+$	31.8	1	0.5	10	0.5	1				
323–344	$H_xGe_3Fe(CO)_2^+$	51.5					10	1	0.5	0.5	
306–319	$H_xGe_3Fe(CO)^+$	44.2					10	0.5	0.3		
266–285	$H_xGe_3Fe^+$	100							?	0.5	10
313–326	$H_xGe_2Fe(CO)_4^+$	9.0					10	?			
284–298	$H_xGe_2Fe(CO)_3^+$	48.0			3	2	10	?			
253–269	$H_xGe_2Fe(CO)_2^+$	29.9				0.5	10	1	1	0.5	
228–240	$H_xGe_2Fe(CO)^+$	55.9					10				
199–212	$H_xGe_2Fe^+$	57.0					10	6			
238–246	$H_xGeFe(CO)_4^+$	4.9							1	1	10
210–218	$H_xGeFe(CO)_3^+$	36.9							2	1	10
182–190	$H_xGeFe(CO)_2^+$	15.8							2	5	10
158–166	$H_xGeFe(CO)^+$	23.9							3	6	10
126–134	H_xGeFe^+	40.6							2	2	10
216–234	$H_xGe_3^+$?	1.1					10				
140–155	$H_xGe_2^+$	15.8						1	10	2	1
70–79	H_xGe^+	24.5						5	10	1	2
169	$HFe(CO)_4^+$	0.6									
168	$Fe(CO)_4^+$	7.7									
141	$HFe(CO)_3^+$	0.6									
140	$Fe(CO)_3^+$	10.1									
113	$HFe(CO)_2^+$	0.6									

Table 6.4 (Cont.)

112	$Fe(CO)_2^+$	7.2
85	$HFe(CO)^+$	0.6
84	$Fe(CO)^+$	4.9
57	HFe^+	0.6
56	Fe^+	5.9
28	CO^+	(c)

Footnotes:

(a) Summed over x = 8-0 and over GeFe combinational isotopes where appropriate.

(b) Strongest component of family assigned 10, with other components relative to this.

(c) Peak includes N_2^+

Table 6.5 The Vibrational Spectrum of $GeH_3GeH_2(GeH_3)Fe(CO)_4$ (cm^{-1})

I.r. (solution)(a)	I.r.(solid)	Assignment
	2105 vvw	
2090 s	2090 ms	νCO, a'
2064 w,sh		νGeH, a' + a"
2055 m	2050 mw	
	2039 mw	νCO, a' + a"
2039 w,sh	2022 s	
2023 vvs	2000 s	
2007 vvs	1991 vs	νCO, a'
1986 vw		$\nu^{13}CO$
1973 vw		
874 w	872 w	$\delta_{asym.}$ $GeH_{3(1)}$, $GeH_{3(2)}$ a' + a"
860 w	856 vw	
	822 vw	$\delta_{sym.}$ $GeH_{3(1)}$, $GeH_{3(2)}$ a'
813 ms	810 w	
	799 vw	
790 mw	787 w	
679 m	674 w	GeH_2 wag, a'
	658 vw	
617 s	610 s	δFeCO, a'
434 vw	438 vw	GeH_3 rock
(b) 434 s,p		νFeC, a'
(b) 268 m,p		νGe–Ge, a'
(b) 223 vs,p		νGe–Fe, a'
(b) 202 s,p		νGe–Fe, a'
(b) 104 s,dp		Skeletal deformation, a"

Table 6.5 (Cont.)

Footnotes:

(a) Infrared solution spectrum in cyclohexane

(b) Raman spectrum of neat liquid.

The spectrum shows absorptions in regions where vibrational modes were earlier observed for $(Ge_2H_5)_2Fe(CO)_4$. The carbonyl stretches assignable to 3a' + a" modes and the three strong polarised metal-metal stretching bands are all expected of a C_s symmetry. Overall, only about a quarter of the possible 54 vibrations are observed.

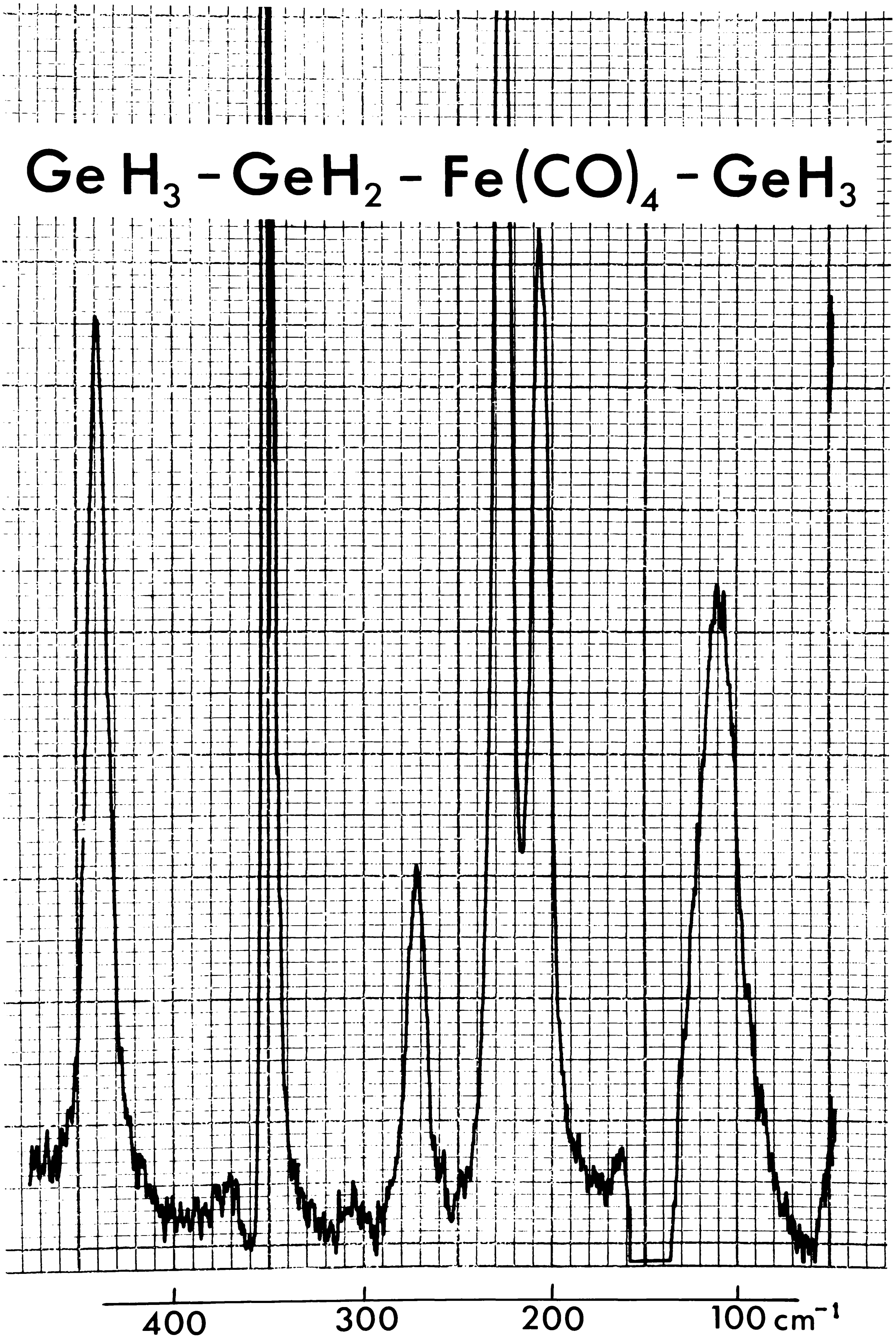
In the GeH_x deformation region, the spectrum shows features which can be assigned to the GeH_3 and GeH_3GeH_2 groups by comparison with $(GeH_3)_2Fe(CO)_4$ (173) and $(Ge_2H_5)_2Fe(CO)_4$. The symmetric deformation of the germyl group is assigned to the sharp band at 790 cm^{-1}, compared with the in- and out-of-phase combinations of this mode at 835 cm^{-1} and 809 cm^{-1} for $(GeH_3)_2Fe(CO)_4$. Similarly, the prominent GeH_2 wag is found at 679 cm^{-1} compared with 692 cm^{-1} and 662 cm^{-1} for the modes in $(GeH_3GeH_2)_2Fe(CO)_4$ (see Table 6.2). The third prominent deformation at 813 cm^{-1} is then assigned to GeH_3 of the GeH_3GeH_2 group. The asymmetric GeH_3 modes of both groups are assigned to the broader, more complex band about 870 cm^{-1} – the characteristic frequency for such modes. Thus while $(GeH_3)_2Fe(CO)_4$ and $(GeH_3GeH_2)_2Fe(CO)_4$ both show a pair of bands for the combined symmetric deformations of the α-GeH_x groups, $GeH_3GeH_2(GeH_3)Fe(CO)_4$ shows single bands at approximately the average frequency of each pair. The vibrational spectra of the GeH_x deformation region of $(GeH_3GeH_2)_2Fe(CO)_4$ and $GeH_3GeH_2(GeH_3)Fe(CO)_4$ can be found in Chapter 7.

The Raman spectrum of the metal-metal stretching of $GeH_3GeH_2(GeH_3)Fe(CO)_4$ is given in Fig. 6.4.

Figure 6.4

Raman Spectrum (0 - 500 cm^{-1})

of $GeH_3GeH_2(GeH_3)Fe(CO)_4$



$GeH_3-GeH_2-Fe(CO)_4-GeH_3$

The strong polarised band at 434 cm^{-1} assigned to Fe-C stretch matches the 433 cm^{-1} and 436 cm^{-1} bands in $(GeH_3GeH_2)_2Fe(CO)_4$ and $(GeH_3)_2Fe(CO)_4$ (173). The three strong polarised metal-metal stretching bands confirm the C_s symmetry of $Ge_2H_5(GeH_3)Fe(CO)_4$. While the medium, polarised Ge-Ge stretch of $(GeH_3GeH_2)_2Fe(CO)_4$ (a_1) and $GeH_3GeH_2(GeH_3)Fe(CO)_4$ (a') both occur at exactly the same frequency as that found for digermane (92) the two Ge-Fe frequencies show drops from $(GeH_3)_2Fe(CO)_4$, through $Ge_2H_5(GeH_3)Fe(CO)_4$ to $(Ge_2H_5)_2Fe(CO)_4$. Both the a_1 and b_1 modes of $(Ge_2H_5)_2Fe(CO)_4$ show equal drops of 18 cm^{-1} from $(GeH_3)_2Fe(CO)_4$, while the lower frequency band in $Ge_2H_5(GeH_3)Fe(CO)_4$ seems to be the more sensitive. Thus the 202 cm^{-1} is probably the νGe_2-Fe Stretch and the 223 cm^{-1} band the νGe_1-Fe stretch.

6.3.5 Substitution Reactions

$(GeH_3)_2Fe(CO)_4$ (279) shows initial reaction with $SiCl_4$ after 4 hours, while the first sign of change was observed after 1½ months with $(Ge_2H_5)_2Fe(CO)_4$; $Ge_2H_5(GeH_3)Fe(CO)_4$ reacts at an intermediate rate with changes recorded after 1 week, all under similar conditions. Thus, it appears that addition of GeH_3 groups introduces steric hindrance towards substitution of the reactive hydrogens on the α-germanium by $SiCl_4$. The two non-reactive GeH_3 groups in $(GeH_3GeH_2)_2Fe(CO)_4$ seem to provide a protective cover over the two α-GeH_2 groups.

Although no characterisation was obtained for the chloro-substituted product of the reaction between $(Ge_2H_5)_2Fe(CO)_4$ and $SiCl_4$, the doublet (6.0 τ) and quartet (4.3 τ) signals (J = 4.0 Hz) of intensity ratio 3:1 are clearly due to either $GeH_3GeH_2(GeH_3GeHCl)Fe(CO)_4$

or $(GeH_3GeHCl)_2Fe(CO)_4$, reaction reaching equilibrium after 10% of the $(Ge_2H_5)_2Fe(CO)_4$ had been consumed,

$$(GeH_3GeH_2)_2Fe(CO)_4 + SiCl_4 \longrightarrow (GeH_3GeH_2)(GeH_3GeHCl)Fe(CO)_4$$

$$\text{or} \qquad (GeH_3GeHCl)_2Fe(CO)_4 + SiHCl_3$$

Incidentally, the coupling constant of 4 Hz of the well separated product signals confirms the earlier analysed coupling constant for $(Ge_2H_5)_2Fe(CO)_4$ and $Ge_2H_5(GeH_3)Fe(CO)_4$, the nmr spectra of which are a complex of overlapping signals. The chloro-product showed no tendency to undergo self-reaction, commonly observed for the halo-substituted products of $(GeH_3)_2Fe(CO)_4$ (174) and $(MeGeH_2)_2Fe(CO)_4$ (177). In fact this chloro-compound showed no decomposition at all over 4½ months.

The changes in the nmr spectrum for the reaction between $Ge_2H_5(GeH_3)Fe(CO)_4$ and $SiCl_4$ suggest substitution of the more accessible GeH_3Fe part:

$$Ge_2H_5(GeH_3)Fe(CO)_4 + SiCl_4 \longrightarrow Ge_2H_5(GeH_2Cl)Fe(CO)_4 + SiHCl_3$$

Further changes involve self-reaction and can be rationalised by the following equation, supported by the recovery of Ge_2H_6 and the mass spectrum of the cyclised product:

$$2Ge_2H_5(GeH_2Cl)Fe(CO)_4 \longrightarrow 2Ge_2H_6 + [GeHClFe(CO)_4]_2$$

The chloro-substituted product of $(Ge_2H_5)_2Fe(CO)_4$ does not undergo self-reaction probably because the two GeH_3 groups do not allow the close approach of a pair of the reactants to allow the condensation reaction. It also further demonstrates previous observations that the halo-substituted product of a transition metal carbonyl derivative is more stable than the halides of the polygermanes.

The reaction between $(Ge_2H_5)_2Fe(CO)_4$ and CCl_4 is much faster than with $SiCl_4$ showing the effect of reactant size in rate determination. However, it is a little more complicated by the lack of signals attributable to any chloro-substituted products, but chloro-substitution is obvious by the production of $CHCl_3$ and CH_2Cl_2. The evolution of GeH_4 also suggests Ge–Ge bond cleavage. Taken together, it could mean a combination of two reactions. The first involves chloro-substitution perhaps even of the GeH_3 groups, to form a very unstable product under the reaction conditions. This is probably followed by a rapid self-reaction to form a high molecular weight compound, evidenced by the precipitation of yellow deposits as the reaction proceeded, with elimination of monogermane. The yellow product may possibly be $[GeH_3GeCl(GeHCl)Fe(CO)_4]_2$.

CHAPTER 7. DISCUSSION

7.1 The NMR Patterns of the Polygermanyl-Transition Metal Compounds

A considerable amount of nmr data has been reported at various stages throughout this thesis. The data obtained for the polygermanyl-transition metal carbonyls are collected together and discussed here.

The 60 MHz ^1H nmr of the digermanylmanganese and cobalt compounds are of the second-order A_3B_2 type where the triplet and quartet multiplicities are just identifiable. In such complex signals the easiest to recognise is the A_{13} (293) peak which is the strongest peak giving the chemical shift of the GeH_3 resonance. By using this peak and by guessing the coupling constant J and Δ value (Δ = the difference in the chemical shifts of the GeH_3 and GeH_2 resonances), the chemical shifts of the B_8 and B_5 peaks of the GeH_2 resonance are found. B_8 and B_5 are the two peaks to the extreme right and extreme left of the GeH_2 resonance. The average of these gives the chemical shift of the GeH_2 resonance. This method by trial and error was first used by Narasimhan and Rogers (294,295) and later successfully applied by Mackay and Watt (296,297) to halide derivatives of ethyldigermane and ethylsilane. The full analysis of the nmr spectrum of $GeH_3GeH_2Mn(CO)_5$ has previously been made by the author (53) using this method. A matching theoretical spectrum was also obtained using the method of analysis supplied by Corio (293,298) where the above descriptive notations were obtained. Here, it is shown that the same methods of analysis can be applied to the second-order A_3B_2 spectrum of $GeH_3GeH_2Co(CO)_4$ to derive the true GeH_2 chemical shift. The theoretical spectrum is also obtained and matches well with the practical spectrum. The practical and theoretical spectra of $GeH_3GeH_2Mn(CO)_5$ (53) are reproduced in Fig. 7.1 and Fig. 7.2 together with those of $GeH_3GeH_2Co(CO)_4$ in Fig. 7.3 and Fig. 7.4. By coincidence the spectrum of $GeH_3GeH_2Co(CO)_4$ is a near mirror-image of that of the manganese analogue. The spectrum of $(GeH_3GeH_2)_2Fe(CO)_4$ (Fig. 7.5) is a second-order A_3B_2 complex of two overlapping resonances, which on low resolution appears as a broad singlet with fine structure. Several trial theoretical spectra of the second-order A_3B_2 type were worked out, one of which is given in Fig. 7.6, but none showed as good a match to the practical spectrum as in the earlier cases.

The nmr parameters obtained for the digermanyl-transition metal compounds are as follows:

	Chemical shifts (tau)		J(Hz)
	GeH_3Ge	GeH_2M	
GeH_3GeH_3	6.92		
$GeH_3GeH_2Mn(CO)_5$	6.53	6.85	4.4
$(GeH_3GeH_2)_2Fe(CO)_4$	6.53	6.48	4.3
$GeH_3GeH_2Co(CO)_4$	6.51	6.25	4.2

Figure 7.1

Nmr Spectrum of $GeH_3GeH_2Mn(CO)_5$

(53)

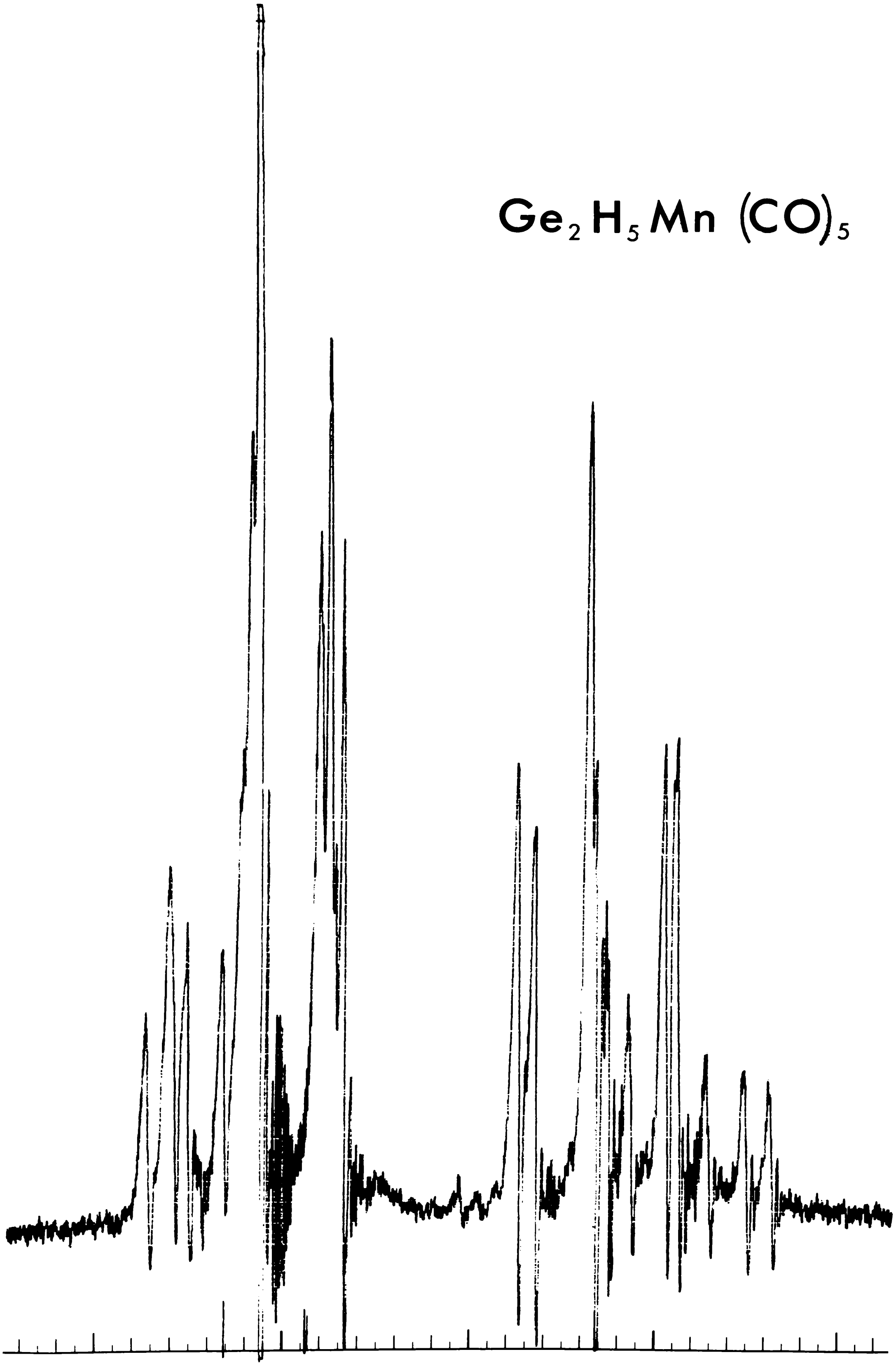

Ge$_2$H$_5$Mn (CO)$_5$
6.5
7 τ

Figure 7.2

Theoretical Nmr Spectrum of $GeH_3GeH_2Mn(CO)_5$

(53)

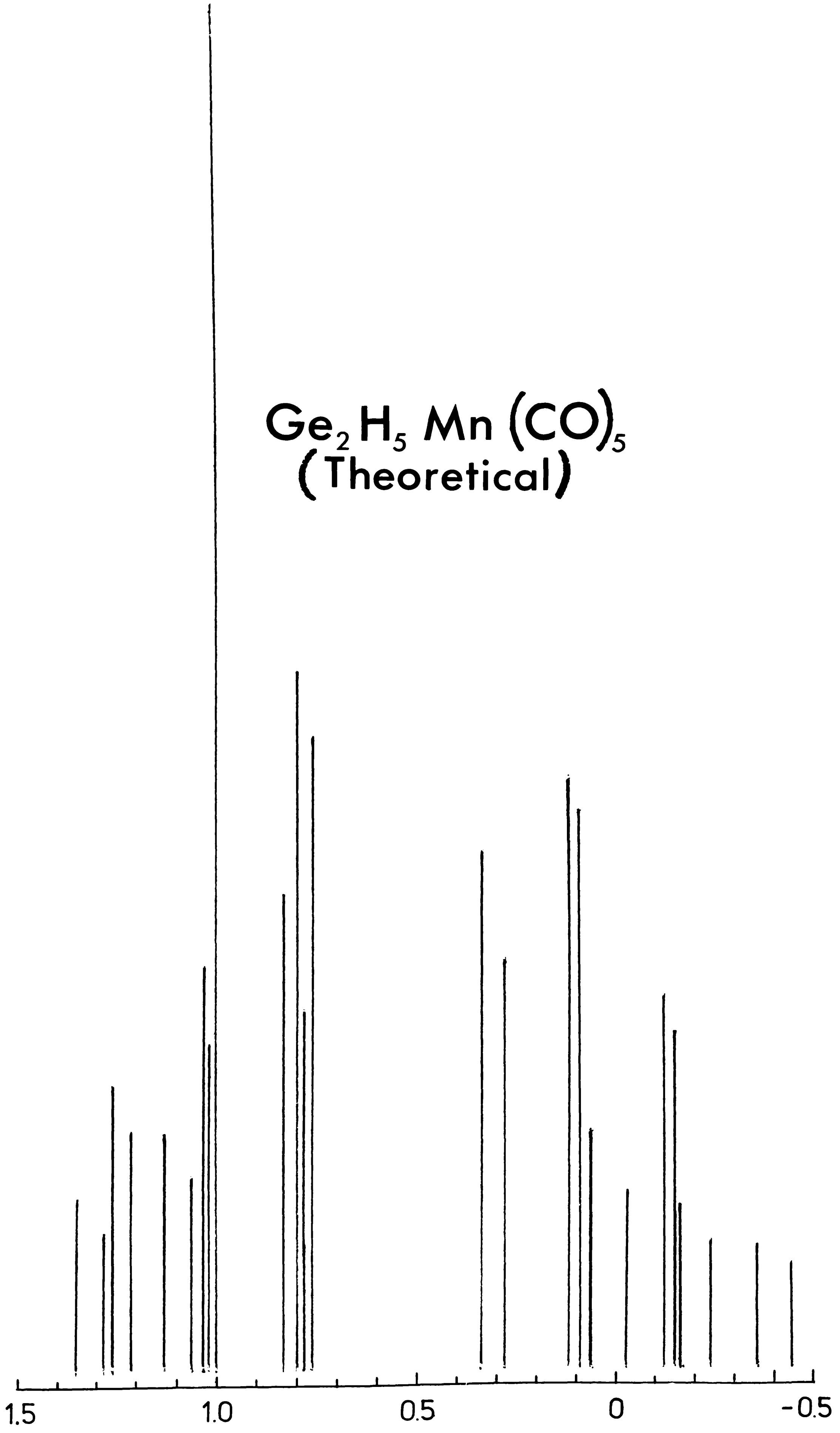

$Ge_2H_5Mn(CO)_5$
(Theoretical)
1.5
1.0
0.5
0
-0.5

Figure 7.3

Nmr Spectrum of $GeH_3GeH_2Co(CO)_4$

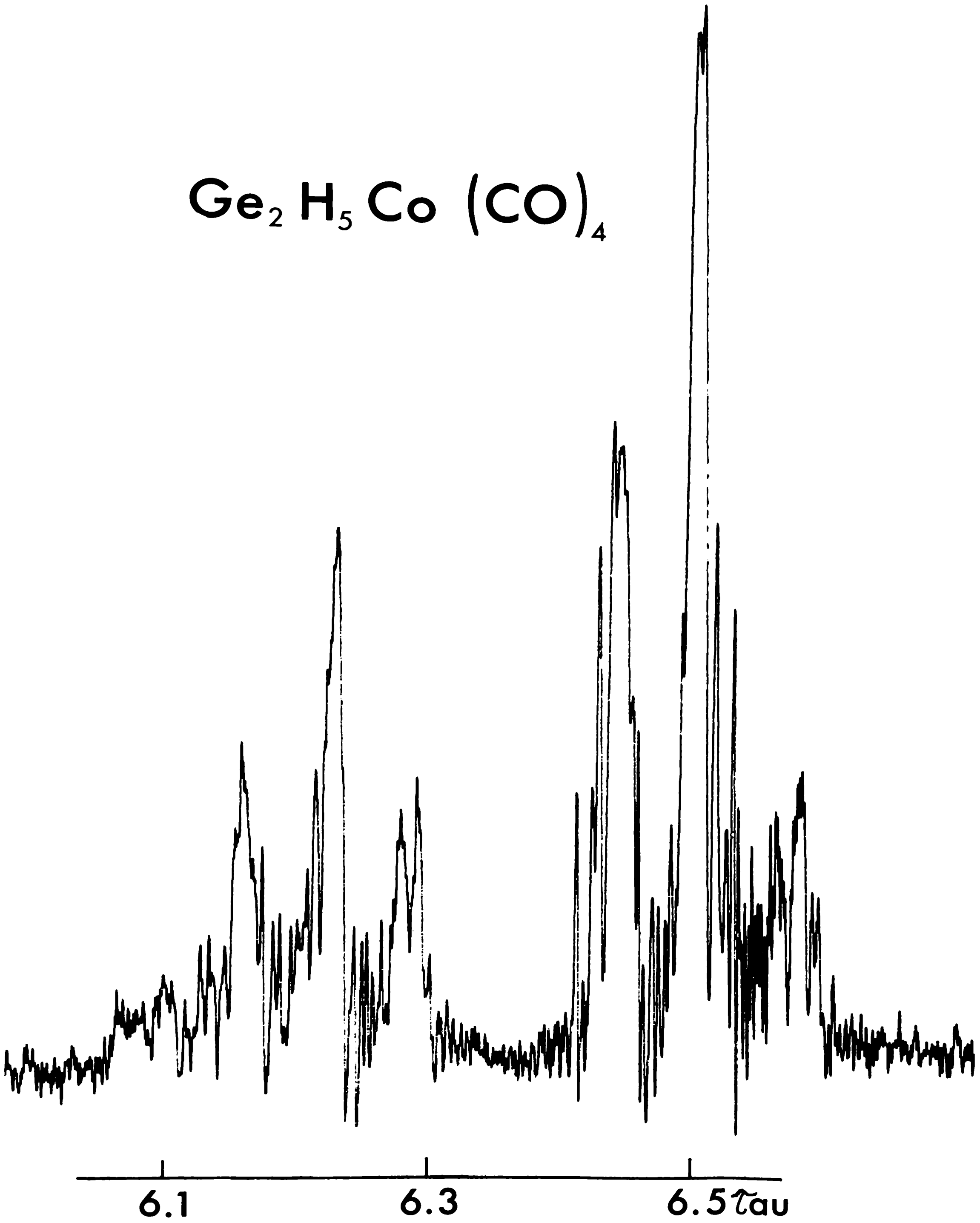

$Ge_2H_5Co(CO)_4$
6.1
6.3
6.5 τau

Figure 7.4

Theoretical Nmr Spectrum of $GeH_3GeH_2Co(CO)_4$

$Ge_2H_5Co(CO)_4$
(Theoretical)

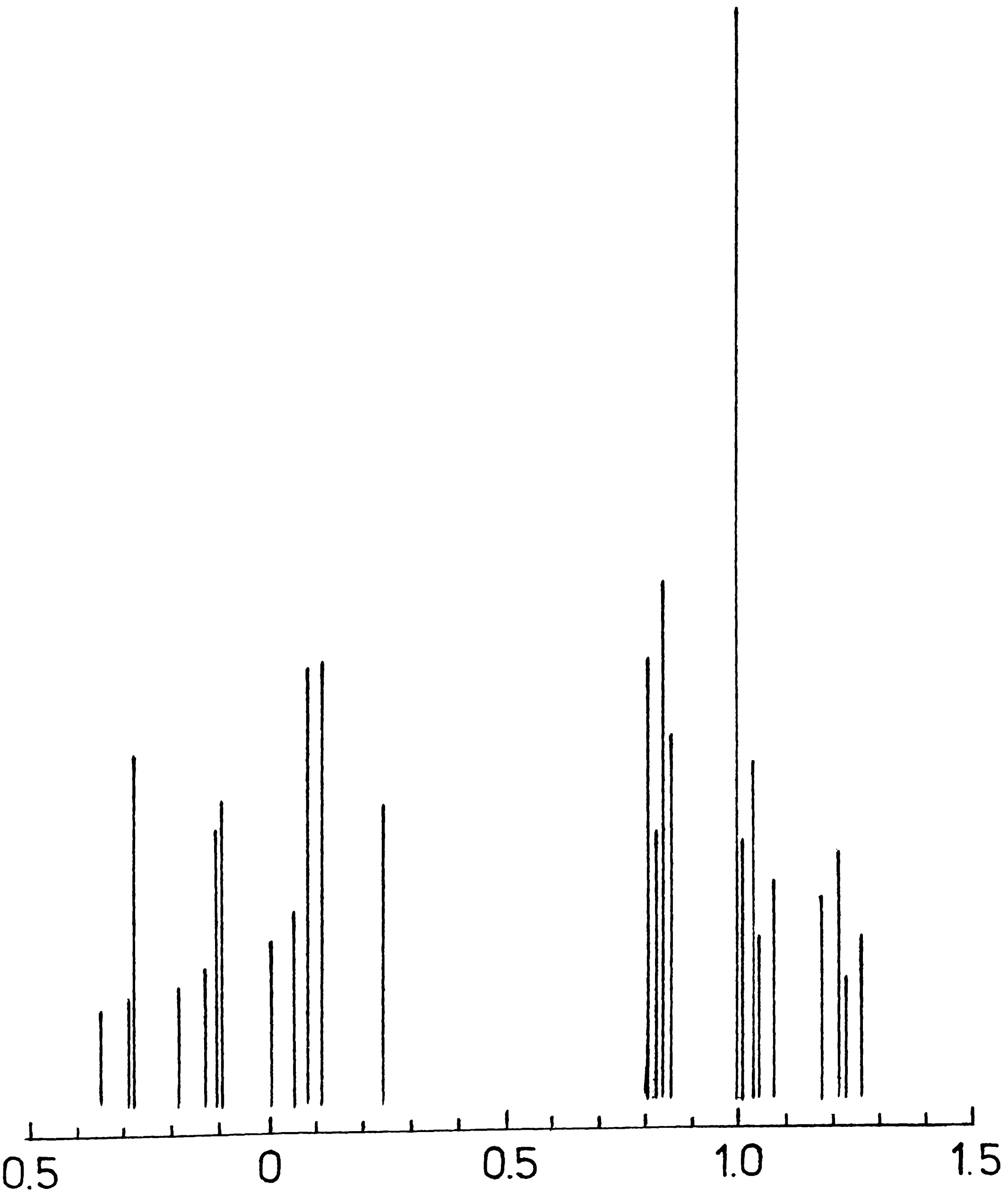
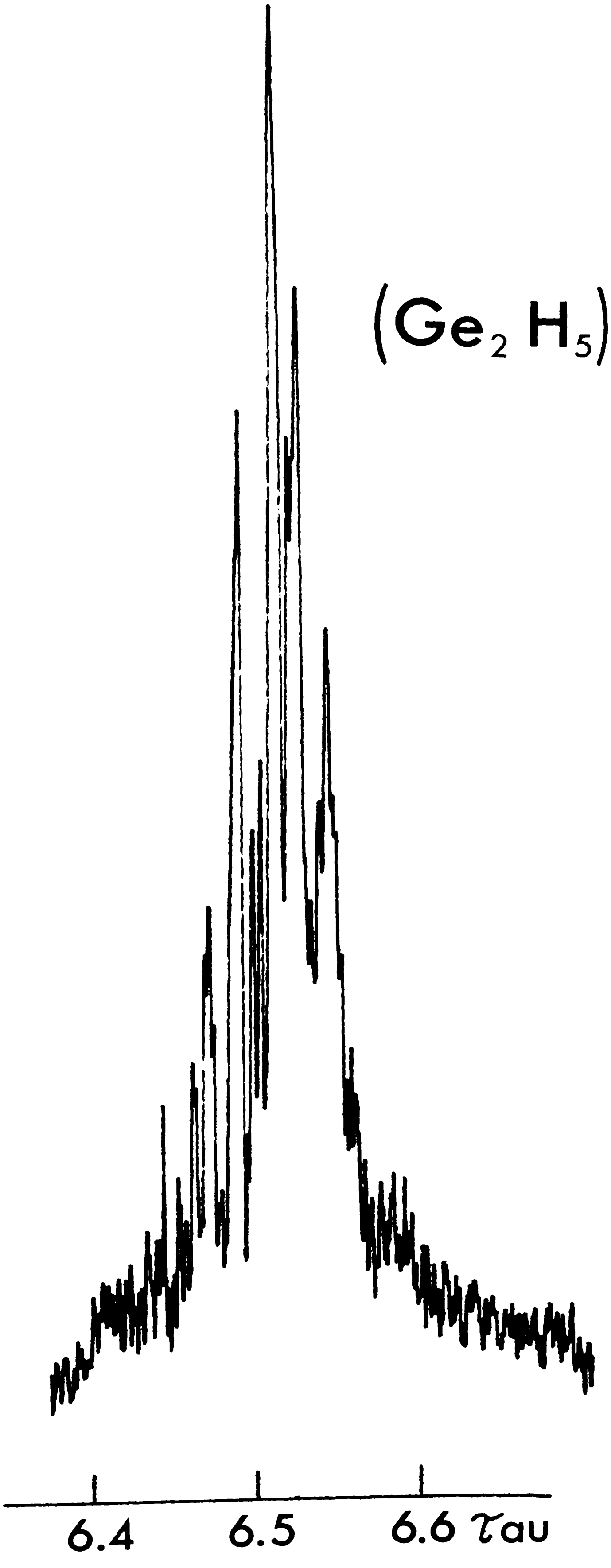


Figure 7.5

Nmr Spectrum of $(GeH_3GeH_2)_2Fe(CO)_4$



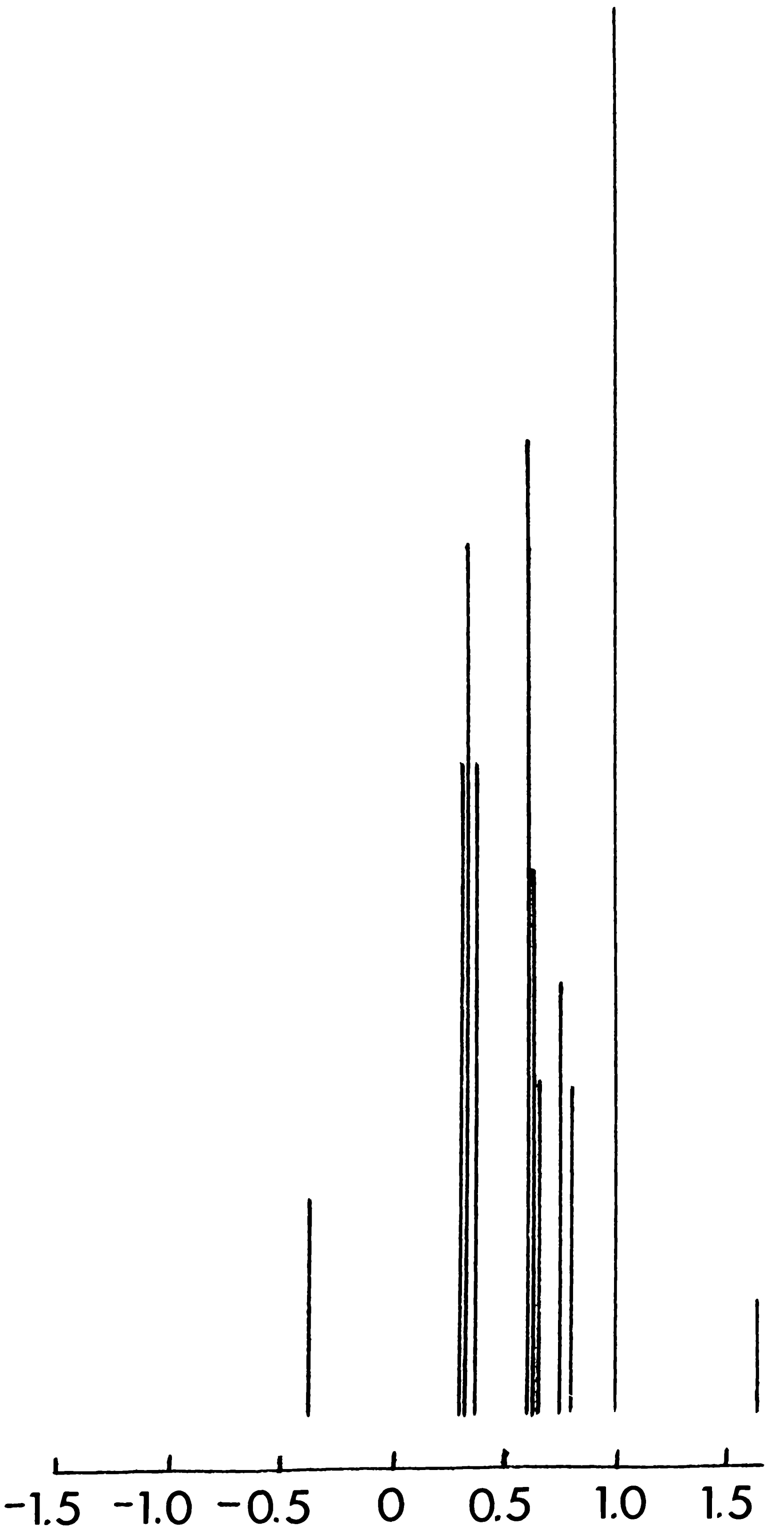
$(Ge_2H_5)_2Fe(CO)_4$

Figure 7.6

Theoretical Nmr Spectrum of

$(GeH_3GeH_2)_2Fe(CO)_4$

$(Ge_2H_5)_2\ Fe(CO)_4$
(Theoretical)

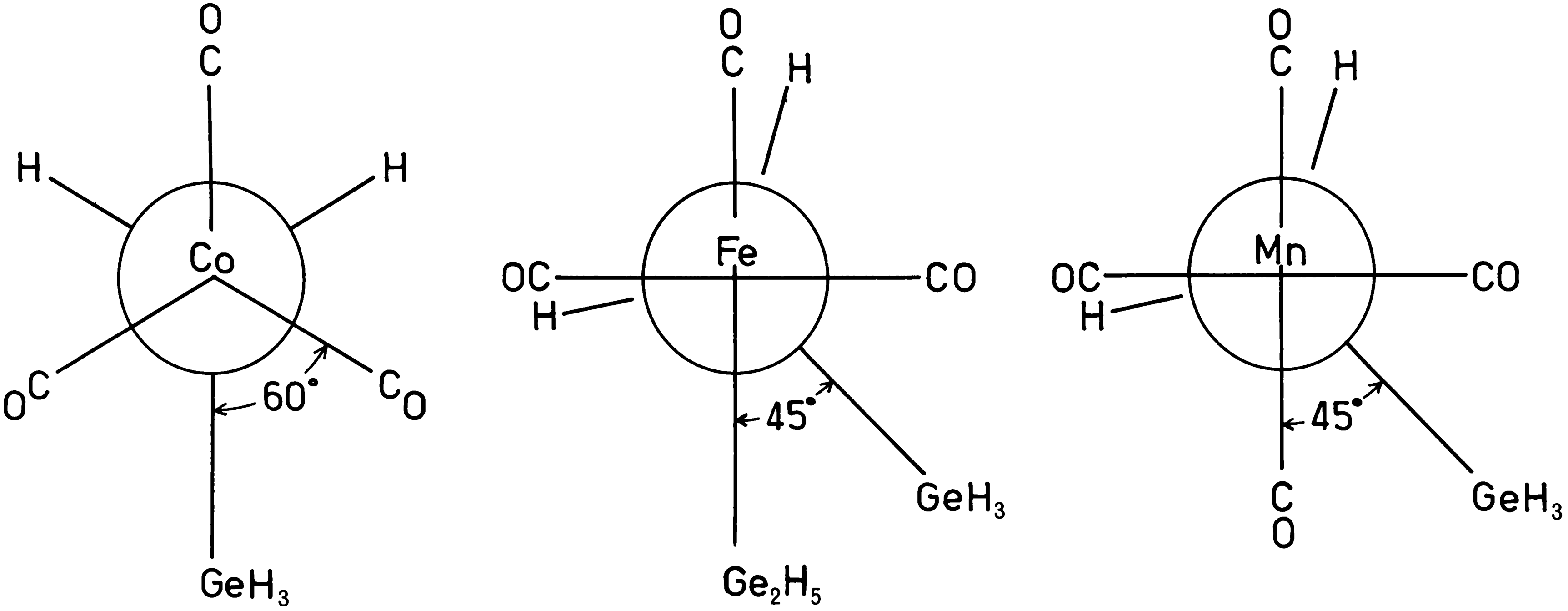


There are several interesting features. The first is that the GeH_3Ge chemical shifts of the transition metal derivatives are all about the same value and occur approximately 0.4 ppm downfield from Ge_2H_6. They appear to be unaffected by the change of transition metal carbonyl. The second is the marked effect of the transition metal on the GeH_2M shifts, with the GeH_2Mn shift occurring just downfield from the Ge_2H_6 resonance, the GeH_2Fe in the region of the GeH_3Ge shift while that of the GeH_2Co appearing downfield from the GeH_3Ge shift. The third is that the coupling constants of about 4 Hz are close to those of the polygermanes (54). It appears possible to explain the shift patterns in terms of an induced magnetic field by the π-cloud in the $M-(C-O)_x$ bonds. The effect is felt most strongly by the hydrogens on the α-germanium and probably weakly by the more distant and freely rotating GeH_3 group. Furthermore, the GeH_3 group may also be under the influence of magnetic anisotropy in the Ge-Ge bond. It may only be by coincidence that the GeH_3Ge resonance of the three compounds all occur at about 0.4 ppm downfield from Ge_2H_6 as the nett result of these two effects. The downfield shift of the GeH_2M resonance from the manganese compound to the cobalt compound is probably due to the configurations of the various metal carbonyl groups and this is more clearly seen in Fig. 7.7 which shows the Newman projection diagrams of the three digermanyl derivatives viewed down the transition metals. The bond lengths have been drawn approximately to scale. The diagrams show the proximity of the various hydrogens of the GeH_2M groups to the carbonyls and also the number of carbonyls influencing these

Figure 7.7

Newman Projection Diagrams of the Digermanyl Derivatives of Manganese, Iron and Cobalt Carbonyls.

CO Inductive Effect



Co < Fe < Mn

hydrogens. Viewed in this manner, the hydrogens of the GeH_2M group of the manganese compound are most greatly affected, those in the cobalt compound least, and those in the iron compound, intermediate. There have also been suggestions of a direct "across-space" ($p \rightarrow d$) π interaction between the equatorial carbonyls and the group IV element (208,228). This may be an alternative explanation.

The ^1H nmr data of the mono-, di- and tri-germanyl transition metal derivatives and related compounds are listed in Table 7.1. The table clearly shows the familiar downfield trend of the $M'H_xM$ chemical shifts from the $M'H_4$ signal of the silyl and germyl compounds in the order of manganese to iron to cobalt. In the M-M'-M'-M system, the shift is even more pronounced. The chemical shift of $Co(CO)_4GeH_2GeH_2Co(CO)_4$ is by coincidence downfield from the Ge_2H_6 signal by the sum of the downfield shifts of the GeH_3Ge and GeH_2Co resonances in $GeH_3GeH_2Co(CO)_4$, each GeH_2Ge group seems to be experiencing both the earlier mentioned effects causing these downfield shifts, brought on by two cobalt carbonyl groups. However, this is not the case in $Mn(CO)_5GeH_2GeH_2Mn(CO)_5$. This is probably due to a more rigid structure in the manganese compound with two extra carbonyls.

Addition of Cl shifts the GeH_x signal in GeH_3GeH_2Cl and $GeH_3GeHClMn(CO)_5$ considerably downfield from the Ge_2H_6 resonance to the 4-5 τ region. This is mainly an inductive effect by the strongly electronegative Cl. This effect is felt to a much lesser extent by the GeH_3 group which also shows a downfield shift proportional to the number of chlorine atoms bonded to the

Table 7.1 ^{1}H Nmr Parameters of the Polygermanyl-Transition Metal Derivatives and Related Compounds

	Solvent	Chemical shifts (τ)		J(Hz)	Ref
		M'HX	M'H_3	(HGeGeH)	
SiH_4	C_6H_{12}		6.80		299
$SiH_3Mn(CO)_5$	neat	6.41			157
$(SiH_3)_2Fe(CO)_4$	neat	6.33			169
$SiH_3Co(CO)_4$	neat	5.96			200
GeH_4(b)	C_6H_6		6.80		(a)
$GeH_3Mn(CO)_5$	C_6H_6	6.72			(a)/162
$GeH_2[Mn(CO)_5]_2$	$CHCl_3$	6.67			159
$(GeH_3)_2Fe(CO)_4$	C_6H_6	6.50			(a)/173
$GeH_3Co(CO)_4$(g)	C_6H_6	6.27			(a)
Ge_2H_6(c)	C_6H_6		6.92		(a)
GeH_3GeH_2Cl(d)	C_6H_6	4.98	6.71	4.1	(a)
$GeH_3GeH_2Mn(CO)_5$(e)	C_6H_6	6.85	6.53	4.4	(a)
$GeH_3GeHClMn(CO)_5$	C_6H_6	4.08	6.18	4.0	(a)
$GeH_3GeCl_2Mn(CO)_5$	C_6H_6		5.96		(a)
$GeH_3GeMe_2Mn(CO)_5$	C_6H_6	(9.31 Me)	6.54		53
$(GeH_3GeH_2)_2Fe(CO)_4$	C_6H_6	6.48	6.53	4.3	(a)
X or Y	$SiCl_4$	4.3	6.0	4.0	(a)
$GeH_3GeH_2(GeH_3)Fe(CO)_4$	C_6H_6	6.55 6.52(GeH_3Fe)	6.60	4.0	(a)
$GeH_3GeH_2(GeH_2Cl)Fe-(CO)_4$	$SiCl_4$	6.57 4.93(GeH_2Cl)	6.60		(a)
$[GeHClFe(CO)_4]_2$	$SiCl_4$	4.60			(a)
$GeH_3GeH_2Co(CO)_4$	C_6H_6	6.25	6.51	4.2	(a)

Table 7.1 (Cont.)

	Solvent	Chemical shifts (τ)		J(Hz)	Ref
		M'HX	M'H_3	(HGeGeH)	
$ClGeH_2GeH_2Cl$	C_6H_6	5.09			(a)/139
$Mn(CO)_5GeH_2GeH_2Mn(CO)_5$	C_6H_6	6.03			(a)
$Co(CO)_4GeH_2GeH_2Co(CO)_4$	C_6H_6	5.69			(a)
$Co(CO)_4GeH_2GeH_2Cl$	C_6H_6	5.97(GeH_2Co) 4.75(GeH_2Cl)			(a)
Ge_3H_8(f)	C_6H_6	6.95	6.79	4.0	(a)
$(GeH_3)_2GeHCl$	C_6H_6	4.65	6.53	4.0	(a)
$(GeH_3)_2GeHMe$(h)	C_6H_6	6.43	6.70	3.9	137
$(GeH_3)_2GeHMn(CO)_5$	C_6H_6	6.36	7.09	4.4	(a)
$(GeH_3)_2GeClMn(CO)_5$			6.05		(a)

Notes:

X = $(GeH_3GeH_2)(GeH_3GeHCl)Fe(CO)_4$

Y = $(GeH_3GeHCl)_2Fe(CO)_4$

(a) This work,

compare with, in cyclohexane:

(b) 6.85 τ (280)

(c) 6.76 τ (280)

(d) 4.61 τ, 6.37 τ, 4.1 Hz (122)

(e) 6.91 τ, 6.56 τ, J not given (135)

(f) 6.88 τ, 6.68 τ, 4.0 Hz (54)

(g) This value incorrectly reported in ref. 183

(h) τMe = 9.66, HCGeH = 4.2 Hz

α-germanium atom as in $GeH_3GeHClMn(CO)_5$ and $GeH_3GeCl_2Mn(CO)_5$. This probably also reflects magnetic anisotropy in the Ge-Ge bond. An interesting observation here is that chlorosubstitution does not show a marked decrease in the HGeGeH coupling constant in the above chlorosubstituted compounds, nor in the chlorosubstituted compound of $(GeH_3GeH_2)_2Fe(CO)_4$ (X or Y, see Table 7.1) in contrast to the HCGeH coupling constant of $MeGeH_2Mn(CO)_5$ (4.0 Hz) to $MeGeHClMn(CO)_5$ (3.1 Hz) (141). Methyl substitution does not seem to affect the chemical shift of the β-GeH_3 group in the digermanyl system as seen between $GeH_3GeH_2Mn(CO)_5$ and $GeH_3GeMe_2Mn(CO)_5$. The difference in the degree of shift by a methyl group and a manganese carbonyl group on the GeH_x resonance results in the lone GeH resonance of the central germanium atom in $GeH_3GeHMeGeH_3$ and $GeH_3GeH[Mn(CO)_5]GeH_3$ being on opposite sides of the strong doublet signal of the GeH_3 groups, which is in the region of the Ge_3H_8 signals:

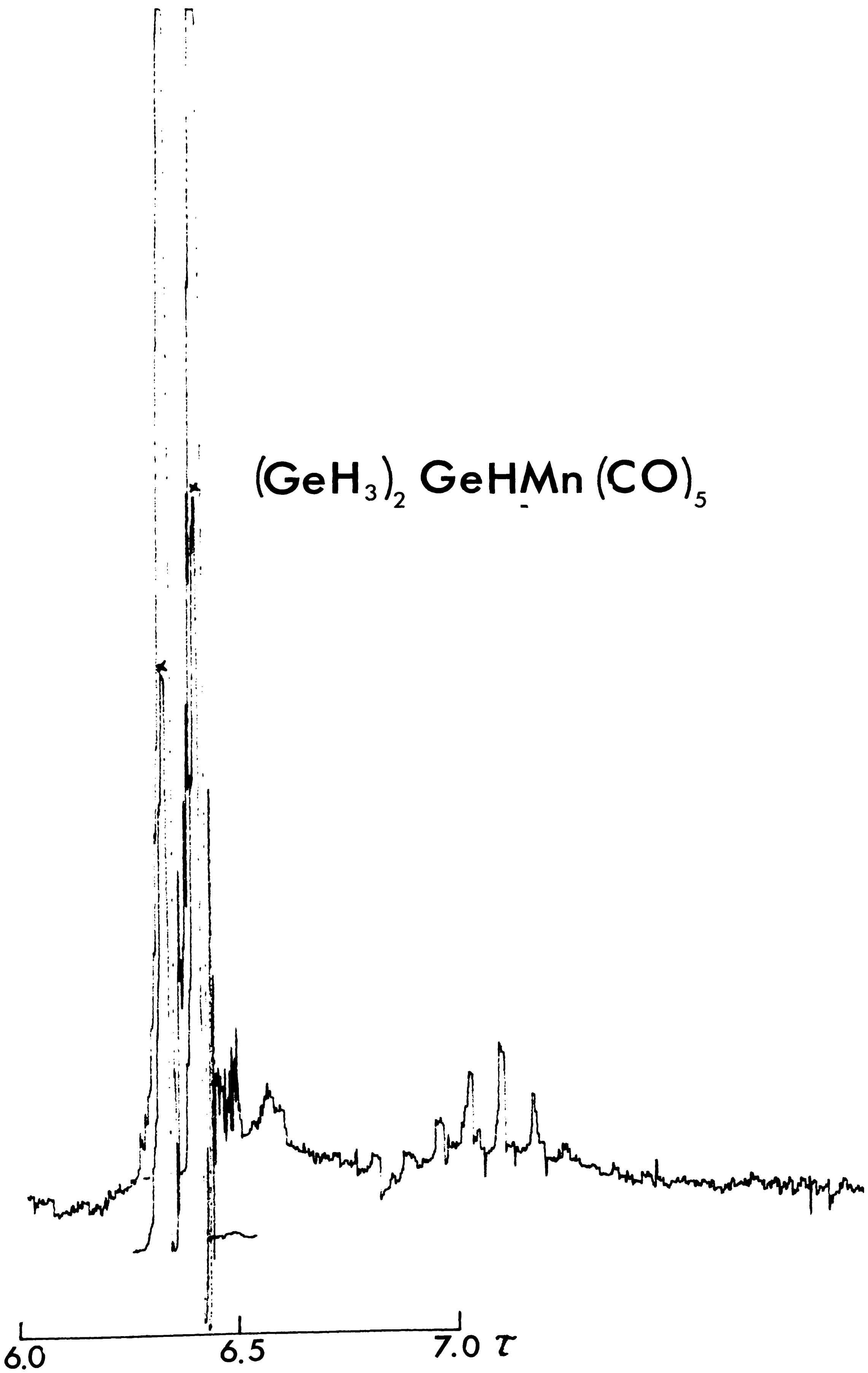
	τGeH_3	τGeH_x	J(Hz)
$GeH_3GeH_2GeH_3$	6.79	6.95	4.0
$GeH_3GeHMeGeH_3$	6.70	6.40	3.9
$GeH_3GeH[Mn(CO)_5]GeH_3$	6.36	7.09	4.4

These features are better illustrated in Fig. 7.8 and Fig. 7.9.

Figure 7.8

Nmr Spectrum of

$(GeH_3)_2GeHMn(CO)_5$

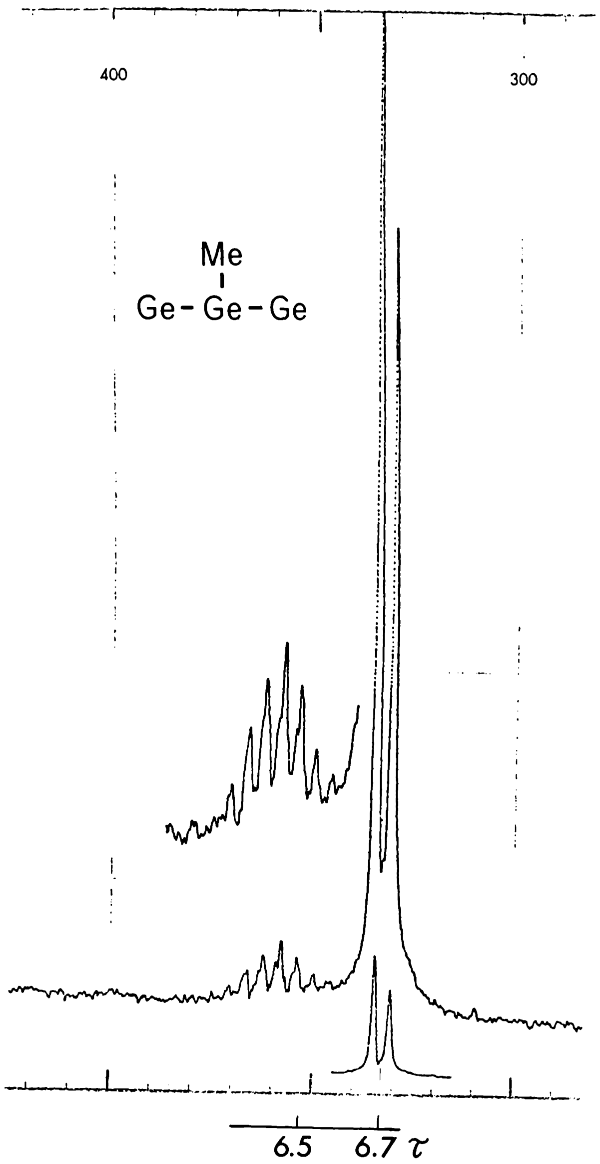


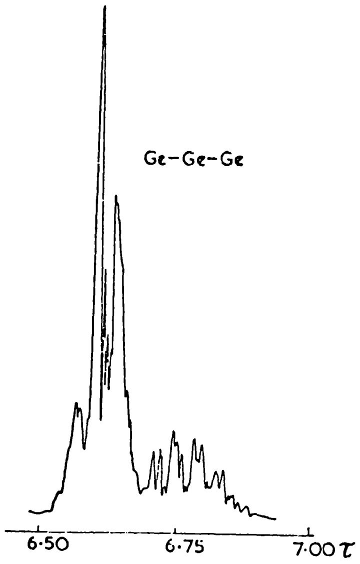
$(GeH_3)_2 Ge\underline{H}Mn(CO)_5$

Figure 7.9

Nmr Spectrum of

Ge_3H_8 (54) and $(GeH_3)_2GeHMe$ (147)


400
300
Me
Ge - Ge - Ge
6.5
6.7 τ


Ge–Ge–Ge
6·50
6·75
7·00 τ

7.2 The GeH_3 and GeH_2 Deformations

In Chapters 3, 4, 5 and 6, the vibrational spectra of the various polygermanyl-transition metal carbonyls have been discussed. The spectra were assigned by comparing with the spectra of compounds containing the polygermanyl fragment and with compounds containing the metal carbonyl moiety. The most prominent peaks in the spectra of the polygermanyl derivatives not containing the metal carbonyl group e.g. Ge_2H_5Cl (133) are usually the GeH stretches in the 2000 cm^{-1} region, the symmetric GeH_3 deformation and the GeH_2 wags in the 700 cm^{-1} to 800 cm^{-1} region. The GeH_3 rocks at about 400 cm^{-1} are usually described as medium peaks. The carbonyl stretches and MCO deformations are very intense vibrational modes. As the compounds studied in this work contain both the polygermanyl and the metal carbonyl groups, the absorptions due to the metal carbonyl moiety have been described as strong or very strong while those due to the polygermanyl fragment appear as medium to very weak peaks.

There are several interesting features in the GeH_3 and GeH_2 deformations of the compounds presented in the earlier chapters worthy of further consideration. These modes are listed in Table 7.2 and illustrated by Fig. 7.10 and Fig. 7.11. The asymmetric and symmetric GeH_3 deformations, and the GeH_2 wags are all of about the same contour in all the compounds listed in Table 7.2, with the asymmetric GeH_3 deformation band the weakest of the three. While the GeH_2 wag is strongest in Ge_2H_5Cl, this band is of similar intensity as the symmetric GaH_3 deformation mode in Ge_2H_5Me and in the transition metal derivatives. The GeH_3

Table 7.2 GeH_3 and GeH_2 Deformations of the Polygermanyl-Transition Metal Compounds.

(a) GeH_3GeH_2X (X = Cl, Me, $Mn(CO)_5$, $\frac{1}{2}$ $Fe(CO)_4$, $Co(CO)_4$)

	Cl (133)	Me (134)	$Mn(CO)_5$	$\frac{1}{2}Fe(CO)_4$	$Co(CO)_4$
		886			
$\delta_{asym.}GeH_3$	873R	879	870	875	876
	869Q	873		860	
(+GeH_2 scissors)	863P	862			
				789	
	796R	786R	792	(810,	791
$\delta_{sym.}GeH_3$	792Q	781Q		787 in-phase and out-of-phase in solid-film spectrum)	
	787P	775P			
	728R	678R	683	692	673
GeH_2 wag	721Q	672Q		662 (in-phase and out-of-phase symmetric wags)	
	716P	668P			

(b) $(GeH_3)_2GeHMn(CO)_5$ and $GeH_3GeH_2(GeH_3)Fe(CO)_4$

	$(GeH_3)_2GeHMn(CO)_5$	$GeH_3GeH_2(GeH_3)Fe(CO)_4$
	(a)	874
$\delta_{asym.}GeH_3$ (+ GeH_2 Scissors)		860
	800) in-phase) and	813 ($GeH_{3(1)}$)
$\delta_{sym.}GeH_3$	774) out-of-phase	790 ($GeH_{3(2)}$)
GeH_2 wag		679
δGeH	673	

Note:

(a) Extremely weak.

Figure 7.10

GeH_3 and GeH_2 Deformations

of GeH_3GeH_2X Compounds

GeH_3 and GeH_2 Deformations

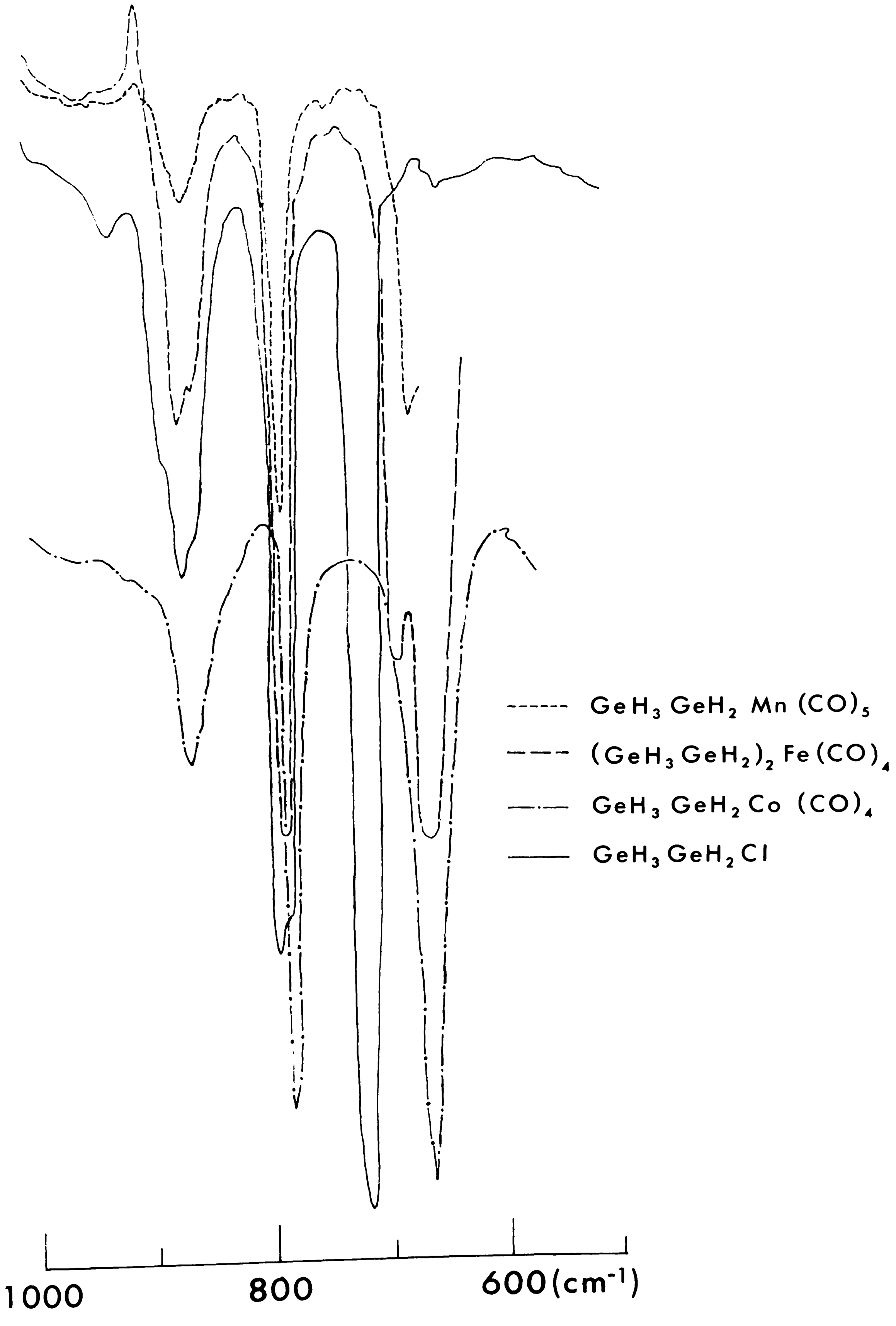


Figure 7.11

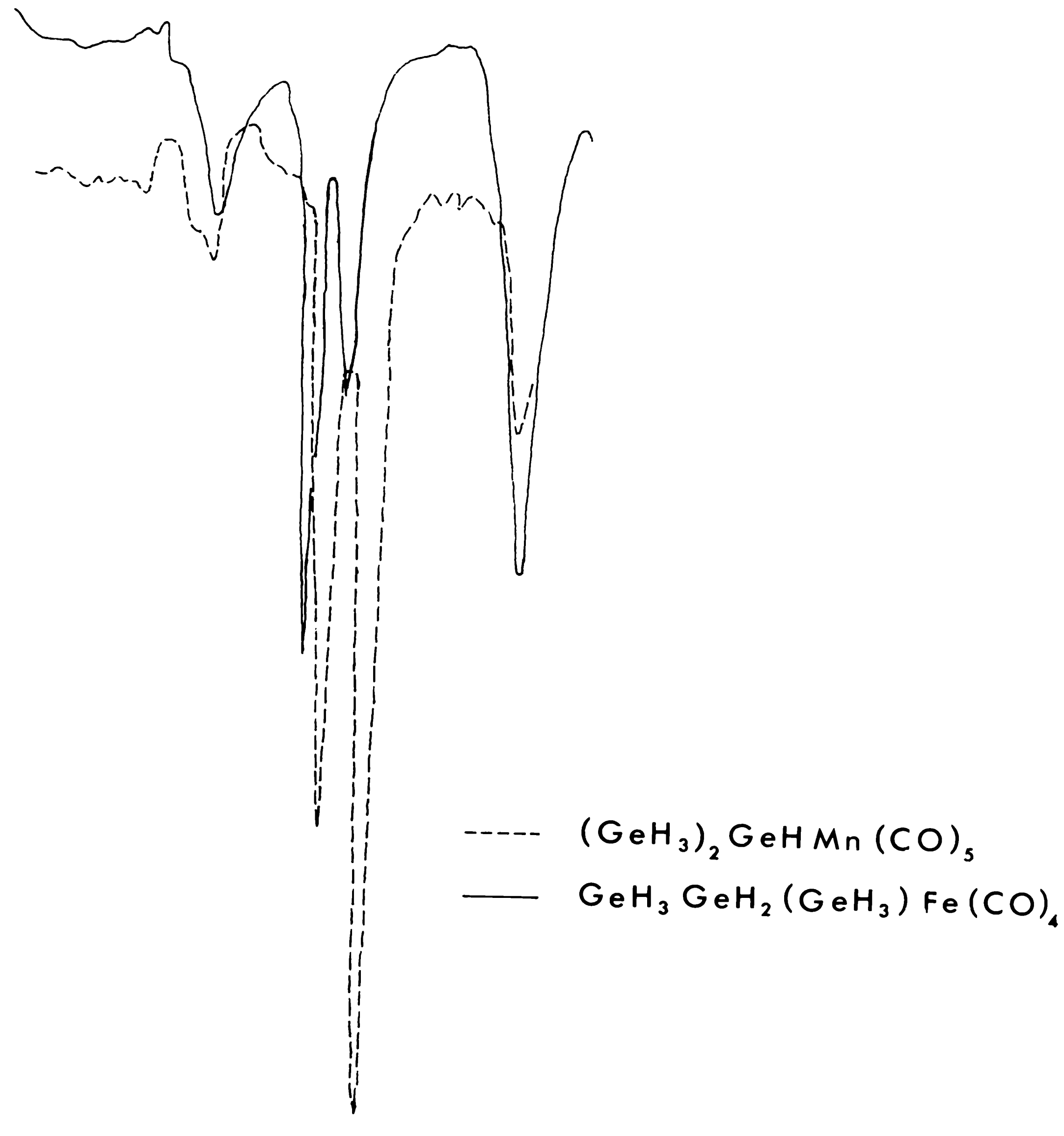
GeH_3 and GeH_x Deformations

of

$(GeH_3)_2GeHMn(CO)_5$ and

$GeH_3GeH_2(GeH_3)Fe(CO)_4$

GeH_3 and GeH_2 Deformations



deformation modes are fairly constant, but the GeH_2 wag shifts considerably showing highest vibrational frequencies in GeH_3GeH_2Cl followed by $GeH_3GeH_2Mn(CO)_5$, $(GeH_3GeH_2)_2Fe(CO)_4$ and $GeH_3GeH_2Co(CO)_4$ in that order. This band and the symmetric GeH_3 deformation in the solid spectrum of $(GeH_3GeH_2)_2Fe(CO)_4$ are split into two, and are assigned to the in-phase and out-of-phase symmetric GeH_2 wags and GeH_3 deformations, although the extra GeH_3 band in the solid spectrum may arise from crystal splitting. In $GeH_3GeH_2(GeH_3)Fe(CO)_4$ only one band is observed in the GeH_2 wag region and occurs at about the average of the two bands obtained for the bis(digermanyl) compound. This is in much the same sense as the two symmetric GeH_3 deformation bands observed for $(GeH_3)_2Fe(CO)_4$ (835 cm^{-1}, 809 cm^{-1}) whereas only one is present in $GeH_3(H)Fe(CO)_4$ (821 cm^{-1}) occurring near the average of the two former bands (173).

Two symmetric GeH_3 deformation bands are observed in the spectra of $(GeH_3)_2GeHMn(CO)_5$ and $GeH_3GeH_2(GeH_3)Fe(CO)_4$ (see Fig. 7.11). In the manganese compound, these are the in-phase and out-of-phase symmetric GeH_3 deformations, whereas in the iron compound the two bands are the symmetric GeH_3 deformations of the two non-equivalent GeH_3 groups, $GeH_{3(1)}$ and $GeH_{3(2)}$.

7.3 Stability Order and Spectroscopic Evidences

So far, the stabilities of compounds have mainly been discussed in terms of decomposition during handling, in the dark and on exposure to light. By these physical observations, it was established that the polygermanyl-transition metal derivatives are more stable than the germyl analogues. A second stability order has previously been established (173) for the germyl-transition metal compounds:

$$GeH_3Mn(CO)_5 > (GeH_2)_2Fe(CO)_4 > GeH_3Co(CO)_4$$

The studies in this work show that such a stability order also holds with the polygermanyl derivatives. Thus it seems the manganese group confers the highest degree of stability, cobalt carbonyl lowest and the iron carbonyl intermediate stability to the analogous complexes they form. Addition of a second metal carbonyl group to form the M–M'–M'–M systems as in $[GeH_2Mn(CO)_5]_2$ and $[GeH_2Co(CO)_4]_2$ further enhances the stabilities of the digermanyl systems. Fig. 7.12 provides a rough guide to the stabilities of the germyl and polygermanyl derivatives. Addition of a GeH_3 group to form the M'–M'–M system appears to be more stable than the M'–M system. The Pauling-type electronegativities (300) of the group IV elements are as follows:

$$C = 2.55, \quad Si = 1.90, \quad Ge = 2.01, \quad Sn = 1.96, \quad Pb = 2.33.$$

Thus, excluding carbon, lead is the most electronegative group IV metal while the electronegativities of silicon, germanium, and tin are very similar. Photoelectron spectroscopy of $M'H_3M(CO)_x$ (M' = C, Si, Ge; M = Mn, Re, Co) compounds (249) shows the $M'H_3$ groups to be weak σ-acceptors in the order

$$SiH_3 > GeH_3 > CH_3$$

No explanation is available as to why the SiH_3 group should act as a better σ-acceptor than the CH_3 group, although an interpretation may be that the larger size of the Si atom or of the SiH_3 group

Figure 7.12 Relative Stabilities (a) of the Germyl and Polygermanyl Derivatives

GeH_4		$[GeH_2Mn(CO)_5]_2$		
Ge_2H_6		$(GeH_3)_2GeHMn(CO)_5$		
Ge_3H_8		$GeH_3GeH_2Mn(CO)_5$		
Ge_4H_{10}	GeH_3Cl	$GeH_3Mn(CO)_5$	$(GeH_3GeH_2)_2Fe(CO)_4$	$[GeH_2Co(CO)_4]_2$
			$GeH_3GeH_2(GeH_3)Fe(CO)_4$	
			$(GeH_3)_2Fe(CO)_4$	$GeH_3GeH_2Co(CO)_4$
				$GeH_3Co(CO)_4$
	GeH_3GeH_2Cl			
	$(GeH_3)_2GeHCl(?)$			

↓

Decreasing Stability

Note:

(a) The relative stabilities are based on physical observations in a vacuum system, i.e. rate and extent of decomposition during handling, in the dark, on exposure to light at room temperature and thermal decomposition.

allows for more diffusion of charge, or the polarities and polarisabilities of the M'–H bonds may be a determining factor.

In studies with the permethylpolysilanyl-manganese system (257), $(Me_3Si)_nMe_{3-n}SiMn(CO)_5$ (n = 1-3), the results have been interpreted in terms of $\Delta\sigma$ -donor/$\Delta\pi$ -acceptor Graham parameters of the Me_3Si groups. The trend in the calculated parameters are consistent with the postulation of two conflicting effects. Starting with the Me_3Si derivative there is an initial increase in σ -donor/π -acceptor ability with β -silicon substitution (n - 1) which is explained in terms of electron release by the Me_3Si group and d-orbital availability for delocalised π -bonding. Further substitution (n = 2,3), however, reverses this trend as the steric requirements of the polysilyl ligand increase and non-bonded interactions lengthen the Si–Mn bond. (The Si–Mn bond in $(Me_3Si)_3SiMn(CO)_5$ has been shown (258) to be significantly longer than that in $Me_3SiMn(CO)_5$). The results also infer the existence of π-contributions to the M–Mn bonds. No attempt is made at calculating the Graham parameters in the studies with the polygermanyl systems here for two reasons. Firstly, such a calculation requires accurate measurements and assignments of the carbonyl modes of vibration. The spectra of the series of compounds should preferably be recorded under exactly similar conditions including similar sampling method to avoid phase shifts. Unfortunately, the spectra of the reported germyl compounds (162,173,183) were recorded as gas samples, while the vapour pressures of the polygermanyl derivatives are too low to allow this and the spectra have thus been recorded using solution samples. Although, in many cases, solid state spectra were also obtained, assignments of the vibrational modes are least reliable due to the possibility of crystal splitting effects. Secondly, Raman studies were not recorded of the carbonyl regions, partly because of decomposition of the compounds, particularly the iron and cobalt ones in the laser beam of the Raman spectrometer. Only the 0–500 cm^{-1} region was scanned in most cases. However, $GeH_3GeH_2Mn(CO)_5$ and $(GeH_3)_2GeHMn(CO)_5$, and $GeH_3GeH_2(GeH_3)Fe(CO)_4$ and $(GeH_3GeH_2)_2Fe(CO)_4$ can be compared as they were all recorded under similar conditions. The strongest carbonyl band between the manganese compounds (the e mode, see Tables 3.2 and 5.4) and the two strongest bands between the iron compounds (the a' or $a_1 + b_2$ modes, see Tables 6.5 and 6.2) show little variation which may indicate absence of $\Delta\sigma$-donor/$\Delta\pi$ -acceptor contributions or that such effects are cancelled by the increasing non-bonded interactions.

Table 7.3 gives the M–C, M'–M and M'–M' stretching frequencies along with the force constants based on a "pseudodiatomic" model. The M–C stretching frequency of the various compounds of each transition metal group remains almost constant and mass alteration by addition of GeH_3 groups does not seem to affect the vibration of this bond, probably because of the large energy difference between the metal-metal and metal-carbon bonds. Thus, the increasing trend of the force constants calculated for the M–C stretching frequencies is a clear indication of the inadequacy of the "pseudodiatomic" model. The decreasing frequencies of the M'–M bond with addition of GeH_3 group does not necessarily mean a decrease in bond strength. In fact, the reverse is reflected by the bond

Table 7.3 M–C, M'–M and M'–M' Stretching Frequencies (cm^{-1}) and Force Constants (mdyn. Å^{-1})(a)

Compound	νM–C	f_{M-C}	νM'–M	$f_{M'-M}$	νM'–M'	$f_{M'-M'}$
$GeH_3Mn(CO)_5$	409	2.48	219	1.56	-	-
$GeH_3GeH_2Mn(CO)_5$	409	2.54	205	2.12	273	2.63
$(GeH_3)_2GeHMn(CO)_5$	408	2.56	191	2.24	264(b)	2.58
$GeH_3(H)Fe(CO)_4$	432	2.72	226	1.59	-	-
$(GeH_3)_2Fe(CO)_4$	436	2.86	223(b)	1.72	-	-
$GeH_3GeH_2(GeH_3)Fe(CO)_4$	434	2.89	223	1.82	268	2.62
			202	2.25		
$(GeH_3GeH_2)_2Fe(CO)_4$	433	2.91	205(b)	2.54	268(c)	2.66
$GeH_3Co(CO)_4$	421	2.59	228	1.63	-	-
$GeH_3GeH_2Co(CO)_4$	415	2.59	205	1.99	269	2.50
GeH_3GeH_3	-	-	-	-	266	1.63
$GeH_3GeH_2GeH_3$	-	-	-	-	266(b)	1.60(d)

(a) Based on "pseudodiatomic" model.

(b) This is the average value of the asymmetric and symmetric stretches.

(c) The asymmetric stretch, if present, has been considered weak and overlapping with the strong polarised symmetric Ge–Ge stretch (see text in 6.3.3).

(d) This value is obtained by more accurate valence force field calculations (54,58).

force constants, but unfortunately, the "pseudodiatomic" model seems to overcompensate the increased mass effect thus giving the exaggerated values. The values obtained for the M'-M' bond appear to be better approximations showing the expected small differences between values as observed between Ge_2H_6 and Ge_3H_8 obtained by more accurate means. It is reasonable, where the asymmetric and symmetric modes occur, to use the average value of these. For example, the asymmetric Ge-Ge stretch in $GeH_3GeH_2GeH_3$ is at 288 cm^{-1} and symmetric is at 245 cm^{-1} averaging to give a value of 266 cm^{-1}, which is close to the Ge-Ge stretch of 268 cm^{-1} in GeH_3GeH_3. The Ge-Ge bonds in these two metal hydrides have been shown to have near equal force constants (<u>ca</u>. 1.6 mdyn. $\mathring{A}^{-1}$) (54,58) by valence force field calculations. Although there appears to be interaction between the Ge-Ge and Ge-Mn bonds in $GeH_3GeH_2Mn(CO)_5$ by comparing the frequencies of these bonds with those in $GeH_3Mn(CO)_5$ and Ge_2H_6, the Ge-Ge stretching frequencies are hardly changed in $GeH_3GeH_2(GeH_3)Fe(CO)_4$, $(GeH_3GeH_2)_2Fe(CO)_4$ and $GeH_3GeH_2Co(CO)_4$, which may suggest little interaction, but because there is little energy difference between the Ge-Ge and Ge-M bonds in these compounds, interaction is likely. The constant Ge-Ge stretching frequencies in the latter compounds may reflect mass compensation effects.

Evidence for possible increase in the M'-M bond strength is drawn from the ion abundance of species retaining this bond in mass spectroscopic studies. Table 7.4 lists the ion abundance of this species for the various compounds in this work. There is a clear trend of increased ion abundance of Ge-M retaining species from the germyl to digermanyl cases. Further addition of a GeH_3 group to the

Table 7.4 Ion Abundance of Species Retaining the Ge-M Bond in Mass Spectroscopic Fragmentation of the Germyl and Polygermanyl-Transition Metal Compounds

	Ion Abudance of Ge-M Retaining Species (%)
$GeH_3Mn(CO)_5$	80
$GeH_3GeH_2Mn(CO)_5$	88
$(GeH_3)_2GeHMn(CO)_5$	88
$(GeH_3)_2Fe(CO)_4$	83
$GeH_3GeH_2(GeH_3)Fe(CO)_4$	87
$(GeH_3GeH_2)_2Fe(CO)_4$	(86)
$GeH_3Co(CO)_4$	78
$GeH_3GeH_2Co(CO)_4$	(86)
$Mn(CO)_5GeH_2GeH_2Mn(CO)_5$	88
$Co(CO)_4GeH_2GeH_2Co(CO)_4$	96

Note: Values within parentheses are calculated values (see text in 4.3.2 and 6.3.2).

α-germanium in $GeH_3GeH_2Mn(CO)_5$ to give $(GeH_3)_2GeHMn(CO)_5$ does not seem to alter this ion abundance. This may be explained by the supposition of two conflicting effects. Addition of the GeH_3 group increases σ -electron withdrawal from the carbonyls presumably increasing the Ge–M bond stretch; but this extra GeH_3 group also increases steric crowding, possibly with increased repulsion between the GeH_3 groups and the $Mn(CO)_5$ group and probably increased Ge–M bond length leading to a weaker bond. Thus the retention of the Ge–Mn bond remains unaltered. This is, perhaps, again seen between $GeH_3GeH_2(GeH_3)Fe(CO)_4$ and $(GeH_3GeH_2)_2Fe(CO)_4$. The high ion abundances of such species in the compounds containing the M–M'–M'–M skeleton seem to suggest further stabilisation of the Ge–M bond on addition of a second $Mn(CO)_5$ or $Co(CO)_4$ group to the digermane system. The increased ion abundance of species retaining the Ge–M bond may also be an artefact of increased statistical probability of obtaining such species during mass spectral fragmentation. We must, however, recall the uncertainty in the $H_xGe_2^+$ and H_xGe^+ abundances in the mass spectra of the digermanyl-cobalt and bis(digermanyl)iron compounds, thus the ion abundance of Ge–M bonded species in the fragmentation of these compounds must be treated with some caution.

Nonetheless, the above evidence appears to be compatible for comparison within the family, i.e. of compounds containing the same transition metal (even if it does not allow cross-comparison between compounds of different transition metals) which may help explain the observed stability order:

$$Mn > Fe > Co$$

This was also the case in mass spectral studies by Lappert et al. (241), Stobart (234,242,243) and Spalding (244) on $X_3M'ML_x$ compounds (X = Me, Ph, Cl; M' = Si, Ge, Sn; M = Cr, Mo, W, Mn, Re, Fe, Co; L = $(CO)_x$, $(CO)_xC_p$). These have been discussed in the introductory chapter (see pages 34, 37 and Table 1.8). In many instances the ion-abundances showed good supporting evidence for conclusions reached from the M'–M bond dissociation energies calculated from appearance potentials.

The group IV metal–group IV metal exchange reaction between Ge_2H_5Cl and $GeH_3Co(CO)_4$ gives chemical evidence suggesting the digermanylcobalt compound to be more stable than the germyl one, and the reverse for the chloride. Although the above spectroscopic evidence is somewhat sketchy, this reaction offers good support to physical observations of the greater stability of the polygermanyl-transition metal compounds.

7.4 Reactions

The reactions of the polygermanyl-transition metal carbonyls have been discussed to some extent in their respective experimental chapters. Comparisons with the germyl analogues of these compounds have shown there to be little difference in the substitution patterns, cleavage reactions and transition metal exchange reactions. $HgCl_2$ cleaves only the Ge–Co bonds in $GeH_3GeH_2Co(CO)_4$ (4.3.5) and $Co(CO)_4GeH_2GeH_2Co(CO)_4$ (5.3.5) with little evidence for Ge–Ge bond cleavage. The transition metal exchange order in the germyl compounds,

$$Co \longrightarrow Fe \longrightarrow Mn$$

is retained with the polygermanyl compounds (4.3.6 and 6.3.4). It has also been established that halide-transition metal carbonyl exchange or group IV metal-group IV metal exchange is possible between two compounds with a weak M'-X bond (X = functional group = Cl or $Co(CO)_4$) with exchange giving a thermodynamically more favoured system (4.3.4).

Substitution is mainly of the hydrogens on the α-germanium. The substitution rates have been found to be dependent on reagent size as observed by the decreasing rate of substitution at the α-germanium in the order,

$$CCl_4 \gg SiCl_4 > GeCl_4 <<< SnCl_4$$

Although $SnCl_4$ reacts extremely fast, largely because of the weak Sn-Cl bond, no 1,1-dichlorosubstitution has been observed. Reactions have revealed evidences for some 1,2-dichlorosubstitution. It has also been shown how addition of extra GeH_3 groups as between $GeH_3Mn(CO)_5$, $GeH_3GeH_2Mn(CO)_5$ and $(GeH_3)_2GeHMn(CO)_5$, and between $(GeH_3)_2Fe(CO)_4$, $GeH_3GeH_2(GeH_3)Fe(CO)_4$ and $(GeH_3GeH_2)_2Fe(CO)_4$ introduces steric hindrance to substitution by decreasing rates and less extensive substitutions (see sections 3.3.3, 5.3.4 and 6.3.5). Comparing the rates of reaction of the Ge_2H_5X compounds ($X = Mn(CO)_5$, $\frac{1}{2}Fe(CO)_4$, $Co(CO)_4$) another reaction order is recognised,

$$Mn(CO)_5 > \tfrac{1}{2}Fe(CO)_4 > Co(CO)_4$$

The $Mn(CO)_5$ group appears to activate the hydrogens on the α-germanium towards substitution, the $Fe(CO)_4$ group conferring activation to a lesser degree. $Co(CO)_4$ group is completely non-activating, and no hydrogen substitution of a group IV (hydride)-cobalt compound has yet been observed. Substitution reaction allows the possibility of stepwise addition of a metal carbonyl group but substitution with the metal tetrahalides $M'X_4$ has the disadvantage of some polychlorosubstitution or incompletely specific substitution. For example, $Ge_2H_5Mn(CO)_5$ reacts with CCl_4 to yield $GeH_3GeHClMn(CO)_5$ (7%) and $GeH_3GeCl_2Mn(CO)_5$ (40%); with $GeCl_4$ the yields are reversed - $GeH_3GeHClMn(CO)_5$ (52%), $GeH_3GeCl_2Mn(CO)_5$ (6%). With $SnCl_4$ (53) a mixture of $GeH_3GeHClMn(CO)_5$ (78%), $GeH_2ClGeHClMn(CO)_5$ (14%) and $GeH_2ClGeH_2Mn(CO)_5$ (6%) is obtained. Several attempts by the author to prepare $GeH_3GeH\,[Mn(CO)_5]_2$ were unsuccessful. The problem was mainly in the difficulty of obtaining some pure $GeH_3GeHClMn(CO)_5$. An attempt at direct $Mn(CO)_5^-$ coupling with the products of $GeH_3GeH_2Mn(CO)_5/SnCl_4$ reaction was also unsuccessful as $NaMn(CO)_5$ anion is sensitive to $SnCl_2$.

The substitution reactions have also established the halo-substituted polygermanyl-transition metal carbonyls to be very much more stable than the halides of the polygermanes. This is presumably because the α-germanium atom and substituents on it are protected by both the GeH_3 and metal carbonyl groups. The strong electonegativity of the chloride is reflected by the higher carbonyl vibrational frequencies showing a reduced back-donation of electrons from the transition metal to the π^*-orbital of the carbonyls.

Sodium-ammonia solution mainly cleaves the metal-metal bonds in Ge_3H_8 and $GeH_3GeH_2Mn(CO)_5$ in a quantitative manner. It is also shown that evolution of hydrogen may not only be due to high e^- concentration in the solution but also that one or more of the anions produced may also be reactive. This side-reaction can, perhaps, be reduced by direct quantitative reaction instead of titration. This way the anions produced will have little chance of further reaction with the parent hydrides. This is a potentially useful analytical reaction for studying compounds containing metal-metal bonds as in, for example, the ring structure $[GeH_2Fe(CO)_4]_2$.

7.5 Conclusion

It is probably proper as a conclusion to briefly speculate on the greater stability of the polygermanyl-transition metal carbonyl derivatives. It appears possible to interpret the increased stability as one involving synergic contributions. Photoelectron spectroscopy (249) shows the GeH_3 group to be a weak σ-acceptor. Increased withdrawal of carbonyl σ-electrons <u>via</u> the Ge-M bond (M = Mn, Fe, Co) on addition of a GeH_3 group is presumably reciprocated by an increased back-donation of available d-orbital electrons of the transition metal into the π^*-orbital of the carbonyl. Such a possibility would mean an increase in the M-C, and possibly even the Ge-M and Ge-Ge bond strengths. Alternatively, the increased stability may be due to an increased protective cover of the reactive α-GeH_x group by the addition of a GeH_3 group.

APPENDIX I. ATTEMPTED SYNTHESIS OF GERMYL(SILYL)IRONTETRACARBONYL

As described in Chapter 1 (1.4.3(e)), the equimolar reaction between $Mn(CO)_5^-$ and $(GeH_3)_2Fe(CO)_4$ formed only $GeH_3Fe(CO)_4^-$ (198). The analogous transition metal exchange with $(Ge_2H_5)_2Fe(CO)_4$ was successfully used to synthesise the unsymmetric compound, $Ge_2H_5(GeH_3)Fe(CO)_4$ (Chapter 6; 6.3.4). The only known transition metal derivatives of mixed group IV metals are of the type $Me_3SiRu(CO)_4M'R_3$ ($M'R_3$ = Me_3Sn, Ph_3Sn or Bu_3Ge) (301). Treatment of $[R_3SiRu(CO)_4]_2$ with sodium amalgam affords the anion $Me_3SiRu(CO)_4^-$ which was used in alkali-halide elimination reactions to produce the above series of compounds.

In this first part of the Appendix, the attempted preparation of $GeH_3(SiH_3)Fe(CO)_4$ <u>via</u> metal-metal exchange, and its partial characterisation are described. The preparation was approached from opposite directions starting from $(GeH_3)_2Fe(CO)_4$ (173) and from $(SiH_3)_2Fe(CO)_4$ (168,169).

Summary of data relating to preparation of starting materials:

SiH_3Cl (140)

$$SiH_4 + SnCl_4 \xrightarrow[R.T]{12\ hours} SiH_2Cl_2 + SiH_3Cl$$

ca. 7 mmol 4.3 mmol $< 5\%$ ca. 1.7 mmol

$+ HCl + SnCl_2$

SiH_3Br (302)

$$C_6H_5SiCl_3 \xrightarrow[Et_2O]{LiAlH_4} C_6H_5SiH_3 \xrightarrow[ca.\ 40\ mmol]{HBr} C_6H_6$$

ca. 18 mmol. ca. 15 mmol.

$+ SiH_3Br$ + HBr

ca. 11 mmol (excess)

(6.29τ)

HBr was prepared by action of bromine on tetralin (305).

$(GeH_3)_2Fe(CO)_4$ (173)

$$Na + Fe(CO)_5 \xrightarrow[30\ min.]{-63\ ^{o}C} Na_2Fe(CO)_4$$

Na: 4.27 mmol in 13 ml NH_3

$Fe(CO)_5$: 2.62 mmol

$+ Fe(CO)_5$ (unreacted, 0.93 mmol)

$$GeH_3Br + Na_2Fe(CO)_4 \xrightarrow[R.T.]{n\text{-}pentane} (GeH_3)_2Fe(CO)_4$$

GeH_3Br: 3.79 mmol.

$Na_2Fe(CO)_4$: ca. 1.69 mmol

25 min.

$(GeH_3)_2Fe(CO)_4$: 0.59 mmol, 34.9% based on Fe, 6.57τ (c.f. 6.50τ ref.173)

$+ GeH_3(H)Fe(CO)_4$
trace

$+ GeH_3Br$/pentana/$H_2Fe(CO)_4$ mixture

$+ GeH_4$
0.3 mmol.

$(SiH_3)_2Fe(CO)_4$ (168,169)

$$Na + Fe(CO)_5 \xrightarrow[30\ min.]{-63\ ^{o}C} Na_2Fe(CO)_4$$

Na: 7.4 mmol in 25 ml of NH_3

$Fe(CO)_5$: 5.29 mmol

$+ Fe(CO)_5$ (unreacted, 2.01 mmol)

$$SiH_3Br + Na_2Fe(CO)_5 \xrightarrow[R.T.]{n\text{-}hexane} (SiH_3)_2Fe(CO)_4$$

SiH_3Br: ca. 7.50 mmol

$Na_2Fe(CO)_5$: ca. 3.27 mmol

$(SiH_3)_2Fe(CO)_4$: 1.1 mmol, 33.6% based on Fe, 6.45τ (c.f. 6.33τ neat, ref. 169)

$+ SiH_3(H)Fe(CO)_4$
0.16 mmol, 4.4%

$+ H_2Fe(CO)_4$
traces

$+ SiH_3Br$/hexane mixture

Data relating to preparation of $GeH_3Fe(CO)_4SiH_3$:

From $(GeH_3)_2Fe(CO)_4$

$$(GeH_3)_2Fe(CO)_4 + NaMn(CO)_5 \xrightarrow[\text{R.T.}\ \text{30 min.}]{Et_2O} GeH_3Mn(CO)_5$$

$(GeH_3)_2Fe(CO)_4$: 0.55 mmol

$NaMn(CO)_5$: (1% Na/Hg, 0.21 mmol $Mn_2(CO)_{10}$)

$GeH_3Mn(CO)_5$: 0.35 mmol, 6.71τ

+ $GeH_3Fe(CO)_4Na$
(yellow-orange residue)

+ $(GeH_3)_2Fe(CO)_4$
(unreacted, *ca.* 0.1 mmol)

$$GeH_3Fe(CO)_4Na + SiH_3Cl \xrightarrow[\text{R.T.}\ \text{30 min.}]{Et_2O} GeH_3Fe(CO)_4SiH_3$$

$GeH_3Fe(CO)_4Na$: *ca.* 0.35 mmol

SiH_3Cl: 1.1 mmol

$GeH_3Fe(CO)_4SiH_3$: 0.254 mmol,
(72% based on $GeH_3Mn(CO)_5$)

+ X + NaCl

+ SiH_3Cl
(0.05 mmol)

No incondensibles noted.

From $(SiH_3)_2Fe(CO)_4$

$$\begin{array}{llll} (SiH_3)_2Fe(CO)_4 & +\ NaMn(CO)_5 & \xrightarrow[\text{R.T.}]{Et_2O} & SiH_3Mn(CO)_5 \\ 0.59\ \text{mmol} & (1\%\ NaHg, & 1\ \text{hour} & 0.39\ \text{mmol}, \\ & 0.27\ \text{mmol}\ Mn_2(CO)_{10}) & & 6.40\tau \\ & & & +\ SiH_3Fe(CO)_4Na \\ & & & +\ (SiH_3)_2Fe(CO)_4 \\ & & & \quad \text{(unreacted, traces)} \\ & & & +\ \text{some incondensibles.} \end{array}$$

$$\begin{array}{llll} SiH_3Fe(CO)_4Na & +\ GeH_3Br & \xrightarrow[\text{R.T.}]{Et_2O} & SiH_3Fe(CO)_4GeH_3 \\ \underline{ca.}\ 0.39\ \text{mmol} & 0.50\ \text{mmol} & 25\ \text{min.} & 0.33\ \text{mmol},\ 84.6\% \\ & & & \text{based on}\ SiH_3Mn(CO)_5 \\ & & & +\ X\ +\ NaBr \\ & & & +\ GeH_3Br/\text{ether mixture} \end{array}$$

Spectroscopic data show the products of the preparations by the two approaches above, to be identical. It consisted of a white crystalline mixture later identified as $GeH_3(SiH_3)Fe(CO)_4$, together with traces of $(GeH_3)_2Fe(CO)_4$ and a third component X, liquid at room temperature and having near equal vapour pressure so that separation was difficult. This accompanying liquid phase seemed to increase in quantity with manipulation.

Like $(GeH_3)_2Fe(CO)_4$ (173) or $(SiH_3)_2Fe(CO)_4$ (168,169), $GeH_3(SiH_3)Fe(CO)_4$ forms white crystals with a vapour pressure ca. 2 mm Hg at room temperature. The compound does not show any decomposition in the dark, but rapidly turns brown on exposure to light. When exposed to air there is a flash but no explosion, leaving a brown solid film on the wall of the vessel.

The nmr spectra of the product mixtures from the two preparations were similar. Two singlets of equal intensities at 6.35τ and 6.63τ were assigned to the SiH_3 and GeH_3 resonances respectively. A third singlet at 6.58τ about 1.5 times the intensity of the two singlets above was assigned to X which is possibly $(GeH_3)_2Fe(CO)_4$ or $SiH_3(H)Fe(CO)_4$ or both although no Fe-H signal could be found in the 20τ region because of high noise levels in the recorded spectra. The above assignments compare well with other germyl-silyl derivatives listed in Table AI.1. It is interesting to note that the resonance signal of the SiH_3 group in $GeH_3(SiH_3)Fe(CO)_4$ falls to lower field than the SiH_3 signal in $(SiH_3)_2Fe(CO)_4$, but the GeH_3 signal falls to high field of GeH_3 signal in $(GeH_3)_2Fe(CO)_4$. Hence the positions of the signals of the SiH_3 and GeH_3 in $GeH_3Fe(CO)_4SiH_3$, if they are controlled primarily by inductive effects, suggest that the electronegativity of germanium may be greater than that of silicon. This is consistent with the electronegativities of 1.90 and 2.01, respectively, which have been proposed for silicon and germanium (300). This is again featured between SiH_3GeH_3 and SiH_3SiH_3 and GeH_3GeH_3 in cyclohexane solutions (see Table AI.1). Further characterisations were obtained from mass and infrared spectra.

The mass spectrum listed in Table AI.2 again showed the presence of at least two components in the product mixture, but the monogermyl envelopes attributable to $H_xGeSiFe(CO)_n$ featured prominently.

Table AI.1 ^{1}H NMR Data of some Germyl-Silyl Derivatives and Related Compounds

	Solvent	Chemical shifts,τ		Ref.
		SiH_3	GeH_3	
$(SiH_3)_2Fe(CO)_4$ (b)	C_6H_6	6.45		(a)
$SiH_3Fe(CO)_4GeH_3$	C_6H_6	6.35	6.63	(a)
$(GeH_3)_2Fe(CO)_4$ (c)	C_6H_6		6.57	(a)
$GeH_3(H)Fe(CO)_4$	C_6H_6(19.87 FeH)		6.65	173
SiH_3GeH_3 (d)	C_6H_6	6.74	7.05	58
$SiH_3CH_2GeH_3$ (e)	C_6H_{12}	6.29	6.37	303
Si_2H_6	C_6H_{12}	6.75		304
Ge_2H_6 (f)	C_6H_6		6.92	(a)

(a) This work

(b) c.f. 6.33 τ of neat liquid, ref. 169

(c) c.f. 6.50 τ in C_6D_6, ref. 173

(d) J(HSiGeH) = 3.5 Hz; c.f. SiH_3 = 6.60τ , GeH_3 = 6.98τ in C_6H_{12}, ref. (36).

(e) τCH_2 = 9.60, J(HCGeH) = J(HCSiH) = 3.9 Hz. in C_6H_{12}

(f) 6.76τ in C_6H_{12}, ref. 280.

Table AI.2 The Mass Spectrum of $GeH_3(SiH_3)Fe(CO)_4$

m/e observed	Relative intensity	Assignment
269–277	vw	$H_xGeSiFe(CO)_4^+$ x = 3,2,1 in ratio 2 : 10 : 2
238–245	w	$H_xGeSiFe(CO)_3^+$ or $H_xGeFe(CO)_4^+$ x = 1,0 in ratio 8 : 10
210–218	m	$H_xGeSiFe(CO)_2^+$ or $H_xGeFe(CO)_3^+$ x = 3,2,0 in ratio 5 : 5 : 10
182–190	m	$H_xGeSiFe(CO)^+$ or $H_xGeFe(CO)_2^+$ x = 2,1,0 in ratio 5 : 10 : 5
154–162	s	$H_xGeSiFe^+$ or $H_xGeFe(CO)^+$ x = 2,1,0 in ratio 6 : 4 : 10
126–136	s	H_xGeFe^+ x = 1,0 in ratio 1 : 10

Also present in the mass spectrum are digermanyl envelopes attributable to $(GeH_3)_2Fe(CO)_4$ (173,279) with a very weak parent ion envelope but moderate to strong $H_xGe_2Fe(CO)_n^+$ (n = 0-3) envelopes, strongest being $H_xGe_2Fe^+$. The monogermyl envelopes in Table AI.2 except m/e 269-277 could in part be contributed by $H_xGeFe(CO)_n^+$ species resulting from Ge-Fe cleavage of $(GeH_3)_2Fe(CO)_4$ followed by CO loss but the presence of the m/e 269-277 envelope clearly indicates the parent ion $H_xGeSiFe(CO)_4^+$. The expected base peak of $GeH_3(SiH_3)Fe(CO)_4$ is $H_xGeSiFe^+$ at m/e = 154-162. A strong envelope was observed which may also in part be attributable to $H_xGeFe(CO)^+$ from $(GeH_3)_2Fe(CO)_4$. The $H_xGeFe(CO)^+$ envelope in the mass spectrum of a pure sample of $(GeH_3)_2Fe(CO)_4$ is of medium-weak intensity. The spectrum obtained of the impure $GeH_3(SiH_3)Fe(CO)_4$ showed this envelope to be as strong as the base peak $H_xGe_2Fe^+$ of the bis(germyl)iron by-product. Thus the envelope at m/e = 154-162 is largely due to $H_xGeSiFe^+$. Another distinguishing feature is the weak peak at m/e = 196. This was probably due to $SiFe(CO)_4^+$. The possible presence of $SiH_3(H)Fe(CO)_4$ was difficult to analyse from the mass spectrum as fragment ions that can arise are in regions of the fragment ions of the above two compounds.

The infrared spectrum of the product mixture is summarised in Table AI.3 below. The infrared spectrum shows absorptions in regions expected for νSiH_3, νGeH, δSiH_3, δGeH_3 and $\delta FeCO$. The contours of the SiH_3 and GeH_3 deformation bands closely resemble those for SiH_3GeH_3 (36). Two weak doublets at 755 cm^{-1} and 728 cm^{-1} tentatively assigned to δFeH, and the peaks tentatively assigned to δSiH_3 varied in intensities in different spectra, possibly

Table AI.3 Infrared Spectrum of Product in $GeH_3(SiH_3)Fe(CO)_4$ Preparations (cm^{-1}).

	Tentative Assignment
2126 vvw	νSiH
2099 mw	νCO_{ax}
2068 vw	νGeH
2041 vvs	νCO
2019 vs	
1985 vvw	$\nu ^{13}CO$
962 vw	δSiH_3
954 vw	
831 w	δGeH_3
822 mw	
807 mw	
755 vvw	δFeH ?
728 w	
666 vw	
628 m	$\delta FeCO$
598 vvw	δFeH ?

indicating presence of the slightly more volatile $SiH_3(H)Fe(CO)_4$. The absorptions assigned to δGeH_3 and $\delta FeCO$ weakened over 6 hours with deposition of a brown film in the gas cell, possibly indicating decomposition of the less stable $(GeH_3)_2Fe(CO)_4$.

An infrared spectrum was also recorded of a cyclohexane solution of the non-volatile orange residue left in the preparative reaction vessel after removal of all volatiles. It showed νCO and $\delta FeCO$ absorptions and weak peaks at 940, 860, 870, 805–830, 770, 715 and 650–658 (cm^{-1}) possibly indicating some high molecular weight iron compound containing SiH or GeH or both.

$GeH_3(SiH_3)Fe(CO)_4$ + $SiCl_4$

A sample of $GeH_3(SiH_3)Fe(CO)_4$ together with by-product component(s?) in $SiCl_4$ was observed with the nmr. The singlet at 6.63 τ assigned to GeH_3Fe of $GeH_3(SiH_3)Fe(CO)_4$ weakened slowly over 45 days when it was a third of its original intensity. The singlet at 6.35 τ assigned to SiH_3Fe remained unchanged. No signals attributable to any chlorosubstituted products were observed, thus whether the weakening of the GeH_3Fe signal indicated chlorosubstitution on GeH_3 is still open to doubt. The singlet at 6.58τ earlier assigned to either $(GeH_3)_2Fe(CO)_4$ or $SiH_3(H)Fe(CO)_4$ or both weakened only slightly.

$(GeH_3)_2Fe(CO)_4$ has been reported to monosubstitute with $SiCl_4$ readily (174). $(SiH_3)_2Fe(CO)_4$ does not substitute with $SiCl_4$ (see Appendix II). Thus the singlet at 6.58τ is probably due to overlapping singlets due to $(GeH_3)_2Fe(CO)_4$ and $SiH_3(H)Fe(CO)_4$ as it showed only slight weakening. Preliminary studies with GeH_3SiH_3 (36) and with $GeH_3CH_2SiH_3$ (303) indicated Si-H substitution.

APPENDIX II. OTHER RELATED REACTIONS

These reactions were studied either to clarify some reactions presented in earlier chapters or for comparisons.

$(SiH_3)_2Fe(CO)_4$ + $SiCl_4$

$(SiH_3)_2Fe(CO)_4$ (0.058 mmol, 6.37 τ) in $SiCl_4$ with TMS as reference was observed with the nmr. No changes were observed over 100 hours.

This experiment shows the Si–H bond in $(SiH_3)_2Fe(CO)_4$ to be resistant to substitution by $SiCl_4$, unlike the Ge–H bond in $(GeH_3)_2Fe(CO)_4$ which undergoes substitution readily (174) with $SiCl_4$. $GeH_3CH_2SiH_3$ is the only compound containing both a GeH_3 and a SiH_3 group to have clearly shown substitution (330). Reaction with HCl at room temperature over $AlCl_3$ forms $GeH_3CH_2SiH_2Cl$ and $GeH_3CH_2SiHCl_2$.

$(SiH_3)_2Fe(CO)_4$ + GeH_3Br

$(SiH_3)_2Fe(CO)_4$ (0.28 mmol) and GeH_3Br (0.23 mmol) were sealed in a nmr tube with benzene and observed at intervals at room temperature. Although a trace of SiH_3Br was observed at 6.29 τ, no significant changes occurred over 50 hours except some disproportionation of GeH_3Br (6.01 τ) after 24 hours to give GeH_4 (6.96 τ) and GeH_2Br_2 (5.23 τ).

This experiment was performed to see if an alternative approach to $GeH_3(SiH_3)Fe(CO)_4$ is available, <u>via</u> direct halide-transition metal exchange without going through metal-metal exchange as in Appendix I, where by-products were also obtained together with $GeH_3(SiH_3)Fe(CO)_4$.

$SiH_3Co(CO)_4$ + GeH_3Br

$SiH_3Co(CO)_4$ was prepared as in (200). $SiH_3Co(CO)_4$ (0.13 mmol) and GeH_3Br (0.10 mmol) were combined with benzene in a nmr tube. Reaction was fast and complete in 5 hours. Initial reaction was observed after 30 minutes. The GeH_3Br singlet (6.01τ) weakened faster than the $SiH_3Co(CO)_4$ singlet (6.08τ) to give rise to two new singlets at 6.40τ and at 6.96τ, the latter attributable to GeH_4. A weak singlet at 5.08τ and towards the end of the reaction another weak singlet at 6.29τ also started to show. The solution became increasingly brown as reaction proceeded. GeH_4 was confirmed on opening of the tube and examination of volatiles. The tail fraction consisted of a colourless liquid of very low volatility. I.r. spectrum of a gas sample showed strong carbonyl stretching bands in the 2000 cm^{-1} region and three weak absorptions at 950 cm^{-1}, 825 cm^{-1} and 550 cm^{-1}. A non-volatile brown-red residue was left in the tube.

This reaction was performed to see if a halide-cobalt carbonyl exchange would occur in the system. The changes observed were difficult to interpret, especially the evolution of GeH_4. This could not have arisen from GeH_3Br disproportionation as this is a slow process. As no $GeH_3Co(CO)_4$ or SiH_3Br were observed, an exchange was unlikely to have taken place. It was initially thought the exchange did occur followed by a rapid disproportionation between SiH_3Br and GeH_3Br, but a separate experiment showed no reaction between the two.

Trial Reaction Between $Ge_2H_5Mn(CO)_5$ and $GeH_3Co(CO)_4$.

$Ge_2H_5Mn(CO)_5$ (24.5 mg, 0.07 mmol) and $GeH_3Co(CO)_4$ (20.0 mg, 0.08 mmol) were combined with benzene and the ^1H nmr observed at room temperature. A weak triplet-like signal of unequal separation between peaks (6 Hz, 4.2 Hz) was observed after a week. This is probably a doublet signal (6.0 τ, J = 4.2 Hz) with a singlet signal near to it. A further singlet at 6.86τ assigned to GeH_4 was discernible after a second week. The tube was opened and all volatiles, including unreacted starting materials, were removed and the solid residue subjected to prolonged pumping on the vacuum line. GeH_4 (ca. 0.03 mmol, identified by i.r.) was detected amongst the volatiles.

The residues were again dissolved in benzene and an nmr spectrum recorded. It showed the doublet and singlet signals near 6.0 τ with the possibility of another two sets of triplets at 5.78 τ and 6.38 τ (J = 6 Hz). A mass spectrum of the residues showed masses up to m/e = 440. Both characteristic Ge_2^+ and Ge^+ envelopes were observed. Also present was the carbonyl loss pattern showing the presence of at least 9 carbonyls. Overall, however, the mass spectrum showed a mixture of compounds, although the envelope at m/e = 440 represented the $Co(CO)_4GeMn(CO)_5^+$ species. An i.r. spectrum recorded showed absorptions assignable to νCO, δGeH_x, $\delta MnCO$, $\delta CoCO$ and νCoC.

This experiment was performed out of interest to see if there is reaction, and if there is, whether it is a metal-metal exchange, a $Co(CO)_4$ substitution on the α-germanium of $Ge_2H_5Mn(CO)_5$ or because of steric crowding at the α-germanium, a substitution on the GeH_3 group. Metal-metal exchange would resemble the halide-transition metal carbonyl exchange between Ge_2H_5Cl and $GeH_3Co(CO)_4$ but this is unlikely because of the high stability of $Ge_2H_5Mn(CO)_5$. Substitution on the α-germanium by $Co(CO)_4$ is expected the most likely.

The results are not at all clear, especially interpretation of the nmr. The doublet signal at 6.0 τ may in fact be the GeH_3 signal of $GeH_3GeHMn(CO)_5Co(CO)_4$ although the two weak triplet signals may indicate presence of $GeH_2Co(CO)_4GeH_2Mn(CO)_5$. The ion of $m/e = 440$ attributable to $Co(CO)_4GeMn(CO)_5^+$ may arise by, say, H_xGe elimination of $GeH_3GeHMn(CO)_5Co(CO)_4$. Alternatively, this ion could have arisen from $Co(CO)_4GeH_2GeH_2Mn(CO)_5$ by H_xGe elimination accompanied by a 1,2-migration of a transition metal group as seen elsewhere in this thesis. The infrared spectrum offers further evidence for the presence of both $Mn(CO)_5$ and $Co(CO)_4$. Although the final product may be a mixture of the 1,1- and 1,2-disubstituted species, this reaction shows it is possible to substitute a hydrogen on $Ge_2H_5Mn(CO)_5$ with $Co(CO)_4$.

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