PREPARATION, CHARACTERISATION, AND REACTION STUDIES OF GROUP IV-TRANSITION METAL COMPOUNDS

A thesis submitted to the University of Waikato for the degree of Doctor of Philosophy

by

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by B.W.L. GRAHAM

ABSTRACT

The compounds germylpentacarbonylmanganese, methylgermylpentacarbonylmanganese, and methylgermyltetracarbonylcobalt have been prepared by alkali-halide elimination reactions between the appropriate germyl halides and metal carbonyl anions. The two methyl derivatives were characterised by vibrational and nmr spectroscopy and mass spectrometry, with assignments being proposed for most of the observed features of the spectra.

Some reactions of $H_3GeMn(CO)_5$ and $MeGeH_2Mn(CO)_5$ were investigated. Reagents used included the halogens, hydrogen halides, group III and group IV-halides, mercuric halides, phosphorus trihalides, triarylphosphines, and ethylene. The reaction of $MeGeH_2Co(CO)_4$ with mercuric chloride was also investigated, as were a number of

related reactions of $MeGeH_3$ and the methylgermyl halides. Most of the reactions were studied by nmr spectroscopy, and in some cases products were further characterised by infrared spectroscopy.

The reactions of $MeGeH_3$ and $MeGeH_2Co(CO)_4$ with $Co_2(CO)_8$ were investigated and in both cases the compound $MeGeCo_3(CO)_{11}$ was isolated as a major product. Some exchange reactions of $MeGeH_2Co(CO)_4$ and $(H_3Ge)_2Fe(CO)_4$ with $Mn(CO)_5^-$ were also investigated as a new synthetic route to group IV-transition metal compounds.

The identification of the various reaction products is reported and discussed, and the reactions of group IV-transition metal compounds are reviewed.

CHAPTER 1. INTRODUCTION

1.1 Definitions

The class of compounds referred to by the title of this thesis is that in which a main group IV metal is bonded to a transition metal. This definition will also be extended to the group IV metalloids, silicon and germanium, and for convenience these will be referred to in the text as metals when all or some of the group IV elements are being discussed.

It will also be convenient to refer at times to a generalised formula for these compounds, $R_3M'ML_n$ where M' = Si, Ge, Sn and Pb; M = any transition metal; R_3 = substituents on the group IV metal; and L_n = n other ligands on the transition metal (n = 0, 1, 2 ---). For example, $H_3M'M(CO)_n$ signifies the group IV hydride derivatives of the metal carbonyls.

Occasionally particular transition metal compounds will be referred to according to their periodic groups (e.g. Group VI = Cr, Mo, W). This should not be confusing as it should normally be obvious from the text that it is the transition metal group being referred to

rather than the corresponding main group.

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; although with the exception of germanium the prefix mono- is usually omitted for the n = 1 compounds. These parent compounds form the basis of a nomenclature system similar to that of methane and its derivatives. Thus "germyl" derivatives are those compounds of the general form GeH_3X, "methylgermyl" derivatives are represented by $MeGeH_2X$, and "digermanyl" compounds have the form Ge_2H_5X. The latter term should be distinguished from "digermyl" which indicates $(GeH_3)_2X$ compounds.

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

THF	:	tetrahydrofuran
Et_2O	:	diethyl ether
Me	:	CH_3, methyl
Et	:	C_2H_5, ethyl
Ph	:	C_6H_5, phenyl
Cp	:	C_5H_5, cyclopentadienyl
diphos	:	$(Ph_2PCH_2)_2$
TMS	:	tetramethylsilane

1.2 Group IV-Transition Metal Compounds - General Introduction

The first compounds containing a Group IV metal-to-transition metal bond were some alkyl lead derivatives of Iron carbonyl reported in 1941 by Hein and Pobloth (1). In the next twenty or so years progress in this field was relatively slow, being confined to reports of a few of the more stable and readily accessible compounds. By the early 1960's however interest was beginning to intensify, as in so many other aspects of organometallic chemistry at this time, with the result that the field of group IV-transition metal compounds is now one of considerable proportions.

The most recent general review of group IV-transition metal compounds by Glockling and Stobart (2) covers developments in the literature over the period 1968-70. These authors do not attempt a detailed listing of all of the reported compounds in this field but two earlier reviews by Brooks and Cross (3) and Vyazankin *et al.* (4) provide complementary lists of references for over five hundred compounds for the period up to 1970. Earlier general reviews have appeared (5,6,7) as have others of a more specific

nature. Thus derivatives of germanium have been covered in a book by Glockling (8) and more recently in another book by Lesbre et al. (9). A review of the silicon hydrides by Aylett (10) includes a discussion of transition metal derivatives while silicon-transition metal compounds have been treated more recently by Ang and Lau (11) and a review of σ-complexes of platinum(II) compounds (12) briefly covers the silicon, germanium, and tin derivatives. Two reviews by Abel and Stone (13,14) of transition metal carbonyl compounds also include discussion of the group IV derivatives and the recent Chemical Society Specialist Periodical Report on Organometallic Chemistry (15) contains a small section on compounds containing a group IV-to-transition metal bond.

One of the major interests in metal-metal bonded compounds is their spectroscopic properties, and a review by Watters and Risen (16) considers some aspects of these, while part of a recent survey of structural tin (IV) chemistry (17) covers the transition metal derivatives of this metal. In addition to the specific reviews listed above there are an increasing number of publications which include discussions of one or more

aspects of group IV-transition metal compounds.

Within the field of group IV-transition metal compounds there have been a number of general areas of interest. This class of compounds provides useful comparisons with the corresponding class of organo-transition metal compounds and some workers have been interested in this aspect. Usually the heavier group IV congeners are relatively more stable and less reactive than their corresponding carbon analogues so that they are easier to handle and more amenable to physical and chemical studies. For example $SiH_3Co(CO)_4$ (18) and $GeH_3Co(CO)_4$ (19) are moderately stable compounds at room temperature and readily manipulated in a vacuum line, whereas the corresponding $CH_3Co(CO)_4$ (20) decomposes at -35°C. On the other hand $CH_3Co(CO)_4$ readily undergoes CO insertion to give $CH_3COCo(CO)_4$, while attempts by Aylett and Campbell (18) to observe the same reaction with $SiH_3Co(CO)_4$ were unsuccessful even with CO pressures of over 20 atmospheres and temperatures of 70°C.

As with organo-transition metal compounds the heavier group IV metal derivatives have been of some interest as potential homogeneous catalysts. Numerous hydrosilylation catalysts have been reported, some initially containing a silyl group, as in $(SiEtCl_2)(H)Pt(PPh_3)_2Cl$

which catalyses the addition of R_3SiH (R = Ph,Et,Cl) to hex-1-ene, and many others in which a silicon-transition metal compound is possibly formed during the catalytic cycle. Some examples of this latter type are $RhCl(PPh_3)_3$ (22), $Ni(PPh_3)_2Cl_2$ (23), and $Co_2(CO)_8$ (24,25). Fewer examples of hydrogermylation catalysts have been reported but these are quite similar to the hydrosilylation catalysts given above (e.g. $RhCl(PPh_3)_3$, $Pt(PPh_3)_2Cl_2$, ref. 26), while some $SnCl_3$-derivatives of platinum(II) are well-known hydrogenation catalysts (27). Good general reviews of homogeneous catalysis are given in ref. 28.

Another area of interest has been based on a possible difference between the organo- and other group IV-transition metal compounds. That is, in compounds of silicon, germanium, tin, and lead there is the possibility of involvement of the low-lying unfilled d orbitals in bonding to suitable substituents. Thus in silicon-oxygen compounds there is evidence for $p \longrightarrow d$ π-bonding from oxygen to silicon, shown by increased Si-O bond strengths and decreased bond lengths from those expected by comparison with related carbon compounds (ref. 10 summarises this effect quite well);

and similar results may be expected in bonding to transition metals. Here the bonding could be between filled d orbitals on the transition metal and the unfilled d orbitals on the group IV metal, and this may be expected to have significant effects on the relative bond strengths in these compounds.

Most physical techniques have been used at some time or other in studies of the bonding in group IV-transition metal compounds. Thus the frequencies of carbonyl stretching vibrations in the infrared have been measured for many compounds and force constant calculations usually suggest some π-contribution to the M-M' bonding. (This work is summarised in section 3.4.2 of ref. 2). X-ray structural studies (e.g. 17,29) often show a reduction of the predicted M-M' bond lengths, although here there is usually some doubt in the assignment of covalent radii for the metal, M. Mössbauer studies (17,30) on tin- and iron-containing compounds, ^{55}Mn nmr studies of Mn-M' compounds (31), and ^{59}Co nqr studies of cobalt compounds (32) have all been carried out, with the results indicating some π-bonding in these compounds; and esr measurements have also been made on some titanium compounds (33). Some recent molecular

orbital calculations (20) on $R_3SiCo(CO)_4$ compounds suggest some π-bonding in the Si-Co bond, but these also show the possible presence of non-bonded interactions between the group IV ligands and equatorial carbonyl groups, and this is supported by mass spectral results (34) as well as X-ray and electron diffraction studies (20). Finally, and by comparison, a recent photoelectron spectral study of silicon- and germanium-hydride-metal carbonyl compounds (34) provides evidence for the absence of any (d-d) π-bonding in these compounds. Earlier references to these and other studies may be found in the reviews.

The group IV-transition metal compounds have aroused much spectroscopic interest, in the specific properties of the metal-metal bond as discussed above, and because of the variety of bond types and structures exhibited by these compounds. In the case of heterogeneous metal-metal systems, there is an added advantage in that these are more amenable to examination by a wider range of techniques than are homogeneous systems. To a lesser extent there has also been some interest in the fact that metal-metal bonded compounds may serve as useful models for the bonding in actual metals, alloys, and metal polymers. Both of these points are discussed by Watters and Risen (16) in a review of metal-metal

bonded systems which includes references to some of the more complete spectroscopic studies which have been carried out on group IV-transition metal compounds. Thus detailed force field calculations have been performed on the series of molecules, $Cl_3M'Co(CO)_4$ (35), $J(^{119}Sn-CH_3)$ coupling constants have been correlated with substituent electronegativity from the nmr spectra of a series of $Me_nSn[M(CO)_x]_{4-n}$ compounds (36), and the numerous ^{119}Sn mössbauer studies of tin-containing compounds have been collected together and analysed by Watters and Risen (16).

These general aspects have been the main areas of interest in group IV-transition metal compounds, and this is reflected in the present state of development of the field. The possible synthetic routes to these compounds are now well-established and it appears that any compound for which these details have not yet been reported should be prepared without much difficulty by a judicious selection of appropriate conditions. Spectroscopic studies continue to be reported and there is still intense interest in these details. A great mass of data is now available for most of the common spectroscopic techniques and reviews of these could well be useful at this stage to collect all of the results together and perhaps produce a clearer picture than

exists at present. Perhaps the area of least endeavour has been in the study of the reactions of these compounds. Only in the last few years has the number of reports of reaction studies begun to increase and, as with the spectroscopic investigations, there is now a reasonable number of results available. Again these are quite fragmented however and could be quite usefully collected together in a review article.

1.3 General Aims of this Work

With these general points in mind the overall aims of this work were established. The basic aim was to carry out an investigation into some of the reactions of a few selected group IV-transition metal compounds within the context of existing studies, to gain a greater understanding of the factors determining reactivity in these systems. The group IV hydride-transition metal carbonyl compounds, $H_3M'M(CO)_n$, were chosen for this study for reasons which are detailed in the introduction to chapter 3. In addition it was felt that the methyl derivatives, $MeM'H_2M(CO)_n$, would provide complementary information to that found for the H_3M'- compounds and some of these had not been reported in the literature.

Thus, another aim was to prepare examples of such compounds and characterise them by the normal spectroscopic methods, as well as using them in the reaction studies. Incidental to these aims, a number of other unreported compounds were expected as products in the reaction studies and partial characterisation of these would also be attempted.

Thus there are a number of parts to this thesis. In chapter 3 the preparation and characterisation of some $H_3M'M(CO)_n$ and $MeM'H_2M(CO)_n$ compounds is reported and discussed. This is then followed in chapters 4 and 5 by the reaction studies carried out on these compounds, and the incidental characterisation of the products of some of the reactions. In the process of this work a considerable number of nmr spectra were recorded and in chapter 6 the data from these are collated and discussed. In chapter 2 the existing $H_3M'M(CO)_n$ compounds will be surveyed and general experimental details given. These however will be preceded by a brief discussion of the preparative aspects of the general field of group IV-transition metal compounds, with particular emphasis on recent developments.

CHAPTER 2. GROUP IV-TRANSITION METAL COMPOUNDS

2.1 Preparative Aspects

With over five hundred reported compounds in this field it is not surprising that there are now well-established preparative routes to most of the possible combinations of the group IV metals with transition metals. Table 2.1 summarises the more widely used methods with recent examples of, and comments on, their applicability. Further examples can be found in the Brooks and Cross Review (3) and more detailed discussion is not necessary as this aspect is well covered in this and other review articles (3,4). Some recent developments are worth noting however and discussion of these follows.

2.1.1. Abnormal Products

As noted in the table the use of method 1(a) has been generally unsuccessful with most silyl halides. Attempted preparations by this route have usually resulted in conversion of the silyl halide to a siloxane derivative and formation of complex metal carbonyl compounds from the anion. Curtis (51) has recently studied these reactions in some detail and finds that the oxygen in the siloxane most probably comes from the carbonyl groups

TABLE 2.1. Preparative Routes to Group IV-Transition Metal Compounds

Method	References	Applicability and Other Comments
1. Alkali-Halide Elimination		
a) Group IV Halide + Transition Metal Anion		
$H_3M'Cl+NaMn(CO)_5 \longrightarrow H_3M'Mn(CO)_5+NaCl$ (M'=Si,Ge)	(37,38)	Cr,Mn,Fe, and Co groups. Useful for polymetallic derivatives. Unsuccessful for many silyl derivatives.
$Me_3SiCl+NaMo(CO)_3Cp \longrightarrow Me_3SiMo(CO)_3Cp+NaCl$	(39)	
$H_2SiI_2+2NaCo(CO)_4 \longrightarrow H_2Si[Co(CO)_4]_2+2NaI$	(18)	
b) Transition Metal Halide + Alkali Metal-Group IV Derivative		
$H_3SiK+BrFe(CO)_2Cp \longrightarrow H_3SiFe(CO)_2Cp+KBr$	(40)	Ti,Fe,Ni, and Cu groups. Useful for polymetallic derivatives. More suitable for aryl derivatives of the group IV metals.
$4Ph_3SiK+TiCl_4 \longrightarrow (Ph_3Si)_4Ti+4KCl$	(41)	

Method	References	Applicability and Other Comments
2. Oxidative Addition Reactions		
a) Addition of $H_3M'X$		
$H_3M'X + trans\text{-}(Et_3P)_2PtI_2 \longrightarrow (M'H_2X)(H)PtI_2(PEt_3)_2$ (M'=Si,Ge; X=Cl,I)	(42)	Mainly group VIII transition metal compounds. Often coupled with elimination reactions (see method 3)
b) Addition of $M'X_2$ (X=halogen)		
$SnX_2 + M(CO)_3Cp_2 \longrightarrow X_2Sn[M(CO)_3Cp]_2$ (X=Cl,Br,I; M=Cr,Mo,W)	(43)	Limited to availability of $M'X_2$ (Sn,Pb and GeI_2). Occurs more readily in metal carbonyls with bridging CO's.
3. Elimination Reactions (Other than Alkali-Halide)		
a) Oxidative Addition - Elimination Reactions		
$H_3M'X + trans\text{-}XPt(PEt_3)_2H \longrightarrow trans\text{-}XPt(PEt_3)_2 M'H_2X + H_2$ (M'=Si,Ge; X=F,Cl,Br,I)	(42)	As for method 2(a)

Method	References	Applicability and Other Comments
$2HSiCl_3+(PPh_3)_2Pt(C_2H_4)\longrightarrow(SiCl_3)_2Pt(PPh_3)_2+H_2+C_2H_4$	(44)	

b) **Elimination of Neutral Molecules**

(i)	$2PhGeH_3+3Co_2(CO)_8\longrightarrow 2PhGeCo_3(CO)_{11}+3H_2+2CO$	(45)	(i) Widely applicable to metal carbonyls and Si and Ge hydrides. Higher substitution in $RM'H_3$ and $R_2M'H_2$ is more common for Ge.
	$2SiF_3H+Mn_2(CO)_{10}\longrightarrow 2SiF_3Mn(CO)_5+H_2$	(46)	
(ii)	$Me_3M'C_5H_5+M(MeCN)_3(CO)_3\longrightarrow Me_3M'M(CO)_3Cp+3MeCN$ (M'=Ge,Sn; M=Cr,Mo,W)	(47)	(ii) These are rather specific methods and not widely applicable.
	$3Ph_3SnH+Ti(NMe_2)_3\longrightarrow(Ph_3Sn)_3Ti+3HNMe_2$	(48)	
	$Me_3SnN{:}CR_2+HMo(CO)_3Cp\longrightarrow Me_3SnMo(CO)_3Cp+HNCR_2$	(49)	

Method	References	Applicability and Other Comments
4. Mercurial Reagents		
$2(Me_3M')_2Hg+(chelate)PtCl_2 \longrightarrow (Me_3M')_2Pt(chelate) + 2Me_3M'Cl+2Hg$	(50)	Mainly for Si and Ge derivatives. So far reported for Cr, Co, Fe and Ni group compounds.

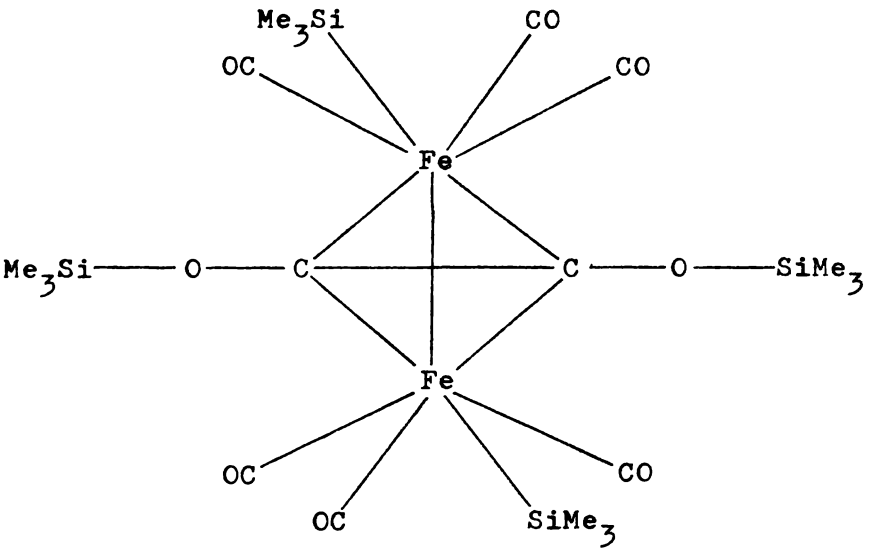
5. Indirect Syntheses

A large class of group IV-transition metal compounds is of course formed via the reactions of other group IV-transition metal compounds. Examples of these will be seen in the two chapters on reaction studies.

of the metal carbonyl anion, while the solvent for the reactions (usually tetrahydrofuran) also appears to be involved in the rearrangement of this anion. Involvement of the solvent in the reactions must be quite important as it has been found that the M-M' couplings can be successfully carried out in the absence of solvent (52). Another observation by Curtis is that the nucleophilicity of the metal carbonyl anion is also a contributing factor and he reports that the more nucleophilic anions $Co(CO)_3(PPh_3)^-$ and $Fe(CO)_2Cp^-$ give successful preparations while $Co(CO)_4^-$ and $Mn(CO)_5^-$ do not. Thus the problem appears to be rather complex and Curtis suggests that more than one mechanism may be involved in these reactions.

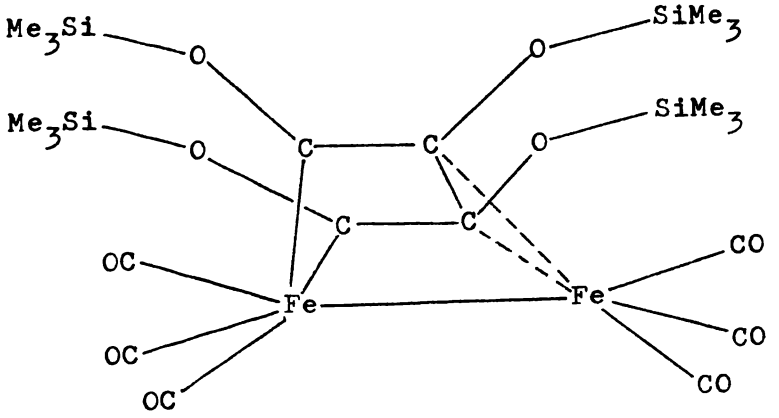
A further clue to this behaviour comes in some other recent reports of unusual results from another type 1(a) reaction. Two rather interesting compounds have been isolated from similar preparations by MacDiarmid et al. (53) and Graham and his co-workers (54), and these may indicate possible types of intermediates present in the more complete rearrangements discussed above. Initially MacDiarmid reported that a dimeric compound of empirical formula $(Me_3Si)_2Fe(CO)_4$ had been isolated from the reaction between Me_3SiI and $Na_2Fe(CO)_4$ and the structure shown in Fig. 2.1 (a) was proposed for it.

FIGURE 2.1


Me3Si
CO
OC
CO
Fe
Me3Si
O
C
C
O
SiMe3
Fe
OC
CO
OC
SiMe3

(a)

(b)


Me3Si
O
SiMe3
Me3Si
O
SiMe3
C
C
O
C
C
OC
CO
Fe
Fe
OC
CO
OC
CO

Other compounds in which a silyl group is attached to an oxygen atom of a metal carbonyl compound have been reported (55,56) and the high Si-O bond strength is probably a contributing factor in the formation of these. This structure was supported by infrared, mass, and nmr spectral data, and a reaction with HCl in which only the two Me_3Si groups on oxygen were cleaved to give Me_3SiCl and the H-O-C- moiety.

One discrepancy in MacDiarmid's report however was in the interpretation of the mass spectrum of the compound. Peaks were observed at m/e values corresponding to $(P+CO)^+$ and $(P+2CO)^+$ and Graham *et al.* point out, quite reasonably, that this is a rather unlikely occurrence. Instead they propose that the product actually contains ten carbonyl groups and support this by X-ray data which gives the structure shown in Fig. 2.1.(b). It may be significant that this was formed in the reaction of $Na_2Fe(CO)_4$ with Me_3SiBr, whereas MacDiarmid *et al.* used Me_3SiI. This is an even more intriguing structure than that proposed by MacDiarmid, but it is not reconcilable with all of MacDiarmid's evidence. The same cleavage of two Me_3Si groups by HCl is reported by Graham and it is difficult to see how only two of the four silyl groups can be differentiated in this way. This situation

does not appear to be fully resolved as yet and more than one complex product may exist, but the results still provide some worthwhile indications of the kind of structural variations likely to occur in these anomalous systems.

The question of how far the solvent affects these reactions is not really resolved by the above results. Both unusual products were prepared in THF solution while MacDiarmid's product was also found from the same reaction carried out in hexane. It is pointed out, though, that traces of THF may still have been present from the anion preparation, so that this cannot be taken as conclusive evidence against solvent involvement. Another recent report by MacDiarmid and Ingle (57) does lend some support to THF involvement in the reactions. These workers report that there is a rapid reaction at room temperature between $Me_3SiCo(CO)_4$ and THF to give high yields of the complex $Me_3SiOCCo_3(CO)_9$, in which the silyl group is again attached to oxygen. Furthermore, when $Me_3SiCo(CO)_4$ is heated at 105°C for 50 h in the absence of solvent the same compound is formed, as well as a new compound, $(Me_3SiOC)_4Co_2(CO)_4$. This report comes from an abstract only and it will be interesting to see whether the latter compound is structurally related to

that found by Graham *et al.* for the related iron system.

Thus this particular aspect of the preparations of silicon-transition metal compounds is by no means clear. The situation does not appear to be simple and there are obviously many different effects to be considered. It also seems likely that no one explanation will be satisfactory for all of the results discussed above. So far, there is no report of similar complexity in germanium compounds.

2.1.2. Polymetallic Derivatives

Another area in which interest appears to be intensifying is in the preparation of polymetallic derivatives. Compounds in which two, three, or four transition metal atoms are bonded to one group IV atom have been known for some time. These are interesting structurally and are also the types of compounds on which models of metallic systems may be based. In contrast with this situation the number of compounds with a single transition metal group attached to polysily-, germyl-, or stannyl-derivatives is quite small, and only in the last few years has any interest been shown in these compounds. These derivatives are interesting from the point of view of the group IV-to-transition metal bond, as the increasing bulkiness of the group IV substituent may be expected to

have some effect on any bonded or non-bonded interactions between the two parts of the molecule. In addition any (d-d) π-bonding in the M-M' bond may be transmitted through the M'-M' bonds as well, using the vacant M' d orbitals. Reaction studies on such compounds should also be quite interesting, especially in systems where competition may occur for attack by a reagent at the M-M' bond or an M'-M' one. Similarly reactions occurring specifically at the M'_nR_{2n+1} moiety may, by comparison with similar reactions of the parent M'_nR_{2n+2} compounds, demonstrate any bonding modifications caused by the transition metal.

These polymetallic derivatives are prepared by the normal methods, 1a, 3a, and 3b having been used so far, as well as addition of hexamethylditin across a metal-metal bond (which does not fit any of the classifications of table 2.1). Some examples are given below.

$$Ge_2H_5I + NaMn(CO)_5 \xrightarrow{\text{ether}} Ge_2H_5Mn(CO)_5 \qquad (58)$$

$$(Me_3Si)_nMe_{3-n}SiH + Mn_2(CO)_{10} \xrightarrow[36\ h]{130^oC} 2(Me_3Si)_nMe_{3-n}SiMn(CO)_5 + H_2 \qquad (59)$$

$(n=1,2,3)$

$$Me_6Sn_2 + (PPh_3)_2PtC_2H_4 \longrightarrow (Me_3Sn)_2Pt(PPh_3)_2 + C_2H_4 \qquad (60)$$

$$Ph_6Pb_2 + M(PPh_3)_4 \longrightarrow (PbPh_3)_2M(PPh_3)_2 + 2PPh_3 \qquad (61)$$

$(M=Pd,Pt)$

The compound $Ge_2H_5Mn(CO)_5$ is the first reported group IV analogue of a σ-bonded ethyl complex and shows a considerable increase in stability compared with $C_2H_5Mn(CO)_5$ (20,58).

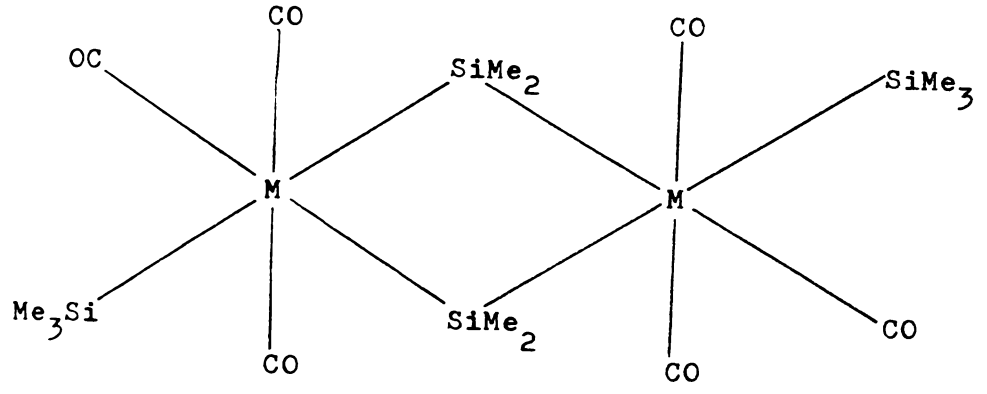
The use of partially substituted silanes in these preparations is quite interesting. When the R_6M_2' derivatives of tin and lead are used, cleavage of the group IV metal-metal bond occurs to give normal R_3M'- derivatives (60,61). This is to be expected as the M'-M' bond is the weakest in these compounds. Similarly the same result is observed for Si_2Cl_6 (62). However, with derivatives of the form $R_5M'_2H$ the M'-H bond may become comparable in energy to the M'-M' bond so that more than one type of product may be formed. Thus Nicholson and Simpson (59) find that in the reaction between pentamethyldisilane and $Mn_2(CO)_{10}$ under relatively forcing conditions (36 h at 130°C), hydrogen elimination takes place to give $Me_5Si_2Mn(CO)_5$. In contrast with this Stone *et al.* (63) observe that Me_5Si_2H reacts with some carbonyl derivatives of ruthenium and osmium to give both H_2 elimination and Si-Si bond cleavage. Thus the compound shown in Fig. 2.2.(a) is formed by the reaction between Me_5Si_2H and either $M_3(CO)_{12}$, $(Me_3Si)_2M(CO)_4$, or $[Me_3SiM(CO)_4]_2$ under conditions of heating (up to 160°C), or ultraviolet irradiation.

In addition some reactions of tetramethyldisilane were reported. The Ru and Os dodecacarbonyls did not give any stable products with 1,1,2,2-$Me_4Si_2H_2$ other than the hydride $H_4Ru_4(CO)_{12}$. With $[Me_3SiRu(CO)_4]_2$ however $(Me_2Si)_3Ru_2(CO)_6$, which has three Ru-Si-Ru bridges, (Fig. 2.2.(b)) was formed under mild conditions, while $[Me_3SiOs(CO)_4]_2$ gave small quantities of $(Me_2Si)_2[Os(CO)_3SiMe_3]_2$ with the structure shown in Fig. 2.2.(a).

Thus, in reactions of this type the products formed are going to depend on the relative M'-H and M'-M' bond strengths, as well as on the relative stabilities of the different possible products. More detailed study of such preparations could therefore yield some useful qualitative information on relative bond strengths as well as an interesting variety of structures for different compounds. Some work (64) is now under way in this laboratory on the reactions of derivatives of di- and trigermane with transition metal carbonyls.

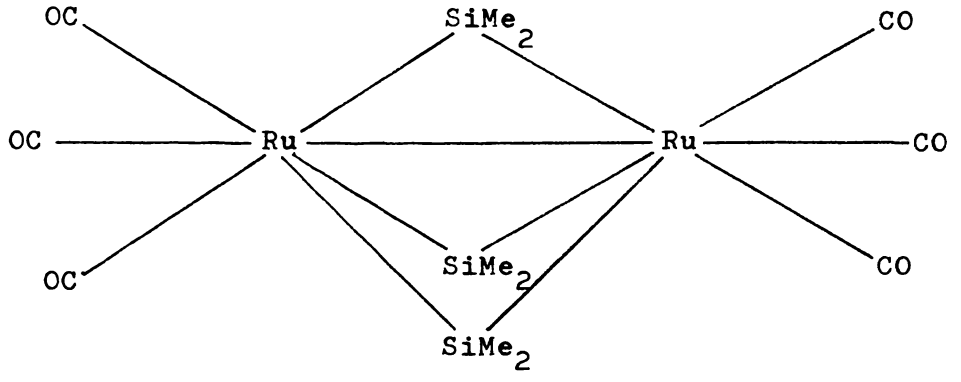
At present there is not enough data available from which to draw any general conclusions about changes in the bonding in these polymetallic derivatives. However in the case of the polysilanylmanganese derivatives reported by Simpson *et al.* (59,65) the Si-Mn bond length

FIGURE 2.2



(M = Ru, Os)

(a)



(b)

in $(Me_3Si)_3SiMn(CO)_5$ shows no significant shortening due to (d-d) π-bonding, while distortion about the silicon atom bonded directly to manganese suggests some steric repulsion between the two parts of the molecule. There is also no evidence for any transmission of charge from manganese to the β-silicon atoms.

2.1.3 Carbene Analogues

Finally, there have been three recent reports of the preparation of a number of group IV analogues of the so-called "carbene complexes". This latter class of compounds is receiving much attention at present and it seems likely that with these discoveries of analogous compounds of the heavier group IV elements, interest in this particular aspect of group IV-transition metal compounds should increase quite dramatically.

Thus Schmid and Balk (66) find that when $(PPh_3)_2Pt(SiX_3)_2$ (X=Cl,Br) is treated with excess triphenylphosphine, a complex formulated as $(PPh_3)_2Pt(SiX_2)_2$ is formed in high yield. This is believed to have either of the structures shown in Fig. 2.3.(a) on the basis of infrared spectra, and a reaction with diphenylacetylene which yields the complex shown in Fig. 2.3.(b).

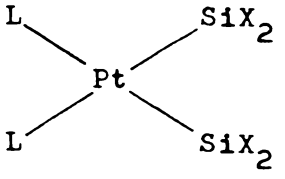
Similarly, Marks and Newman (67,68) report germylene-, stannylene-, and plumbylene- derivatives. The low temperature (-78^o) reaction between $Na_2Cr_2(CO)_{10}$ and dialkyl-

germanium and -tin dihalides in THF yields complexes formulated as shown in Fig. 2.3.(c). The products are extremely air sensitive and only the $(t\text{-}C_4H_9)_2Sn$- derivative is stable for any length of time at room temperature. Tetrahydrofuran cannot be removed from the complexes without decomposition and the preparations are unsuccessful in non-coordinating solvents. Further characterisation is by infrared and mass spectroscopy.

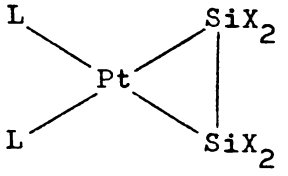
In a subsequent paper (68) derivatives of iron were reported. The compounds $[R_2M'Fe(CO)_4]_2$ (R=Me,Ph, $t\text{-}C_4H_9$; M'=Ge,Sn,Pb) were prepared by the reaction of $R_2M'X_2$ with $Na_2Fe(CO)_4$ in THF. All of these molecules possess considerable thermal and chemical stability and are undissociated in non-coordinating solvents. However, the infrared spectra in coordinating solvents (pyridine, acetone, tetrahydrofuran, diethyl ether) show that dissociation takes place, and it is proposed that the products are related to the chromium complexes mentioned above, as shown in Fig. 2.3.(d). Further evidence for these carbene analogues comes from nmr and mössbauer spectroscopic measurements, analytical data, and conductivity measurements.

Whether the above compounds are analogous to carbene compounds is still a matter of conjecture. All of the

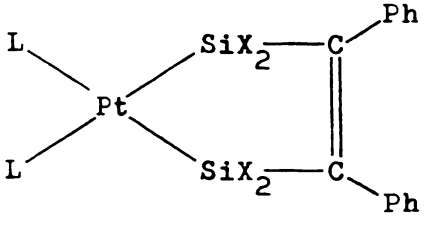
FIGURE 2.3



(a)

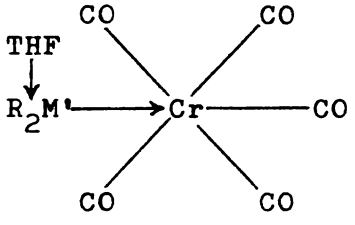


(L= PPh_3 ; X= Cl, Br)



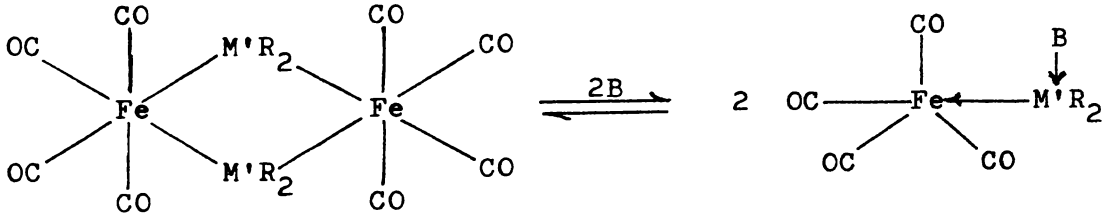
(L= PPh_3)

(b)



(M'= Ge, Sn; R= Me, Et, $t\text{-}C_4H_9$)

(c)



(M'= Ge, Sn, Pb; B= base)

(d)

evidence presented so far is indirect so that the actual formulation of these compounds is largely dependent on the individuals involved in the investigation. More direct physical evidence, such as an X-ray structure, may help to resolve the matter.

2.1.4. Conclusion

The three particular aspects discussed in this section are some of the more significant recent developments in the preparations of group IV-transition metal compounds. They have been presented here to give some indication of the sort of work which has already been done in this field, to indicate where the emphasis is likely to be placed in work in the near future, and to supplement the review articles listed in section 1.2. which pre-date most of these developments. The first two points are also relevant to some of the work covered in this thesis.

General descriptions of the characterisation and reaction studies of group IV-transition metal compounds need not be given here. These points will be covered later, and more specifically and usefully in the relevant chapters.

2.2 Group IV-Hydride Derivatives of the Transition Metals

The known group IV-hydride-transition metal compounds are listed in Table 2.2. There have been no reports of tin- or lead-containing derivatives and this probably reflects the low Sn-H and Pb-H bond strengths, and perhaps also the undesirable nature of such compounds. The methods of preparation of the compounds are given in the table, as are the spectroscopic techniques used for characterisation of each compound.

The most commonly used preparative method for these compounds is alkali-halide elimination and interestingly this has been successful for silyl, as well as germyl, derivatives. All of the type 1(a) preparations of the germyl derivatives were carried out in an ether solvent (THF or Et_2O) with the exceptions of $(H_3Ge)_2Fe(CO)_4$ which was prepared in n-butane and $(MeGeH_2)_2Fe(CO)_4$ in pentane. Similarly the silicon derivatives of Mn, Fe and Co were prepared in the same solvents by this method. Aylett and Campbell (18) note that the yield of $H_3SiCo(CO)_4$ is increased from 55% to about 70% when diethyl ether is replaced by dimethyl ether as solvent, but other than this most of the yields of the silyl derivatives are quite comparable with those of their germyl analogues. The group VI compounds, $H_3SiM(CO)_3Cp$, were prepared by the same method

TABLE 2.2.

GROUP IV-HYDRIDE-TRANSITION METAL COMPOUNDS

	Preparation (a)	Characterisation (b)	Ref.
A) Silicon			
$H_3SiM(CO)_3Cp$ M=Cr,Mo, W	1a	IR,NMR,MS,EA,RP	69
$(SiHCl_2)M(CO)_3Cp$ M=Mo,W	1a	IR,NMR,MS,EA	39
$(MeSiHCl)M(CO)_3Cp$ M=Mo,W	1a	IR,NMR,MS,EA	39
$H_3SiMn(CO)_5$	1a	IR,NMR,MS,PE,EA, RP	34,37
$H_3SiRe(CO)_5$	1a	PE	34
$(H_3Si)_2Fe(CO)_4$	1a	IR,NMR,EA,RP	70
$H_3Si(H)Fe(CO)_4$	1a	IR,NMR,EA(d)	70
$H_3SiFe(CO)_2Cp$	1b	IR,NMR,EA	40
$Me_2SiHFe(CO)_2Cp$	1a	IR,NMR,MS,EA,RP	71
$H_3SiCo(CO)_4$	1a	IR,NMR,MS,PE,ED, EA,RP	18,34 86
$H_2Si[Co(CO)_4]_2$	1a	IR,EA	18
$MeSiH_2Co(CO)_4$	3b	IR,NMR,MS,RP	25,72
$Ph_2SiHCo(CO)_4$	3b	IR,EA	24
trans-$(SiH_xX_{3-x})Pt(PEt_3)_2X'$ (X=F,Cl,Br,I; X'=Cl,Br, I; x=0,1,2,3)	3a,5	IR,NMR,EA,RP	42,73

	Preparation (a)	Characterisation (b)	Ref.
trans-$(SiH_2NMe_2)Pt(PEt_3)_2Cl$	5	IR,NMR,EA	42
$(SiH_2X)_2Pt(Et_3P)_2(H)I_2$ (X=Cl,I)	2a,5	IR,NMR,EA,RP	42,73
$(Ph_2SiH)_2Pt(diphos)$	3a	IR,EA,RP	74
$(Ph_2SiH)(H)Pt(PEt_3)_2$	3a	IR,NMR	75
$(Me_2SiH)(H)Pt(PEt_3)_2$	3a	IR,NMR	75
B) <u>Germanium</u>			
$H_3GeMn(CO)_5$	1a	IR,RA,NMR,MS,PE, EA,RP	34,38
$H_2Ge[Mn(CO)_5]_2$	?	IR,NMR,EA	76
$H_5Ge_2Mn(CO)_5$	1a	IR,RA,NMR,MS	58
$MeGeH_2Mn(CO)_5$	1a	IR,RA,NMR,MS,RP	(C)
$H_3GeRe(CO)_5$	1a	IR,RA,NMR,MS,PE, RP	34,77
$H_2Ge[Re(CO)_5]_2$	?	IR	77
$(H_3Ge)_2Fe(CO)_4$	1a	IR,RA,NMR,MS,EA, RP	78
$H_3Ge(H)Fe(CO)_4$	1a	IR,RA,NMR,MS	78
$(MeGeH_2)_2Fe(CO)_4$	1a	IR,NMR,RP	64
$H_3GeFe(CO)_2Cp$	1a	IR,NMR	78
$H_2Ge[Fe(CO)_2Cp]_2$	5	IR,NMR,EA	79
$(Ph_2Ge)(PhGeH)Fe_2(CO)_6$	3b		80

	Preparation (a)	Characterisation (b)	Ref.
$(H_3Ge)_2Os(CO)_4$	1a	IR,NMR,EA	81
$H_3Ge(H)Os(CO)_4$	1a	IR,NMR	81
$H_3GeCo(CO)_4$	1a	IR,RA,NMR,MS, PE,EA,RP	19,34
$MeGeH_2Co(CO)_4$	1a	IR,RA,NMR,MS,RP	(c)
$Ph_2GeHCo(CO)_4$	3b		82
trans-$(GeH_xX_{3-x})Pt-(PEt_3)_2X'$ ($X \neq X'$=Cl,Br,I; x=0, 1,2,3)	3a	IR,NMR,EA,RP	42
$(GeH_2X)_2Pt(PEt_3)_2(H)-I_2$ (X=Cl,I)	2a,5	IR,NMR,EA,RP	42
$(GeH_2Cl)_n(GeHCl_2)_{3-n}-Pt(H)(PEt_3)_2$ (n=1,2,3)	2a	NMR	83

Footnotes: a) Numbers refer to the classification of Table 2.1.

b) IR-infrared spectroscopy; RA-raman spectroscopy; NMR-nuclear magnetic resonance spectroscopy; MS-mass spectrometry; PE-photoelectron spectroscopy; ED-electron diffraction; EA-elemental analysis; RP-reaction products also characterised.

c) This work. d) Molecular weight only.

in yields of 20-40% in the absence of solvent (69) while $(SiHCl_2)M(CO)_3Cp$ and $(MeSiHCl)M(CO)_3Cp$ (M=Mo,W) were prepared in non-polar solvents (cyclohexane or methylcyclohexane). Malisch *et al.* (39) attribute these latter successful preparations to the use of the non-polar solvents as the products decompose readily in solvents other than cyclohexane, methylcyclohexane, and pentane. This observation also lends some support to the idea of solvent involvement in the formation of abnormal products from the coupling of other silyl halides with metal anions discussed in section 2.1.1.

There is a useful implication in the fact that compounds such as $H_3SiMn(CO)_5$ may be formed by alkali-halide elimination whereas other derivatives such as $Me_3SiMn(CO)_5$ are only formed successfully with this method in the absence of solvent (51,52). The formation of abnormal products from organo-silyl halides such as Me_3SiCl has already been discussed (section 2.1.1) and it was suggested that the explanation for these results may be a mechanistic one. If this is the case and if the mechanisms for the formation of the abnormal products involve intermediates such as $R_3Si^{\bullet}$ radicals or R_3Si^{+} cations, then the H_3Si-derivatives may not be expected to be involved as the formation of $H_3Si^{\bullet}$ or H_3Si^{+} would be less favourable due to the lack of any

stabilisation by the substituents. In fact Curtis (51) suggests that one of the mechanisms for the formation of anomalous products may involve free-radicals, so that the above observations support this.

The compounds $H_3Ge(H)Fe(CO)_4$, $H_3Si(H)Fe(CO)_4$, and $H_3Ge(H)Os(CO)_4$ are all formed as byproducts in the preparations of the $(H_3M')_2M(CO)_4$ compounds (70,78,81) by method 1a. Another product in the preparations of the iron compounds is $H_2Fe(CO)_4$ and it is interesting to consider the origin of the hydrogen in forming these additional products. Aylett et al. (70) have observed that $H_3Si(H)Fe(CO)_4$ is one of the decomposition products of $(H_3Si)_2Fe(CO)_4$ while Stobart (78) reports that the yield of $H_2Fe(CO)_4$ in the preparation of $(H_3Ge)_2Fe(CO)_4$ increases with longer reaction times. Thus, these results suggest that for the iron compounds the transition metal hydride compounds may be formed by decomposition of the digermyl derivatives. It is also significant in this respect that $HMn(CO)_5$ is formed in the preparation of $H_3SiMn(CO)_5$, as well as in its decomposition (37).

The digermyl-osmium compound (81) has only recently been reported and this was formed by the reaction between H_3GeBr and an anion produced from the reduction of $Os_3(CO)_{12}$ with sodium in liquid ammonia. There is some conjecture

as to the nature of the anion, so that in this case $H_3Ge(H)Os(CO)_4$ may either be formed by decomposition of $(H_3Ge)_2Os(CO)_4$ or by the reaction between H_3GeBr and $NaHOs(CO)_4$.

There are four group IV-hydride compounds of the form $H_2M'[MLn]_2$. Of these $H_2Si[Co(CO)_4]_2$ is formed quite normally by the reaction of H_2SiI_2 with 2 moles of $NaCo(CO)_4$ (18). Also $H_2Ge[Fe(CO)_2Cp]_2$ is an example of what have been called "indirect methods" of preparation (method 5). In this case (79) $I_2Ge[Fe(CO)_2Cp]_2$ was formed by the reaction between GeI_2 and $[Fe(CO)_2Cp]_2$ (method 2b) followed by reduction with $NaBH_4$ in THF to give the hydride derivative. The remaining compounds $H_2Ge[Mn(CO)_5]_2$ and $H_2Ge[Re(CO)_5]_2$ are somewhat more interesting. The former was the first reported group IV-hydride-transition metal compound (76) and was produced by the reaction between GeH_4 and $HMn(CO)_5$. This reaction took place over eight days at room temperature in the presence of tetrahydrofuran and did not appear to proceed by any simple substitution mechanism, as there was no evidence for either $H_3GeMn(CO)_5$ or $HGe[Mn(CO)_5]_3$ in the products. It now seems likely that $H_2Ge[Mn(CO)_5]_2$ may have been formed in this preparation by the disproportion of $H_3GeMn(CO)_5$. The decomposition of this latter compound has not been studied under the same

conditions used for the formation of $H_2Ge[Mn(CO)_5]_2$, but both $H_2Si[Mn(CO)_5]_2$ and $H_2Si[Co(CO)_4]_2$ are products of the decomposition at room temperature of $H_3SiMn(CO)_5$ and $H_3SiCo(CO)_4$ respectively (37,18). It is also quite significant that the preparation of $H_2Ge[Mn(CO)_5]_2$ was carried out in THF, which is likely to promote the decomposition of $H_3GeMn(CO)_5$. The compound $H_2Ge[Re(CO)_5]_2$ was isolated by Mackay and Stobart (77) as a minor product in the preparation of $H_3GeRe(CO)_5$, and GeH_4 was also identified. The H_3GeBr used in the preparation had been freed from H_2GeBr_2 so that the disubstituted compound must have been formed by a disproportionation reaction. Thus both the Mn and Re compounds were probably formed by a reaction of the form:

$$2H_3GeM(CO)_5 \quad H_2Ge[M(CO)_5]_2 + GeH_4.$$

Some other examples of indirect syntheses are seen with some of the platinum compounds shown in table 2.2. The following equations are typical of the sorts of reactions used:

$$trans\text{-}(SiH_2Cl)Pt(PEt_3)_2Cl + HNMe_2 \quad trans\text{-}(SiH_2NMe_2)Pt(PEt_3)_2Cl + HCl \qquad (42)$$

$$trans\text{-}(SiH_2Cl)Pt(PEt_3)_2Cl + HCl \quad trans(SiHCl_2)Pt(PEt_3)_2Cl + H_2 \qquad (73)$$

$$\left.\begin{array}{l} trans\text{-}(Et_3P)_2PtI_2 + M'H_3X \\ \text{or} \\ trans\text{-}(M'H_2X)Pt(PEt_3)_2I + HI \end{array}\right\} \rightarrow (M'H_2X)_2Pt(PEt_3)_2(H)I_2 \quad (42,73)$$

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

As shown in the last example the same compounds may be formed by different methods. This is especially the case with the platinum compounds and most of these have been prepared by one or more oxidative addition or addition-elimination reactions as indicated in the table.

Finally some of the type 3b preparations should be considered. These were used initially for the preparation of cobalt compounds, but Graham and his co-workers (80,84, 85) have been able to extend the method to compounds of W, Mn, Re, and Fe by the use of more rigorous conditions. The following equations are simple examples of this method, and under mild conditions these reactions (especially with

$$2MeSiH_3 + Co_2(CO)_8 \rightarrow 2MeSiH_2Co(CO)_4 + H_2 \quad (72)$$

$$MeSiH_3 + HCo(CO)_4 \rightarrow MeSiH_2Co(CO)_4 + H_2 \quad (25)$$

silanes) proceed in this way. However under more forcing conditions, and more commonly for germanium derivatives, higher degrees of substitution may be achieved. Thus from the reaction of diphenylgermane with $Fe_3(CO)_{12}$ as many as four products may be isolated depending on conditions (80); that is $Ph_2GeFe_2(CO)_8$, $Ph_2GeFe(CO)_4$ 2, $(Ph_2Ge)_2Fe_2(CO)_7$, and $(Ph_2Ge)(PhGeH)Fe_2(CO)_6$. Similarly

the compound $Ph_2GeHCo(CO)_4$ given in the table has not actually been isolated (82)but it is a likely intermediate in the reaction between Ph_2GeH_2 and $Co_2(CO)_8$ to give $Ph_2GeCo_2(CO)_7$. There are many more examples of these reactions with a corresponding wide variety of products being reported (see e.g. ref. 2,3), and some of these will be discussed more specifically in chapter 5.

The infrared, raman, nuclear magnetic resonance, and mass spectral data for the compounds of table 2.2 will not be discussed here. Particular examples will be considered, where appropriate, in the later chapters. An electron diffraction study has been reported (86) for $H_3SiCo(CO)_4$. The Co-Si bond length is 238.1 pm and the Si-Co-C angle is 81.7°, and these values are compared with 225.4 pm and 85° respectively for $Cl_3SiCo(CO)_4$. Robiette et al. (86) interpret these differences on the basis of $(d \longrightarrow d)$ π-bonding in the Si-Co bond. The shorter bond length in the chloro derivative reflects a lowering of the size and energy of the silicon d orbitals (due to the greater electronegativity of chlorine compared with hydrogen) so that they are more effective in π-bonding, and the greater Si-Co-C angle is explained as a result of the increased σ-accepting ability of the Cl_3Si moiety compared with H_3Si. These results are complementary to the numerous

x-ray diffraction results reported for group IV-transition metal compounds, which are summarised in the Brooks and Cross review (3).

A recent photoelectron spectral study of some $H_3M'M(CO)_n$ compounds by Ebsworth *et al.* (34) presents a new approach to the investigation of the nature of the M-M' bond. The photoelectron spectra of $H_3M'Mn(CO)_5$, $H_3M'Re(CO)_5$, $H_3M'Co(CO)_4$ (M'=Si,Ge); $HRe(CO)_5$, $HCo(CO)_4$, and $Me_3SiMn(CO)_5$ were recorded and similar results for $HMn(CO)_5$ and $CH_3Mn(CO)_5$ were already known. By comparing these various spectra, as well as considering previously reported results for $H_3M'X$ compounds, and a detailed study of $XMn(CO)_5$ compounds it was possible to assign the observed absorptions to electron excitations from particular molecular orbitals in each compound. For the manganese compounds the results show that both the e and b_2 metal d orbitals shift with variation of the attached ligands (H_3M' and CH_3) and this was taken to indicate that there was no (d$\longrightarrow$d) π-bonding in the Mn-M' bonds. Such bonding would be expected to influence only the e-level in the transition metal. Instead the order of binding energies for the manganese d orbitals indicates that the net positive charge on Mn varies in the

order Si > Ge > C, and this is taken to mean that the order of σ-accepting power of the $M'H_3$ groups is $SiH_3 > GeH_3 > CH_3$. Similar results were found for the cobalt and rhenium compounds.

With more extensive studies this new technique could be increasingly useful in establishing the nature of the bonding in $H_3M'M(CO)_n$ compounds. At present, though, the work can only be semi-quantitative and comparative when dealing with compounds with this degree of complexity, and more detailed molecular orbital calculations are needed to support assignments of the observed spectra.

2.3 General Experimental Details

2.3.1 General

Many of the compounds mentioned in this thesis are volatile and many of them are air-sensitive. They were therefore handled in a conventional multi-purpose vacuum frame which was used for all reactions unless otherwise stated. A rotary oil pump was used to maintain a vacuum which was usually adequate, but if a lower pressure was required (e.g. for manipulations of the less-volatile metal carbonyl derivatives) a mercury diffusion pump was available. Normal greased taps and mercury manometers were

employed, but since the germyl-metal carbonyl compounds appeared to be soluble in the tap grease some particular pieces of apparatus were constructed with grease-less teflon taps fitted. Teflon taps were also used when there was a possibility of "streaking" of the greased taps due to the presence of, say, an ether solvent, and when leak-free systems were required.

Constant low temperatures used for fractional distillations and some reactions were obtained by partially freezing a suitable liquid, usually by the addition of liquid nitrogen, to form a fluid slush, which maintained the temperature at the melting point of the compound for as long as the solid phase remained. The most common materials used for these slush baths, and their melting points are (87):

benzene	5.5°C
carbon tetrachloride	-22.6°C
chlorobenzene	-45.2°C
chloroform	-63.5°C
ethyl acetate	-82.5°C
toluene	-95.0°C
n-propyl alcohol	-127.0°C

Air-sensitive solids, or solid reaction products which may have been air-sensitive, were handled in a

glove box flushed continuously with oxygen-free nitrogen which was supplied by New Zealand Industrial Gases Ltd.

2.3.2 Physical Techniques

A number of physical techniques were used as follows.

a) Infrared Spectroscopy

A few millimetres pressure in a 10 cm infrared gas cell is usually sufficient to give strong spectra for most germyl and metal carbonyl species. Thus infrared spectroscopy is a useful technique for the identification of many of the compounds prepared in this thesis, and was in some cases the sole means of identification of particular reaction products. Conventional 10 cm gas cells fitted with KBr windows were used for sampling volatile compounds while the spectra of solids were recorded as nujol or kel-F mulls on KBr plates. Far-infrared measurements (below 400 cm^{-1}) were recorded using polythene cell windows or polythene discs. Some solids were also studied in solution using a 0.1 mm KBr solution cell, with a variable path length cell placed in the reference beam and containing pure solvent. Appropriate peaks from the spectra of polystyrene, CO_2, NH_3, DCl and water vapour (88)

were used for calibration.

Routine and high-resolution spectra were recorded on Shimadzu IR-27G or Beckmann IR-20A grating spectrophotometers with ranges of 4000 - 400 cm^{-1} and 4000 - 250 cm^{-1} respectively. The latter instrument was more suitable for high resolution work through having longer scan times and greater slit width variation, but was not available until the later stages of this work.

The far-infrared spectra of $MeGeH_2Mn(CO)_5$ and $H_xBr_{3-x}GeMn(CO)_5$ (x=1,2,3) were recorded on a Grubb-Parsons DM4 instrument at the University of Auckland, with the helpful assistance of Dr. G.A. Bowmaker and Mr. K.R. Grundy.

b) Raman Spectroscopy

Raman spectra were recorded at the Victoria University of Wellington with the helpful assistance of Dr. G. Burns of that University, and Dr. M.J. Taylor of the University of Auckland. The instrument utilises an argon ion laser with Spex optics, and spectra were recorded at 5145Å. Samples were recorded in thin-walled capillary tubing (2 mm o.d.) sealed at both ends for air-sensitive compounds.

It has been observed in this laboratory that compounds such as $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$, which are only moderately volatile, can be manipulated quite satisfac-

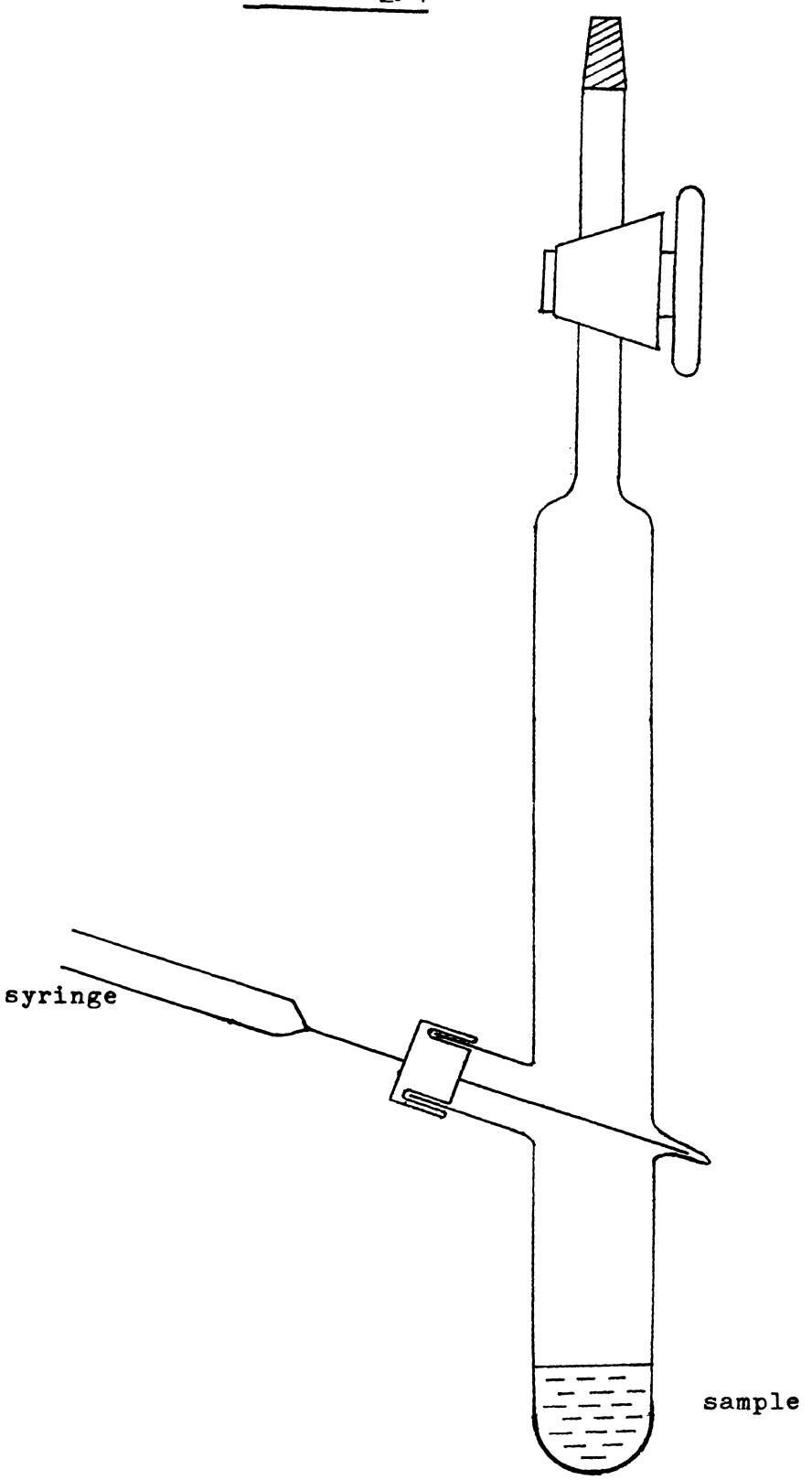
torily as liquids in a glove box at room temperature. This simplifies the transfer of these samples into narrow tubes such as those for the raman instrument, as vacuum line manipulation can be a slow and tedious process in such situations. Thus for the two germyl-metal carbonyl compounds mentioned above, samples were distilled on the vacuum line into the tube shown in Fig. 2.4 and then transferred in the glove box to the capillary tubes using a microlitre syringe.

c) Nuclear Magnetic Resonance Spectroscopy

A Jeol C-60HL spectrometer was used for most of the ^{1}H measurements. Some of the earlier ^{1}H spectra were also recorded by Mr. D. Calvert of the University of Auckland on a Varian T60 instrument. ^{19}F measurements were recorded on the Jeol instrument with a fluorine probe loaned by Massey University, and some of these spectra were also recorded by Dr. K. Jolley of that university on a similar instrument.

All spectra were recorded at 60 MHz using normal 5 mm o.d. nmr sample tubes. For volatile samples B10 cones were glass-blown onto the ends of the tubes and the samples were transferred into these on the vacuum line. The tubes were then sealed below the cone with a hand-torch, with the samples kept frozen in liquid nitrogen.

FIGURE 2.4



Tetramethylsilane was used as internal reference for most of the proton spectra but in some cases, where signals came rather close to this region of the spectrum benzene was used instead. Perfluorobenzene, C_6F_6, was the reference compound for the ^{19}F spectra. The solvents used for the various spectra are specified in the appropriate parts of the text.

d) Mass spectrometry

The mass spectra of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ were recorded on a Varian CH7 instrument by Dr. J. Simpson of the University of Otago, with the samples being introduced in the vapour phase *via.* a cold inlet. The spectrum of $MeGeCo_3(CO)_{11}$ was recorded by Dr. P. Holland of Ruakura Agricultural Research Centre, Hamilton, on a Varian CH5 spectrometer. This sample was admitted as a solid on the end of a temperature-controlled probe at 25°C.

e) Vapour Pressure Measurements

The vapour pressures of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ were measured between about 0°C and 50°C using an apparatus modelled on that shown by Jolly (89) and reproduced in Fig.2.5. A null method was used in making the measurements. That is, the vapour pressure of the sample on the left-hand side of the apparatus was balanced against the pressure in

the vacuum line, which was connected to the vertical tube in the centre of the apparatus. Mercury was admitted to, or removed from, the apparatus *via.* the Teflon needle valve and by adjustment of the "rough vacuum" on the right-hand side of the apparatus. The mercury levels in the system and in the manometers on the vacuum line were measured with a cathetometer to ± 0.1 mm, and the temperature of the bath surrounding the apparatus was measured to ± 0.2°C with an ordinary mercury-in-glass thermometer.

2.3.3 Starting Materials

a) Germanium Hydride Derivatives

Monogermane, GeH_4, was prepared by the hydrolysis of an aqueous germanate with potassium borohydride, as described by Jolly (90). Phosphoric acid (3M) was used instead of acetic acid and yields of up to 80% were obtained. Other products in the reaction were Ge_2H_6, Ge_3H_8, and a yellow GeH_x polymeric material.

Methylgermane, $MeGeH_3$, was prepared similarly, using the method of Griffiths (91). That is, an aqueous solution of potassium borohydride was added to an acidic solution of methyltrichlorogermane, $MeGeCl_3$. Yields in this preparation were from 30 to 50% with some partially reduced products being formed as well.

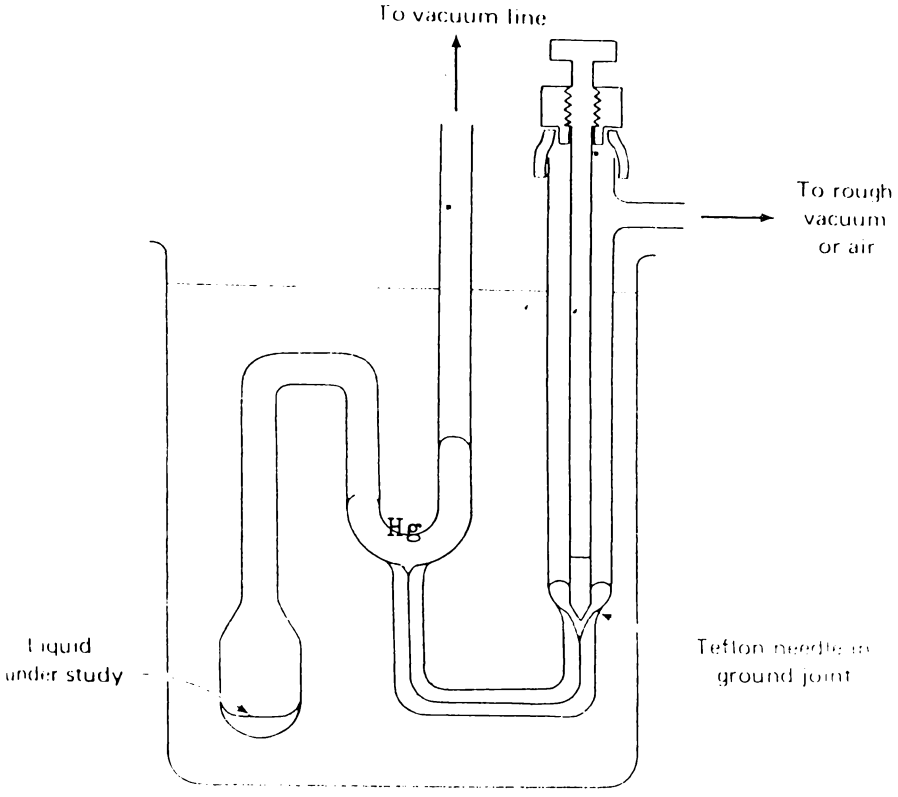


FIG. 8.31. Apparatus for measuring vapor pressures above room temperature

FIGURE 2.5.

(Reproduced from Ref. 89)

Germyl bromide, GeH_3Br, and methylgermyl bromide, $MeGeH_2Br$, were prepared by the direct bromination of GeH_4 and $MeGeH_3$, respectively. Initially the method of Freeman *et al.* (92) was used for these preparations. That is, successive small amounts of bromine were condensed onto the germane and the mixture allowed to warm up after each addition. When the bromine colour was no longer discharged the reaction was terminated and the products fractionated on the vacuum line. With this method yields of about 30% of GeH_3Br and 40% of $MeGeH_2Br$ were obtained (based on total germanium present) and the remaining germanium was largely accounted for by the more highly substituted products (GeH_2Br_2, $MeGeHBr_2$, *etc.*).

During the course of this work a note by Geisler *et al.* (93) reported yields of GeH_3Br of up to 96% from the direct reaction between bromine and an excess of monogermane at -112°C. The author has found that, using the same general method, 75% conversion of $MeGeH_3$ to $MeGeH_2Br$ can be achieved, based on the amount of bromine used. The preparation is best carried out at -127°C in a well-made (that is, high initial solids content) and insulated slush bath. At this temperature the reaction is very slow and the system can be left overnight (*ca.* 12 h) to react. The most suitable scale for the reaction

is about 5 mmol $MeGeH_3$ and 3 mmol Br_2. If larger quantities are used, or if the slush bath is not kept cold enough the reaction proceeds a lot faster and the production of $MeGeHBr_2$ increases at the expense of the yield of $MeGeH_2Br$. Successful preparations can also be carried out at *ca.* -82.5°C but vigorous stirring of the slush bath is required to moderate the reaction, which takes less than an hour to go to completion under these conditions.

Finally, large amounts of mixtures of monogermane and hydrogen bromide gas, and methylgermane and hydrogen bromide, are produced in the above bromination reactions. These mixtures cannot be separated by fractionation and it has been found in this laboratory (94) that if they are placed in a gas storage bulb on the vacuum line and in contact with the mercury surface of a manometer, within a few days further amounts of the mono-brominated products are produced. This reaction has not been investigated in any detail but it is likely that mercuric bromide (from the reaction between mercury and HBr) is catalysing the reaction between the germane and HBr.

i.e. $GeH_4 + HBr \xrightarrow{HgBr_2} GeH_3Br + H_2$.

A similar reaction can be observed if these mixtures are placed in contact with anhydrous aluminium bromide; and

the author has found that if mixtures of GeH_4 or $MeGeH_3$ and HBr are sealed in heavy-walled glass tubes in the presence of aluminium bromide, and the tubes then stored in a deep freeze for at least a month; almost complete conversion of the germane to its mono-bromo-derivative is achieved.

Methylgermyl chloride, $MeGeH_2Cl$, was prepared by treating $MeGeH_3$ with a large excess of $SnCl_4$. Mixtures of the two reagents were shaken together until deposition of $SnCl_2$ appeared to be complete and then the products were fractionated. Unreacted stannic chloride was held at $-45^{\circ}C$, $MeGeH_2Cl$ at $-127^{\circ}C$, and unreacted $MeGeH_3$ and HCl were collected at $-196^{\circ}C$. This method has been described by Ebsworth et al. (95) for some silanes and germanes.

(b) Solvents and Other Materials

The solvents used in the preparations of the metal carbonyl derivatives were diethyl ether and tetrahydrofuran. These were stored over sodium wire and distilled off lithium aluminium hydride before use.

Solvents used for spectroscopy (infrared and nmr) were benzene and cyclohexane which were dried with sodium wire before use. Silicon tetrachloride was also used

as an nmr solvent and this was distilled on the vacuum line before use. Carbon tetrachloride, another nmr solvent, was stored over molecular sieves and used without further treatment.

All of the above reagents were B.D.H. laboratory grade with the exception of cyclohexane and carbon tetrachloride which were spectroscopic grade.

Manganese carbonyl, $Mn_2(CO)_{10}$, and cobalt carbonyl, $Co_2(CO)_8$, were supplied by Strem Chemicals. The former compound was used without any special treatment, but the cobalt compound was normally sublimed before use, except when taken from a freshly-opened bottle.

Boron trifluoride, BF_3, was prepared by treating boron trifluoride diethyl etherate with concentrated sulphuric acid. The product was purified by fractionation through a $-127^{\circ}C$ trap.

Phosphine, PH_3, was produced from the treatment of phosphonium iodide, PH_4I, with alkali, and purification of the product by fractionation through a $-127^{\circ}C$ trap.

Phosphorus trifluoride, PF_3, was prepared by a direct exchange reaction between SbF_3 and PCl_3 at room temperature, followed by purification through a $-127^{\circ}C$ trap.

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

CHAPTER 3. PREPARATION AND CHARACTERISATION OF GERMANIUM HYDRIDE DERIVATIVES OF SOME METAL CARBONYLS

3.1. INTRODUCTION

The major aim of this work was to study the preparation and characterisation of group IV-transition metal compounds and to investigate their reactions with various reagents. Compounds of the type $H_3GeM(CO)_n$ (M=transition metal, n=4,5) were chosen for this study for a variety of reasons. The compounds $H_3GeMn(CO)_5$ (38), $H_3GeCo(CO)_4$ (19), $H_3GeRe(CO)_5$ (77), $(H_3Ge)_2Fe(CO)_4$ (78), and $H_5Ge_2Mn(CO)_5$ (58) have all been reported in the last few years and their syntheses are well-established. They are relatively stable compounds and sufficiently volatile to be suitable for vacuum line manipulation. The vibrational spectra have all been recorded and have been interpreted on the basis of separate $M'H_3$- and $-M(CO)_n$ moieties, with little mixing observed between the two. Thus any lowering of the symmetry of the compounds produced by chemical reactions should show up quite clearly in the infrared spectra, making this technique quite useful for the reaction studies. Preliminary reaction studies have also been reported (19,38,77, 78,96) and suggest that further work may well reveal some

interesting properties.

Of these compounds $H_3GeMn(CO)_5$ is the most easily manipulated and this was chosen as a starting point. The reported synthesis (38) of this compound was used for its preparation.

Another of the techniques available for studying the reactions in this work was nuclear magnetic resonance spectroscopy. This method can be used to detect intermediate species formed during a reaction, while the wide range of temperature variation usually available allows a certain amount of control over the rate at which these are produced or consumed. In addition the technique requires relatively small amounts of material, has a high degree of sensitivity towards changes in molecular composition of the compounds under study and, by the use of vacuum line or glove box techniques, is applicable to most organometallic compounds. The first point, the detection of reaction intermediates, was of some importance in this work, and for this reason it was decided to extend the study to the compound methylgermylpentacarbonylmanganese, $MeGeH_2Mn(CO)_5$. The multiplicity produced in the nmr by coupling between the methyl and germyl protons would be an aid to interpretation of the spectra and to identification of the components of any reaction system. From other workers' observations

on related systems (see chapter 4) it was expected that the presence of the methyl group on germanium would not seriously affect the reactivity of the compound.

$MeGeH_2Mn(CO)_5$ has not been reported before. Since both $H_3GeMn(CO)_5$ (38) and $Me_3GeMn(CO)_5$ (97) can be prepared by alkali halide elimination (see chapter 2) it seemed likely that $MeGeH_2Mn(CO)_5$ could be formed in this way. Details of the synthesis of this compound and of its characterisation are given in part 2.2 of this chapter.

The work on the reactivity of germyl-metal carbonyl compounds described in chapters 4 and 5 is concerned with determining some of the factors affecting the position of reaction sites and the overall reactivities of the compounds. As well as variation of the reagents used, a logical course for this work to take was variation of the particular parts of the compounds under study. Of the group IV hydride-metal carbonyl derivatives known at this stage some reaction details have been reported for $H_3SiMn(CO)_5$ (37), $H_3SiCo(CO)_4$ (18), and $(H_3Si)_2Fe(CO)_4$ (70). Similarly studies on tri-methyl derivatives are reported for $Me_3M'Mn(CO)_5$ and $Me_3M'Co(CO)_4$ (2) (M'=Si, Ge,Sn). It was therefore decided to extend our studies

to the germyl-cobalt derivatives; and to this end the compound methylgermyltetracarbonylcobalt, $MeGeH_2Co(CO)_4$, was prepared. Alkali halide elimination was again used for the synthesis, and this, and the characterisation of the compound are also reported in section 3.2.3.

The spectroscopic properties of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ are given in this chapter as part of the characterisation of these new compounds. These details are also usefully compared with similar results for the higher symmetry tri-hydride derivatives, $H_3GeMn(CO)_5$ (38), and $H_3GeCo(CO)_4$ (19), as well as with the related compounds $H_3GeRe(CO)_5$ (77), $(H_3Ge)_2Fe(CO)_4$ (78), and the H_3Si- (18,37) and $MeSiH_2$- (98) analogues. Part 3.3 includes discussion of the spectra on this basis.

3.2. EXPERIMENTAL

3.2.1 Preparation of Germylpentacarbonylmanganese

The method used for the preparation of $H_3GeMn(CO)_5$ was essentially that of Mackay *et al.* (38)

$$GeH_3Br + NaMn(CO)_5 \longrightarrow GeH_3Mn(CO)_5 + NaBr$$

The following procedure was used in a typical preparation:

Manganese carbonyl anion was prepared by treatment of a solution of manganese carbonyl (349 mg, 0.90 mmol) in 15 ml of dry tetrahydrofuran with excess of a 1-2% sodium amalgam. The amalgam was removed after fifteen minutes and most of the ether pumped off on the vacuum line, leaving a dark green slurry of the sodium salt in ether. Germyl bromide (272 mg, 1.75 mmol) was condensed onto this and the mixture allowed to warm to room temperature and shaken for fifteen minutes, in which time the colour lightened and sodium bromide was deposited. Then the volatile products were fractionated through traps held at -45°C and -127°C into one held at -196°C. Monogermane (12 mg, 0.16 mmol, 9%) was recovered from the liquid nitrogen trap, tetrahydrofuran was held at -127°C, and germylpentacarbonylmanganese (333 mg, 1.23 mmol, 70% based on total germanium present) was held at -45°C. The product was identified by its infrared spectrum (38).

Table 3.1 summarises the details of most of the syntheses of $GeH_3Mn(CO)_5$ performed by the author, and there are a number of points worth noting. Result 1 shows the effect of decomposition caused by impurities present in the sodium used for that preparation, and this is discussed in more detail below. The production of monogermane is related to this and is also discussed below.

TABLE 3.1

Details of $H_3GeMn(CO)_5$ Preparations

No.	Time(a), min	$NaMn(CO)_5$: GeH_3Br	Time(b), min	% Yields (c) $GeH_3Mn(CO)_5$	% Yields (c) GeH_4
1	30	1:1	30	5	95(d)
2	15	1:1.04	15	73	16
3	15	1.02:1	20	70	9
4	60	1:1.05	10	69	(e)
5(f)	100	1:1.03	15	66	(e)
6(f)	120	1:1.01	15	59	(e)

(a) Time for treatment of $Mn_2(CO)_{10}$ with Na/Hg.

(b) Time for treatment of $NaMn(CO)_5$ with GeH_3Br.

(c) % yields based on total germanium present.

(d) Impure sodium was used in this preparation. In all others it was distilled before use (see text).

(e) Small amounts only, detected by their infrared absorptions.

(f) These preparations were carried out in the presence of $NaCo(CO)_4$ as discussed in the text.

GeH_4 was produced in all preparations but normally in such small yields that the actual quantities were not measured.

With the exception of the first preparation yields range from 59% to 73% and this may be compared with the results of Mackay *et al.* (38) who report varying yields of between 55% and 80%. These workers also note that occasionally up to 50% of the germanium appeared as GeH_4, but overall their results appear to show the effect of a much purer supply of sodium than was available in this laboratory.

Results 5 and 6 are interesting in that these preparations were carried out with a mixture of $NaMn(CO)_5$ and $NaCo(CO)_4$. These experiments were a first investigation into the possibility of metal/metal exchange at the transition metal; the question being whether a mixture of $H_3GeMn(CO)_5$ and $H_3GeCo(CO)_4$ would be produced, or whether one product would be formed in preference to the other. In preparation 5 the ratio of cobalt to manganese was about 1:10 and in 6 this was about 1:1. In both cases only traces of $H_3GeCo(CO)_4$ were found in the final product, but it is possible that the 59% yield of preparation 6 is significant as this is slightly lower than all the other results. This work will be considered

again in more detail in chapter 5 in the section on metal/metal exchange reactions.

In all of the preparations given in the table the times taken for the two parts of the synthesis were varied as shown. There are no significant changes in yields due to this variation however and the times listed may be compared with those of George (99), who used one hour for the anion synthesis and 15 minutes for the latter stage of the preparation.

When this preparation was first attempted by the author it was unsuccessful and the problem was tracked down to impurities in the sodium used in the amalgam. BDH "Dry Sodium" was used untreated, and this resulted in extremely low yields (less than 5%) of $H_3GeMn(CO)_5$ and associated high yields of monogermane (95%). Vacuum distillation of the sodium before use overcame this problem however, to give yields of between 55% and 70% in later preparations. It seemed, therefore, that the sodium must have contained impurities which promoted the decomposition of $H_3GeMn(CO)_5$, and the most likely candidates were alkaline organic compounds. To test this out a number of qualitative and semi-quantitative tests were performed.

Initially a mixed sample of $H_3GeMn(CO)_5$ and tetrahydrofuran was condensed onto a large excess of sodium ethoxide and warmed to room temperature. After fifteen minutes the only volatile material detected in the infrared spectrum was monogermane. This experiment was then repeated using $H_3GeMn(CO)_5$ (39 mg, 0.14 mmol) free from tetrahydrofuran, and in 18 hours a mixture of GeH_4 and Ge_2H_6 had been formed, which accounted for about 30% of the total germanium. Some incondensible gases had also been produced (about 0.03 mmol) and germanium was detected in the solid residue by precipitation of GeS_2 from a solution of the solid in 50% sulphuric acid treated with H_2S. There was no evidence for any unreacted $GeH_3Mn(CO)_5$ present in the gas phase.

With sodium hydroxide similar results were found. When $H_3GeMn(CO)_5$ (20.4 mg, 0.08 mmol) contaminated with tetrahydrofuran was condensed onto dry sodium hydroxide and warmed to room temperature, none of the original material remained after a few minutes, and the monogermane produced accounted for about 25% of the total germanium used. In a control experiment, $H_3GeMn(CO)_5$ (51.8 mg, 0.19 mmol) in the presence of sodium hydroxide but free from ether showed no signs of decomposition over 36 hours at room temperature. When the system was warmed to about

50°C some incondensible gas was produced (about 0.03 mmol) but no GeH_4 could be detected. Finally, another sample of $H_3GeMn(CO)_5$ (39 mg, 0.14 mmol) containing a small amount of tetrahydrofuran, showed only slow and partial decomposition to mono- and di-germane at room temperature in the presence of sodium hydroxide. There was still some unreacted carbonyl present after 15 minutes, and when more ether was added to this system the decomposition proceeded to completion.

To summarise, it appears that basic compounds promote the decomposition of $H_3GeMn(CO)_5$ and production of GeH_4 and Ge_2H_6, especially in the presence of ether. Since the untreated sodium may contain basic organic impurities it is likely that these were responsible for the low yield found in the first preparation.

3.2.2. Preparation of Methylgermylpentacarbonylmanganese

$MeGeH_2Mn(CO)_5$ was prepared by a similar method to that used for $H_3GeMn(CO)_5$ (38), using THF or diethyl ether as solvent.

i.e. $MeGeH_2Br + NaMn(CO)_5 \longrightarrow MeGeH_2Mn(CO)_5 + NaBr.$

As with $H_3GeMn(CO)_5$ the synthesis was carried out a number of times and the details of each preparation are summarised in Table 3.2. Again yields varied over a fairly wide

TABLE 3.2.

Details of $MeGeH_2Mn(CO)_5$ Preparations

No.	$NaMn(CO)_5$: $MeGeH_2Br$	Solvent	Times, min (a)	(b)	% Yields $MeGeH_2Mn(CO)_5$	$MeGeH_3$
1	1:1.3	THF	30	30	32	9
2	1:1.0	THF	60	15	69	(c)
3	1.1:1	Et_2O	60	15	44	(c)
4	1:1.0	THF	60	15	45	-

(a) Time for treatment of $Mn_2(CO)_{10}$ with Na/Hg

(b) Time for treatment of $NaMn(CO)_5$ with $MeGeH_2Br$

(c) Small amounts detected only by their infrared spectra

range and $MeGeH_3$ was detected in all cases. There are no obvious changes in yields with particular changes in reaction conditions, but one point worth noting, of a more practical nature, is that the more volatile diethyl ether is more readily separated from the product than is tetrahydrofuran. A typical synthesis follows:

$NaMn(CO)_5$ (457 mg, 2.10 mmol) was prepared by treating manganese carbonyl with excess sodium amalgam as described previously. All but a few ml of the solvent (tetrahydrofuran) were removed and $MeGeH_2Br$ (368 mg, 2.17 mmol) was condensed into the anion suspension. The mixture was shaken in the glove box for fifteen minutes and then the volatiles were fractionated through traps held at -45°C and -127°C into one held at -196°C. Methylgermane (identified by its i.r. spectrum) was held at -196°C, tetrahydrofuran at -127°C, and methylgermylpentacarbonylmanganese (413 mg, 1.45 mmol, 69% based on total Ge present) was collected at -45°C.

The product is a colourless volatile liquid when pure but usually appears pale yellow due to small amounts of decomposition. Despite this, the compound is quite stable and shows no signs of further decomposition at

room temperature over normal manipulation periods (up to ½ h) on the vacuum line, whereas a sample held in an infrared gas cell, to which air had been admitted, appeared to be completely decomposed in two days. Vapour pressures were measured between 0°C and 50°C and decomposition was observed at the latter temperature with some incondensible gases being produced. The actual vapour pressure data is shown in Table 3.3 and plotted in Figure 3.1. In this figure some estimate of

TABLE 3.3

Vapour Pressure Data for $MeGeH_2Mn(CO)_5$

Temp., °C	Pressure, mmHg	Temp., °C	Pressure, mmHg
1.0	11.0	30.0	46.3
10.0	19.8	35.0	58.1
15.0	21.6	40.0	72.4
20.0	28.1	45.0	92.4
25.0	35.5	50.0	123.7

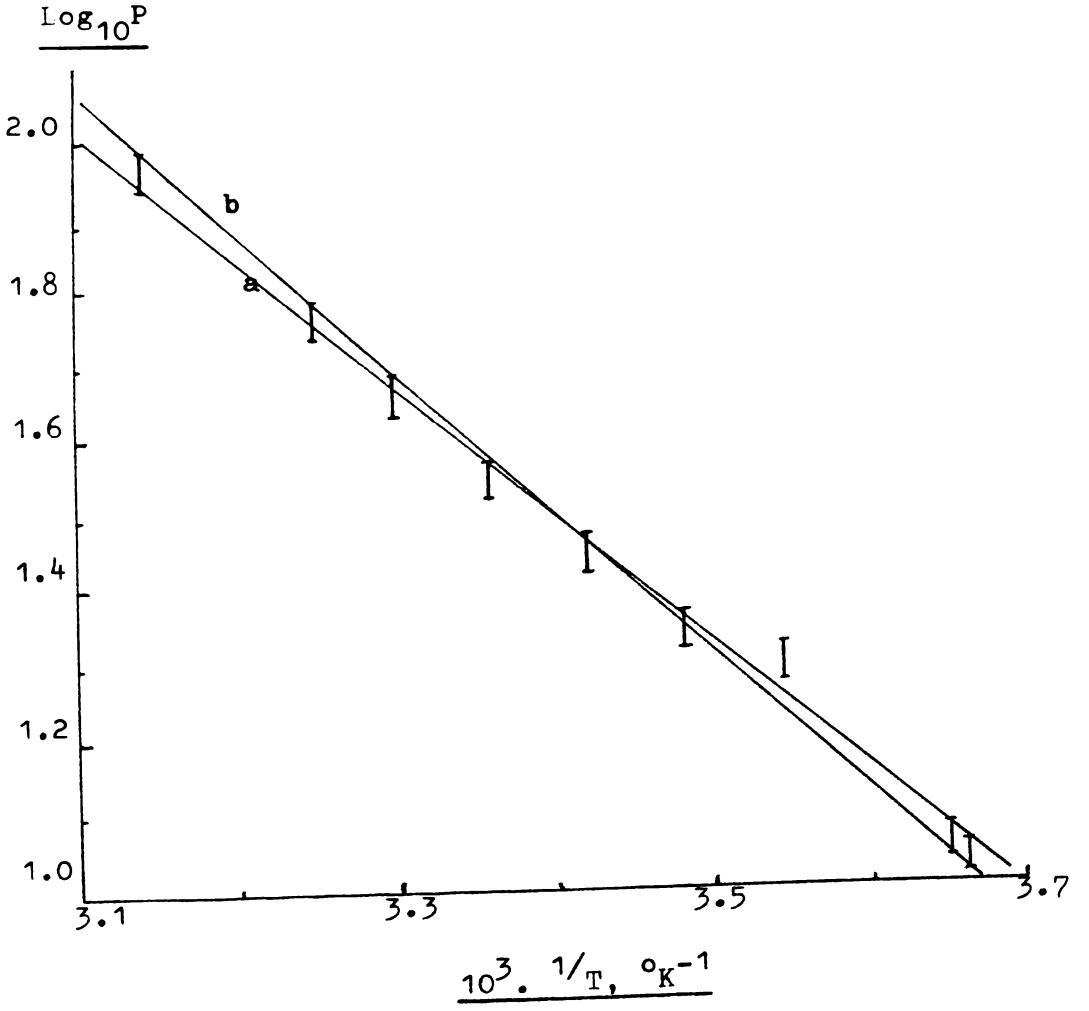
the possible range of results has been made as the method of determining the vapour pressures was not a very accurate one (see 2.3.2.(e)). The two lines fit the relationships:

FIGURE 3.1

Vapour Pressure Data for $MeGeH_2Mn(CO)_5$

(a-: $\quad \text{Log } P = \frac{-1710}{T} + 7.3$)

(b-: $\quad \text{Log } P = \frac{-1880}{T} + 7.9$)



(a) $\log_{10}P = \frac{-1710}{T} + 7.3$

(b) $\log_{10}P = \frac{-1880}{T} + 7.9$

and the extrapolated boiling point range is 103 - 115°C. The vapour pressure at room temperature is about 35 mmHg so that this compound is readily manipulated on the vacuum line.

The 60 MHz ^1H nmr spectrum, run in silicon tetrachloride, shows a triplet at 9.32τ and a quartet at 6.34τ in the approximate ratio 3:2, with $J_{HH'}$ approximately 4.0 Hz. These signals are in the regions normally found for methyl and germyl protons respectively, and the multiplicity is as expected for an A_3X_2 system. Silicon tetrachloride is a rather unusual solvent for nmr spectroscopy but it was found to be a convenient alternative to carbon tetrachloride. This latter solvent was more desirable than most other common organic solvents for its lack of an nmr spectrum, but it was found to react with the hydride derivatives being studied in this work. On the other hand silicon tetrachloride has similar solvent properties but was found to be relatively inert in these systems.

Further characterisation was obtained from the vibrational and mass spectra, and these are reported and discussed in some detail in the latter parts of this chapter.

3.2.3. Preparation of Methylgermyltetracarbonylcobalt

In view of the success of the alkali halide elimination reaction for the preparations of $H_3GeMn(CO)_5$ (38), $H_3GeCo(CO)_4$ (19), and $MeGeH_2Mn(CO)_5$ (this work), it seemed likely that the same method could be used for the synthesis of $MeGeH_2Co(CO)_4$.

i.e. $MeGeH_2Br + NaCo(CO)_4 \longrightarrow MeGeH_2Co(CO)_4 + NaBr$

This proved to be the case and Table 3.4 summarises the experimental details for the syntheses performed by the author. Some difficulty was experienced in obtaining the product completely free from tetrahydrofuran when this solvent was used and diethyl ether was found to be more satisfactory. In most cases unreacted $MeGeH_2Br$ was found in the preparation, even though a deficiency of this reagent was normally used. The incomplete reaction was probably due to impure cobalt carbonyl which decomposed slowly when stored in the glove box, and in the later stages of this work had to be re-sublimed before use. Yields in all the preparations accounted for 35% to 45% of the total germanium present in the system. This is quite comparable with the results obtained by Mackay *et al.* (19) for the preparation of $H_3GeCo(CO)_4$, where yields rose from 36% to 48% with experience.

TABLE 3.4.

Details of $MeGeH_2Co(CO)_4$ Preparations (a)

No.	$NaCo(CO)_4$: $MeGeH_2Br$	Solvent	% Yields	
			$MeGeH_2Co(CO)_4$	Other Products
1	1.2 :1	THF	(b)	$MeGeH_2Br$, GeH_4 (5%)(c)
2	1.15:1	Et_2O	44	$MeGeH_2Br$, $MeGeH_3$, $HCo(CO)_4$
3	1.3 :1	Et_2O(d)	39	None observed
4	1.2 :1	Et_2O	44	$MeGeH_2Br$
5	1 :1.1	THF(e)	39	$MeGeH_2Br$
6	1 :1.1	Et_2O(e)	37	$MeGeH_2Br$, $HCo(CO)_4$

(a) The times taken for each step in these syntheses were not varied and are given in the accompanying text.

(b) Product not completely separated from tetrahydrofuran.

(c) Monogermane was probably admitted to this system as an impurity. It is unlikely that it would have been formed by any decomposition process.

(d) This preparation was performed initially without solvent, but diethyl ether was added when the reaction did not proceed more than a few per cent (see text).

(e) 5 and 6 were performed in parallel with each other, using different solvents (see text).

Other minor products of the reaction were $HCo(CO)_4$ and $MeGeH_3$, the latter compound probably being formed by decomposition of the product along similar lines to that noted earlier for $H_3GeMn(CO)_5$ and $MeGeH_2Mn(CO)_5$. Most of the minor products in the $MeGeH_2Co(CO)_4$ syntheses could not be separated from the solvent or were present in very small amounts and the yields of these are not given in the table.

The third synthesis in Table 3.4 was attempted initially without solvent. That is, dry $NaCo(CO)_4$ was treated with $MeGeH_2Br$, and changes in the composition of the volatile components of the system were monitored by infrared spectroscopy. Some product formation was detected after two minutes at room temperature, but no further changes were observed over the next fifteen minutes. Diethyl ether was then added and the preparation continued in the normal method. The fifth and sixth syntheses in the table are also interesting in that they were performed in parallel with each other. Sufficient cobalt carbonyl anion for both syntheses was prepared in diethyl ether and then the solution divided into two approximately equal portions. One of these was treated as for a normal preparation in diethyl ether. The other was pumped completely free of solvent on the vacuum line,

dry tetrahydrofuran distilled in and the preparation then carried out in this medium. The yields of the two preparations are not significantly different, but more effort was needed in the preparation with tetrahydrofuran to obtain the product completely free of solvent.

The following example is typical of the method used in the various preparations.

Cobalt carbonyl, $Co_2(CO)_8$, (313 mg, .92 mmol) was treated with excess sodium amalgam in dry diethyl ether (15 ml) for one hour at room temperature. The amalgam was removed to leave a clear, pale pink solution from which the ether was distilled, leaving an off-white solid. This was pumped overnight on the vacuum line to remove any unreacted cobalt carbonyl and then diethyl ether (about 2 ml) and $MeGeH_2Br$ (271 mg, 1.60 mmol) were condensed onto the remaining solid. On warming to room temperature sodium bromide deposition occurred and, after the mixture had been shaken for fifteen minutes, the volatiles were fractionated through traps held at -45^oC, -63^oC, -127^oC, and -196^oC. Methylgermane was collected at -196^oC, ether, $HCo(CO)_4$ and unreacted $MeGeH_2Br$ at -127^oC (all identified by their infrared spectra) and $MeGeH_2Co(CO)_4$ was found in both the -45^oC

and -63°C traps, with a total yield of 182 mg (0.70 mmol, 44% based on total Germanium present).

The product, when pure, is a colourless volatile liquid. However, as with $H_3GeCo(CO)_4$ the colour darkens quite rapidly at room temperature in the light to give a yellow or orange coloured liquid. Mackay *et al.* (19) find though, that the colour due to the decomposition product of $H_3GeCo(CO)_4$ is very intense so that very little decomposition produces a rather strong discolouration. In fact after the initial stage, decomposition does not proceed very far at all and these workers found that only 0.017 mmol of incondensible gas was produced from 0.273 mmol of $H_3GeCo(CO)_4$ after 3 days at room temperature. The decomposition is more marked at high temperatures, so that any heating of the sample is undesirable.

$MeGeH_2Co(CO)_4$ appears, from the author's general observations, to show a somewhat similar stability to $H_3GeCo(CO)_4$. In view of this the vapour pressure of the compound was only measured at a few temperatures between 0°C and room temperature. Above this, incondensible gases were produced and discolouration of the sample increased. Values recorded (in mmHg) were: 5 at 0°C, 7 at 9°C, 9 at 15°C, and 12 at 22°C; and from these, by

a long and dubious extrapolation, the boiling point range is 187 to 247°C. Fig. 3.2 shows the plots of this data.

As for $MeGeH_2Mn(CO)_5$, the 60 MHz ^1H nmr spectrum appears as a triplet and a quartet, in the approximate ratio 3:2 with chemical shifts of 9.16τ and 5.67τ respectively (in $SiCl_4$), and $J_{HH'}$ of 3.5 Hz. The mass spectrum and vibrational spectra were also recorded as part of the characterisation of this compound and these are reported and discussed, along with those for $MeGeH_2Mn(CO)_5$, towards the end of this chapter.

3.3 Discussion

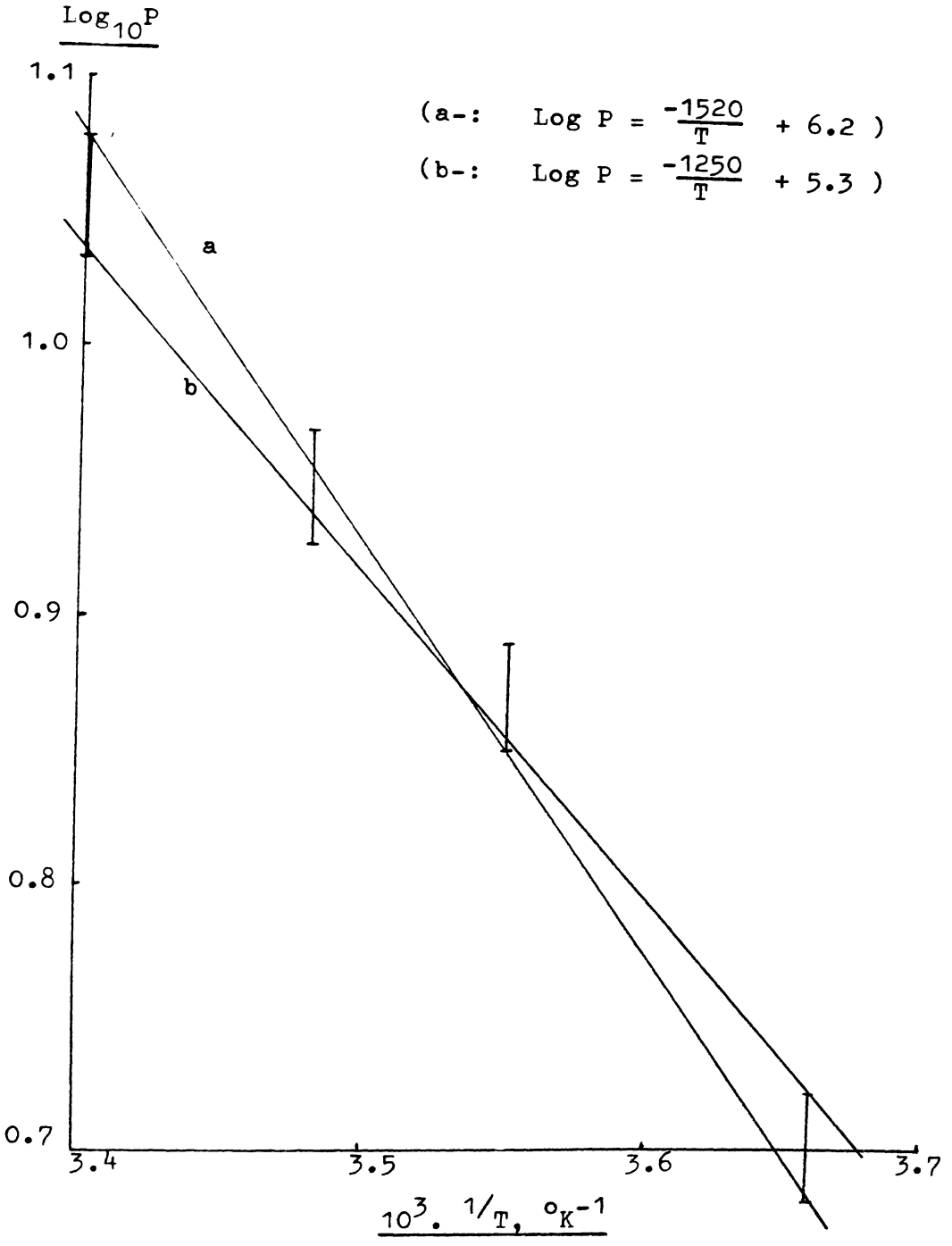
3.3.1. General: The new compounds $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ have been prepared *via.* the reaction:

$$MeGeH_2Br + NaM(CO)_n \longrightarrow MeGeH_2M(CO)_n + NaBr$$

with results similar to those found for the germyl analogues (19,38). The preparations can be carried out in either diethyl ether or tetrahydrofuran with no difference in yields, although the former more volatile solvent appears to be more suitable from a practical point of view. Yields for the syntheses are affected by the presence of basic impurities, but in the absence of such contaminants

FIGURE 3.2

Vapour Pressure Data for $MeGeH_2Co(CO)_4$



they are quite comparable with those reported for the parent compounds.

The general handling properties of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ can be usefully compared with those of the parent germyl compounds and the related silyl derivatives. In both the GeH_3- (19,38) and SiH_3- (18,37) systems the manganese derivatives are found to be the more stable, and this appears to be the case with the $MeGeH_2$- compounds as well. $MeGeH_2Co(CO)_4$ shows much more evidence of decomposition than does $MeGeH_2Mn(CO)_5$ during normal manipulations, and this is also the case at elevated temperatures. Although no quantitative data are available for the decomposition of the methylgermyl derivatives, these compounds seem to have a comparable stability to their germyl analogues. This is as expected since the introduction of one Ge-C bond into these molecules should not significantly affect the reactivity of the Ge-H and Ge-M bonds, and it is the latter which will determine the overall stability of the compounds.

Vapour pressures of the new compounds were recorded at various temperatures between 0^oC and 50^oC and Figs. 3.1 and 3.2 show the plots of $\log P \propto \frac{1}{T}$ for each compound.

In both graphs upper and lower limits have been taken for the "best fit" lines and these give a range of possible boiling points for each compound. The wide range of boiling points quoted for the cobalt compound reflects the small temperature range over which measurements were made for this compound due to its instability at higher temperatures. Table 3.5 compares the boiling point data with similar values for related compounds. The agreement is not good but there is not really enough data available to draw any significant conclusions about the present results.

Table 3.5: Boiling Points of Some Group IV-Transition Metal Compounds

Compound	B.Pt., ^{o}C	Ref.	Compound	B.Pt., ^{o}C	Ref.
$MeGeH_2Mn(CO)_5$	103-115	(a)	$MeGeH_2Co(CO)_4$	187-247	(a)
$H_3GeMn(CO)_5$	150	38	$H_3GeCo(CO)_4$	120	19
$H_3SiMn(CO)_5$	134	37	$H_3SiCo(CO)_4$	102	18
			$MeSiH_2Co(CO)_4$	121.8	72

(a) This work

3.3.2. NMR Data of Group IV-hydride-Transition Metal Compounds

The nmr spectra of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ were recorded as part of the characterisation of these compounds. Both spectra show the multiplicity expected for an A_3X_2 system and the signals have the correct relative intensities. Initially carbon tetrachloride was chosen as a suitable solvent for these compounds, but it was found that this gave fairly rapid reactions of the type:

$$MeGeH_2Mn(CO)_5 + CCl_4 \longrightarrow MeGeHClMn(CO)_5 + CHCl_3,$$

and: $$MeGeHClMn(CO)_5 + CCl_4 \longrightarrow MeGeCl_2Mn(CO)_5 + CHCl_3,$$

so that another solvent had to be used. (The above reactions are considered in more detail in chapter 4). Subsequently the spectra of $MeGeH_2Mn(CO)_5$ were recorded in silicon tetrachloride, tetramethylsilane and germanium tetrachloride, while all $MeGeH_2Co(CO)_4$ spectra were measured in $SiCl_4$. This latter solvent was a satisfactory substitute for CCl_4 as it showed no signs of reaction over a period of a few months and produced no additional handling difficulties as most samples were prepared on the vacuum line, or in the glove box. There were no pronounced changes in chemical shift with any of the above solvents, most values being within 0.1 ppm of each other.

TABLE 3.6: NMR Spectral Data for $MeGeH_2M(CO)_n$ and Related Compounds

Compound	solvent	Chemical Shifts, τ(a) GeH	CH_3	$J_{HH'}$, Hz	Ref.
$MeGeH_2Mn(CO)_5$	CCl_4	6.34	9.27	4.0	(b)
"	$SiCl_4$	6.34	9.32	4.0	(b)
"	$GeCl_4$	6.27	9.32	4.0	(b)
"	TMS	6.25	9.38	4.0	(b)
$MeGeH_2Co(CO)_4$	$SiCl_4$	5.67	9.16	3.5	(b)
$(MeGeH_2)_2Fe(CO)_4$	$SiCl_4$	6.18	9.30	3.9	64
$MeGeH_3$	CCl_4	6.58	9.65	4.3	(c)
$MeGeH_2Br$	$SiCl_4$	5.12	9.06	3.1	(c)
$H_3GeMn(CO)_5$	C_6H_6	6.72	-	-	38
$H_3GeCo(CO)_4$	C_6H_6	6.95	-	-	19
$(H_3Ge)_2Fe(CO)_4$	C_6D_6	6.50	-	-	78
GeH_4	$SiCl_4$	6.82	-	-	(c)
GeH_3Br	C_6H_{12}	5.50	-	-	100

(a) Measured at 60 MHz, 30°C, relative to internal TMS.

(b) This work.

(c) These values were obtained from solutions of known samples prepared by the author. The values are in close agreement with those given in ref. 100.

Table 3.6 gives the chemical shift data for the new transition metal compounds, as well as values recorded during this work or reported by other workers for related compounds. A more extensive tabulation of data appears in chapter 6 and the results will be discussed in more detail at that point. It can be seen from the table, however, that the observed chemical shifts of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ appear in the same general region as those for related compounds, thus providing further characterisation of these new compounds.

3.3.3. The Mass Spectra of Methylgermylpentacarbonylmanganese and Methylgermyltetracarbonylcobalt

The mass spectra of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ were recorded on a Varian CH7 mass spectrometer by Dr. J. Simpson of the University of Otago. Tables 3.7 and 3.8 list the observed spectra along with the assignments and relative ion intensities of the various peaks. As may be seen in these tables the assignments have been made for groups of peaks corresponding to all of the ions of the same general stoichiometry but containing different germanium isotopes and/or due to the loss of one, two, or three hydrogen atoms.

TABLE 3.7: Mass Spectrum of $MeGeH_2Mn(CO)_5$ (Mono-Isotopic)

m/e	Assignment(d)	Relative Intensity(a)	Hydrogen Ratios(b) x=3	2	1	0
288-280	$MeGeH_xMn(CO)_5^+$	10.0		10.0	3.2	0.3
260-252	$MeGeH_xMn(CO)_4^+$	32.9		10.0	0.7	0.7
232-224	$MeGeH_xMn(CO)_3^+$	14.2		3.3	3.3	10.0
204-196	$MeGeH_xMn(CO)_2^+$	20.1		10.0	2.1	0.4
176-168	$MeGeH_xMn(CO)^+$	12.2		10.0	4.7	0.2
148-140	$MeGeH_xMn^+$	100		10.0	2.8	6.4
94-85	$MeGeH_x^+$	24.1		1.9	0.6	10.0
274-265	$GeH_xMn(CO)_5^+$	4.0	1.3	10.0	2.6	0.5
246-237	$GeH_xMn(CO)_4^+$	7.4	1.5	4.9	4.1	10.0
218-209	$GeH_xMn(CO)_3^+$	3.6	4.3	9.3	7.2	10.0
190-181	$GeH_xMn(CO)_2^+$	4.3	2.8	10.0	3.2	3.2
162-153	$GeH_xMn(CO)^+$	7.4	4.4	10.0	8.5	8.1
134-125	GeH_xMn^+	49.4	0.3	1.4	7.2	10.0
79-70	GeH_x^+	4.7	2.2	2.2	5.6	10.0
196	$HMn(CO)_5^+$	0.4				
195	$Mn(CO)_5^+$	0.3				
168	$HMn(CO)_4^+$	0.6				
167	$Mn(CO)_4^+$	1.0				
140	$HMn(CO)_3^+$	2.9				
139	$Mn(CO)_3^+$	1.9				
112	$HMn(CO)_2^+$	0.6				
111	$Mn(CO)_2^+$	4.2				

TABLE 3.7 (cont.)

m/e	Assignment(d)	Relative Intensity(a)	Hydrogen Ratios(b) x=3	2	1	0
84	$HMn(Co)^+$	1.7				
83	$Mn(CO)^+$	7.6				
70	$MeMn^+$	6.7				
56	HMn^+	4.8				
55	Mn^+	37.5				
28	CO^+	(c)				

Footnotes

(a) Summed over x=0,1,2,3 and over Ge isotopes where appropriate.

(b) Relative to strongest component of family = 10.0. These are approximate values only due to overlap of peaks from different Ge isotopes.

(c) Strong peak but includes N_2^+.

(d) Other weak peaks observed at m/e 210, 154, 98 assigned to $MeMn(CO)n^+$, n=5,3,1. However these accounted for less than 0.5 relative intensity, in total. A stronger peak was present at m/e 69 (Rel Int 6.7) with two very weak ones at m/e 68, 67, and these may be due to CH_2Mn^+, $CHMn^+$, and CMn^+ respectively. No similar fragmentations were observed in other CH_3 containing ions.

TABLE 3.8: Mass Spectrum of $MeGeH_2Co(CO)_4$ (Mono-Isotopic)

m/e	Assignment(d)	Relative Intensity(a)	Hydrogen Ratios(b) x=3	2	1	0
264-256	$MeGeH_xCo(CO)_4^+$	3.4		10.0	2.3	1.5
236-228	$MeGeH_xCo(CO)_3^+$	12.7		10.0	0.8	1.8
208-200	$MeGeH_xCo(CO)_2^+$	26.7		4.7	0.7	10.0
180-172	$MeGeH_xCo(CO)^+$	24.0		0.9	1.7	10.0
152-144	$MeGeH_xCo^+$	37.7		2.1	3.7	10.0
94-85	$MeGeH_x^+$	100		10.0	8.3	8.6
250-241	$GeH_xCo(CO)_4^+$	2.5			(e)	
222-213	$GeH_xCo(CO)_3^+$	3.2			(e)	
194-185	$GeH_xCo(CO)_2^+$	7.6	5.6	2.6	5.6	10.0
166-157	$GeH_xCo(CO)^+$	10.4	4.1	4.1	5.9	10.0
138-129	GeH_xCo^+	35.3	0.8	1.5	4.1	10.0
79-70	GeH_x^+	64.5	4.2	10.0	4.2	10.0
172	$HCo(CO)_4^+$	0.3				
171	$Co(CO)_4^+$	0.4				
144	$HCo(CO)_3^+$	1.3				
143	$Co(CO)_3^+$	1.8				
116	$HCo(CO)_2^+$	0.8				
115	$Co(CO)_2^+$	10.6				
88	$HCo(CO)^+$	1.8				
87	$Co(CO)^+$	15.3				
60	HCo^+	0.5				
59	Co^+	7.3				
28	CO^+	(c)				

TABLE 3.8 (cont.)

Footnotes

(a) Summed over x=0,1,2,3 and over Ge isotopes where appropriate.

(b) Relative to strongest component of family = 10.0. These are approximate values only due to overlap of peaks from different Ge isotopes.

(c) Strong peak but includes N_2^+.

(d) Other weak peaks observed due to $MeCo(CO)n^+$ (n=4,3,2,1,0), but the total intensity is only 1.7 for this family.

(e) Peaks too weak for any meaningful separation into components.

The presence of five naturally occurring isotopes of germanium (^{76}Ge 7.8%, ^{74}Ge 35.6%, ^{73}Ge 7.8%, ^{72}Ge 27.4%, ^{70}Ge 20.5%) produces characteristic intensity patterns in the mass spectra of compounds containing this element. This is a useful aid to the identification of such compounds as the observed spectra can be compared with that expected on the basis of the relative abundances of these isotopes. In the case of the hydride derivatives of germanium the spectra are complicated further, however, by hydrogen atom removal which may produce additional peaks overlapping with those for other isotopes (e.g. $^{72}GeH^+$ and $^{73}Ge^+$). For H_3Ge- and H_2Ge- derivatives this makes the assignment of the spectra a little more complicated, but the problem is not insoluble, and relative intensities for the individual ions within each group can still be calculated. Thus, in the case of the manganese compound, it was possible to assign all of the observed peaks (about 150 altogether) on the basis of the fragmentation of $MeGeH_2Mn(CO)_5$ and this provided strong support for the formulation of this compound. For $MeGeH_2Co(CO)_4$ the spectrum was not as intense as that for the manganese compound and the assignment of all the observed peaks was not as precise. The spectrum may have also been complicated further by decomposition of the compound inside the spectro-

meter as some weak peaks were observed above m/e 264, the ion due to $Me^{76}GeH_2Co(CO)_4^+$. Most of the stronger families of peaks in the spectrum could be analysed as fragments of $MeGeH_2Co(CO)_4$, however, so that this formulation was also supported by the mass spectral results.

The spectra will now be discussed in more detail, with the manganese compound being considered first.

The most prominent series of ion families is derived from $MeGeH_2Mn(CO)_5$ by successive loss of carbon monoxide, with weaker series due to $GeH_xMn(CO)_n^+$ and $Mn(CO)_n^+$ (x=0 to 3, n=0 to 5). Rearrangement ions, $HMn(CO)_n^+$ (n=0 to 5) and $MeMn(CO)_n^+$ (n=5,3,1,0) are also present as weak peaks, although some of the $HMn(CO)_n^+$ series are quite comparable in intensity with the similar hydrogen-free ions, and $MeMn^+$ is a relatively strong peak. The peak at m/e 69 due to CH_2Mn^+ has the same intensity as this latter ion, and very weak peaks were observed for $CHMn^+$ and CMn^+.

Within the germanium-containing series fragmentation by loss of H is also observed, to give overlapping patterns of peaks due to Ge^+, GeH^+, GeH_2^+, and GeH_3^+ in combination with all the germanium isotopes. The latter ions with three hydrogen atoms on germanium must also be due to a

rearrangement process. The strongest peak in the spectrum is that due to $^{55}Mn^+$, but the total intensity of the $MeGeH_xMn^+$ family (m/e 140-148) is greater than this and has been used as a composite base peak.

Of the four major fragmentation processes, CO H and Me loss, or Ge-Mn cleavage, the former appears to be considerably more favourable than all the others, and this is in agreement with mass spectral studies of other metal carbonyl derivatives (101,102) where CO loss often takes preference over the removal of other ligands. Cleavage of the Ge-Mn bond does not become important until most of the carbonyls have been removed, as shown by the low relative intensities of the $Mn(CO)_n^+$ ions for n=5,4 and 3, compared with n=2,1, and 0; and H and Me loss appear to be of intermediate importance between this process and CO loss.

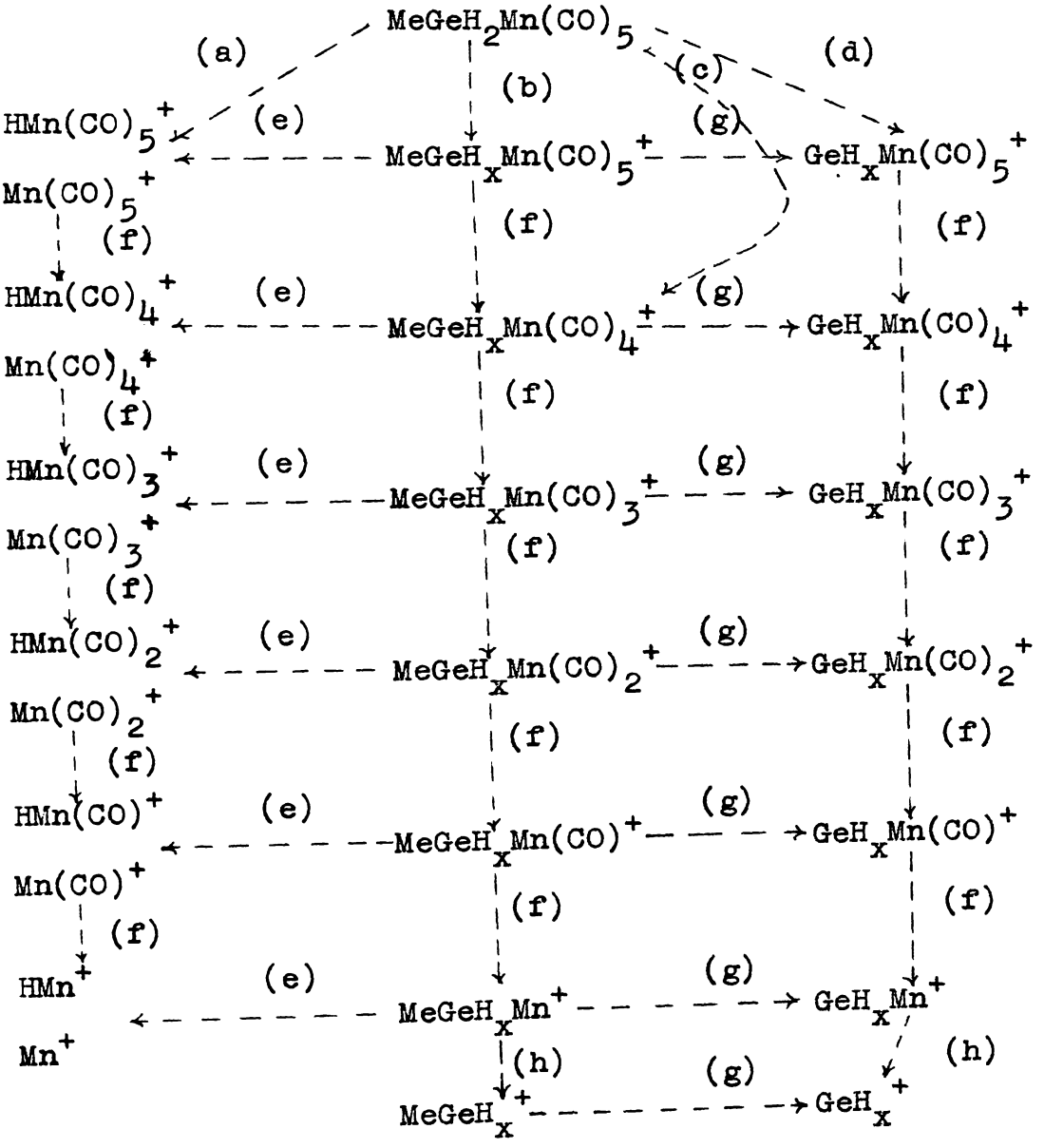
In the $MeGeH_xMn(CO)_n^+$ families of ions the loss of hydrogen is not very significant for n=5 and 4, more significant for n=2,1, and 0, and considerably more significant when n=3. Thus, the ratio of $MeGeH_2Mn(CO)_n^+$: $MeGeHMn(CO)_n^+$:$MeGeMn(CO)_n^+$ is 10.0:0.7:0.7 for n=4, 10.0:2.8:6.4 for n=0, and 3.3:3.3:10.0 when n=3. The situation is similar in the $GeH_xMn(CO)_n^+$ families in that,

while H loss appears to be on the whole more important than in the methyl-containing ions, those ions in which it is most significant are $GeH_xMn(CO)_3^+$, $GeH_xMn(CO)^+$, and GeH_xMn^+. The rearrangement ions, $HMn(CO)_n^+$, $MeMn(CO)_n^+$, and $GeH_3Mn(CO)_n^+$, on the whole give rather weak peaks, as might be expected.

In Fig. 3.3 the probable major fragmentation routes of $MeGeH_2Mn(CO)_5$ are shown. These are quite tentative, however, as none of the proposed routes to each ion are supported by metastable peaks, which were not observed in the spectrum. Hydrogen loss is not represented in the diagram for simplicity, but may be expected from any of the GeH-containing ions, by elimination of a single hydrogen radical, or loss of molecular hydrogen. The $MeMn(CO)_n^+$ ions are also not shown, and these are probably due to GeH_x elimination from the appropriate ions. Another possible fragmentation route which is not shown is the simultaneous loss of more than one carbonyl group from any of the appropriate ions. This has been reported for a number of metal carbonyl compounds (103,104,105), and in the mass spectra of $Me_9Si_4Mn(CO)_5$ and $Me_3SiCo(CO)_4$ metastable peaks have been observed (106) for the loss of two and three carbonyl groups, respectively, from some ions.

Figure 3.3.

Probable Fragmentation Routes of $MeGeH_2Mn(CO)_5$



(a) elimination of $MeGeH_x^-$

(b) elimination of e^-

(c) elimination of CO^-

(d) elimination of CH_2^-, CH_3^-, etc.

(e) elimination of $MeGeH_x$

(f) elimination of CO

(g) elimination of CH_2, CH_3, etc.

(h) elimination of Mn

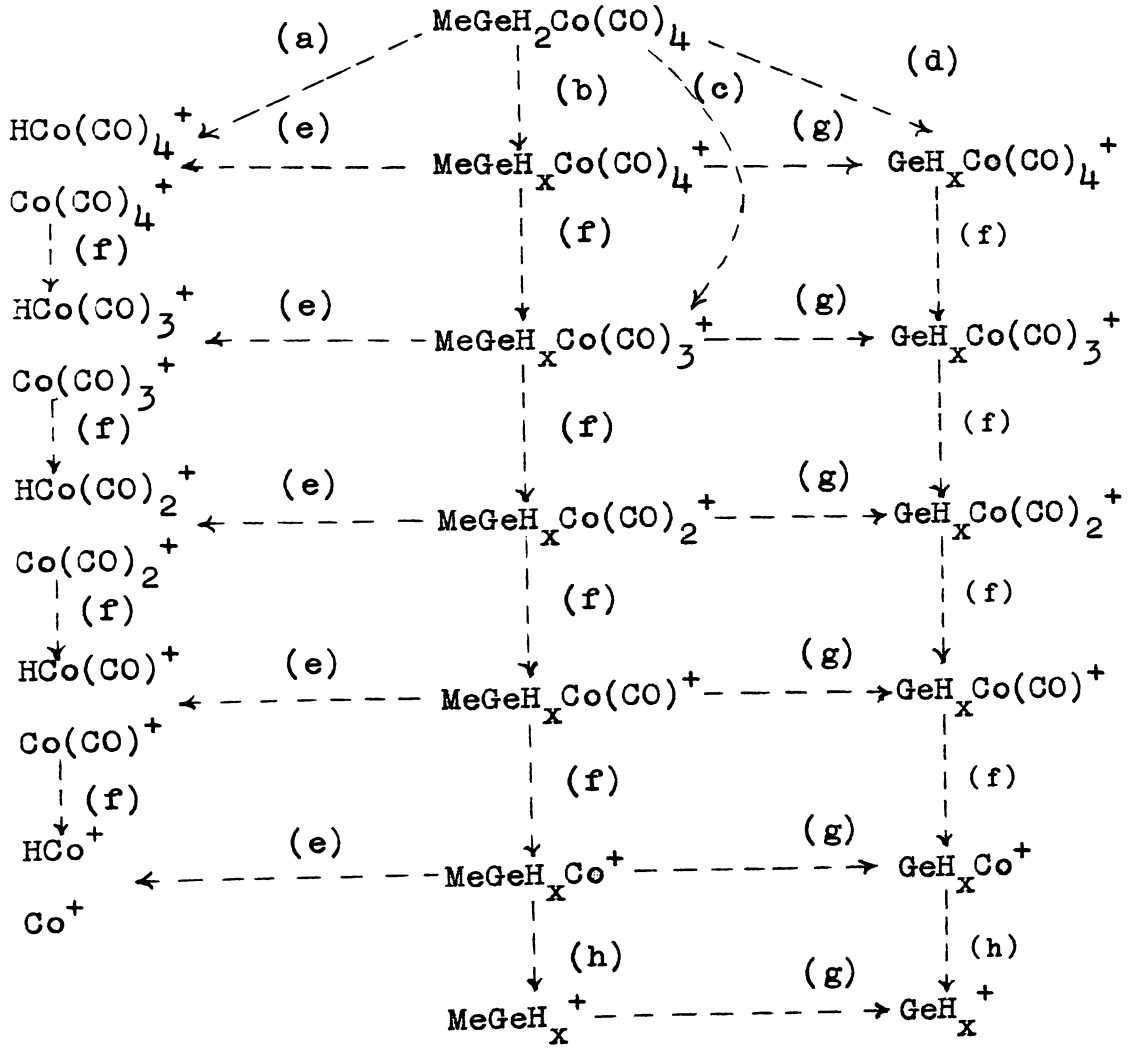
Similar fragmentation patterns were observed for the cobalt compound. Thus, the strongest families are in the $MeGeH_xCo(CO)_n^+$ (n = 4 to 0) series, with the $GeH_xCo(CO)_n^+$ ions being the next strongest. The $Co(CO)_n^+$ and $HCo(CO)_n^+$ ions were also observed as relatively weak peaks, and the $MeCo(CO)_n^+$ ions were weaker still.

The fragmentation pattern of $MeGeH_2Co(CO)_4$ is shown in Fig. 3.4. Again no metastable peaks were detected so that none of the proposed routes are supported by these transitions. Hydrogen loss, the formation of $MeCo(CO)_n^+$ ions, and fragmentation by multiple CO loss are not shown.

There are some interesting differences between the fragmentation patterns of the two compounds. Significantly, Ge-Co cleavage appears to be more strongly favoured than Ge-Mn cleavage. Thus, of the total ion current carried by metal-containing ions in each of these spectra, only 44% is carried by ions containing both Ge and Co, while 72% is carried by ions with both Ge and Mn present. This possibly reflects the relative M-M' bond strengths in these compounds, but interpretations of such results in this way should always be made with some caution, and this point will be discussed

Figure 3.4.

Probable Fragmentation Routes of $MeGeH_2Co(CO)_4$



(a) elimination of $MeGeH_x^-$

(b) elimination of e^-

(c) elimination of CO^-

(d) elimination of CH_2^-, CH_3^-, etc.

(e) elimination of $MeGeH_x$

(f) elimination of CO

(g) elimination of CH_2, CH_3, etc.

(h) elimination of Co

in more detail later. Another significant difference between the two fragmentation patterns is the greater proportion of hydrogen removal in the $MeGeH_xCo(CO)_n^+$ and $GeH_xCo(CO)_n^+$ ions, compared with the corresponding manganese ions. Thus $MeGeCo(CO)_n^+$ and $GeCo(CO)_n^+$ are the most important ions, in the GeH_x-containing series, for n = 2,1 and 0, whereas in the manganese system this is only the case for the GeH_xMn^+ family and $MeGeH_xMn(CO)_3^+$.

Finally, the rearrangement ions $HM(CO)_n^+$ and $MeM(CO)_n^+$ (M = Mn,Co) appear to be less favoured in the cobalt system. For example $Mn(CO)^+$ is about 4.5 times as intense as $HMn(CO)^+$, whereas $Co(CO)^+$ is 8.5 times as strong as $HCo(CO)^+$. Similarly the total relative intensity of the $MeCo(CO)_n^+$ ions is 1.7, while that of $MeMn(CO)_n^+$ is 7.2. These differences probably reflect the relative stabilities of the hydride and methyl derivatives of the manganese and cobalt carbonyls.

Both of these spectra are quite similar to those of some related group IV-transition metal compounds. Thus, in the $H_3GeM(CO)_n$ (M = Mn, Re, $\frac{Fe}{2}$, Co) compounds (19,38,77,78) fragmentation by CO and H loss and Ge-M cleavage are all observed. From chemical and other

physical studies an approximate order of stability of these compounds is $Co < \frac{Fe}{2} < Mn < Re$ and it is interesting to compare this order with the fragmentation data. That is, in the spectra of these compounds the percentage of ion current carried by compounds containing both metal atoms is 77% for Co, 79% for Mn, 47% for Re, and in the iron compound 57% of the ion current is carried by Ge_2Fe fragments and a further 26% by GeFe-containing ions. The two methylgermyl derivatives in this study appear to show similar stabilities to their GeH_3 analogues, and yet the corresponding % values are 44% and 72% for $MeGeH_2Co(CO)_4$ and $MeGeH_2Mn(CO)_5$, respectively. Thus it is obvious that this data cannot be directly related to the M-M' bond strength in these compounds.

In a mass spectral study (107) of the series of compounds $Me_3M'M(CO)_3Cp$ (M = Cr,Mo,W; M' = Ge,Sn) the fraction of ions retaining both M and M' was:

Cr-Ge (16%), Mo-Ge (34%), W-Ge (57%)

Cr-Sn (22%), Mo-Sn (53%), W-Sn (80%)

and it was suggested by Lappert *et al.* that these values might possibly be interpreted in terms of the relative M-M' bond strengths. In this case appearance potential measurements were also made and the calculated bond

dissociation energies were (in eV):

Cr-Ge	2.03	Cr-Sn	2.32
Mo-Ge	2.60	Mo-Sn	3.08
W -Ge	2.81	W -Sn	3.28

so that within the series of the Ge or Sn compounds it does appear that the relative ion abundances may be related to the M-M' bond energies. Since the data are not comparable between the two series of compounds, however, other factors must be important as well.

It is not surprising that the above data for the $H_3GeM(CO)_n$ and $MeGeH_2M(CO)_n$ compounds are inconsistent with the observed stabilities of these compounds. It has often been emphasised (101,102) that there is a danger in relating mass spectral fragmentation patterns to thermodynamic data because there are so many factors other than bond strengths that may be involved in the production of particular ions. That is, this will be determined to some extent by the stabilities of the ions themselves, and also by the stabilities of the neutral species lost in forming the ions. For example, in organometallic compounds of the group IV elements ($M'R_4$), CH_4, CH_2, and H_2 elimination are usually strongly favoured

processes, regardless of the relative bond strengths in the parent ions (8,101). The rate at which fragmentation occurs may also be important, and in addition the spectra will be affected by the particular conditions under which they are recorded. In the above series of group VI transition metal derivatives most of these factors are eliminated within the Ge or Sn series so one may expect a correlation between the calculated bond dissociation energies and the fragmentation data, as was observed. In the germanium hydride derivatives also considered above this is not the case as there are greater physico-chemical differences between most of the compounds, and no correlation is observed.

The mass spectra of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ have not produced any unexpected features. Thus in the related $H_3GeM(CO)_n$ and $H_3SiM(CO)_n$ compounds (18,19,37, 38) the major fragmentation processes have been competitive CO and H loss, and M-M' cleavage. Similarly in compounds such as the $Me_3M'M(CO)_3Cp$ series discussed previously (107) methyl and CO loss, and M-M' cleavage are all competitive processes, with removal of Cp being much less favoured. Rearrangement ions such as $HM(CO)_n^+$ and $MeM(CO)_n^+$ are quite

common for the hydride and methyl derivatives, respectively, and in the spectra of polysilanyl derivatives, such as $Me_3Si(SiMe_2)_nFe(CO)_2Cp$ (n = 1,2,3; ref. 71) and $Me_3Si(SiMe_2)_nMn(CO)_5$ (n = 1,2; ref. 106), the observation of ions such as $Me_3Si(SiMe_2)_{n-1}Fe(CO)_n,Cp^+$ and $Me_3Si(SiMe_2)_{n-1}Mn(CO)_{n'}^+$ are approximately analogous to the $H_3GeM(CO)_n^+$ ions in the $MeGeH_2M(CO)_n$ (M = Mn,Co) spectra.

As other workers (19) have already noted, there is an interesting difference between the fragmentation of germyl groups attached to transition metals and those in the related polygermanes. Thus, in R_3GeX compounds (19,101) hydrogen removal is often one of the major fragmentation processes, as the R groups appear to be removed roughly in the order of R-Ge bond strengths. This is a rather simplified view of course, as when R = Ph, for example, the stabilisation by this group of the ions or radicals formed in the fragmentation processes becomes a significant factor. In the case of the $H_3GeM(CO)_n$ compounds, however, and as has been seen here for the $MeGeH_2$- derivatives, hydrogen atom removal is much less significant, and this suggests some sort of stabilisation by the transition metal moieties. The effect is probably not a bond energy one as the chemical

reactivity of the Ge-H bond is much the same in $H_3GeM(CO)_n$ and H_3GeX compounds (see chapter 4), but it may be related to stabilisation of the ions and radicals formed in the fragmentation processes. Another possible explanation may be the kinetics involved in the particular fragmentations of the ions.

Finally, an attempt has been made by Saalfeld et al. (29,108) to relate mass spectral fragmentations to bonding interactions in the M-M' bond. These workers have used molecular structure data from X-ray and electron diffraction studies and mass spectral data, combined with molecular orbital calculations, to demonstrate the presence of (d—d) π-bonding in the Si-Co bond, and intramolecular interactions between silicon and the equatorial carbonyl groups in silyl derivatives of cobalt carbonyl (i.e. $R_3SiCo(CO)_4$, ($R_3 = F_3, Cl_3, MeF_2, Me_3$).

These workers calculated the ratios of $Co(CO)_n^+$/ $R_3SiCo(CO)_{n-1}^+$ from the mass spectral data for n = 4,3,2,1, and the results were taken as an indication of the relative Si-Co and OC-Co bond strengths. Such an interpretation must be made with the same reservations discussed earlier in the text. In addition, this is based on a rather simplified idea of the fragmentation of the various ions in that it assumes that the only processes to be considered are:

$$R_3SiCo(CO)_n^+ \longrightarrow R_3SiCo(CO)_{n-1}^+ + CO$$

$$R_3SiCo(CO)_n^+ \longrightarrow Co(CO)_n^+ + R_3Si.$$

No allowance has been made for any of the following fragmentations, which will all affect the observed intensities of the $R_3SiCo(CO)_{n-1}^+$ and $Co(CO)_n^+$ ions, and therefore the validity of the interpretation.

$$R_3SiCo(CO)_n^+ \longrightarrow R_3Si^+ + Co(CO)_n$$

$$R_3SiCo(CO)_n^+ \longrightarrow CO^+ + R_3SiCo(CO)_{n-1}$$

$$R_xSiCo(CO)_n^+ \longrightarrow Co(CO)_n^+ + R_xSi \quad (x = 0,1,2)$$

$$R_3SiCo(CO)_n^+ \longrightarrow R_3SiCo(CO)_{n-y}^+ + yCO \quad (y = 2,3)$$

With the above reservations in mind it is still interesting to compare the present results with those of Saalfeld *et al.* This comparison is made in Table 3.9. It is probably not valid to include the manganese compound in this table, and, as can be seen, the results for this compound are quite different from those of the cobalt derivatives. The comparison of $MeGeH_2Co(CO)_4$ with the other cobalt compounds is quite good and Mackay *et al.* (19) have reported a similar result for $H_3GeCo(CO)_4$.

Table 3.9.

Mass Spectral Analysis According to the Method of Saalfeld et al. (108)

	$F_3SiCo(CO)_4$	$Cl_3SiCo(CO)_4$	$MeSiF_2Co(CO)_4$	$Me_3SiCo(CO)_4$	$MeGeH_2Co(CO)_4$(a)	$MeGeH_2Mn(CO)_5$(a)
$M(CO)_5^+/RM(CO)_4^+$						0.01
$M(CO)_4^+/RM(CO)_3^+$	0	0	0	0	0.04	0.36
$M(CO)_3^+/RM(CO)_2^+$	0	0	0	0	0.22	0.12
$M(CO)_2^+/RM(CO)^+$	4.30	0.76	0.83	4.64	6.23	0.53
$M(CO)^+/RM^+$	1.51	0.86	0.65	2.20	3.06	0.15

(a) This work. The ratios are calculated for $MeGeH_2M(CO)_n^+$, not $MeGeH_xM(CO)_n^+$ ions.

3.3.4. The Vibrational Spectra of Methylgermyl-pentacarbonylmanganese and Methylgermyl-tetracarbonylcobalt.

The vibrational spectra of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ are listed in tables 3.10 and 3.11, respectively. The infrared spectra of gaseous samples were recorded between 400 and 4000 cm^{-1}, while raman spectra were measured with liquid samples from 20 to 2200 and 20 to 800 cm^{-1} for the manganese and cobalt compounds, respectively. When the infrared spectrum of $MeGeH_2Co(CO)_4$ was recorded decomposition took place, producing additional bands in the CO-stretching region. These were identified by recording the spectrum at regular intervals for about twelve hours, and this enabled the identification of those bands in the spectrum due to the original compound. Decomposition of the cobalt compound was also a problem when the raman spectrum was recorded. The liquid sample darkened rapidly in the laser beam and absorbed sufficient energy so that it "boiled" out of the light path. Thus, the spectrum had to be recorded a number of times with cooling of the sample in between.

TABLE 3.10

Vibrational Spectrum of $MeGeH_2Mn(CO)_5$

IR (gas)	Raman (liquid)	Assignment
2963 w 2926 w 2877 w		C-H stretches (2a' + a")
2107 m	2106 s,p	CO stretches (3a' + 2a"), Ge-H stretches (a' + a")
2029 vs	2031 s,p	
2018 vs	2012 s	
1985 w		^{13}CO stretch
1460 w		CH_3 assymmetric deformation (a")
1080 w 1035 w		combination bands?
877 w 838 s	881 w	CH_3 rocks (a' + a"), GeH_2 bend (a')
695 w,sh 670 s,sh 660 s		Mn-C-O bends (5a' + 5a"), GeH_2 wags (a' + a")

TABLE 3.10 (cont'd).

IR (gas)	Raman (liquid)	Assignment
609 w,br		
583 m	582 w	Ge-C stretch (a')
482 m		
	429 s,sh	Mn-C stretches (3a' + 2a")
	416 s,p	
	220 s,p	Mn-Ge stretch (a')
	169 w	skeletal bending modes (5a' + a")
	109 s,br	

TABLE 3.11

Vibrational Spectrum of $MeGeH_2Co(CO)_4$

IR (gas)	Raman (liquid)	Assignment
2994 w		C-H stretches (2a' + a")
2931 w		
2868 w		
2106 s		CO stretches (3a' + a"), Ge-H stretches (a' + a")
2047 vs		
2017 vs		
2012 vs		
1982 m		^{13}CO stretch
1425 w,br		CH_3 assymmetric deformation (a")
1248 w		CH_3 symmetric deformations (2a')
1137 w,br		combination bands?
1060 w,br		
877 m		CH_3 rocks (a' + a"), GeH_2 bend (a')
873 m,sh		
843 m		
838 m,sh		
831 s		

TABLE 3.11 (cont'd)

IR (gas)	Raman (liquid)	Assignment
702 m		GeH_2 wags
691 sh		(a' + a")
615 w		Ge-C stretch (a')
587 m	594 w	
549 s		Co-C-O deformations
542 s,sh		(4a' + 4a")
	525 w	
504 m		Co-C stretches
485 m		(3a' + a")
413 vw	421 s,p	
393 m		GeH_2 rocks (a' + a")
	262 w	
	221 s,p	Co-Ge stretch (a')
	158 w	skeletal bending
	80 s,p	modes
	38 w	(4a' + 5a")

Even with this method, however, the relative intensities given in the table for the raman spectrum of $MeGeH_2Co(CO)_4$ may not be very meaningful. The spectra of both compounds should contain similar absorptions due to the $MeGeH_2$-moiety so that it will be convenient to consider the two sets of results together.

Both $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ may be assumed to have C_s symmetry and will possess 48 and 42 fundamental modes of vibration, respectively. Obviously all of these vibrations have not been distinguished in the spectra so that complete assignments can not be made. However, Mackay et al. (19,38) have found that in the case of $H_3GeMn(CO)_5$ and $H_3GeCo(CO)_4$ qualitative assignments of the observed vibrational spectra can be made by comparison with the spectra of other compounds containing the H_3Ge, $Mn(CO)_5$, and $Co(CO)_4$ moieties. Thus, it should also be possible to do this for the similar $MeGeH_2$ derivatives, and this has been used as the basis for the assignments given in the tables.

The vibrations due to the $MeGeH_2$ group can be assigned partially on the basis of similarities between the spectra of the two compounds and also by comparison with the reported spectra of other $MeGeH_2X$ compounds (109,110,111). Thus, the three weak absorptions between

2860 and 3000 cm^{-1} which occur in both spectra are in the region normally observed for C-H stretching vibrations. Absorptions due to the CH_3 symmetric and assymmetric deformations can be expected at about 1220-1260 cm^{-1} and 1420-1460 cm^{-1}, respectively. These are both observed as weak absorptions at 1248 and 1425 cm^{-1} in the infrared spectrum of the cobalt compound, while only the latter is present as a weak absorption at 1460 cm^{-1} for the manganese compound.

The methyl rock vibrations and a GeH_2 assymmetric deformation mode (bend) should occur between 800 and 900 cm^{-1}. Both compounds show a number of bands in this region but a more exact assignment is not possible. Other deformation modes of the GeH_2 group should be observed at ca. 700 cm^{-1} (GeH_2 wag) and ca. 400 cm^{-1} (GeH_2 rock). In the manganese compound these two vibrations have not been observed, although the GeH_2 wag absorptions could lie under the much stronger metal carbonyl deformation modes at ca. 695 cm^{-1}. For $MeGeH_2Co(CO)_4$ the GeH_2 deformations are assigned to the absorptions at 702, 691 and 393 cm^{-1}.

The germanium-carbon stretching vibration is usually observed between 550 and 650 cm^{-1} and for

$MeGeH_2Mn(CO)_5$ this is assigned to the medium intensity absorption at 583 cm^{-1} in the infrared and the weak counterpart at 582 cm^{-1} in the raman spectra. The weak band at 594 cm^{-1} in the raman spectrum of $MeGeH_2Co(CO)_4$ may also be assigned to this vibration, but in the infrared spectrum of the cobalt compound no assignment is possible because of the presence of the metal carbonyl deformation modes in the same region. Finally, the Ge-H stretching vibrations should be present as strong bands near 2035 cm^{-1} in the spectra of both compounds. However these are swamped by the much stronger carbonyl stretching bands in the same region, and no particular absorptions can be assigned to the Ge-H stretches in any of the spectra.

Most of the remaining absorptions observed in the spectra can be assigned to vibrations of the metal carbonyl moieties. For $MeGeH_2Mn(CO)_5$ there is a good comparison with the corresponding vibrations observed for $H_3GeMn(CO)_5$ (38) and this supports the assumption that the $Mn(CO)_5$ moiety retains its local C_{4v} symmetry in these molecules. Thus, the carbonyl stretches are observed at 2107, 2029, and 2018 cm^{-1} in the infrared spectrum of $MeGeH_2Mn(CO)_5$, while in the parent germyl compound these are assigned

to absorptions at 2115, 2022, and 2019.5 cm^{-1}. In the latter spectrum the bands were assigned to the a_1, a_1, and e modes respectively (for C_{4v}), and the raman polarisation data for the methylgermyl compound suggests that the same assignment can be made in the present case. If the C_{4v} symmetry had not been retained in this compound five absorptions would have been required for the 3a' + 2a" modes predicted for C_s symmetry.

The carbonyl deformation modes, and metal carbon stretches in $MeGeH_2Mn(CO)_5$ are also comparable with those of $H_3GeMn(CO)_5$ (38,112). In the former compound the MnCO bends are assigned to bands at 695, 670, and 660 cm^{-1} in the infrared spectrum, while for the latter compound these bands appear at 685, 672, and 663 cm^{-1}. Similarly the Mn-C stretching modes are observed at 482 (IR), 429, and 416 (raman) cm^{-1} for the $MeGeH_2$ compound, and at 497, 474 (IR), 437, and 409 (Raman) cm^{-1} for the H_3Ge derivative. Polarisation data indicate that the 416 and 409 cm^{-1} vibrations are of a_1 or a' symmetry. The weak absorptions at 1080 and 1035 cm^{-1} in the infrared spectrum of $MeGeH_2Mn(CO)_5$ also have counterparts in the infrared spectrum of $H_3GeMn(CO)_5$ at 1090, and 1040 cm^{-1}. These could be combination bands involving funda-

mental vibrations of the $Mn(CO)_5$ moiety. Another absorption at 1985 cm^{-1} in the infrared spectrum of $MeGeH_2Mn(CO)_5$ can be assigned to vibrations of ^{13}CO.

In the spectra of $MeGeH_2Co(CO)_4$ there is significant evidence for a lowering of symmetry of the $Co(CO)_4$ moiety from C_{3v} to C_s. For $H_3GeCo(CO)_4$ (19) three carbonyl stretching vibrations were observed in the infrared spectrum at 2109, 2046, and 2025 cm^{-1}, corresponding to the $2a_1 + e$ modes expected for C_{3v} symmetry. In the spectrum of the $MeGeH_2$ derivative the first two bands are present at 2106 and 2047 cm^{-1}, but the third absorption is split into two bands at 2017 and 2012 cm^{-1}. This corresponds to loss of the degeneracy of the e mode in going from C_{3v} to C_s symmetry ($e \longrightarrow a' + a''$, ref. 113) and has also been observed in the infrared spectrum of $MeSiH_2Co(CO)_4$ (98). Further to this, there are more absorptions in the vibrational spectra of $MeGeH_2Co(CO)_4$ in the regions expected for the CoCO deformation and Co-C stretching modes (ca. 400 - 600 cm^{-1}, ref. 19,35,114) than in the corresponding regions of the spectra of $H_3GeCo(CO)_4$. This could also be indicative of loss of the degeneracy of the e modes in these vibrations, but since assignment of the individual bands is not possible no definite conclusions

can be made in this respect.

The low frequency vibrations in the spectra of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ include the M-M' stretching modes and a number of skeletal deformation modes (CMC and GeMC bends, and torsional vibrations). In the parent H_3Ge compounds the Ge-Mn and Ge-Co stretching modes were observed at 219 and 224 cm^{-1}, respectively, so that the strong bands observed in the raman spectra at 220 and 221 cm^{-1} can be assigned to the corresponding vibrations in the $MeGeH_2$ derivatives. The polarisation data support this assignment also, as these vibrations are of a' symmetry. None of the remaining bands in this region can be assigned to any particular vibrations.

CHAPTER 4

REACTION STUDIES OF GROUP IV-TRANSITION METAL COMPOUNDS - PART I

4.1. INTRODUCTION AND GENERAL REVIEW

Up until the last five years or so reaction studies of group IV-transition metal compounds were relatively neglected. Interest in this aspect is now increasing, however, and reaction studies of these compounds should become increasingly important in the development of a clear understanding of their chemical nature. The most recent reviews (2,3,11) include some of the more specific reaction studies that were carried out prior to 1971, and, as with the preparative aspects covered in chapter 2, the following discussion will emphasise the more recent examples.

It is possible to classify many of the reactions of group IV-transition metal compounds into three categories, depending on the position in the molecule at which the reaction occurs. Thus, in the $R_3M'-ML_n$ system the three general classes of reactions likely to be observed are:

i) Reactions of M'-R

ii) Reactions of M'-M

iii) Reactions of ML_n,

and these will be discussed, with examples, in the following sections of this chapter.

4.1.1. Reactions of M'-R and M'-M

These reactions are to some extent complementary to each other in that the same reagents can participate in either reaction with different compounds, or with the same compound under different reaction conditions. For example bromine readily cleaves the metal-metal bond of $Ph_3GeMn(CO)_5$ in an n-heptane/benzene (1:1) solution at room temperature in 2 to 3 h,

$$Ph_3GeMn(CO)_5 + Br_2 \longrightarrow Ph_3GeBr + BrMn(CO)_5,$$

while, under the action of three equivalents of bromine in dibromoethane, substitution of the phenyl groups occurs when the temperature is raised from 20° to 130°C over 5 h (115),

$$Ph_3GeMn(CO)_5 + 3Br_2 \longrightarrow Br_3GeMn(CO)_5 + 3PhBr.$$

As well as being dependent on reaction conditions, the path taken by any of these reactions will be determined by a number of factors, including the relative energies of the bonds being formed and those being broken, and

also on the nature of the reagent. This leads to a number of useful comparisons, especially as regards relative bond strengths. Thus, in $H_3SiMn(CO)_5$ the Si-Mn bond is unaffected by HCl, while in $H_3SiCo(CO)_4$ the Si-Co bond is cleaved by the same reagent under similar conditions, and this suggests that the Si-Co bond may be weaker or more polar than the Si-Mn bond.

i.e. $H_3SiMn(CO)_5 + xHCl \longrightarrow H_{3-x}Cl_xSiMn(CO)_5 + xH_2$ (37)

$(x = 1,2)$

$H_3SiCo(CO)_4 + HCl \longrightarrow H_3SiCl + HCo(CO)_4$ (18)

The halogens and hydrogen halides are common reagents for these reactions, the former usually being more vigorous than the latter. This is demonstrated by Clark *et al.* (116) who find that the Sn-Mn bond in $Me_3SnMn(CO)_5$ is cleaved by Cl_2 and I_2, while HCl, HBr, and HI give methyl substitution, under similar conditions.

i.e. $Me_3SnMn(CO)_5 + X_2 \longrightarrow Me_3SnX + XMn(CO)_5$

$Me_3SnMn(CO)_5 + HX \longrightarrow Me_2XSnMn(CO)_5 + \text{hydrocarbon.}$

Other commonly-used reagents are the organic and inorganic halides, and again the course of the reactions with these reagents varies from compound to compound.

Carbon tetrachloride is a relatively mild reagent and as observed in this work (see chapter 3, and part 2

of this chapter) is a useful reagent for chlorination of group IV-hydride compounds. Such reactions have been observed with group IV-transition metal compounds also, and the most recent example is that reported by King *et al.* (71).

$$Me_2SiHFe(CO)_2Cp + CCl_4 \longrightarrow Me_2SiClFe(CO)_2Cp + CHCl_3.$$

By comparison, the Zr-Si bond in the recently reported d^0 compound, $Ph_3Si(Cl)ZrCp_2$, is cleaved by $CDCl_3$ within 24 h (117), even though this compound shows appreciable thermal stability.

$$Ph_3Si(Cl)ZrCp_2 + CDCl_3 \longrightarrow Cl_2ZrCp_2 + ?$$

Trifluoroiodomethane has been reported (116) to give both methyl substitution and Sn-Mn cleavage in its reaction with $Me_3SnMn(CO)_5$,

$$Me_3SnMn(CO)_5 + CF_3I \longrightarrow Me_3SnI\ (40\%) + IMn(CO)_5\ (13\%) + Me_2ISnMn(CO)_5\ (30\%) + C_2F_6,$$

while 1,2-dibromoethane has been observed to quantitatively cleave the metal-metal bond in the same compound (118), and in a similar germyl complex of platinum (50).

$$Me_3SnMn(CO)_5 + C_2H_4Br_2 \longrightarrow Me_3SnBr + C_2H_4 + BrMn(CO)_5$$

$$Ph_3Ge(H)Pt(diphos) + C_2H_4Br_2 \longrightarrow Br_2Pt(diphos) + Ph_3GeH + C_2H_4.$$

A mechanism for this latter reaction is discussed.

Other organic halides that have been used in similar reactions are MeI, EtCl, C_6F_5Br, CF_3COCl (118) and $C_2H_4Cl_2$ (119).

The mercuric halides and organomercurial halides have been reported to give a number of metal-metal bond cleavage reactions, and those of the latter class of compounds also produce some unusual organomercury derivatives as byproducts.

e.g. $Ph_3Si(Cl)ZrCp_2 + HgCl_2 \longrightarrow Ph_3SiCl + Hg + Cl_2ZrCp_2$ (117)

$Me_3SnM(CO)_3Cp + HgX_2 \longrightarrow Me_3SnX + XHgM(CO)_3Cp$ (120)

(M = Mo, W; X = Cl,Br,I)

$Me_3SnFe(CO)_2Cp + MeHgCl \longrightarrow Me_3SnCl + MeHgFe(CO)_2Cp$ (121)

$\downarrow$

$Me_4Sn + Me_2Hg + Hg[Fe(CO)_2Cp]_2$

$+ ClHgFe(CO)_2Cp$

An R-substitution reaction has also been reported for the mercuric halides (120).

$(CH_2{=}CHCH_2)_3SnM(CO)_3Cp + HgX_2 \longrightarrow$

$CH_2{=}CHCH_2HgX + (CH_2{=}CHCH_2)Sn(X)M(CO)_3Cp$

(M = Mo,W; X = Cl,Br,I)

Metal-metal cleavage reactions have been observed with $TiCl_4$, $ZnCl_2$ (121), and $MgCl_2$ (122), producing some interesting grignard reagents in the latter case.

$$Me_3SnFe(CO)_2Cp + TiCl_4 \longrightarrow Me_3SnCl + Cl_3TiFe(CO)_2Cp$$

$$Me_3SnMn(CO)_5 + ZnCl_2 \longrightarrow Me_3SnCl + ?$$

$$R_3GeM(CO)_3Cp + MgBr_2 \xrightarrow{THF} R_3GeBr + Cp(CO)_3MMgBr(THF)$$

(M = Mo,W; R = Me,Et)

A number of organo or halide derivatives of the group IV metals have been used in what may be classified as M'-R substitution, and M-M' cleavage reactions, but are more commonly called redistribution and exchange reactions. Thus with $Me_3SnMn(CO)_5$ in $M'Cl_4$ solution (M' = C,Si,Ge,Sn), substitution of the methyl groups was observed to take place quite rapidly with $SnCl_4$, very slowly with $GeCl_4$, and not at all in $SiCl_4$ and CCl_4 (118).

i.e. $Me_3SnMn(CO)_5 + xSnCl_4 \longrightarrow Me_{3-x}Cl_xSnMn(CO)_5 + xMeSnCl_3$

(x = 3,2,1)

This behaviour is consistent with the report by Ebsworth et al. (95) of the use of $SnCl_4$ as a selective chlorinating agent. A similar reaction has been reported between $Me_3SnFe(CO)_2Cp$ and $SnCl_4$ (121).

$$Me_3SnFe(CO)_2Cp + SnCl_4 \longrightarrow Cl_3SnFe(CO)_2Cp + Me_3SnCl$$

In the same report two related reactions using silyl halides are mentioned in which Si-Fe bonds are formed.

$$Me_3SnFe(CO)_2Cp + Me_3SiCl \longrightarrow Me_3SnCl + Me_3SiFe(CO)_2Cp$$

$$Me_3SnFe(CO)_2Cp + SiCl_4 \longrightarrow Me_3SnCl + Cl_3SiFe(CO)_2Cp$$

The latter result suggests that the above reaction between $Me_3SnFe(CO)_2Cp$ and $SnCl_4$ need not proceed by stepwise chlorination but could involve a direct M-M' cleavage to give the same product. Further examples of this latter type of reaction are reported by Clemmit and Glockling (50) and Glockling and Irwin (123) for compounds of platinum and iridium respectively, but in these cases the reactions probably proceed by oxidative addition mechanisms which are not very likely in the iron and manganese compounds considered above.

Some interesting redistribution reactions have also been reported recently by Clark and Hunter (124), and these workers propose that the reactions may proceed through a four-centre transition state.

$$Me_3M'Mn(CO)_5 + Me_3SnCF_3 \longrightarrow CF_3Me_2SnMn(CO)_5 + Me_4M'$$
$$(M' = Ge,Sn)$$

$$CF_3Me_2SnMn(CO)_5 + Me_3SnMn(CO)_5 \longrightarrow Me_2Sn[Mn(CO)_5]_2 + Me_3SnCF_3$$

The reactions of halide compounds of boron and phosphorus with some group IV-transition metal compounds have also been investigated. The Si-Co bond in $H_3SiCo(CO)_4$

is cleaved by PF_3, probably to give the products shown (125).

$$H_3SiCo(CO)_4 + PF_3 \longrightarrow H_3SiF + PF_2Co(CO)_4$$

On the other hand no reaction was observed between this reagent and $Me_3SiCo(CO)_4$ even when the temperature was raised to 100° (25). No reaction was observed with PF_5 at room temperature either, while $MeSiH_2Co(CO)_4$ is reported to give $MeSiF_2Co(CO)_4$ under similar conditions (72,126). The mechanism suggested for this reaction involves more than one step, and is necessary to explain all of the observed products.

$$MeSiH_2Co(CO)_4 + PF_5 \longrightarrow MeSiF_2H + PF_3 + HCo(CO)_4$$

$$HCo(CO)_4 + MeSiF_2H \longrightarrow MeSiF_2Co(CO)_4 + H_2$$

$$HCo(CO)_4 + xPF_3 \longrightarrow HCo(CO)_{4-x}(PF_3)_x + xCO$$

As shown in this last equation, PF_3 can also function as a ligand on the transition metal, and some reactions of the group IV-transition metal compounds with this reagent have produced such complexes. These reactions will be considered in part 4.1.2.

The boron trihalides have been used in a similar manner to the group IV halides in the halogenation of some silanes and germanes (127,128), and it might be expected that similar reactions would be observed with

the transition metal compounds. However, no reaction has been observed between BF_3 and either $Me_3SiCo(CO)_4$ or $MeSiH_2Co(CO)_4$ (25,72) under mild conditions. Clark *et al.* (116) report a reaction with $Me_3SnMn(CO)_5$ in which the Sn-C bonds appear to be cleaved, but the final product observed in the reaction must be formed by a further reaction with the reagent.

$$Me_3SnMn(CO)_5 + BF_3 \longrightarrow MeBF_2 (+Me_2BF) + Me_2SnFMn(CO)_5$$

$$Me_2SnFMn(CO)_5 + BF_3 \longrightarrow [Me_2SnMn(CO)_5]BF_4$$

The same product can be formed by treating $Me_2SnClMn(CO)_5$ with $AgBF_4$.

A novel reaction has recently been reported (129) in which BF_4^- is used as a fluorinating reagent, rather than in its usual role of a large stabilising anion. Thus, treatment of compounds of the form $R_{3-n}Cl_nM'ML_m$ with $AgBF_4$ in either coordinating or non-coordinating solvents produces the fluoro-substituted compounds, with precipitation of AgCl and elimination of BF_3.

i.e. $R_{3-n}Cl_nM'ML_m + nAgBF_4 \longrightarrow R_{3-n}F_nM'ML_m + nAgCl + nBF_3$

(M = Mo,Mn; M' = Ge; R = Ph; n = 1,3)

(M = Fe; M' = Si; n = 3)

(M = Co; M' = Ge; R = Ph; n = 1,3)

(L_m = CO,Cp as appropriate)

The precipitation of AgCl probably provides the driving force for these reactions.

Another type of reaction which may be classified as M-M' cleavage is the insertion reaction. Here the M-M' bond is broken, but both parts of it are retained in the final product molecule. Many examples of this type of reaction have been reported by Clark and his co-workers (130, and references therein) for the insertion of fluorocarbons into group IV-transition metal bonds. Some examples follow:

$$Me_3SiMn(CO)_5 + C_2F_4 \xrightarrow{U.V.} Me_3SiCF_2CF_2Mn(CO)_5$$

$$Me_3GeMn(CO)_5 + F_3C-C\equiv C-CF_3 \xrightarrow{U.V.} Me_3GeC(CF_3)-C(CF_3)=C(CF_3)-C(CF_3)(Mn(CO)_5)$$

Similar reactions have been observed by these workers for $Me_3M'Mn(CO)_5$ (M' = Ge,Sn) and $Me_3M'Fe(CO)_2Cp$ (M' = Si, Ge,Sn) with various fluorinated olefins and acetylenes, usually under free-radical conditions of U.V. irradiation or heating, in non-polar solvents. The products are normally those of insertion into the metal-metal bond, or compounds derived from such products by decomposition.

Some attempts have also been made at inserting small molecules such as CO, CS_2, and SO_2 into metal-metal bonds. Such reactions would be analogous to those of $MeMn(CO)_5$ and other similar compounds, as indeed are the above reactions with fluorocarbons (20). So far, however, such insertion reactions have not been achieved for $H_3SiCo(CO)_4$ (18), $H_3SiMn(CO)_5$ (37), and $Me_3SiMn(CO)_5$ (52), while Carey and Clark (131) find that the reactions of SO_2 with $R_3SnMn(CO)_5$ (R = Me,Ph) produce compounds of stoichiometries $R_3SnMn(CO)_5.xSO_2$, x = 1.5,2.5; but with indeterminate structures.

Finally, there have been a number of reports of adduct-formation reactions between group IV-transition metal compounds and amines (2,3). These are well-established for many of the silyl derivatives in particular, and are quite similar to the reactions of halosilanes with many amines (10). Some of the more recent examples of these reactions have been reported for $H_3SiM(CO)_3Cp$ (M = Cr,Mo,W; ref. 69) and $H_3GeCo(CO)_4$ (19), and, as with most of the adducts reported earlier, these probably have an ionic structure $R_3M':B_m^+\square M(CO)_n\square^-$ (B = base, m = 1,2).

Adduct formation in group IV-transition metal compounds can have a significant effect on the reactivity of the metal-metal bond. This was demonstrated by Aylett and Campbell (125) who found that while $H_3SiMn(CO)_5$ is inert to HCl at room temperature, and only the Si-H bonds are attacked on heating, the pyridine (py) adduct reacts with HCl at -100°C as shown.

$$H_3SiMn(CO)_5.2py + 3HCl \longrightarrow H_3SiCl + HMn(CO)_5 + 2py.HCl$$

Since the adducts usually have a higher thermal stability than the parent group IV-transition metal compounds, this increased reactivity is probably due to the ionisation, or polarisation, of the metal-metal bond, which would facilitate attack by ionic or polarisable reagents.

4.1.2. Reactions of ML_n

Reactions of the ML_n moiety in group IV-transition metal compounds should follow the same sort of pattern as XML_n compounds in general. This has been observed, and of course it is possible in such reactions to determine whether the presence of the group IV ligand has any effect on the rest of the molecule, in comparison with, say, X = CH_3, halogen, *etc.* The following

discussion will be concerned mainly with the metal carbonyl derivatives.

Two of the simplest substitution reactions of metal carbonyls, CO exchange and isomerisation, have recently been studied for $(Cl_3Si)_2Ru(CO)_4$, using ^{13}CO labelling and infrared spectroscopy (132). A further study (133) of the related osmium compounds $(R_3M')_2Os(CO)_4$ (R_3 = Me_3,Me_2Cl,$MeCl_2$,Cl_3; M' = Si; R_3M' = Me_3Sn) has also been carried out using ^1H nmr coalescence studies, and ^{13}CO labelling and infrared spectroscopy. In the ruthenium system evidence was found for a 5-coordinate intermediate in the cis-trans isomerisation, and ^{13}CO exchange occurred by the same mechanism. In the osmium compounds, however, no ^{13}CO exchange was observed and the cis-trans isomerisation was proposed to occur by an intramolecular process.

Carbonyl substitution reactions have been observed on a number of occasions with the group IV derivatives, but as mentioned in 4.1.1. these reactions are not accompanied by insertion into the metal-metal bond. Some of the more recent examples have been reported by Curtis (51) and George (134).

$$Ph_3M'Co(CO)_4 + PPh_3 \xrightarrow{120\text{-}150^\circ C} Ph_3M'Co(CO)_3PPh_3 \quad (51)$$

(M' = Si,Sn)

$$Me_3SnMo(CO)_3Cp + PPh_3 \xrightarrow{160^\circ C} Me_3SnMo(CO)_2(PPh_3)Cp \quad (134)$$

Some kinetic studies (135,136) have recently been carried out on the reactions of $Ph_3GeMn(CO)_5$ and $Ph_3SnMn(CO)_5$ with various phosphines, and these indicate two competing mechanisms in which the rate-determining steps involve slow fission of Mn-CO bonds, and nucleophilic attack by the phosphine on the substrate. Interestingly, Ross et al. (136) also report that with phosphite compounds substitution of the group IV ligand occurs in preference to CO-substitution, and a carbonyl insertion product is ultimately produced.

$$Ph_3SiMn(CO)_5 + P(OR)_3 \longrightarrow RCOMn(CO)_3\,P(OR)_3\,_2 + OP(OSiPh_3)_3$$

A driving force for this reaction may be the formation of the Si-O bonds; and a mechanism for this reaction is also discussed.

Another phosphine compound which has been used in carbonyl substitution reactions is PF_3, which has similar ligand properties to CO. When a mixture of $Me_3SiMn(CO)_5$ and excess PF_3 was irradiated with ultraviolet light for 10 h, a number of products were isolated (52).

$$Me_3SiMn(CO)_5 + PF_3 \longrightarrow Me_3SiMn(CO)_4(PF_3) + Me_3SiMn(CO)_3(PF_3)_2 + Me_3SiMn(CO)_2(PF_3)_3$$

Some trifluorophosphine complexes of rhodium and iridium containing group IV ligands have recently been prepared by two elimination reactions (137), which are analogous to those discussed in chapter 2 for metal carbonyls and related compounds.

$$Ph_3M'Cl + KM(PF_3)_4 \longrightarrow Ph_3M'M(PF_3)_4 + KCl$$

(M' = Sn,Pb; M = Rh,Ir)

$$R_3SiH + M_2(PF_3)_8 \longrightarrow R_3SiM(PF_3)_4 + HM(PF_3)_4$$

(R = Ph,EtO,Cl; M = Rh,Ir)

4.1.3. A Comparison with Organo-derivatives of the Transition Metals

Some of the reactions discussed in sections 4.1.1. and 4.1.2. can be compared with those of the related σ-organo-derivatives of the transition metals. Thus, the metal-carbon bond in some complexes is cleaved by halogens, the hydrogen halides, or alkyl halides (20).

$$cis\text{-}(Et_3P)_2PtMe_2 + HCl \longrightarrow cis\text{-}(Et_3P)_2PtMeCl + CH_4$$

$$cis\text{-}(Et_3P)_2PtMe_2 + Br_2 \longrightarrow cis\text{-}(Et_3P)_2PtBr_2 + C_2H_6$$

$$cis\text{-}(Et_3P)_2Pt(CH_2Ph)_2 + 2PhCH_2I \longrightarrow trans\text{-}(Et_3P)_2PtI_2 + 2(PhCH_2)_2$$

In a recent kinetic study (138) the cleavage reactions of acyl- and methylmanganese pentacarbonyls have been examined using a variety of nucleophiles. This paper reports the cleavage of the Mn-CH_3 bond in $MeMn(CO)_5$ by HCl, $HgCl_2$, and $Hg(OOCCH_3)_2$.

$$MeMn(CO)_5 + HCl \longrightarrow ClMn(CO)_5 + CH_4$$

$$MeMn(CO)_5 + HgX_2 \longrightarrow XMn(CO)_5 + MeHgX \quad (X = Cl, CH_3CO_2)$$

As already discussed in 4.1.1. insertions of fluorocarbons, CO, and SO_2 into metal-carbon bonds are quite common reactions, and these occur under mild conditions (20). The failure to observe any such reactions between CO and group IV-transition metal compounds has been attributed to the loss of the stabilisation of the metal-metal bond through (d-d) π-bonding, which would occur if insertion took place. However, recent calculations (29) suggest that the size of this contribution to the metal-metal bond is relatively small (*ca.* 5%), so that this explanation is not very satisfactory.

Carbonyl substitution reactions are also relatively common in σ-organo-transition metal compounds. These occur more readily than in the heavier group IV derivatives and this may be due to the assistance of the accompanying insertion reaction, which provides a vacant site on the transition metal (20).

i.e. $MeMn(CO)_5 \rightleftharpoons MeCOMn(CO)_4$

$MeCOMn(CO)_4 + PPh_3 \longrightarrow MeCOMn(CO)_4PPh_3$

$MeCOMn(CO)_4PPh_3 \xrightarrow{-CO} MeMn(CO)_4PPh_3$

Amines also take part in CO-substitution reactions with the σ-organo-transition metal compounds, and this compares with the adduct-formation reactions discussed in 4.1.1. for the heavier group IV derivatives. Hagen *et al.* (69) have recently investigated the reactions of some amines with the compounds $H_3M'M(CO)_3Cp$ (M' = C,Si; M = Cr,Mo,W), and observe CO-substitution accompanied by insertion, and adduct formation, for the carbon and silicon derivatives, respectively.

Comparisons of the relative stabilities of organo-transition metal compounds and the heavier group IV analogues have often been cited as evidence for the existence of a (d-d) π-contribution in the metal-metal

bonds of the latter class of compounds. In fact, a recent report by Braterman and Cross (139) suggests that metal-carbon bonds are in no way qualitatively different from metal-hydrogen, metal-metal, or metal-nitrogen bonds. These authors suggest that the observed instability of many organo-transition metal compounds can be explained on the basis of available low-energy decomposition pathways such as β-elimination, reductive elimination, and binuclear interactions, so that the decomposition of the compounds is kinetically rather than thermodynamically controlled. In view of this theory it is probably invalid to draw any conclusions about the differences in bonding between organo-transition metal compounds and group IV-transition metal compounds on the basis of relative reactivities or stabilities. More meaningful comparisons may be gained from considerations of the mechanisms of the various reactions of these compounds, but at present there is not enough information available to do this.

4.2. EXPERIMENTAL

The reactions studies carried out in this work will be considered in the remainder of this chapter, and in chapter 5. As well as studies of the reactions of germyl-

transition metal compounds, a number of reactions of the parent germanes and the germyl halides were also investigated. These were used as model systems to test the suitability of the various physical techniques for particular reaction studies, and also to assist in the identification of some of the products of these studies.

4.2.1. Halogenation Reactions of $MeGeH_3$ and $MeGeH_2X$

(i) $MeGeH_3 + GeCl_4$

A sample of methylgermane was condensed into an nmr tube with $GeCl_4$ as solvent, and TMS as internal reference. On warming the tube to room temperature only the two quartets of $MeGeH_3$ were observed in the nmr spectrum at 6.52 and 9.68 τ. After 3 weeks at room temperature very weak multiplets were observed at 4.68 (quartet) and 9.23 (triplet) τ, and these can be assigned to $MeGeH_2Cl$ (ref. 111, and part (iii) of this section). This product accounted for only 2% of the total germanium present.

(ii) $MeGeH_3 + SnCl_4/CCl_4$

Methylgermane (0.84 mmol) and stannic chloride (0.21 mmol) were condensed into an nmr tube with CCl_4

(*ca.* 1 ml) as solvent and TMS as internal reference. This tube was not sealed properly so that the system was exposed to the atmosphere. However, the tube was capped, and the results do not show any significant effects due to this exposure.

When the tube was warmed to room temperature a reaction occurred immediately, and a white solid was deposited on the walls of the tube in a similar manner to that observed with other reactions of stannic chloride (see chapter 2, and ref. 95). When the nmr spectrum was recorded after ten minutes signals due to $MeGeH_3$ and $MeGeH_2Cl$ were observed and the latter compound accounted for approximately 54% of the total germanium in the system. Thus the reaction with stannic chloride appeared to be complete (solid deposition had also ceased) and, interestingly, two chlorine atoms appeared to have been removed from each molecule of reagent.

i.e. $SnCl_4 + 2MeGeH_3 \longrightarrow 2MeGeH_2Cl + SnCl_2 + H_2$

No details of this reaction can be obtained from the nmr spectra but it probably proceeds by the following steps.

$$MeGeH_3 + SnCl_4 \longrightarrow MeGeH_2Cl + SnCl_3H$$

$$SnCl_3H \longrightarrow HCl + SnCl_2$$

$$MeGeH_3 + HCl \longrightarrow MeGeH_2Cl + H_2$$

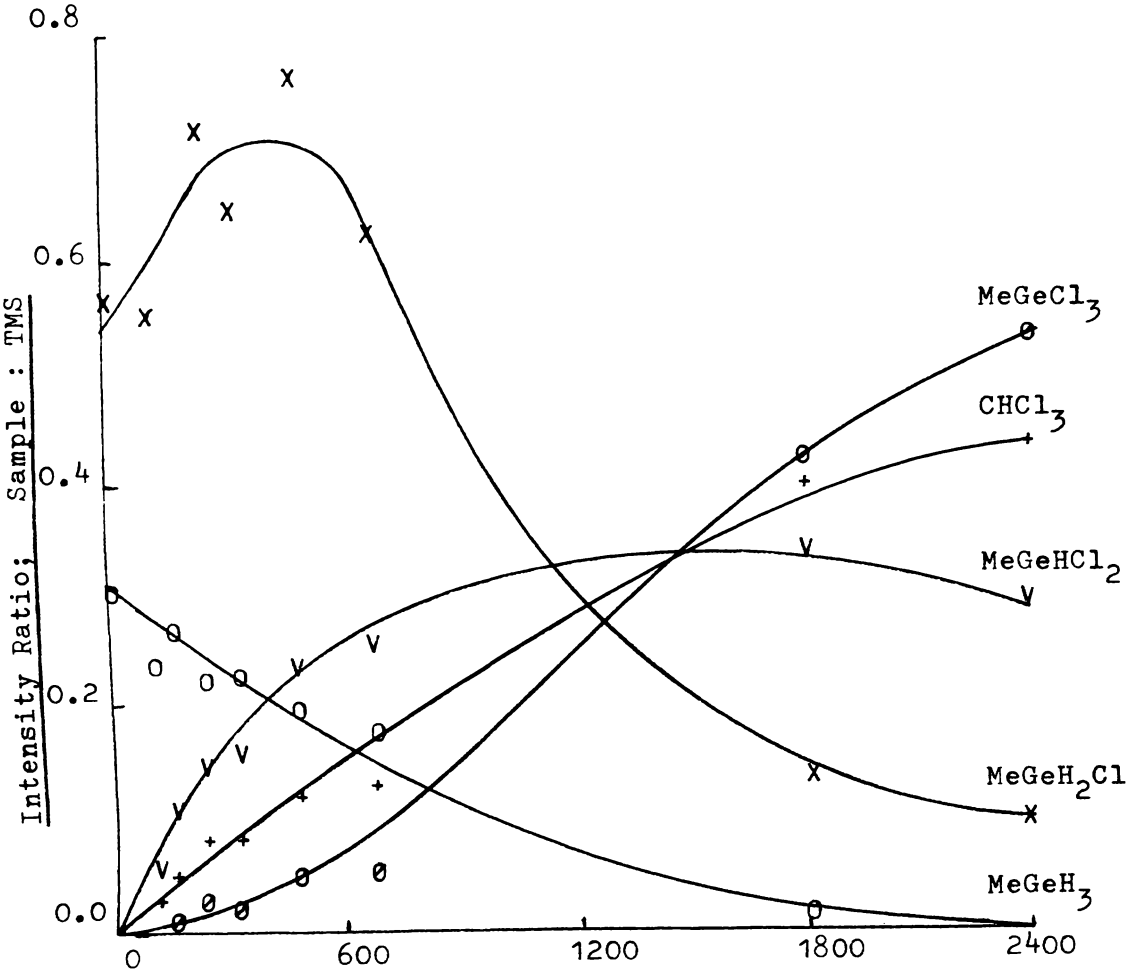
Further changes in the spectrum were observed for a total of four hours, by which time all reaction appeared to have ceased. In this time the mixture of $MeGeH_3$ and $MeGeH_2Cl$ reacted with CCl_4 as indicated by the production of $CHCl_3$, while the other products of the reaction were $MeGeHCl_2$ and $MeGeCl_3$. The nmr data for the components of the system is given in Table 4.1.

Table 4.1: NMR Data for $MeGeH_3$ + $SnCl_4/CCl_4$

Signal τ,ppm	Multiplicity	$J_{HH'}$, Hz	Intensity Ratios, CH:GeH	Assignment
9.65	4	4.3	1:1	$MeGeH_3$
6.58	4			
9.12	3	3.1	3:2	$MeGeH_2Cl$
4.68	4			
8.70	2	1.6	3:1	$MeGeHCl_2$
3.17	4			
8.35	1			$MeGeCl_3$
2.77	1			$CHCl_3$

FIGURE 4.1

Progress of the Reaction Between $MeGeH_3$ + $MeGeH_2Cl$ and CCl_4. (See Section 4.2.1.(ii))



In Fig. 4.1 the changes in the relative concentrations of each component of the system are plotted against time. This data was produced by measuring the relative peak heights for each compound in the various spectra, and it demonstrates the stepwise formation of $MeGeH_2Cl$, $MeGeHCl_2$, and $MeGeCl_3$, combined with the gradual consumption of $MeGeH_3$, and production of $CHCl_3$.

i.e. $MeGeH_3 + CCl_4 \longrightarrow MeGeH_2Cl + CHCl_3$

$MeGeH_2Cl + CCl_4 \longrightarrow MeGeHCl_2 + CHCl_3$

$MeGeHCl_2 + CCl_4 \longrightarrow MeGeCl_3 + CHCl_3$

When the reaction was complete the amount of chloroform produced accounted for 27% of the total hydrogen initially present as GeH_3 in $MeGeH_3$. The amount of $MeGeH_2Cl$ and $MeGeHCl_2$ remaining contained a further 12%, and with the initial 54% conversion due to $SnCl_4$, there is a further 7% unaccounted for. This is probably an indication of the accuracy of these measurements, which were based on peak heights rather than areas.

(iii) $\underline{MeGeH_2Cl + GeCl_4}$

The nmr spectrum of $MeGeH_2Cl$ in $GeCl_4$ was recorded for the purposes of comparison with other results. This showed a quartet at 4.70τ and a triplet at 9.25τ,

with $J_{HH'}$, 3.1 Hz, and relative intensities 2:3. No reaction was observed between the two components of this system.

(iv) $MeGeH_2Br + GeCl_4$

A sample of $MeGeH_2Br$ and $GeCl_4$ (solvent) was sealed in an nmr tube with TMS. The first spectrum recorded, after ten minutes, at room temperature, contained a number of components, and the system showed no further change, even after being stored in the dark for six months. The spectrum can be analysed as shown in Table 4.2 (refs. 111,127), with the relative quantities being calculated from relative peak heights.

Table 4.2. NMR Data for $MeGeH_2Br + GeCl_4$

Signal τ,ppm	Multiplicity	$J_{HH'}$, Hz	Assignment	Relative quantities, %
9.28	3	3.1	$MeGeH_2Cl$	5
4.72	4			
8.90	2	1.3	$MeGeHCl_2$	30
3.29	4			
8.77	2	1.6	$MeGeHClBr$ or $MeGeHBr_2$	2
8.47	1		$MeGeCl_3$	57
8.37	1		$MeGeCl_2Br$ or $MeGeClBr_2$	6

(v) $\underline{MeGeH_2Br + SiCl_4}$

The nmr spectrum of $MeGeH_2Br$ was recorded in $SiCl_4$, with TMS as internal reference. A quartet and a triplet were observed at 5.12 and 9.06τ, respectively, with J_{HH}, 3.1 Hz, and relative intensities of approximately 2:3. In addition a very weak multiplet (ca. 0.1%) was present at 4.68τ and this may be due to $MeGeH_2Cl$. No further reaction between $MeGeH_2Br$ and $SiCl_4$ was observed however, so that the small amount of $MeGeH_2Cl$ may have been due to a reaction with traces of HCl, which could have been introduced into the system by hydrolysis of $SiCl_4$.

4.2.2. Halogenation Reactions of $H_3GeMn(CO)_5$ and $MeGeH_2Mn(CO)_5$

(i) $\underline{MeGeH_2Mn(CO)_5 + Br_2}$

$MeGeH_2Mn(CO)_5$ (22.8 mg, 0.08 mmol) and an excess of bromine (crude estimation) were condensed into an nmr tube with $SiCl_4$ as solvent and TMS as internal reference. When the tube was warmed to room temperature an instantaneous reaction was indicated by the rapid discharge of most of the bromine colour. The spectrum was recorded within 5 minutes of warming but

the reaction appeared to be virtually complete and very little change took place in the spectrum in the next 24 h. The only change observed was the formation of a new minor peak, and a few white crystals formed in the bottom of the tube. The spectrum is summarised in Table 4.3.

Table 4.3. NMR Data for $MeGeH_2Mn(CO)_5 + Br_2$

Signal τ, ppm	Multiplicity	$J_{HH'}$, Hz	Assignment	Relative Quantities%	Refs.
8.18	1		$MeGeBr_3$	30	111, 127
8.75	1		$MeGeBr_2Mn(CO)_5$	50	Chapt. 6
9.13	3	ca.3	$MeGeH_2Br$		111
9.07	2	ca.2	$MeGeHBrMn(CO)_5$		Chapt. 6
8.60	2	ca.2	$MeGeHBr_2$		111, 127
8.35	1		$MeGeBrCl_2$ or $MeGeBr_2Cl$		127

The two major products of the reaction are assigned as $MeGeBr_3$ and $MeGeBr_2Mn(CO)_5$ which accounted for approximately 30 and 50%, respectively, of the total product. The remaining 20% of the system is accounted for by weak

multiplets in the region 8 - 10τ and assignments of these must be quite tentative in view of the low intensities of the signals, and the presence of overlap between these and the stronger peaks in the spectrum. The weak signals are assigned to $MeGeH_2Br$, $MeGeHBrMn(CO)_5$, and $MeGeHBr_2$ as shown in the table. Signals due to the germyl protons in these compounds were too weak to be observed in the spectrum.

The only change that occurred in the spectrum in 24 h was a decline in the intensity of the $MeGeBr_3$ signal accompanied by the formation of a new singlet at 8.35τ . This can be assigned to either $MeGeBr_2Cl$ or $MeGeBrCl_2$ which could be formed by exchange reactions of $MeGeBr_3$ with the solvent.

(ii) $\underline{H_3GeMn(CO)_5 + HBr}$

Germylpentacarbonylmanganese (0.16 mmol) was sealed inside a thick-walled glass tube with excess hydrogen bromide and stored in the dark at room temperature. Within 36 h white needle-like crystals had formed on the sides of the tube, and no further visible changes were observed over a number of weeks. The tube was opened and its contents examined. Some incondensible gas was

present (H_2?), and the only other volatile component was unreacted HBr (identified by its infrared spectrum). The solid product contained two components, melting at 94 - 96°C and 153 - 154°C (cf. $Br_3GeMn(CO)_5$, m. pt 165 - 166°C, ref. 115) and was soluble in tetrahydrofuran, acetone, and benzene, but not in n-heptane. Qualitative tests showed the presence of Br, Ge, and Mn, and this product is therefore formulated as a mixture of $HBr_2GeMn(CO)_5$ and $H_2BrGeMn(CO)_5$.

Table 4.4. Infrared Spectrum of the Product of $H_3GeMn(CO)_5$ + HBr

Absorption, cm^{-1}		Assignment
2103	(m)	CO stretches + GeH stretches
2060-1980	(s,br)	
858	(vw)	GeH, GeH_2 deformations
730	(vw)	
683	(m,sh)	MnCO bends + GeH, GeH_2 deformations
672	(m)	
654	(m)	
635	(s,br)	
452	(m)	Mn-C stretch
396	(vw)	GeH_2 rock
261	(m,br)	Ge-Br stretch
218	(vw)	Ge-Mn stretch

The infrared spectrum (nujol mull) of the solid showed the absorptions given in Table 4.4. (4000 - 200 cm^{-1}). The lowest absorption may be assigned to the Ge-Mn stretching mode (cf. 219 cm^{-1} in $H_3GeMn(CO)_5$, and 235 cm^{-1} in $Cl_3GeMn(CO)_5$, ref. 38), and the 261 cm^{-1} band is in the region of Ge-Br stretching frequencies (8,110). The strong and medium intensity absorptions between 1980 and 2100 cm^{-1}, and 635 and 683 cm^{-1}, and the absorption at 452 cm^{-1} can be mainly assigned to metal carbonyl absorptions as shown. Weaker bands due to GeH stretching modes and GeH and GeH_2 deformations will also occur in these same regions, however, and the very weak absorptions at 396, 730 and 858 cm^{-1} can also be assigned to these classes of vibrations as indicated in the table (110,140).

(iii) $\underline{MeGeH_2Mn(CO)_5 + HCl/CCl_4}$

$MeGeH_2Mn(CO)_5$ (100.0 mg, 0.35 mmol) and HCl (0.70 mmol) were sealed up in an nmr tube with CCl_4 (*ca.* 1 ml) as solvent and TMS as internal reference. The tube was warmed to room temperature and the spectrum recorded periodically as the reaction proceeded. A number of peaks were detected at various stages of the reaction and these are presented and assigned in Table 4.5.

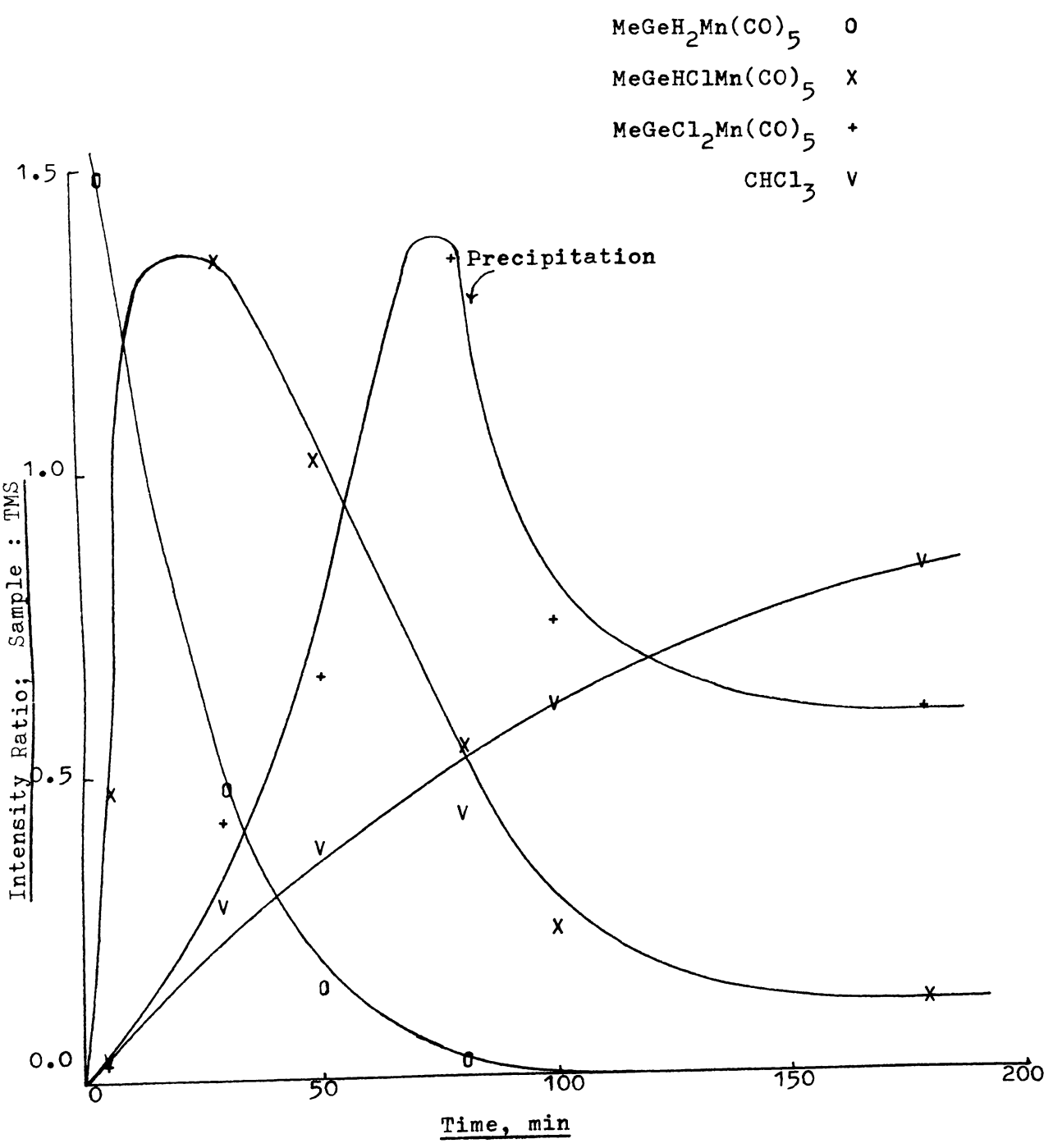
Table 4.5. NMR Data for $MeGeH_2Mn(CO)_5$ + HCl/CCl_4

Signal τ, ppm	Multiplicity	$J_{HH'}$, Hz	Intensity Ratios, CH:GeH	Assignment
9.28	3	4.0	3:2	$MeGeH_2Mn(CO)_5$
6.35				
8.87	2	3.3	3:1	$MeGeHClMn(CO)_5$
4.07	4			
8.54	1			$MeGeCl_2Mn(CO)_5$
9.47	1			impurity
5.37	1			HCl
2.85	1			$CHCl_3$ (ref. 141)

In Fig. 4.2 the changes in relative intensities of these peaks have been plotted against time, demonstrating the progress of the reaction from $MeGeH_2Mn(CO)_5$ to $MeGeHClMn(CO)_5$ and $MeGeCl_2Mn(CO)_5$. Hydrogen chloride was consumed during the reaction as indicated by a decline in the intensity of the singlet at 5.37 τ, while a reaction between the Ge-H-containing compounds and CCl_4 was indicated by the production of $CHCl_3$ throughout the study. A singlet at 9,47τ was assigned to an impurity present in the system as this remained constant throughout the reaction.

FIGURE 4.2

Progress of the Reaction Between $MeGeH_2Mn(CO)_5$ and $HCl + CCl_4$. (See Section 4.2.2.(iii))



The results indicate two competing reactions, involving HCl or CCl_4, with the latter accounting for 47% of the total observed reaction, as calculated from the relative intensities of the various peaks in the final spectrum of the system

i.e. $MeGeH_xCl_{2-x}Mn(CO)_5 + HCl \longrightarrow MeGeH_{x-1}Cl_{3-x}Mn(CO)_5 + H_2$

$MeGeH_xCl_{2-x}Mn(CO)_5 + CCl_4 \longrightarrow MeGeH_{x-1}Cl_{3-x}Mn(CO)_5 + CHCl_3$

Figure 4.2 indicates that the chlorination reactions are stepwise, as the concentration of $MeGeCl_2Mn(CO)_5$ only starts to become significant when that of $MeGeHClMn(CO)_5$ has approached its maximum value. A sharp cut-off can also be seen in this figure at about 100 min, and this was concurrent with precipitation of a solid in the nmr tube, and a general decline in the quality of the spectra. As a result of this precipitation the intensities beyond this point cannot be directly related to the amounts of each compound present in the system. However, very little change was observed in the system beyond this point, even though spectra were recorded for a total of seven days, and the reaction appeared to be complete after ca. 3 hours.

Further characterisation of the components of this system was not carried out. In this, as in a number of

the systems studied, reaction products could not be produced in large enough quantities or free from other components of the same system to allow any further characterisation. However, the spectral assignments may be supported by comparison with related compounds, and these will be discussed in Chapter 6.

(iv) $\underline{MeGeH_2Mn(CO)_5 + CCl_4}$

$MeGeH_2Mn(CO)_5$ (36.4 mg, 0.13 mmol) and CCl_4 (0.13 mmol) were condensed into an nmr tube with $SiCl_4$ as solvent, and TMS. The tube was sealed under vacuum, and then warmed to room temperature, and the nmr spectrum recorded. Five minutes after warm-up the spectrum was essentially that of $MeGeH_2Mn(CO)_5$. Within 1 h a weak doublet due to $MeGeHClMn(CO)_5$ and a weak singlet due to $CHCl_3$ could be observed, and these increased in intensity while the original signals gradually decreased with time. After 3.5 h the singlet of $MeGeCl_2Mn(CO)_5$ could be detected as well as the quartet due to $MeGeHClMn(CO)_5$ and these signals also increased in intensity with time. The system was then left overnight at room temperature, and after 29 h colourless crystals had formed in the tube and the solution had yellowed slightly. In addition the nmr spectrum showed a new weak peak due to CH_2Cl_2, while

the singlets due to $CHCl_3$ and $MeGeCl_2Mn(CO)_5$ had increased in intensity and the multiplets of $MeGeHClMn(CO)_5$ and $MeGeH_2Mn(CO)_5$ had diminished. The system showed no significant changes over the next few weeks and the reaction was assumed to be complete.

The nmr data for the various components of the system is summarised in Table 4.6.

Table 4.6. NMR Data for $MeGeH_2Mn(CO)_5 + CCl_4$

Signal τ,ppm	Multiplicity	$J_{HH'}$, Hz	Intensity Ratios, C<u>H</u>:Ge<u>H</u>	Assignment
9.30	3	4.0	3:2	$MeGeH_2Mn(CO)_5$
6.27	4			
8.83	2	3.0	3:1	$MeGeHClMn(CO)_5$
3.95	4			
8.52	1			$MeGeCl_2Mn(CO)_5$
2.72	1			$CHCl_3$ (ref. 141)
4.83	1			CH_2Cl_2 (ref. 141)

In the final reaction mixture the relative proportions of germanium-containing compounds were $MeGeH_2Mn(CO)_5$ 22%, $MeGeHClMn(CO)_5$ 39%, and $MeGeCl_2Mn(CO)_5$ 39%. A total of 92% of the reacted hydrogen was accounted for by $CHCl_3$ and CH_2Cl_2 combined, and the ratio of $CHCl_3$:CH_2Cl_2 was 10:1.

It is interesting that the reaction did not proceed to completion, even in the presence of an adequate amount of $CHCl_3$. This suggests that the system may have reached a state of equilibrium and would only proceed to completion in the presence of a large excess of the chlorinating reagents (see part (v)).

(v) $\underline{MeGeH_2Mn(CO)_5 + GeCl_4}$

A sample of $MeGeH_2Mn(CO)_5$ was sealed in an nmr tube with $GeCl_4$ as solvent and TMS as internal reference. Initially only the spectrum of the starting material was observed. The tube was then stored overnight at 33°C in the dark and within 24 h a yellow crystalline solid had formed, with corresponding changes in the spectrum. The $MeGeH_2Mn(CO)_5$ signals had completely disappeared and were replaced by peaks due to $MeGeHClMn(CO)_5$, $MeGeCl_2Mn(CO)_5$, and $GeHCl_3$. After a further five days under the same conditions more solid had been deposited in the tube and the spectrum also showed some changes. The signals assigned to $MeGeHClMn(CO)_5$ had disappeared to leave only the two singlets of $GeHCl_3$ and $MeGeCl_2Mn(CO)_5$. In addition, other weak singlets had appeared and these were assigned to GeH_2Cl_2 and GeH_3Cl. No further changes were noticed

in the spectrum over the next 14 days, and Table 4.7 summarises the nmr data for the various compounds observed up to that time.

Table 4.7. NMR Data for $MeGeH_2Mn(CO)_5$ + $GeCl_4$

Signal τ,ppm	Multiplicity	$J_{HH'}$, Hz	Intensity Ratios CH:GeH	Assignment
9.30	3	4.1	3:2	$MeGeH_2Mn(CO)_5$
6.25	4			
8.87	2	3.0	3:1	$MeGeHClMn(CO)_5$
4.02	4			
8.55	1			$MeGeCl_2Mn(CO)_5$
2.50	1			$GeHCl_3$
3.50	1			GeH_2Cl_2
4.90	1			GeH_3Cl

When the reaction study was completed the nmr tube was opened in a dry box and the solid extracted and washed with $GeCl_4$. This solid was soluble in acetone and alcohol, and the bulk of it sublimed at 40 - 50°C (10^{-2} mmHg) to give clear white crystals. Gravimetric analysis of these gave a chloride content of 20.6% (calc. for $C_6H_2O_5GeMnCl_2$ 20.3%), and the infrared spectrum (nujol and kel-F mulls, 4000 - 350 cm^{-1}) showed the absorptions given in Table 4.8 which can be assigned for $MeGeCl_2Mn(CO)_5$ as shown.

Table 4.8. Infrared Spectrum of $MeGeCl_2Mn(CO)_5$ (a)

Absorption, cm^{-1}	Assignment
3200-3100 (w,br)	C-H stretches
2195 (m)	CO stretches
1998 (s,br)	CO stretches
1231 (w)	CH_3 symmetric deformation
790 (m)	CH_3 rock
657 (s,sh)	CO deformations
642 (s,br)	CO deformations
591 (w)	Ge-C stretch
456 (m)	Mn-C stretch
355 (w,br)	Ge-Cl stretch

footnote (a) : Assigned on the basis of refs 8,38,109, 110,111,112.

(vi) $H_3GeMn(CO)_5 + GeH_2Br_2$

A small amount of GeH_2Br_2 was condensed into a trap containing an excess of $H_3GeMn(CO)_5$, on the vacuum line. When the trap was allowed to warm to room temperature a yellow solid was deposited on the sides and GeH_4 was produced (identified by its infrared spectrum). Unreacted $H_3GeMn(CO)_5$ was removed, and the solid was then

dissolved in tetrahydrofuran and transferred to a sublimation apparatus. The solvent was removed and the solid heated under vacuum (10^{-4} mmHg) to approximately 100°C, when a white solid was sublimed, leaving a yellow residue. The infrared spectrum (4000-400 cm^{-1}) of the sublimed solid was identical to that given in part (ii) of this section for the mixture of $HBr_2GeMn(CO)_5$ and $H_2BrGeMn(CO)_5$. The yellow residue showed no infrared absorptions in the 4000 - 400 cm^{-1} region and may have been a $GeBr_x$ species formed by the decomposition of GeH_2Br_2.

4.2.3. Reactions with HgX_2

(i) $H_3GeMn(CO)_5 + HgI_2$

$H_3GeMn(CO)_5$ (198.0 mg, 0.7 mmol) was condensed onto a powdered sample of HgI_2 (650.0 mg, 1.4 mmol) and allowed to warm to room temperature. The system was then left for *ca.* 15 h, with periodic cooling to promote mixing of the reagents, and in this time a yellow solid was deposited. Some incondensible gas was also present as well as unreacted $H_3GeMn(CO)_5$. Unreacted mercuric iodide was removed (crudely) and the

remaining solid dissolved in tetrahydrofuran. The ether was removed under vacuum and, with heating, an orange solid (27.2 mg) was sublimed ($40^{o}C$, 10^{-4} mm-Hg) out of the residue. The infrared spectrum (nujol mull) of this solid showed the following absorptions:

(in cm^{-1})		
	2095 (m)	720 (w,br)
	2060 (w)	645 (s,sh)
	2015 (s)	638 (s)
	1992 (m,sh)	440 (w)
	1987 (m,sh)	

These can be rationalised for compounds of the type $H_xX_{3-x}GeMn(CO)_5$ as in part (ii) of the section 4.2.2., but this is not conclusive evidence for such compounds.

(ii) <u>$MeGeH_2Mn(CO)_5$ + $HgCl_2$, 2:1 Ratio</u>

$MeGeH_2Mn(CO)_5$ (16.1 mg, 0.06 mmol) and $HgCl_2$ (11.4 mg, 0.03 mmol) were sealed inside an nmr tube with CCl_4 as solvent, and TMS. When the tube was allowed to warm to room temperature, and the nmr spectrum recorded, a rapid reaction was observed. In 20 minutes all of the $MeGeH_2Mn(CO)_5$ was converted to $MeGeCl_2Mn(CO)_5$ and the reaction ceased. $MeGeHClMn(CO)_5$ appeared as an intermediate product in the reaction, and $CHCl_3$ was

also produced. The observed signals were:

$MeGeH_2Mn(CO)_5$	9.27, 6.34 τ , J_{HH}, 4.0 Hz
$MeGeHClMn(CO)_5$	8.79 τ, J_{HH}, 3.2 Hz
$MeGeCl_2Mn(CO)_5$	8.47 τ,
$CHCl_3$	2.75 τ.

The GeH proton in $MeGeHClMn(CO)_5$ was not observed, probably because it was too weak. The final intensity of the $CHCl_3$ peak can account for about 75% of the hydrogen initially present as GeH_2.

When the tube was opened and the solvent and other volatile compounds removed, a white solid was produced. This was insoluble in water, and gave a positive test for the presence of monovalent mercury.

(iii) <u>$MeGeH_2Mn(CO)_5 + HgCl_2$, 1:1 Ratio</u>

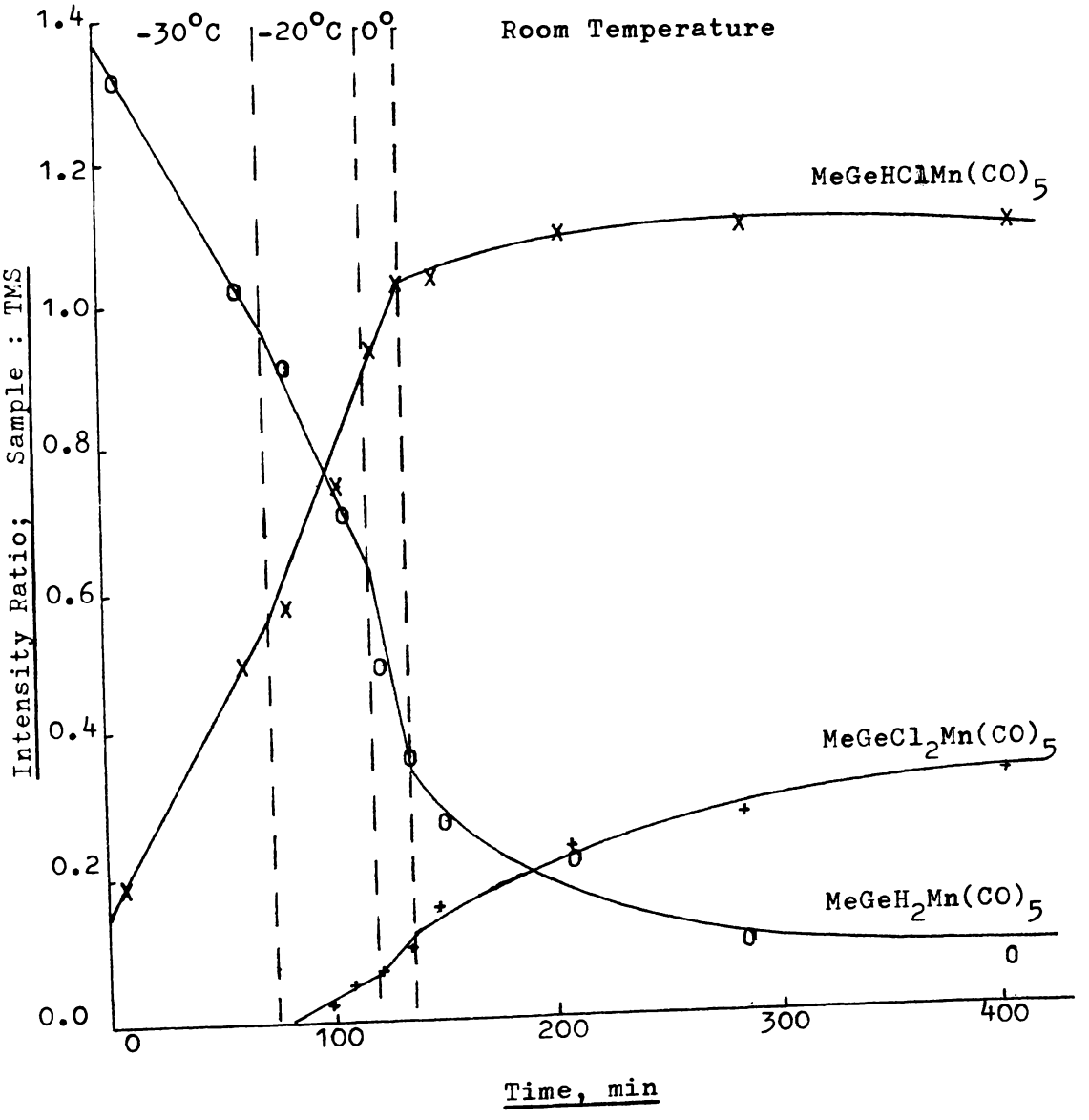
$MeGeH_2Mn(CO)_5$ (55.0 mg, 0.19 mmol) was condensed into an nmr tube containing $HgCl_2$ (53.5 mg, 0.20 mmol). $SiCl_4$ was added as solvent, and TMS as an internal reference, and the tube was sealed under vacuum. The tube was then warmed to allow the solvent to melt and enable the reactants to mix, and was then quickly placed in the nmr spectrometer at -60°C. Less than 5% of the starting material reacted in the brief warming-up period,

to produce $MeGeHClMn(CO)_5$, and at -60°C no further reaction took place over 50 minutes. When the temperature was raised to -30°C a slow reaction was observed and this was studied for 75 min under these conditions, followed by a further 35 min at -30°C, and 15 min at 0°C. The reaction was then about 75% complete and the remaining changes were observed at room temperature. Also at this time metallic mercury was present in the tube, and gas evolution was observed when the temperature was raised.

The products of the reaction are assigned as $MeGeHClMn(CO)_5$ and $MeGeCl_2Mn(CO)_5$. After 405 minutes total reaction time these accounted for 74% and 22%, respectively, of the total germanium in the system; with the remaining 4% being due to unreacted $MeGeH_2Mn(CO)_5$. The progress of the reaction up to this point is shown in Fig. 4.3. After a further 3 days at room temperature, in the dark, no starting material remained and the relative proportions of $MeGeHClMn(CO)_5$ and $MeGeCl_2Mn(CO)_5$ were 78% and 22% respectively, which suggested that the reaction was complete. However, when the tube was stored in the daylight for a further 6 weeks, precipitation of

FIGURE 4.3

Progress of the Reaction Between $MeGeH_2Mn(CO)_5$ and $HgCl_2$. (See Section 4.2.3.(iii))



a white solid occurred and the nmr spectrum showed complete conversion to $MeGeCl_2Mn(CO)_5$. Another weak singlet was present in the spectrum at 4.50τ as well, and this could be due to HCl.

The tube was opened on the vacuum line and the volatile products examined by infrared spectroscopy. As well as $SiCl_4$ and TMS a small amount of HCl was present, and while this latter observation could confirm the above assignment, it is possible that the gas was formed by hydrolysis of $SiCl_4$ after the tube had been opened. An infrared spectrum of the solid product (nujol mull, 4000-400 cm^{-1}) was identical to that of the sample of $MeGeCl_2Mn(CO)_5$ described in part (v) of section 4.2.2.

(iv) $\underline{MeGeH_2Co(CO)_4 + HgCl_2, 1:1 \text{ Ratio}}$

$MeGeH_2Co(CO)_4$ (103.2 mg, 0.40 mmol) was condensed into an nmr tube containing $HgCl_2$ (103.8 mg, 0.39 mmol). A small amount of reaction appeared to take place during this transfer process, as a sublimable yellow solid was observed on the sides of the tube, in the vicinity of traces of $HgCl_2$. $SiCl_4$ and TMS were added to the tube which was then sealed off under vacuum. The nmr spectra were recorded at room temperature, and the data are

summarised in Table 4.9.

Table 4.9. NMR Data for $MeGeH_2Co(CO)_4$ + $HgCl_2$

Signal, τ, ppm	Multiplicity	$J_{HH'}$, Hz	Assignment
9.16	3	3.4	$MeGeH_2Co(CO)_4$
5.66	4		
9.21	3	3.0	$MeGeH_2Cl$
4.67	4		
8.80	2	1.4	$MeGeHCl_2$
3.20	4		
8.38	1		$MeGeCl_3$
5.45	1		HCl

The first spectrum recorded after ten minutes at room temperature showed a mixture of $MeGeH_2Co(CO)_4$ and $MeGeH_2Cl$ (*ca.* 75% and 25%, respectively). In the next few hours the relative intensities of the signals due to these two components gradually changed, until, after 24 h, the proportions were 14% and 78%. In the same time a small amount (8%) of $MeGeHCl_2$ was produced. Within a further 24 h all of the $MeGeH_2Co(CO)_4$ had been

consumed, and the system contained $MeGeH_2Cl$ (73%), $MeGeHCl_2$ (26%), and $MeGeCl_3$ (1%). After 3 days the same components were present, (49, 46, 5%) and in addition a very weak signal was observed due to HCl. Eight days later the spectrum showed the same germanium-containing components in the proportions 39%, 56%, and 5%, as well as the weak peak at 5.45τ, and spectra recorded after this time showed no further changes.

A yellow-green solid was precipitated in the nmr tube during the first few hours of reaction. This product was not examined further but was probably $Hg[Co(CO)_4]_2$.

4.2.4. Reactions With PX_3 and PR_3

(i) $MeGeH_2Mn(CO)_5 + PCl_3$

$MeGeH_2Mn(CO)_5$ (62.6 mg, 0.22 mmol), PCl_3 (0.66 mmol), $SiCl_4$, and TMS were sealed inside an nmr tube. When the tube was warmed to room temperature and the spectrum recorded, a very slow reaction was observed. After 24 h an orange-brown solid had formed on the sides of the tube and the nmr spectrum showed that a small amount of reaction had taken place. After five days approximately 75% of the original starting material

was unreacted and the two products of the reaction $MeGeHClMn(CO)_5$ and $MeGeCl_2Mn(CO)_5$ accounted for 10 and 15%, respectively. It is notable that the dichloro-compound appeared to be formed simultaneously with the monochloro-derivative. The chemical shifts of the components of the system were as follows:

$MeGeH_2Mn(CO)_5$: 9.30, 6.25 τ, J_{HH}, 4.0 Hz

$MeGeHClMn(CO)_5$: 8.83, ? τ, J_{HH}, 3.5 Hz

$MeGeCl_2Mn(CO)_5$: 8.53 τ

(The low field signal due to $MeGeHClMn(CO)_5$ was too weak to be observed).

When the tube was left in the daylight for seven months no visible changes were observed in its appearance. However, the nmr spectrum recorded at this time showed that chlorination had been carried to completion. There were only two signals in the spectrum due to $MeGeCl_2Mn(CO)_5$, and HCl (5.43 τ, very weak). The tube was opened at this stage and the products examined. Some incondensible gas was present and this amounted to 0.2 mmol (measured on a Toepler Pump). An infrared spectrum of the volatile components showed $SiCl_4$, TMS, and some unreacted PCl_3. A white solid was sublimed out of the solid residue in the tube by

pumping overnight at room temperature and 10^{-4} mmHg, and the infrared spectrum of this was identical to that of $MeGeCl_2Mn(CO)_5$ reported in part (v) of 4.2.2. The orange-brown residue that remained was insoluble in hydrocarbon solvents, acetone, and water, and an infrared spectrum of this (4000 - 400 cm^{-1}, KBr disc) showed a broad band at about 460 cm^{-1}, which is in the region of P-Cl stretching vibrations (140).

(ii) $\underline{MeGeH_2Mn(CO)_5 + PF_3}$

In three separate experiments samples of $MeGeH_2Mn(CO)_5$ were treated with an excess of PF_3 in strong sunlight, inside pyrex glass tubes fitted with tap adaptors. In each reaction an incondensible gas was produced and this was identified as CO by molecular weight measurements. The amount of this gas produced was usually less than the amount of PF_3 consumed. The major products of the reaction were intractable yellow oils and the infrared spectra of these were not well resolved. Broad bands in the region 700 - 850 cm^{-1} could have involved Ge-F stretching modes and also P-F stretching modes due to coordinated PF_3 (140). The ^1H nmr spectra of these products were also poorly resolved, showing broad signals in the region 8 - 10 τ. A ^{19}F nmr spectrum of one of

the products showed no signal at all. All of the above spectra showed slight variations for the product of each reaction.

Thus, no definite isolable and identifiable products were observed from these reactions, but the results suggest that both CO substitution and Ge-H fluorination may have occurred.

(iii) $H_3GeMn(CO)_5 + PPh_3$

A thick-walled glass tube containing $H_3GeMn(CO)_5$ (80.6 mg, 0.30 mmol) and PPh_3 (96.0 mg, 0.30 mmol) was sealed up under vacuum, and stored in the dark. After 36 h a yellow solid had formed on the surface of the glass and on the solid PPh_3. No further changes were observed except for a deepening of the colour of this deposit, and after 5 months the tube was reopened. Some incondensible gas was present in the system (0.04 mmol) and GeH_4 and $H_3GeMn(CO)_5$ were identified by their infrared spectra, as the only other volatile compounds present. An infrared spectrum (nujol mull) of the solid showed it to be mainly unreacted PPh_3, with some metal carbonyl-containing species present as well. A pale yellow solid was sublimed from this residue (80°C,

10^{-4} mmHg) and identified as $H_2Ge[Mn(CO)_5]_2$ by its infrared spectrum (73,96).

(iv) $\underline{MeGeH_2Mn(CO)_5 + PH_3}$

Samples of $MeGeH_2Mn(CO)_5$ and PH_3 were placed together in an infrared gas cell. The spectrum was recorded at regular intervals for 3 months but the only change observed was a gradual decline in the absorptions of $MeGeH_2Mn(CO)_5$, probably due to decomposition of the sample. A brown residue formed on the sides of the cell over the same period, but this was not identified.

4.2.5. Other Reactions

(i) Reactions with the Boron Trihalides

$\underline{BF_3}$: Some preliminary investigations were carried out on reactions between $MeGeH_3$ and BF_3, and $MeGeH_2Mn(CO)_5$ and BF_3. With the former system infrared and nmr spectroscopic studies indicated slow formation of $MeGeH_2F$. However the reaction was quite complex with a number of unidentifiable products also being formed. For the latter system an infrared study suggested some reaction between the two compounds but the products could not be identified. Neither of these systems was investigated further.

$\underline{BBr_3}$: A sample of $MeGeH_2Mn(CO)_5$ was sealed inside an nmr tube with excess BBr_3, and $SiCl_4$ and TMS. An instantaneous reaction occurred on warming to room temperature, producing a mixture of products with a complex nmr spectrum. Analysis of this was extremely difficult due to the presence of a number of weak sharp peaks under stronger broad bands. Signals due to $MeGeBr_2Mn(CO)_5$ and $MeGeBr_3$ were identified at 8.73 and 8.17τ, respectively, and $MeGeBrHMn(CO)_5$ may have also been present in the system (weak doublet at 9.13τ, J_{HH}, 1.5 Hz). The remaining peaks in the spectrum could not be assigned (weak singlets at 2.77, 2.92, 7.72, 8.48, 8.54, 9.16τ, and broad bands at 8.71 and 9.09τ).

(ii) Reactions with Ethylene

A number of attempts were made to observe a reaction between $H_3GeMn(CO)_5$ and ethylene, using a variety of reaction conditions. None of the attempts were successful however. Thus, when $H_3GeMn(CO)_5$ was treated with ethylene at a pressure of *ca.* 5 atmospheres no reaction was observed, even at temperatures of up to 130°C, and most of the starting material was recovered unchanged. Irradiation of mixtures of $H_3GeMn(CO)_5$ and

ethylene with ultraviolet light resulted only in decomposition of the former, while in the presence of aluminium chloride such mixtures appeared to react, but no products could be isolated from the system.

4.3. Discussion

The reaction studies reported in the previous section will be discussed in the same general categories in which they have already been considered.

4.3.1. Halogenation Reactions of $MeGeH_3$ and $MeGeH_2X$

As already mentioned, these reactions were investigated to try out the techniques used in the reaction studies, and to assist in the identification of the products of other reactions, from their nmr spectra. The results for $MeGeH_3$ and $MeGeH_2X$ can be summarised on the basis of the exchange reaction,

$$MeGeH_2X + M'X'_4 \rightleftharpoons MeGeH_2X' + M'X'_3X.$$

For $MeGeH_3$ and a large excess of $GeCl_4$ this equilibrium favoured the left-hand side of the equation, with only 2% of $MeGeH_2Cl$ being formed. The other product of the reaction, $GeHCl_3$, was not detected, probably because its nmr signal was not strong enough. The reaction between

$MeGeH_3$ and excess $SnCl_4$ has already been mentioned in Chapter 2, and this favoured the right-hand side of the above equation with $MeGeH_2Cl$ being produced in a fast exothermic reaction.

$$MeGeH_3 + SnCl_4 \longrightarrow MeGeH_2Cl + SnCl_2 + HCl.$$

In the nmr study reported in this chapter a similar result was observed, but in addition a second chlorine atom was exchanged for hydrogen, by the reaction of either $SnHCl_3$ or HCl with $MeGeH_3$, which was present in excess.

$$MeGeH_3 + SnCl_4 \longrightarrow MeGeH_2Cl + SnHCl_3$$

$$MeGeH_3 + SnHCl_3 \longrightarrow MeGeH_2Cl + SnCl_2 + H_2$$

or: $SnHCl_3 \longrightarrow SnCl_2 + HCl$

$$MeGeH_3 + HCl \longrightarrow MeGeH_2Cl + H_2$$

The reactions involving stannic chloride took place within a few minutes. Carbon tetrachloride was also present as solvent in the system and a series of exchange reactions were also observed between this and the $MeGeH_3/MeGeH_2Cl$ mixture produced in the first series of reactions. The second series of reactions was considerably slower than the first, taking four hours to reach equilibrium.

$$MeGeH_3 + CCl_4 \rightleftharpoons MeGeH_2Cl + CHCl_3$$

$$MeGeH_2Cl + CCl_4 \rightleftharpoons MeGeHCl_2 + CHCl_3$$

$$MeGeHCl_2 + CCl_4 \rightleftharpoons MeGeCl_3 + CHCl_3$$

Chloroform, as well as all of the other reaction products, was identified by its nmr spectrum. This reagent did not appear to take part in any further reaction with the germanium-hydride compounds, as no CH_2Cl_2 was detected in the final reaction system.

No reaction was observed between $MeGeH_2Cl$ and excess $GeCl_4$, while in the $MeGeH_2Br/SiCl_4$ system the small quantity of $MeGeH_2Cl$ detected in the nmr spectrum was probably formed by an exchange reaction involving traces of HCl.

$$MeGeH_2Br + HCl \rightleftharpoons MeGeH_2Cl + HBr$$

By comparison, $MeGeH_2Br$ and $GeCl_4$ gave a rapid reaction which resulted in a complex mixture of products. The most likely reactions in this system are:

$$MeGeH_2Br + GeCl_4 \rightleftharpoons MeGeHClBr + GeHCl_3$$

$$MeGeHClBr + GeCl_4 \rightleftharpoons MeGeCl_2Br + GeHCl_3$$

$$MeGeH_2Br + GeCl_4 \rightleftharpoons MeGeH_2Cl + GeCl_3Br$$

$$MeGeHClBr + GeCl_4 \rightleftharpoons MeGeHCl_2 + GeCl_3Br$$

$$MeGeCl_2Br + GeCl_4 \rightleftharpoons MeGeCl_3 + GeCl_3Br$$

These equations explain the existence of the observed products. However, no $GeHCl_3$ was present in the final system and the fate of the reacted hydrogen can not be explained in this way. Since there were no solid products in the system the most likely explanation is that hydrogen was present as molecular H_2, but there is no obvious reason as to why this was produced in this particular system.

There have been many reports (8,95,127,142,143) of exchange reactions of compounds of the group IV elements, similar to those considered above. Generally, it has been observed that for the tetrachloride derivatives the rates of halogen exchange reactions follow the order:

$$SnCl_4 >> GeCl_4 > CCl_4 >> SiCl_4,$$

although, as can be seen from the present results, this is not rigidly adhered to.

4.3.2. Halogenation Reactions of $H_3GeMn(CO)_5$ and $MeGeH_2Mn(CO)_5$

The halogenation reactions of $H_3GeMn(CO)_5$ and $MeGeH_2Mn(CO)_5$ studied in this work follow the same general pattern of the halogenation reactions of similar compounds discussed in section 4.1. Thus,

with Br_2 and $MeGeH_2Mn(CO)_5$ both Ge-H substitution, and Ge-Mn cleavage were observed, with the former reaction being slightly more important.

$$MeGeH_2Mn(CO)_5 + Br_2 \longrightarrow MeGeHBrMn(CO)_5 + MeGeBr_2Mn(CO)_5$$
$$+ MeGeH_2Br + MeGeHBr_2 + MeGeBr_3$$

The other product of the Ge-H substitution reaction, HBr, was not detected in the nmr spectrum of the system. However, since the amount of Br_2 in the system was not known accurately, it is possible that there was a sufficient amount of unreacted Ge(H)-containing species present in the system for further reactions of the type:

$$Ge\text{-}H + HBr \longrightarrow Ge\text{-}Br + H_2$$

to occur. In this case the final product would be H_2 gas and this would not be detected in the nmr spectrum. The fact that partially substituted species were present in the final reaction mixture supports this reasoning but is not conclusive evidence as the reaction could involve a series of equilibria, rather than proceeding completely to the right as shown in the above equations. Some solid products were observed in the reaction and these could have included $BrMn(CO)_5$, the other product of the Ge-Mn cleavage reaction, as well as $MeGeHBrMn(CO)_5$, and $MeGeBr_2Mn(CO)_5$.

By comparison with the above result, when $H_3GeMn(CO)_5$ was treated with excess HBr, Ge-H substitution was the only reaction observed.

$$H_3GeMn(CO)_5 + xHBr \longrightarrow H_{3-x}Br_xGeMn(CO)_5 + xH_2$$
$$(x = 1,2)$$

The mixture of products was identified by its infrared spectrum, and by a comparison of melting points with those of similar compounds. Further to this, Mackay *et al.* (38) report that the reaction between HCl and $H_3GeMn(CO)_5$ gives a mixture of $H_2ClGeMn(CO)_5$ and $HCl_2GeMn(CO)_5$, and these compounds have melting points of 75 - 85°C and 140°C, respectively (*cf.* 94 - 96°C, 153 - 154°C for the corresponding bromo-derivatives).

A similar reaction was observed between $MeGeH_2Mn(CO)_5$ and HCl. In this study the reaction was carried out in CCl_4 solution, and both this and HCl reacted with $MeGeH_2Mn(CO)_5$ in a stepwise fashion to produce a mixture of $MeGeHClMn(CO)_5$ and $MeGeCl_2Mn(CO)_5$.

$$MeGeH_2Mn(CO)_5 + xHCl \rightleftharpoons MeGeH_{2-x}Cl_xMn(CO)_5 + xH_2$$

$$MeGeH_2Mn(CO)_5 + xCCl_4 \rightleftharpoons MeGeH_{2-x}Cl_xMn(CO)_5 + xCHCl_3$$
$$(x = 1,2)$$

In the final reaction mixture $CHCl_3$ accounted for approximately half of the reacted hydrogen, indicating that both reactions occurred to similar extents.

The reaction between $MeGeH_2Mn(CO)_5$ and CCl_4 was also studied in the absence of HCl, and with the reagents in a 1:1 ratio. The same reactions were observed, that is H/Cl exchange, but in addition the reactions occurred at a much slower rate, and the $CHCl_3$ produced in the system also reacted to give CH_2Cl_2.

i.e. $$MeGeH_2Mn(CO)_5 + xCCl_4 \rightleftharpoons MeGeH_{2-x}Cl_xMn(CO)_5 + xCHCl_3$$

$$MeGeH_2Mn(CO)_5 + xCHCl_3 \rightleftharpoons MeGeH_{2-x}Cl_xMn(CO)_5 + xCH_2Cl_2$$

$$(x = 1,2)$$

With $GeCl_4$, as might be expected from the work on $MeGeH_3$ and $MeGeH_2X$, similar H/Cl exchange reactions were observed.

i.e. $$MeGeH_2Mn(CO)_5 + GeCl_4 \longrightarrow MeGeHClMn(CO)_5 + GeHCl_3$$

$$MeGeHClMn(CO)_5 + GeCl_4 \longrightarrow MeGeCl_2Mn(CO)_5 + GeHCl_3$$

In this system $GeCl_4$ was present in a large excess as the solvent and the reaction proceeded completely to $MeGeCl_2Mn(CO)_5$, which was identified by its infrared spectrum and elemental analysis for chloride content. The other product of the reactions, $GeHCl_3$, was identified from its nmr spectrum, and in addition

small quantities of GeH_2Cl_2 and GeH_3Cl were identified in the system. While these may have been produced by exchange reactions with $MeGeH_2Mn(CO)_5$ or $MeGeHClMn(CO)_5$, it is also possible that they may have been the products of redistribution reactions of $GeHCl_3$ and GeH_2Cl_2.

i.e. $2GeHCl_3 \rightleftharpoons GeH_2Cl_2 + GeCl_4$

$2GeH_2Cl_2 \rightleftharpoons GeH_3Cl + GeHCl_3$

There is an interesting comparison between the reactions of $MeGeH_2Mn(CO)_5$ with CCl_4 and with $GeCl_4$. With the former reagent as solvent the reaction was relatively fast, approaching completion within ca. 2 h, and when the reaction was carried out using a 1:1 ratio it was complete after 29 h. In both of these cases a mixture of products was produced, suggesting equilibration of the various components. In contrast with these results, the reaction using $GeCl_4$ as both solvent and reagent was considerably slower, taking 5 days to complete, and yet the final product was that formed by complete chlorination. This observation differs from the order of reactivity of the $M'X_4$ compounds in exchange reactions with other derivatives of germanium mentioned in section 4.3.1, and

possibly indicates that in the above situations the reactions involving CCl_4 are thermodynamically controlled, while that between $GeCl_4$ and $MeGeH_2Mn(CO)_5$ is kinetically controlled. It is also possible that the two reagents react by different mechanisms.

A reaction between $H_3GeMn(CO)_5$ and $GeCl_4$ has been observed by George (99). This reaction was studied using nmr spectroscopy in a similar manner to that used in this work, except that the absence of multiplicity in any of the nmr signals made assignments of these considerably more difficult. A comparison of the results for $H_3GeMn(CO)_5$ and $MeGeH_2Mn(CO)_5$ suggests that both reactions proceeded by H/Cl exchange, but there are additional bands in the nmr spectrum of the former system which cannot be assigned to any of the expected products.

Finally, the reaction between excess $H_3GeMn(CO)_5$ and GeH_2Br_2 studied in this work is another example of a hydrogen/halogen exchange reaction. When these two reagents were allowed to react together at room temperature, GeH_4, $H_2BrGeMn(CO)_5$, and $HBr_2GeMn(CO)_5$ were identified as products, suggesting the following reactions:

$$H_3GeMn(CO)_5 + xGeH_2Br_2 \rightleftharpoons H_{3-x}Br_xGeMn(CO)_5 + xGeH_3Br$$

$$H_3GeMn(CO)_5 + xGeH_3Br \rightleftharpoons H_{3-x}Br_xGeMn(CO)_5 + xGeH_4$$

These reactions took place at a greater rate than either of the corresponding reactions between $GeCl_4$ and $H_3GeMn(CO)_5$ or $MeGeH_2Mn(CO)_5$, and this is probably related to the lower Ge-Br bond energy, compared with that of the Ge-Cl bond (144).

4.3.3. Reactions with HgX_2

Metal-metal cleavage has been reported by Mackay *et al.* (19) for the reaction of $H_3GeCo(CO)_4$ with $HgCl_2$.

$$H_3GeCo(CO)_4 \longrightarrow H_3GeCl + ClHgCo(CO)_4 \text{ or } Hg[Co(CO)_4]_2$$

As discussed in section 4.1 the mercuric halides demonstrate both metal-metal cleavage and R-substitution reactions, and in the present work both of these have been observed. Thus, $MeGeH_2Co(CO)_4$ reacted in the same way as its GeH_3 analogue, giving the products of Ge-Co cleavage.

$$2MeGeH_2Co(CO)_4 + HgCl_2 \longrightarrow 2MeGeH_2Cl + Hg[Co(CO)_4]_2$$

$$\text{or } MeGeH_2Co(CO)_4 + HgCl_2 \longrightarrow MeGeH_2Cl + ClHgCo(CO)_4$$

An additional reaction was observed in this system, in that $MeGeH_2Cl$ was partially converted to $MeGeHCl_2$ and $MeGeCl_3$, and Glockling (8) reports that the mercuric halides have been used on a number of occasions to prepare halide derivatives of other organogermanes in

reactions similar to this.

i.e. $2MeGeH_2Cl + 2HgCl_2 \longrightarrow 2MeGeHCl_2 + Hg_2Cl_2 + H_2$

The reaction between $MeGeH_2Co(CO)_4$ and $HgCl_2$ was the only reaction of the cobalt compound studied in this work, and as has been noted this occurred in the same way as that reported for the parent compound, $H_3GeCo(CO)_4$. In the reaction studies of the corresponding manganese compounds the same general observation applies, in that similar reactions occur in similar ways for both $H_3GeMn(CO)_5$ and $MeGeH_2Mn(CO)_5$. Thus one may reasonably predict at this stage that any further reaction studies of $MeGeH_2Co(CO)_4$ should give similar results to those already reported (19,96) for $H_3GeCo(CO)_4$.

The two reactions of $HgCl_2$ with $MeGeH_2Mn(CO)_5$ studied in this work give some indication of the fate of the mercury in these reactions. In both systems Ge-H substitution occurred to give $MeGeCl_2Mn(CO)_5$ as the final product. For the first system studied CCl_4 was present as solvent and this accounted for 75% of the total reaction. As a result only one chlorine atom would have been removed from each molecule of $HgCl_2$, and since the final Hg-containing product was shown to be a derivative of Hg(I),

this can be reasonably formulated as Hg_2Cl_2. By comparison when both molecules of chlorine were removed from the mercuric chloride, as in the second reaction study, metallic mercury was identified in the reaction products. These observations can be explained by the following sequence of events (x = 0,1):

$$MeGeH_{2-x}Cl_xMn(CO)_5 + HgCl_2 \longrightarrow MeGeH_{1-x}Cl_{x+1}Mn(CO)_5 + HHgCl$$

$$2HHgCl \longrightarrow H_2 + Hg_2Cl_2$$

$$MeGeH_{2-x}Cl_xMn(CO)_5 + Hg_2Cl_2 \longrightarrow MeGeH_{1-x}Cl_{x+1}Mn(CO)_5 + Hg_2HCl$$

$$Hg_2HCl \longrightarrow 2Hg + HCl$$

The last equation explains the observation of HCl in the latter stages of the reaction in $SiCl_4$.

Finally, the results of the reaction between HgI_2 and $H_3GeMn(CO)_5$ suggest that this is also an example of Ge-H substitution. The major products of the reaction were solids, and the only volatile product was an incondensible gas, compatible with H_2 formation. However, the solid products could not be positively identified as $H_{3-x}I_xGeMn(CO)_5$ compounds, and the absence of H_3GeI in the gaseous products could have been due to decomposition of this gas under the reaction conditions (giving H_2?). Thus, the results of this study are not conclusive.

4.3.4. Reactions with PR_3 and PX_3

The reactions of the phosphines with $MeGeH_2Mn(CO)_5$ and $H_3GeMn(CO)_5$, as far as they may be interpreted, demonstrate an interesting trend in reactivity. That is, with PCl_3 Ge-H substitution was observed, with PF_3 the results suggested both CO and Ge-H substitution, while with PPh_3 CO substitution was not observed in this work, but has been observed by George (99). This trend can probably be explained on the basis of the variation in suitability of each of the phosphines as either ligands on the transition metal, or M'-R substitution reagents. The individual reaction studies and their interpretation will now be considered in more detail.

Phosphorous trichloride was observed to give a stepwise chlorination reaction, proceeding to completion over several months. The major product of the reaction was $MeGeCl_2Mn(CO)_5$, identified by its infrared and nmr spectra, and other products were a brown solid, probably a $(PCl_2)_n$ polymer, a trace of HCl, and an incondensible gas, probably H_2. Excess PCl_3 was used in the reaction and some of this was recovered from the system after seven months. The probable reactions in this sytem are:

$$MeGeH_{2-x}Cl_xMn(CO)_5 + PCl_3 \longrightarrow MeGeH_{1-x}Cl_{x+1}Mn(CO)_5 + PHCl_2$$

$$2PHCl_2 \longrightarrow H_2 + (PCl_2)_n$$

$$(x = 0,1)$$

For the PF_3 reactions the results have already been discussed in about as much detail as they possibly can be, in section 4.2.4.(ii). That is, on the basis of CO evolution, and infrared and nmr spectra of the reaction systems, both CO and Ge-H substitution reactions appear to have occurred. No isolable products could be otained, and the intractable oils formed in the various reactions were probably complex mixtures of compounds of the form $MeGeH_{2-x}F_xMn(CO)_{5-n}(PF_3)_n$ ($x = 2,1,0$; $n = 5,4,--,0$).

Triphenylphosphine did not appear to react with $H_3GeMn(CO)_5$ under the conditions given in 4.2.4.(iii). However, the time interval between the addition of reagents and examination of the system was sufficiently long that any products formed may have decomposed again. The $H_2Ge[Mn(CO)_5]_2$ isolated from the reaction mixture could have been produced by decomposition of $H_3GeMn(CO)_5$.

i.e. $2H_3GeMn(CO)_5 \longrightarrow H_2Ge[Mn(CO)_5]_2 + GeH_4$

Interestingly, George (99) has observed that when PPh_3 and $H_3GeMn(CO)_5$ were heated together for 8 h carbon monoxide was evolved, corresponding to substitution of one CO. However, no product could be isolated from the system.

Phosphine, was observed not to react with $MeGeH_2Mn(CO)_5$, and this agrees with the trend in reactivity discussed above, to the extent that PH_3 is not suitable as a ligand on manganese, nor can it act as a Ge-H substitution reagent.

4.3.5. Other Reaction Studies

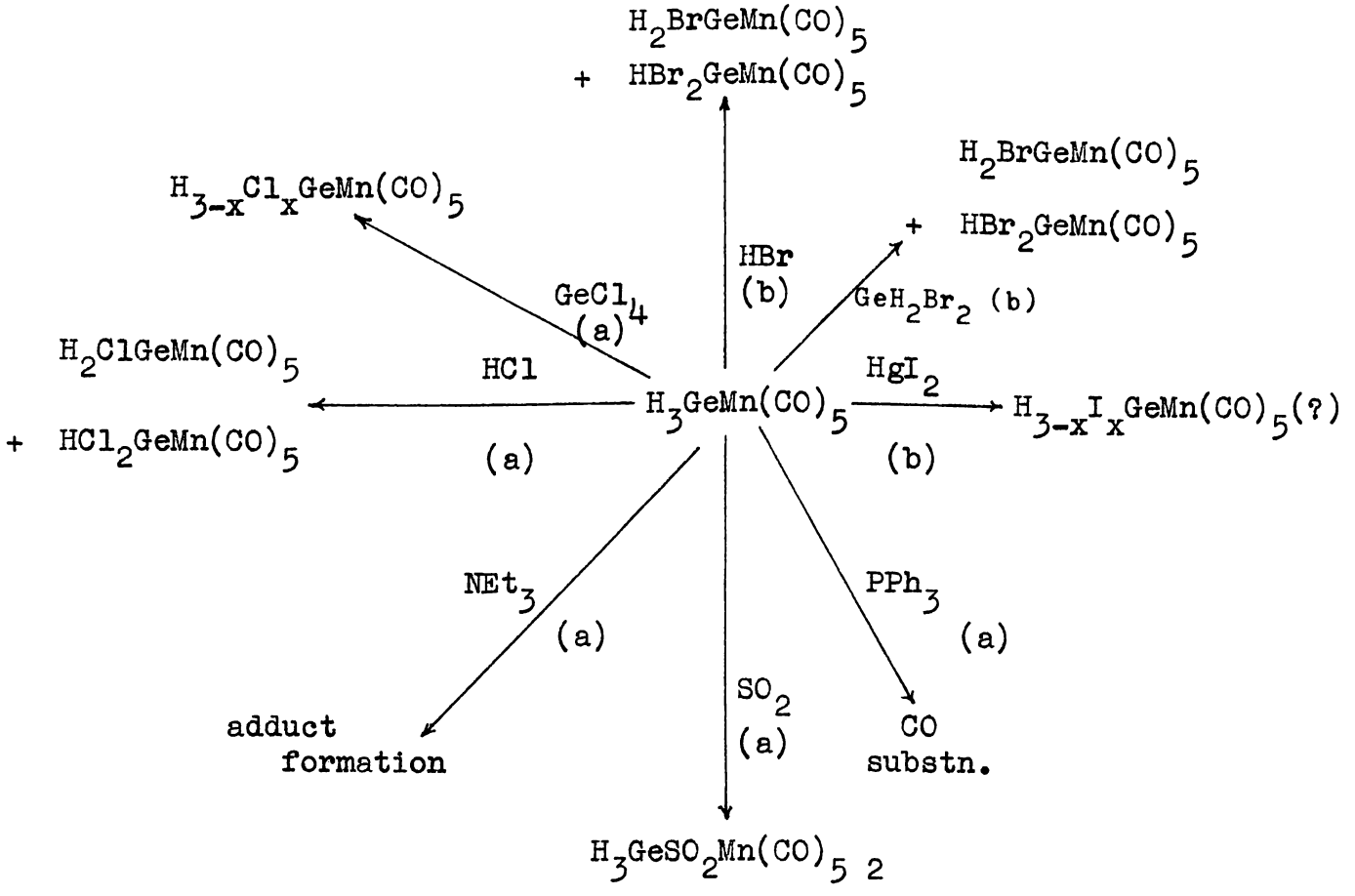
The reaction studies involving the boron halides and ethylene require no further discussion, as no definite conclusions can be drawn from the results.

4.3.6. Summary

The reactions of $H_3GeMn(CO)_5$ and $MeGeH_2Mn(CO)_5$ are summarised in Fig. 4.4 and 4.5, respectively. In addition to the reactions already mentioned in the text, Mackay *et al.* (38) have reported an adduct-formation reaction between $H_3GeMn(CO)_5$ and Et_3N and this appears to have less ionic character than the corresponding adduct of $H_3GeCo(CO)_4$, and the H_3Si analogues. Stobart (96) has also found that $H_3GeMn(CO)_5$ reacts with SO_2, using the latter reagent as solvent, and the product of this reaction was a polymer of empirical formula $[H_3GeSO_2Mn(CO)_5]_n$. An infrared spectrum of the solid suggested the presence of S-O bridges in the compound, but its structure was not determined.

Fig. 4.4

The Reactions of $H_3GeMn(CO)_5$

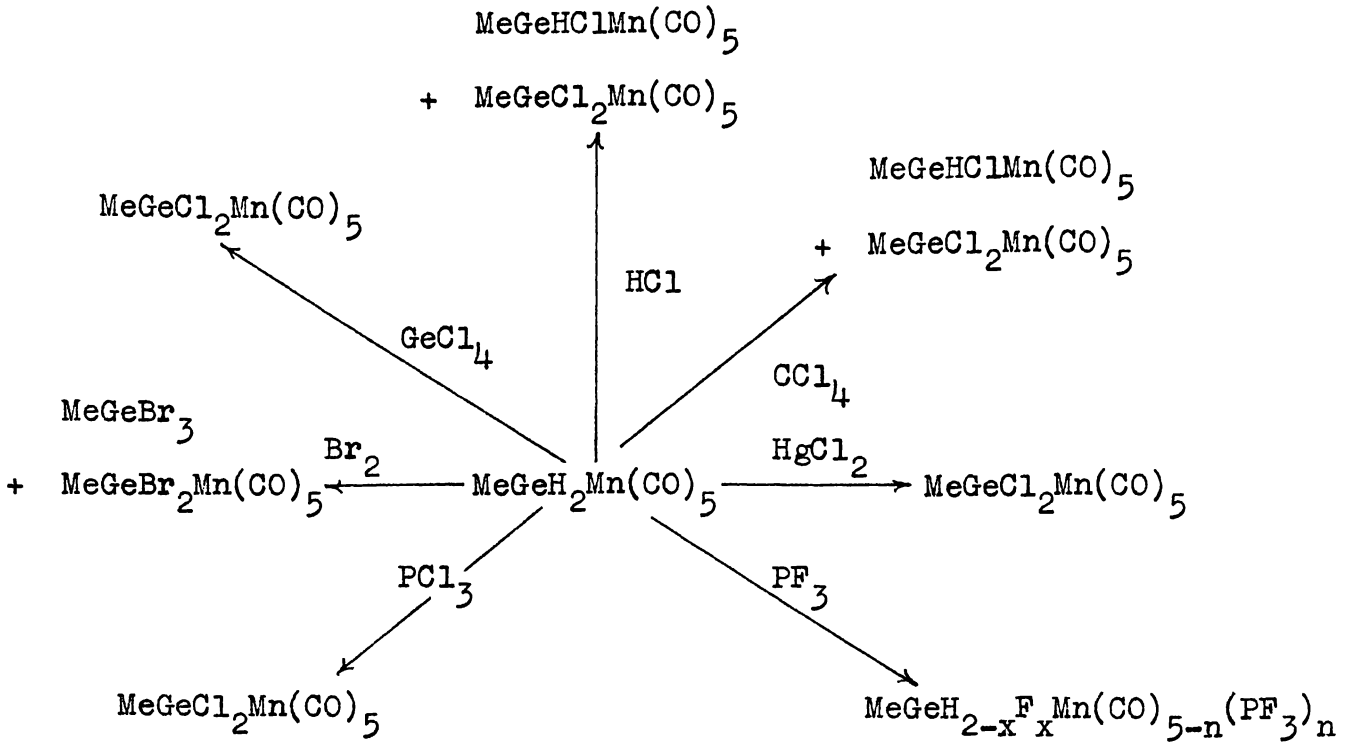


(a) Ref. 39,96,99.

(b) This work.

Fig. 4.5

Reactions of $MeGeH_2Mn(CO)_5$



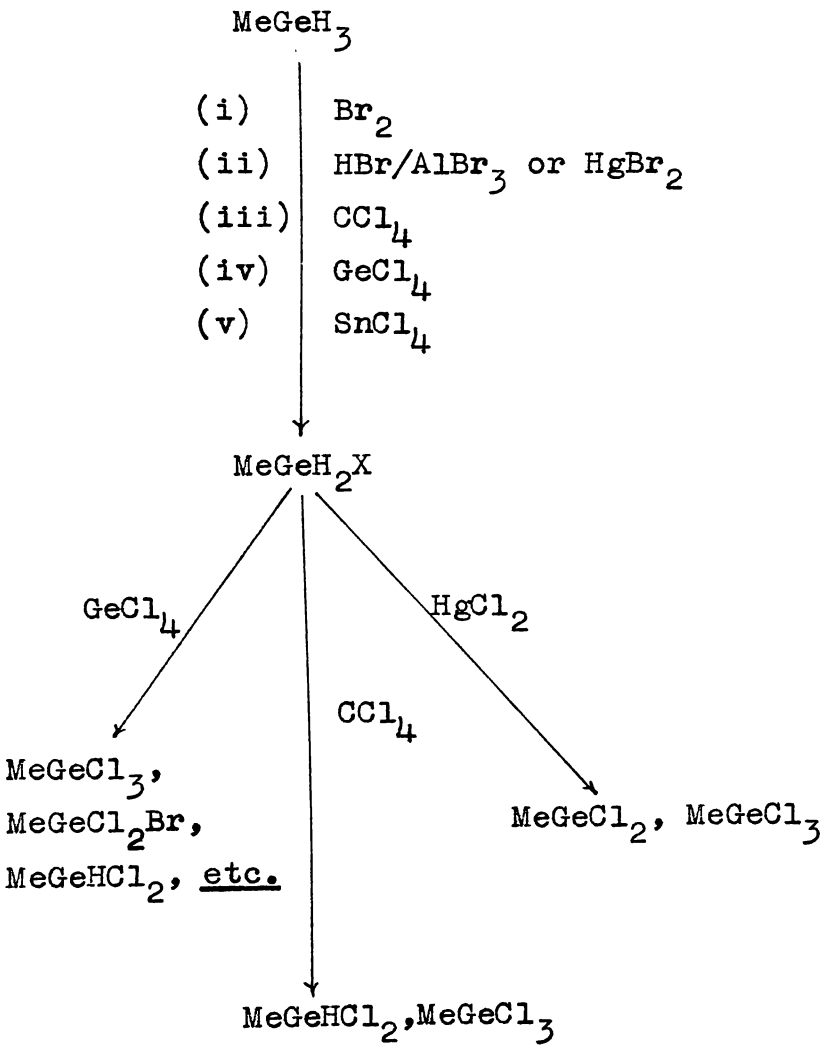
A comparison of the results shown in Fig. 4.4 and 4.5 with the discussion of section 4.1 shows that $MeGeH_2Mn(CO)_5$ and $H_3GeMn(CO)_5$ are quite comparable with other similar group IV-transition metal compounds in their reactions with a variety of reagents. The Ge-H bonds are substituted readily by suitable reagents, while Ge-Mn cleavage is only achieved with the more strenuous reagents such as Br_2. Similarly, CO substitution may only occur under relatively rigorous conditions. Also, a comparison with the reactions of $H_3GeCo(CO)_4$ and $MeGeH_2Co(CO)_4$ suggests that the Ge-Co bond is either weaker, or more polar, than the Ge-Mn bond in these compounds. Finally, it can be noted that the reactions of $MeGeH_2Mn(CO)_5$ are quite similar to those of other $MeGeH_2X$ (X = H,Cl,Br) compounds considered in this work, with the transition metal moiety only affecting the relative rates of the reactions.

The reactions of $MeGeH_3$ and $MeGeH_2X$ (X = Cl,Br) that have been observed in this work are summarised in Fig. 4.6. These results have been taken from the Experimental section of Chapter 2, as well as from this Chapter.

Fig. 4.6

Reactions of $MeGeH_3$ and $MeGeH_2X$

(X = Cl,Br)



CHAPTER 5. REACTION STUDIES OF GROUP IV-TRANSITION METAL COMPOUNDS - PART II.

5.1. INTRODUCTION

The reaction studies to be considered in this chapter have a general theme of synthetic routes to other group IV-transition metal compounds. Two reaction studies will be considered. In the first, some aspects of the reactions between germanium hydride compounds and dicobalt octacarbonyl are investigated; and in the second a new synthetic route is reported for the preparation of some group IV-transition metal compounds.

When the preparation of $MeGeH_2Co(CO)_4$ was first investigated in this study, a synthesis of the type 3(b) (see Table 2.1) was attempted. That is, $MeGeH_3$ and $Co_2(CO)_8$ were mixed together with the aim of initiating a reaction of the form:

$$2MeGeH_3 + Co_2(CO)_8 \longrightarrow 2MeGeH_2Co(CO)_4 + H_2$$

This was not observed however, and the products of the reaction were an incondensible gas, cobalt carbonyl hydride ($HCo(CO)_4$), and an unidentifiable solid. On the basis of the quantities of each reagent consumed,

and the relative amounts of each product formed in the reaction, it was concluded that the reaction was proceeding further than the step shown above, to give substitution of all three hydrogen atoms in $MeGeH_3$. After $MeGeH_2Co(CO)_4$ had been successfully prepared by another route (see Chapter 3), the reactions of both this compound and $MeGeH_3$ with $Co_2(CO)_8$ were investigated in more detail, and this comprises the first reaction study of Chapter 5.

In the second study, some exchange reactions of the group IV-transition metal compounds were investigated. Reactions involving exchange of the group IV substituents have already been reported, and these were discussed in section 4.1.1. However, there have been no reports of similar reactions involving exchange of the transition metal moieties in these compounds, and such reactions should be synthetically useful, as well as providing further information about the chemical nature of group IV-transition metal compounds. Some reactions of this sort have been investigated for derivatives of Mn, Fe, and Co, and the results are reported and discussed in section 5.3.

5.2. The Reactions of $MeGeH_3$ and $MeGeH_2Co(CO)_4$ With $Co_2(CO)_8$.

5.2.1. EXPERIMENTAL

(i) $MeGeH_3 + Co_2(CO)_8$

Methylgermane (1.52 mmol) was condensed into a tube containing $Co_2(CO)_8$ (258.9 mg, 0.76 mmol) and the mixture then warmed to room temperature. After three hours, in the dark, an orange-brown solid was present in the tube as well as a black metallic residue. Some incondensible gas was also present in the tube, and other volatile components were $MeGeH_3$ (1.06 mmol , 70% recovery) and $HCo(CO)_4$ (64.3 mg, 0.38 mmol), which were identified by their infrared spectra. An infrared spectrum (nujol mull, 4000 - 400 cm^{-1}) of the solid material in the tube showed two complex series of absorptions at ca. 2000 cm^{-1} and 400 - 600 cm^{-1}, the regions expected for metal carbonyl stretching and deformation modes.

A similar study was carried out using nmr spectroscopy. $MeGeH_3$ (0.10 mmol) and $Co_2(CO)_8$ (57.9 mg, 0.17 mmol) were sealed in an nmr tube with $SiCl_4$ as solvent, and TMS as internal reference. Upon warming the tube to room temperature a dark brown solution was

produced, and some red-brown solid was also present in the tube. The nmr spectrum of the system, recorded *ca.* 2 minutes after warm-up showed weak signals due to $MeGeH_3$ and a strong singlet at 8.07τ. Other weak signals, all multiplets, were observed at 9.17, 8.80, and 8.42τ, but these were too weak to be resolved. $MeGeH_3$ was rapidly consumed and after *ca.* 5 minutes at room temperature the reaction appeared to be virtually complete. As well as the strong singlet at 8.07τ another weaker singlet was observed in the spectrum at 21.4 τ and this was assigned to $HCo(CO)_4$ (145). The intensity of this signal appeared to decline with time and this was probably due to partial decomposition of the hydride to, say, $H_2 + Co_2(CO)_8$.

After 5 days at room temperature the nmr tube was opened and the products examined. The volatile components were $HCo(CO)_4$, $SiCl_4$, and TMS (identified by their infrared spectra), and a dark-brown solid was also obtained. This latter material was pumped under vacuum, (*ca.* 10^{-4} mmHg) to remove any $Co_2(CO)_8$, which would have sublimed away, and the remaining solid was then examined by infrared spectroscopy (cyclohexane soln. 4000 - 400 cm^{-1}). The infrared data is recorded in Table 5.1 and compared with that reported for

Table 5.1.

Infrared Data for $PhGeCo_3(CO)_{11}$ and the Product of $MeGeH_3 + Co_2(CO)_8$ (a)

$PhGeCo_3(CO)_{11}$ (b), cm^{-1}	Reaction Product, cm^{-1}
2104 w	2105 w
2082 s	2082 s
	2064 w,sh
2056 s	2056 s
2044 w	2047 w,sh
2036 s	2038 s
2025 m	2017 m
2014 m	2009 m
	2003 w,sh
1998 w	1998 w
1850 w	1849 w
1835 w,br,sh	1837 w

(a) Both spectra recorded in cyclohexane solution

(b) Ref. 45.

$PhGeCo_3(CO)_{11}$ (45). In addition to the bands given, other absorptions were present at *ca.* 800 cm^{-1} and 500 cm^{-1}, and these were of weak and medium intensity, respectively. On the basis of the comparison with $PhGeCo_3(CO)_{11}$, and the results given in part (ii) of this section, this product is assigned as $MeGeCo_3(CO)_{11}$. The infrared spectrum was also quite comparable with that of the product of the first reaction reported above, so that both reactions may be summarised by the following equation, with other unidentified intermediates also being formed:

$$MeGeH_3 + 3Co_2(CO)_8 \longrightarrow MeGeCo_3(CO)_{11} + 3HCo(CO)_4 + CO$$

(ii) $MeGeH_2Co(CO)_4 + Co_2(CO)_8$

An nmr tube containing $MeGeH_2Co(CO)_4$ (47.6 mg, 0.18 mmol), $Co_2(CO)_8$ (60.9 mg, 0.18 mmol), $SiCl_4$ as solvent, and benzene as reference, was sealed under vacuum and examined at -40°C. A slow reaction was observed in which $MeGeH_2Co(CO)_4$ was consumed to give, initially, a compound of the type $MeGeHX_2$ (X = $Co(CO)_4$, say), identified by a doublet and quartet in the appropriate regions of the spectra. This, in turn, was consumed to give the same strong singlet observed in the above reaction of $MeGeH_3$, at 8.09 τ (due to

$MeGeCo_3(CO)_{11}$), as well as a much weaker singlet at 8.42 τ . Throughout the reaction $HCo(CO)_4$ was also produced, as indicated by a high field singlet at 21.5 τ . After 1½ h the temperature was raised to 0°C and after a further 2½ h under these conditions the reaction appeared to be complete.

Table 5.2 gives the nmr data for all of the components observed in the reaction. Of these,

Table 5.2. NMR Data for $MeGeH_2Co(CO)_4$ + $Co_2(CO)_8$

Signal τ,ppm	Multiplicity	$J_{HH'}$, Hz	Assignment	Final Relative Intensities
9.18	3	3.2	$MeGeH_2Co(CO)_4$	4
5.71	4			
8.79	2	2.2	$MeGeHX_2$	4
4.52	4			
8.42	1		$MeGeX_3$	1.5
8.09	1		$MeGeCo_3(CO)_{11}$	10
21.5	1		$HCo(CO)_4$	6

$MeGeCo_3(CO)_{11}$ accounted for approximately 50% of the total germanium in the final system, while $HCo(CO)_4$ accounted for about 80% of the reacted hydrogen.

Decomposition of $HCo(CO)_4$ appeared to be reduced by storing the tube at 0^oC, as the intensity of the signal due to this compound did not diminish with time (*cf.* part (i)).

The nmr tube was opened and all the volatile components of the system pumped away to leave a dark-brown solid, the infrared spectrum of which was identical to that observed for the product of the reaction of $MeGeH_3$ and $Co_2(CO)_8$. A mass spectrum of the solid product was also recorded and this can be analysed for a compound of composition $MeGeCo_3(CO)_{11}$, thus confirming the identification made in part (i).

The mass spectrum is recorded in Table 5.3. with the appropriate assignments. The features of this spectrum are extremely simple with the strongest peaks being due to the $MeGeCo_3(CO)_x^+$ (x = 0 to 11) family of ions. A similar result was reported for $PhGeCo_3(CO)_{11}$ (45). As further support for the assignments, each group of peaks in the $MeGeCo_3(CO)_x^+$ series showed the characteristic intensity pattern expected for germanium-containing ions (discussed in section 3.3.3.), with the exception of the peaks due to $MeGeCo_3^+$ where hydrogen loss was also observed.

Table 5.3. Mass Spectrum of $MeGeCo_3(CO)_{11}$

m/e	Assignment	Relative Intensity (a)
576 - 570	$MeGeCo_3(CO)_{11}^+$	11
548 - 542	$MeGeCo_3(CO)_{10}^+$	13
520 - 514	$MeGeCo_3(CO)_9^+$	40
492 - 486	$MeGeCo_3(CO)_8^+$	38
477 - 471	$GeCo_3(CO)_8^+$	vw
464 - 458	$MeGeCo_3(CO)_7^+$	13
449 - 443	$GeCo_3(CO)_7^+$	vw
436 - 430	$MeGeCo_3(CO)_6^+$	50
408 - 402	$MeGeCo_3(CO)_5^+$	100
393 - 387	$GeCo_3(CO)_5^+$	vw
380 - 374	$MeGeCo_3(CO)_4^+$	62
365 - 359	$GeCo_3(CO)_4^+$	vw
352 - 346	$MeGeCo_3(CO)_3^+$	53
337 - 331	$GeCo_3(CO)_3^+$	vw
324 - 318	$MeGeCo_3(CO)_2^+$	74
309 - 303	$GeCo_3(CO)_2^+$	1
296 - 290	$MeGeCo_3(CO)^+$	70
281 - 275	$GeCo_3(CO)^+$	5
268 - 262	$MeGeCo_3^+$	50
253 - 247	$GeCo_3^+$	60
236 - 231	$MeGeCo_2(CO)^+$	8
209 - 203	$MeGeCo_2^+$	43

Table 5.3. (cont'd).

m/e	Assignment	Relative Intensity (a)
194 - 188	$GeCo_2^+$	vw
177	Co_3^+	4
150 - 144	$MeGeCo^+$	10
135 - 129	$GeCo^+$	15
118	Co_2^+	9
91 - 85	$MeGe^+$	vw
87	$Co(CO)^+$	6
76 - 70	Ge^+	vw
59	Co^+	7

(a) vw = very weak (ca. less than 0.5 relative intensity)

Other strong peaks were observed corresponding to $MeGeCo_2^+$, $MeGeCo^+$, $GeCo_3^+$, and $GeCo^+$, and it is quite significant that the latter two ions gave the only strong peaks observed for methyl loss. Fragmentation of the $MeGeCo_3$ framework in the molecule also gave mainly weak ions, and this compares with the retention of similar polymetallic groupings in the mass spectra of other metal carbonyl cluster compounds (101,102).

(iii) Other Reactions of $MeGeH_2Co(CO)_4$.

Reactions between $MeGeH_2Co(CO)_4$ and $Fe(CO)_5$, and $Mn_2(CO)_{10}$, were investigated using infrared spectroscopy. Both systems were studied in the absence of solvent and at temperatures between 0°C and 70°C, while the $MeGeH_2Co(CO)_4/Fe(CO)_5$ system was also studied in the presence of tetrahydrofuran, under similar conditions. In all cases the only reaction observed was decomposition of $MeGeH_2Co(CO)_4$, with the other metal carbonyl compounds being recovered unchanged.

5.2.2. Discussion

The results given in parts (i) and (ii) of the previous section indicate that the final product of the reactions between $MeGeH_3$ and $Co_2(CO)_8$, and $MeGeH_2Co(CO)_4$ and $Co_2(CO)_8$, is $MeGeCo_3(CO)_{11}$. This compound has already been reported in the literature (80) and was produced in the reaction between Me_2GeH_2 and $Co_2(CO)_8$. No physical data were given for the compound however, so that recourse had to be made to a report (45) of the preparation of $PhGeCo_3(CO)_{11}$, for identification of the samples of $MeGeCo_3(CO)_{11}$ produced in this study. The phenyl derivative was formed by the reaction of $PhGeH_3$ with $Co_2(CO)_8$, and x-ray data

shows that it contains a $Co_2(CO)_7$ grouping bridged by germanium, with the remaining $Co(CO)_4$ unit and the phenyl group also attached to the group IV atom. The $Co_2(CO)_7$ unit is also bridged by one of the carbonyl ligands, and the observation of two infrared absorptions in the region of bridging CO's is explained on the basis of there being two possible structural isomers for the compound.

Both $PhGeCo_3(CO)_{11}$ and $MeGeCo_3(CO)_{11}$ react with CO under high pressure to form $RGeCo_3(CO)_{12}$ (R = Me,Ph). It is possible that the unidentified tri-substituted germanium compound observed in the reactions reported in the previous section (weak singlet at 8.42 τ) could also be of this form. However, both of the above $RGeCo_3(CO)_{12}$ compounds readily revert to $RGeCo_3(CO)_{11}$ so that this assignment does not seem very likely. Another, more feasible, assignment could be $RGeCo_3(CO)_9$, which was formed quite readily from the phenyl derivative of $RGeCo_3(CO)_{11}$, and was found to be quite stable (45).

Some reactions of the dialkyl and diaryl germanes and silanes with $Co_2(CO)_8$ give some indication of the possible nature of the other unidentified intermediate in the previous reactions (i.e. the compound giving a quartet at 4.52 τ, and doublet at 8.79 τ in part (ii) of 5.2.1.). As noted above, Graham *et al.* (80) have

reported that the product of the reaction between $MeGeH_3$ and $Co_2(CO)_8$ is $MeGeCo_3(CO)_{11}$. However, Adams and Cotton (146) report that another product of this reaction is $(Me_2Ge)_2Co_2(CO)_6$, which has a $Co_2(CO)_8$ structure with the bridging carbonyl groups replaced by Me_2Ge units. By comparison, Ph_2GeH_2 and $Co_2(CO)_8$ react to give $Ph_2GeCo_2(CO)_7$ in which, presumably, only one of the bridging carbonyls has been replaced by Ph_2Ge. This compound can also be made to react with CO under pressure, to give $Ph_2Ge[Co(CO)_4]_2$. Diphenylsilane reacts with $Co_2(CO)_8$ in a similar fashion to Ph_2GeH_2, to give $Ph_2SiCo_2(CO)_7$ (45). Other products have been isolated, however, and the most recent investigation (55) of this system reveals a progressive series of reactions. The initial product formed is $Ph_2Si(H)Co(CO)_4$, which is then replaced by $Ph_2SiCo_2(CO)_7$. This latter compound also reacts further with excess $Co_2(CO)_8$, giving $Ph_2SiCo_4(CO)_{14}$ as the final product. Similar behaviour was observed for Et_2SiH_2, and the final products in both cases were shown to contain a $Ph_2Si[Co(CO)_4]$ group linked *via.* an oxygen atom to the apical carbon of a $CCo_3(CO)_9$ cluster.

From the above reactions it appears that the favoured path for addition of a group IV-hydride derivative to $Co_2(CO)_8$ is through displacement of the bridging carbonyl groups. This does not fully determine the observed product however, as this may be formed by further reaction with the hydride, or by cleavage of the Co-Co bonds, giving smaller molecules as products. Thus, in the reaction between $MeGeH_3$ and $Co_2(CO)_8$ investigated in this work, it seems likely that the first product to be formed is $MeGeH_2Co(CO)_4$.

i.e. $MeGeH_3 + Co_2(CO)_8 \longrightarrow MeGeH_2Co(CO)_4 + HCo(CO)_4$.

This product then reacts further, giving a disubstituted product, and the most likely formulation of this is $MeGe(H)Co_2(CO)_7$, although $MeGe(H)Co_2(CO)_8$ is another possibility.

i.e. $MeGeH_2Co(CO)_4 + Co_2(CO)_8 \longrightarrow MeGe(H)Co_2(CO)_7 + HCo(CO)_4 + CO$

Finally, either of the disubstituted compounds may react with more $Co_2(CO)_8$ to give $MeGeCo_3(CO)_{11}$.

$MeGe(H)Co_2(CO)_7 + Co_2(CO)_8 \longrightarrow MeGeCo_3(CO)_{11} + HCo(CO)_4$.

The other minor product of the reaction, proposed as $MeGeCo_3(CO)_9$, could be formed by loss of CO from $MeGeCo_3(CO)_{11}$. Another possible reaction in the system is $MeGeH_2Co(CO)_4 + Co_2(CO)_8 \longrightarrow MeGeCo_3(CO)_{11} + H_2 + CO$.

Finally, the failure to observe any reactions between $MeGeH_2Co(CO)_4$ and $Fe(CO)_5$, or $Mn_2(CO)_{10}$, could be due to the absence of bridging carbonyl groups in the latter compounds. The results are not unexpected as it is usually observed (2) that the reactions between these metal carbonyls and the group IV hydrides require more vigorous conditions than similar reactions of cobalt carbonyl.

5.3. TRANSITION METAL EXCHANGE REACTIONS

In section 3.2.1. of this thesis, some reactions between H_3GeBr and mixtures of $NaCo(CO)_4$ and $NaMn(CO)_5$ were discussed. These competition reactions were carried out to determine which of $H_3GeCo(CO)_4$ and $H_3GeMn(CO)_5$ would be formed in preference to the other. Cobalt to manganese ratios of 1:10 and 1:1 were used but in both cases $H_3GeMn(CO)_5$ was produced in good yield, with evidence for traces of $H_3GeCo(CO)_4$ also. From

these results it was concluded that the manganese compound was either being formed initially in preference to the cobalt derivative, or, alternatively, it was being formed from the latter compound. Thus, it seemed likely that any exchange reactions between the manganese and cobalt compounds would favour the direction involving formation of a manganese derivative, and the first reaction described in 5.3.1. was selected on this basis.

The second exchange reaction described in 5.3.1. involves $(H_3Ge)_2Fe(CO)_4$ and $H_3GeMn(CO)_5$. Again, from a comparison of the relative stabilities and chemical reactivities of the germyl derivatives of the $-M(CO)_n$ compounds (M = Mn, Fe, Co; ref. 19, 38, 78), it was expected that formation of the manganese compound would be favoured.

5.3.1. EXPERIMENTAL

(i) $MeGeH_2Co(CO)_4 + NaMn(CO)_5$

A sample of $NaMn(CO)_5$ was prepared by treatment of $Mn_2(CO)_{10}$ with sodium amalgam in ether. The solid was pumped free of ether and a sample of $MeGeH_2Co(CO)_4$

condensed onto its surface. After ½ h at room temperature a trace of $HMn(CO)_5$ had been formed, but no further reaction was observed. After this period, isopentane (*ca.* 5 ml) was distilled onto the mixture, but again no reaction was observed over 15 minutes at room temperature. The hydrocarbon was then removed and a few millilitres of dry tetrahydrofuran added to the system. This time a reaction did occur at room temperature, and examination of the volatile components of the system, by infrared spectroscopy, showed that a mixture of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ had been formed after 15 minutes. In addition, when the solid residue was treated with HCl in the presence of THF, $HCo(CO)_4$, containing only a trace of $HMn(CO)_5$, was produced.

The above reaction was repeated on a quantitative basis, using an excess of $NaMn(CO)_5$. That is, $MeGeH_2Co(CO)_4$ (52.4 mg, 0.20 mmol) was added to a sample of $NaMn(CO)_5$ (0.44 mmol, prepared from 85.3 mg $Mn_2(CO)_{10}$), in the presence of THF. After 15 minutes at room temperature the reaction products were fractionated through a trap held at -45°C, to remove THF, and give the pure product of $MeGeH_2Mn(CO)_5$ (46.8 mg, 0.16 mmol, 80% yield based on $MeGeH_2Co(CO)_4$ consumed).

(ii) $\underline{(H_3Ge)_2Fe(CO)_4 + NaMn(CO)_5}$

$(H_3Ge)_2Fe(CO)_4$ (11.0 mg, 0.04 mmol) was treated with a four-fold excess of $NaMn(CO)_5$, in the presence of THF, in the manner outlined above. The volatile products of the reaction were fractionated at -45°C, and the yield of $H_3GeMn(CO)_5$ was 4.6 mg (0.02 mmol, 50% yield based on $(H_3Ge)_2Fe(CO)_4$ consumed). It is unlikely that the yield of 50% in this reaction is significant as this is a measure of the amount of pure $H_3GeMn(CO)_5$ recovered from the system and makes no allowance for further traces of material carried through the -45°C trap with THF. Normally incomplete fractionation of this magnitude is not significant, but in this case the quantities used are sufficiently small that this effect could account for *ca.* 10% of the total reaction product.

5.3.2. Discussion

The above reactions can be summarised in the following equations.

$$MeGeH_2Co(CO)_4 + NaMn(CO)_5 \xrightarrow{THF} MeGeH_2Mn(CO)_5 + NaCo(CO)_4$$

$$(H_3Ge)_2Fe(CO)_4 + 2NaMn(CO)_5 \xrightarrow{THF} 2H_3GeMn(CO)_5 + Na_2Fe(CO)_4$$

While these results do not establish transition metal exchange reactions as a general route to group IV-transition metal compounds, they provide the first examples of such a process, and it is likely that further examples may be found. In addition, the results suggest that the relative stabilities of the $H_3GeM(CO)_n$ compounds (or $MeGeH_2M(CO)_n$) is

$$Mn > Fe \quad \text{and} \quad Mn > Co,$$

and this agrees with other observations (19,38,78).

The effect of THF on the reaction is interesting. This can probably be compared to the reactions of amine bases with group IV-transition metal compounds, to give $R_3M.2B^+M(CO)_n^-$ adducts. The ether might be expected to interact to a lesser extent than the amines so that the overall effect would be to increase the polarisation of the metal-metal bond, thereby making it more susceptible to attack by a species such as $M(CO)_n^-$. Thus, while the exchange reactions may possibly be thermodynamically feasible in non-polar solvents, the presence of THF makes them kinetically feasible by increasing the reactivity of one of the components. The observation of a THF effect also bears some significance to the discussion of section 2.1.1. of this thesis, where it was suggested that the same solvent could be partially

responsible for the observation of abnormal results in some syntheses of group IV-transition metal compounds.

CHAPTER 6. A DISCUSSION OF THE NMR DATA REPORTED IN THIS WORK.

A considerable amount of nmr data has been reported at various stages throughout this thesis, and in this chapter these results will be collected together and discussed. There will be two parts to the discussion. That is, in section 6.1. the data obtained from the spectra of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ will be compared with the values reported for other group IV-transition metal compounds, and in 6.2. the assignments of the results from the various reaction studies reported in chapters 4 and 5 will be considered in more detail.

6.1. NMR Data for Some Group IV-Transition Metal Compounds.

The nmr data reported for hydride derivatives of the group IV-transition metal compounds is listed in Table 6.1. For the purposes of comparison the following values will also be useful (all values in τ, ppm, and for neat liquids, ref. 10,100).

Table 6.1.: NMR Data for Group IV-Transition Metal Compounds

Compound	Solvent	Chemical Shifts, τ M'H(a)	CH_3	Cp	Ref.
$H_3SiCr(CO)_3Cp$	Et_2O	5.88		5.11	69
$H_3SiMo(CO)_3Cp$	Et_2O	6.15		4.65	69
$H_3SiW(CO)_3Cp$	Et_2O	6.18		4.50	69
$H_3SiMn(CO)_5$	neat	6.41			37
$Me_3SiMn(CO)_5$	C_6H_{12}		9.51		52
$(H_3Si)_2Fe(CO)_4$	neat	6.33			70
$H_3SiFe(CO)_2Cp$	C_6D_6	6.48		6.57	40
$Me_2SiHFe(CO)_2Cp$	neat	5.21	9.55	5.51	71
$H_3SiCo(CO)_4$	neat	5.96			18
$(H_3Si)Pt(PEt_3)_2X$(b)	C_6H_6	6.60-6.78			42
$H_3GeMn(CO)_5$	C_6H_6	6.72			34
$MeGeH_2Mn(CO)_5$	$SiCl_4$	6.34	9.32		(d)
$Me_3GeMn(CO)_5$	$CDCl_3$		9.38		97
$H_2Ge[Mn(CO)_5]_2$	$CHCl_3$	6.67			76
$H_5Ge_2Mn(CO)_5$	$CDCl_3$	6.56,6.91(c)			58
$H_3GeRe(CO)_5$	C_6H_6	6.81			77
$(H_3Ge)_2Fe(CO)_4$	C_6D_6	6.50			78
$H_3Ge(H)Fe(CO)_4$	C_6D_6	6.65			78
$(MeGeH_2)_2Fe(CO)_4$	$SiCl_4$	6.18	9.30		64

Table 6.1. (cont'd)

Compound	Solvent	Chemical Shifts, τ M'H(a)	CH_3	Cp	Ref.
$H_3GeFe(CO)_2Cp$	C_6D_6,$CDCl_3$	6.73		5.20	78
$H_2Ge[Fe(CO)_2Cp]_2$	$CDCl_3$	6.13		5.20	79
$(H_3Ge)_2Os(CO)_4$	C_6H_6	7.10			81
$H_3GeCo(CO)_4$	C_6H_6	6.95			19
$MeGeH_2Co(CO)_4$	$SiCl_4$	5.67	9.16		(d)
$(H_3Ge)Pt(PEt_3)_2X$(b)	C_6H_6	6.92-7.20			42

(a) M' = Si, Ge.

(b) Ref. 42 lists some 24 compounds of the form trans-$XPt(PEt_3)_2Z$, where X = Cl, Br, I and Z = SiH_nX_{3-n}, GeH_nX_{3-n} (n = 1, 2, 3). These show no obvious irregularities however, and it was not considered necessary to list them all here.

(c) (GeH_2) = 6.91, (GeH_3) = 6.56.

(d) This work.

SiH_4	6.80		GeH_4	6.85	
$MeSiH_3$	6.42,	9.81	$MeGeH_3$	6.55,	9.65
Me_2SiH_2	6.18,	9.86	Ge_2H_6	6.76	

From this compilation it can be seen that most of the results fit into fairly limited ranges, and there are no obviously anomalous values. A more detailed examination of the results is worthwhile, however, and this follows.

In considering chemical shift data from nmr spectroscopic studies the simplest assumption that one can make is that the results are indicative of the electron density about the particular atoms under study. That is, the chemical shifts indicate the effective "shielding" or "de-shielding" of the magnetic nucleii, and this effect is related to high or low electron densities, respectively, about these nucleii (147). As a result of this, it is sometimes possible to show that in simple systems, such as CH_3X, the observed chemical shifts are directly related to the electronegativities of the substituents, X. Such studies have been reported for substituted alkanes (148) and silanes (149) and alkyl-substituted silanes and germanes (150), and generally it has been observed that

the above relationship is adhered to, to a limited extent. Deviations from this behaviour are also observed in most cases, however, and as a result it is necessary to consider other factors which may be important in determining chemical shifts.

A discussion of the effects contributing to chemical shift values can be found in most advanced texts on nmr spectroscopy (e.g. 141,147). Generally, it can be shown that changes in the "shielding" of a nucleus depend, not only on the electron density surrounding the nucleus, but also on the existence in the molecule of regions of electric charge which, when placed in a magnetic field, produce their own much smaller magnetic fields. These induced fields can either reinforce or oppose the applied magnetic field, and in this way effectively "de-shield" or "shield" any magnetic nucleii within the range of the effect. This range can extend from any nucleii within the region producing the effect, to those nucleii which are "near neighbours" to this region. Calculations (147) show that the effect is inversely proportional to the cube of the distance from the centre of the effect, so that these "nearest neighbours" are restricted to a separation of only a few Angstroms in length. As a useful guide,

the effects will probably be experienced by a nucleus if it comes within the range of Van der Waal's interactions with the active region. Some typical regions of electric charge which may produce the above effects are large polarisable atoms (e.g. Iodine), polarised covalent bonds (e.g. H-X, or R_3C-X; X = halogen), and multiple covalent bonds (e.g. C=C, C=O, etc.).

In complexes of the transition metals, of the type considered in Table 6.1., it is obvious that any explanations of chemical shift values must be necessarily complex. The presence of large polarisable metal atoms in low formal oxidation states, and regions of high electron density, such as the CO and C_5H_5 ligands, might be expected to be significant factors in determining the chemical shifts of the protons in the group IV ligands. Another possible factor is the presence of (d-d) π-bonding in the M-M' bond which, if present, would also provide a region of electron mobility capable of producing an induced magnetic field. Thus the data of Table 6.1. might be expected to reflect fairly complex interactions within the molecules, and whether this is so, or not will now be considered.

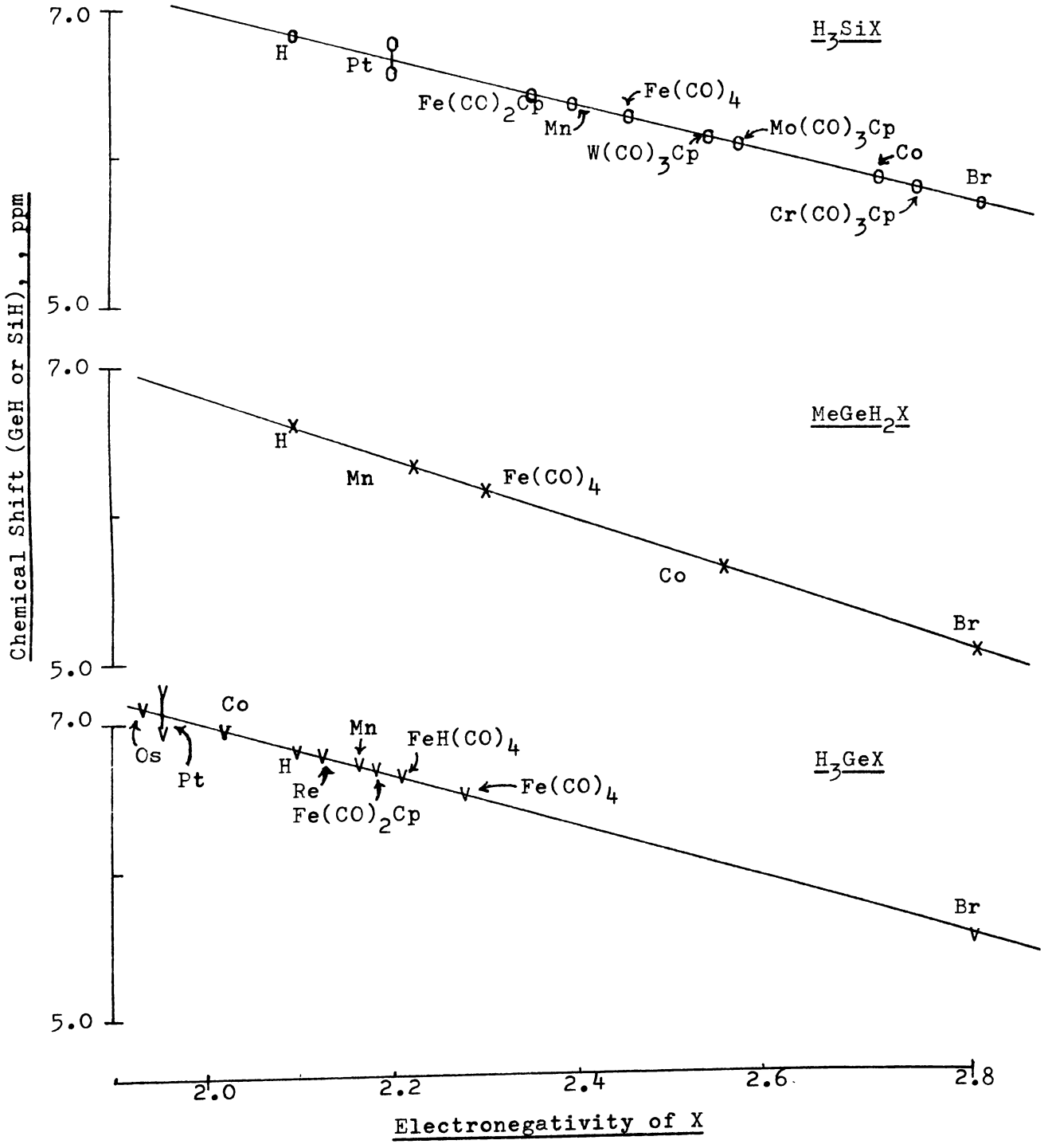
Mackay *et al.* (77) have suggested that the ^1H chemical shifts of $H_3GeM(CO)_n$ (M = Mn, Re, n = 5; M = Co, n = 4), $(H_3Ge)_2Fe(CO)_4$, and $H_3Ge(H)Fe(CO)_4$ can be related to the "effective electronegativities" of the $M(CO)_n$ groups. These workers found that the plot of τ(GeH) against $\delta_{sym}(GeH_3)$ was approximately linear and, from an earlier report by Jolly (151) of the relationship between $\delta_{sym}(GeH_3)$ in GeH_3X compounds and the electronegativity of X, were able to relate τ(GeH) to electronegativity values of $M(CO)_n$. However, the relationship reported by Jolly is not a very rigorous one and any electronegativity values calculated on the basis of this should only be reported to *ca.* ± 0.5, rather than the 3-figure (± 0.01) values quoted by Mackay *et al.* In addition, the range of results reported by these workers are all within a range of 0.4, so that the results are essentially meaningless.

Despite the discussion of the previous paragraph, it is interesting to consider the results of Table 6.1. on the basis of effective electronegativities. In Fig. 6.1. the chemical shifts of M'H in H_3GeX, $MeGeH_2X$, and H_3SiX (X = H, Br) have been plotted against the electronegativities of X. Straight lines were then drawn between each pair of results, and then the chemical shift data from Table 6.1. was fitted onto these lines.

FIGURE 6.1

Chemical Shifts versus Electronegativities of Group IV-Transition Metal Compounds

(Plotted on the basis of Chemical Shifts)



The intention here was not to provide electronegativity values for the ML_n groups, but to demonstrate the extent to which the data fit this sort of relationship. Thus, it can be seen that there is virtually no correlation between any of the lines for the transition metal derivatives, so that any exact electronegativity relationships do not exist. On the other hand, a general trend is apparent, to the extent that the derivatives of Mn, Fe, and Pt occur in the same sequence along each line, and this possibly indicates that in these compounds the electron density about each germyl proton may be the major factor determining the chemical shifts. By comparison the derivatives of cobalt do not fit into the same sequence and this suggests that other effects may be more significant in these compounds. No significant conclusions can be drawn about the positions of the points for the remaining metal compounds in Fig. 6.1.

The chemical shifts for the CH_3 protons of the methyl-substituted compounds shown in Table 6.1. do not show any significant variations between different complexes. This is probably quite reasonable as these protons are a long way removed from the transition metal

moieties, so that any significant changes in the metals could be expected to produce only secondary effects at the CH_3 protons. By comparison, the cyclopentadienyl protons show a considerable degree of variation with different compounds, and this is also as expected. That is, the electron distribution in the C_5H_5 ring will be quite sensitive to changes in the transition metal to which it is attached, as these same electrons can be involved in the bonding of C_5H_5 to the transition metal. This effect has been examined in more detail for compounds of the form $R_3M'M(CO)_nCp$ (M = Fe, Mo; n = 2, 3; M' = Ge, Sn, Pb) by Ugo *et al.* (152).

6.2. THE NMR DATA OBTAINED IN THE REACTION STUDIES OF CHAPTERS 4 AND 5.

In the reaction studies reported in Chapters 4 and 5 a considerable number of nmr results were interpreted entirely on the basis of the observed chemical shifts, multiplicities, and relative intensities of the various spectra. That is, no further analyses were carried out, such as the isolation and characterisation of the various components of each system, or comparison of the observed spectra with those of known samples of the same compounds. The discussion which follows is an attempt to rationalise the assignments made in this way, as well as giving an

indication of the certainty of the assignments made on the basis of the additional evidence mentioned above. The relative intensities and multiplicities of each spectrum will not be repeated here, as in all cases these were in agreement with the assignments made.

The derivatives of monogermane, and methylgermane will be considered first. Table 6.2. lists the results for these compounds, as well as the values reported by other workers, where appropriate. The results from the present work were originally recorded in Parts 4.2.1., (i) - (v); 4.2.2., (i), (v); 4.2.3., (iv); and 4.2.5., (i).

Table 6.2. ^{1}H NMR Chemical Shift Data for Derivatives of Monogermane and Methylgermane (in τ ,ppm)

Compound	This Work	Other Work	Ref.
GeH_4		6.85	100
GeH_3Cl	4.90	4.89	100
GeH_2Cl_2	3.50	3.53	100
$GeHCl_3$	2.50		
$MeGeH_3$	9.67 , 6.54	9.71 , 6.55	111
$MeGeH_2Cl$	9.21 , 4.68	9.27 , 4.70	111
$MeGeHCl_2$	8.80 , 3.20	8.86 , 3.26	111
$MeGeCl_3$	8.38	8.42	111
$MeGeH_2Br$	9.06 , 5.12	9.12 , 5.12	111
$MeGeHBr_2$	8.60 , ?	8.56 , 3.72	111

Table 6.2. (cont'd).

Compound	This Work	Other Work	Ref.
$MeGeBr_3$	8.18	8.02	111
MeGeHClBr	8.77 , ?	8.72 , 3.44	127
$MeGeBrCl_2$	8.36	8.33	127
$MeGeBr_2Cl$		8.21	127

Where more than one value has been reported the average value has been used in the table, and most of the results from this investigation are quoted for $SiCl_4$ solutions.

It can be seen from the table that in most cases there is good agreement between the results reported in this work and those of other workers. Two results may be incorrectly assigned, however. That is, the signals at 8.18τ observed in 4.2.2. (i), and 4.2.5. (i), and assigned to $MeGeBr_3$ could give better agreement with the literature value for $MeGeBr_2Cl$. Formation of such a product would be quite reasonable. Also, the signal observed at 8.36τ in 4.2.1. (iv) and assigned as either $MeGeBrCl_2$ or $MeGeBr_2Cl$ fits the former assignment more satisfactorily. There is one result given in the table for which no literature values could be found for comparison; that is, the signal assigned to $GeHCl_3$. This was assigned on the basis of the trend in chemical shift values for the series GeH_xCl_{4-x} (x = 1,2,3,4), in

which the differences between consecutive values becomes increasingly smaller with increasing chlorination. Such a trend is quite common in series of this sort (100,111,127,143).

In addition to assignments based on comparisons with reported data, the assignments for $MeGeH_3$, $MeGeH_2Cl$ and $MeGeH_2Br$ were supported by the recording of nmr spectra of known samples of the compounds. Such samples were initially identified by their infrared spectra.

The trend in chemical shifts noted above for a series of compounds, GeR_nX_{4-n} (n = 0 to 4), was useful in assigning some of the intermediate species detected in the reactions of the group IV-transition metal compounds. The observed data is listed in Table 6.3, and this also includes an indication of which assignments were further established by other means, and which were based entirely on the observed chemical shifts. The data are taken from the reaction studies of 4.2.2., (i), (iii) - (v); 4.2.3., (ii), (iv); 4.2.5. (i); and 5.2.1. (ii), and where more than one result has been observed for the same compound the range of values is indicated.

Table 6.3. ^{1}H NMR Chemical Shift Data for Derivatives of $MeGeH_2Mn(CO)_5$ and $MeGeH_2Co(CO)_4$ (in τ, ppm)

Compound	Chemical Shifts	Assignment Supported by other means
$MeGeH_2Mn(CO)_5$	9.27-9.38 , 6.25-6.34	Yes
$MeGeHClMn(CO)_5$	8.79-8.87 , 3.95-4.07	No
$MeGeCl_2Mn(CO)_5$	8.52-8.55	Yes
$MeGeHBrMn(CO)_5$	9.07-9.13 , ?	No
$MeGeBr_2Mn(CO)_5$	8.73-8.75	No
$MeGeH_2Co(CO)_4$	9.16-9.18 , 5.66-5.71	Yes
$MeGeHCo_2(CO)_7$(?)	8.79 , 4.52	No
$MeGeCo_3(CO)_9$(?)	8.42	No
$MeGeCo_3(CO)_{11}$	8.09	Yes

The assignments of the spectra of $MeGeH_2Mn(CO)_5$, $MeGeCl_2Mn(CO)_5$, $MeGeH_2Co(CO)_4$, and $MeGeCo_3(CO)_{11}$ have all been supported by independent characterisations. In the case of the parent Mn and Co compounds the characterisations have been fully discussed in Chapter 3, and the nmr spectra were recorded for known compounds. The two substituted compounds were both characterised by isolation of pure samples from particular reaction systems, and investigation of these by spectroscopic and analytical methods. Thus, it is only the intermediate compounds in the various reactions, and

$MeGeBr_2Mn(CO)_5$, which have not been characterised by independent means.

In the case of $MeGeHClMn(CO)_5$ the assignment of the spectra can be supported by a comparison of the trends in chemical shifts in the two series $MeGeH_xCl_{3-x}$, and $MeGeH_xCl_{2-x}Mn(CO)_5$. This shows that the observed chemical shifts for $MeGeHClMn(CO)_5$ are of the right magnitude, although it does not prove the assignment. The only other way to justify this is that the multiplicities of the two signals observed for the compound could be assigned to a monosubstituted derivative of $MeGeH_2Mn(CO)_5$, and in all cases $MeGeHClMn(CO)_5$ fitted logically into the observed reaction sequence as this derivative.

If one accepts the above assignment of $MeGeHClMn(CO)_5$, then the assignments of the shift values of $MeGeHBrMn(CO)_5$ and $MeGeBr_2Mn(CO)_5$ can be supported by comparisons of the series $MeGeH_xX_{3-x}$ and $MeGeH_xX_{2-x}Mn(CO)_5$ for X = Cl and Br. Again the assignments were not proven, but the agreement between corresponding values in the series is sufficiently good to provide strong support for the assignments. Finally, the assignments of the signals in the substituted cobalt compounds shown in the table, were made on the basis of chemical considerations more

than the actual values of the chemical shifts. These assignments have already been discussed in Chapter 5.

Apart from the data already discussed, various spectra were assigned to $CHCl_3$, CH_2Cl_2, $HCo(CO)_4$, and HCl in the reaction studies. The first three assignments were supported by literature data (141), while the latter assignment is unsupported, apart from the fact that its presence can be explained in every system in which it was observed.

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