Journal of Organometallic Chemistry, 182 (1979) 285–298

TRANSITION METAL CARBONYL DERIVATIVES OF THE GERMANES

PART XI* MONO-, DI-, AND TRI-(COBALTCARBONYL)-SUBSTITUTED METHYLGERMANES.

ROBERT F. GERLACH, BRUCE W.L. GRAHAM, AND KENNETH M. MACKAY**
School of Science, University of Waikato, Hamilton, New Zealand

(Received July 24th, 1979)

Summary

CH_3GeH_3 and $CH_3GeH_2Co(CO)_4$ each undergo a complex reaction with $Co_2(CO)_8$ to yield $CH_3GeCo_3(CO)_{11}$ as the principal product. CH_3GeCl_3 and CH_3GeBr_3 react at room temperature with $NaCo(CO)_4$ to form $CH_3GeX_2Co(CO)_4$ which in turn give $CH_3GeX[Co(CO)_4]_2$: further reaction is slight.

Introduction

Etzrodt and Schmid reported recently[1] that CH_3GeCl_3 reacts with $NaCo(CO)_4$ to give $CH_3GeCo_3(CO)_{11}$: $GeBr_4$ similarly yields $BrGeCo_3(CO)_{11}$. This tricobalt-undecacarbonyl germane type was first reported by Graham and colleagues[2] who isolated the phenyl species from $PhGeH_3$ and $Co_2(CO)_8$ and showed crystallographically that it had the structure $(\mu\text{-}PhGe[Co(CO)_4])(\mu\text{-}CO)Co_2(CO)_6$. This group have also mentioned[3] the formation of $CH_3GeCo_3(CO)_{11}$ from $(CH_3)_2GeH_2$ with Ge–C bond cleavage. In contrast, CH_3SiH_3 reacts[4] with $Co_2(CO)_8$ to form $CH_3SiH_2Co(CO)_4$ in 46% yield.

We report here an exploration of routes from hydrides and halides to methylgermanium mono-, di-, or tri-substituted by cobalt carbonyl groups.

---

[*] Part X is reference 6.

Results

Monocobalt Species. The synthesis and properties of $CH_3GeH_2Co(CO)_4$ closely parallel those[5] of $GeH_3Co(CO)_4$. The near-quantitative cleavage[5,6] with mercuric chloride and exchange[7] with $Mn(CO)_5^-$ are characteristic of cobalt-germanes.

The halides $CH_3GeX_2Co(CO)_4$ (X=Cl,Br) result from the 1:1 reaction of CH_3GeX_3 and $NaCo(CO)_4$ for 15 minutes in ether at room temperature followed by work-up at, or below, ambient. These two have not been reported although $CH_3GeI_2Co(CO)_4$[8] and all the halo-tin analogues are known. The properties are consistent with this formulation, although the dimethyl contaminant makes the chloride data less complete.

The vibrational spectra are listed in Table One. The characteristic shift of νCO to higher frequencies in the order H<I<Br<Cl is nicely shown. There is a clear doubling of the lowest carbonyl band compared[5,9] with $GeH_3Co(CO)_4$ or $GeX_3Co(CO)_4$ which (*pace* Ernstbrunner and Kilner[10]) is consistent with the *e* mode of the C_{3v} species going to $a'+a''$ in these C_s molecules. The frequency of the Ge-Co stretch at 221cm^{-1} is the same in $CH_3GeH_2Co(CO)_4$ and[5] in $GeH_3Co(CO)_4$. The main a' modes in the hydride show a lop-sided A contour with the P-branch appearing as a shoulder.

The GeH_2 chemical shift of $CH_3GeH_2Co(CO)_4$ is 0.5ppm downfield of[5] $GeH_3Co(CO)_4$, a similar shift to that found[11] for the pentacarbonylmanganese analogues. The changes among the halides show the induced anisotropic field in the bromide outweighing any electronegativity effects.

Di-substituted species. Under the same mild conditions, but using an excess of $NaCo(CO)_4$, the second halogen is substituted to give $CH_3GeX[Co(CO)_4]_2$ (X=Cl,Br). The mass spectra, as is common with polycobalt carbonyls of Group IV elements, show no parent ion. However, the observation of all the expected fragments shows the basic structure and the species are clearly distinguished from the alternative possibilities $CH_3GeX[Co_2(CO)_7]$ by their carbonyl stretching modes (Table Two). All eight frequencies predicted for the C_s symmetry are

TABLE ONE. Vibrational Spectra of $CH_3GeX_2Co(CO)_4$ Species (cm^{-1})

Description (a)	$CH_3GeH_2Co(CO)_4$ (b)	$CH_3GeCl_2Co(CO)_4$ (c)	$CH_3GeBr_2Co(CO)_4$ (d)	$CH_3GeI_2Co(CO)_4$ (e)
νCO(a')	2106s	2113 (8)	2110 (7.8)	2106 (9)
νCO(a')	2047vs	2057 (9)	2056 (8.3)	2053 (8)
νCO(a'+a'')	2017vs 2012vs	2038 (10) 2024 (10)	2036 (9.6) 2024 (10)	2033 (9.8) 2022 (10)
$\nu^{13}CO$	1982m	1989 (1)	1987 (0.4)	
	877m			
δCH_3(a'+a'')	873m,sh			
	843m		842 (0.2)	
and	838sh			
GeH_2 bend (a')	831s			
		801 (2)	802 (0.8)	
GeH_2 wag (a')	702m 691sh			
δGeH_2(a'') (?)	615w			
νGeC(a')	587m	599 (1)	595 (0.3)	
	549s	550 (6)	549 (1.5)	
δCoCO	542sh			
and	504m		489 (0.3)	
νCoC	485m	472 (2)	473 (0.5)	
	413vw			
δGeH_2(a'')	393m			
νGeCl (a'+a'')		391sh 383 (3)		

(a) CH_3 stretches and deformations appear in the expected regions: relative intensities in brackets

(b) Gas phase. Raman shows 582w,(pol?); 413s,pol; 221s,pol (νGeCo); 158w, 80s,pol and 38w (skeletal bends)

(c) Hexane solution: solid within $5cm^{-1}$ except νGeCl at 378 and 367

(d) Hexane solution: solid within $3cm^{-1}$

(e) Cyclohexane solution, reference 8.

TABLE TWO : Carbonyl Stretches of $CH_3GeX[Co(CO)_4]_2$ (cm^{-1}).

$CH_3GeCl[Co(CO)_4]_2$ (a)	$CH_3GeBr[Co(CO)_4]_2$ (a)	$CH_3GeI[Co(CO)_4]_2$ (b)	$(CH_3)_2Ge[Co(CO)_4]_2$ (c)
2109.2 (3.5)	2108.4 (3.1)	2106 (2.9)	2099.0 (3.1)
2091.1 (10)	2090.5 (10)	2089 (10)	2081.3 (9.6)
2048.6 (5.2)	2048.6 (5.7)	2046 (4.3)	
2042.5 (5.4)	2042.1 (5.7)	2040 (4.4)	2032sh (7.3)
2031.3 (9.3)	2031.4 (9.3)	2030 (9.0)	2024.7 (8.5)
2024.6 (9.5)	2024.8 (9.5)	2024 (9.2)	2018.8 (10)
2014.4 (5.9)	2014.7 (6.1)	2014 (4.9)	2006.7 (9.9)
2001.7 (3.3)	2001.4 (3.5)	2000 (2.9)	1997.0 (6.1)
1980 (0.6) (^{13}CO)			1965 (0.4)

(a) In hexane : values for nujol mull up to 2.5cm^{-1} lower.

(b) In cyclohexane, reference 8.

(c) In hexane under same conditions as (a).

observed, compared with the six main bands found for C_{2v} analogues such as $(CH_3)_2Ge[Co(CO)_4]_2$ and the five terminal and one bridging mode of heptacarbonyls. The frequency sequence $CH_3<I<Br<Cl$ is very slight, indeed the shifts among the halides are smaller than the phase shifts.

Trisubstituted Species from Halides. $CH_3GeX[Co(CO)_4]_2$ react only to a very small extent with $NaCo(CO)_4$ under the mild conditions used. The chloride yields a small amount of product whose infrared spectrum suggests[1] it is $CH_3GeCo_3(CO)_{11}$. The minor product in the reaction of the bromide does not show bridging carbonyl modes but shows terminal modes that are not inconsistent with $CH_3Ge[Co(CO)_4]_3$. Moreover, the minor fraction in the $CH_3GeCl[Co(CO)_4]_2$ preparation has a mass spectrum consistent with $CH_3GeCo_3(CO)_n$ for $n = 11$ *or* 12 (compare, e.g. $CH_3Sn[Co(CO)_4]_3$ which does not show[12] P^+ but $(P-CO)^+$) and anomalous intensity in the infrared, expecially at 2014cm^{-1}, not inconsistent with the dodecacarbonyl.

Hydride Reactions. The ^1H n.m.r. changes show that CH_3GeH_3 reacts with $Co_2(CO)_8$ to form CH_3GeH_2Co, CH_3GeHCo_2 and CH_3GeCo_3 species. The reaction is rapid, and all three types were found to be present when the signal resolution improved after the initial paramagnetic stage. Only one monosubstituted compound was formed and it has parameters identical with those of separately synthesised $CH_3GeH_2Co(CO)_4$. The tri-substituted product, with the 8.07τ methyl singlet, is the main end-product of the reaction. The mass spectrum is similar to that reported[1] for $CH_3GeCo_3(CO)_{11}$ and the infrared spectrum (identical to that of sample B in Table Three) also agrees with the reported[1,2] undecacarbonyls.

$CH_3GeH_2Co(CO)_4$ reacts similarly with $Co_2(CO)_8$ but the reaction is slower so that it is clear, after the initial stages, that a disubstituted species is forming from $CH_3GeH_2Co(CO)_4$ and is itself forming $CH_3GeCo_3(CO)_{11}$. $HCo(CO)_4$ forms in all the reactions and disappears by forming H_2 and $Co_2(CO)_8$. Separate experiments show $HCo(CO)_4$ does not react directly with the germanes.

For both the CH_3GeH_3 and $CH_3GeH_2Co(CO)_4$ reactions with $Co_2(CO)_8$, uncertainties remain about the other species involved which are always minor components of the mixtures. Of the two disubstituted species, the one common to all runs is that giving the CH_3 doublet at 8.75τ, GeH signal at 4.52τ and J = 2.2Hz. The likely candidates are $CH_3GeH[Co(CO)_4]_2$ or $CH_3GeH[Co_2(CO)_7]$. A mixture containing the 8.75τ doublet and the 8.07τ singlet of $CH_3GeCo_3(CO)_{11}$ resulted from hexane extraction of the involatiles from one of the incomplete $CH_3GeH_2Co(CO)_4$ reactions. The carbonyl region is presented as sample A in Table Three, while B was a fraction in which the doublet could not be detected.

Apart from the weak shoulder at 2064cm^{-1} (corresponding to the strongest band in $Co_4(CO)_{12}$ sample B has essentially the same spectrum as $CH_3GeCo_3(CO)_{11}$ and $PhGeCo_3(CO)_{11}$. There are some discrepancies, probably in presentation, in the 2009-38cm^{-1} region. This, with the mass spectrum, identifies the major product of the $CH_3GeH_2Co(CO)_4$ reaction as $CH_3GeCo_3(CO)_{11}$.

A contains an extra component giving the medium band at 2095cm^{-1} and the extra structure on the very strong band at 2030-2000cm^{-1}. The *a''* mode from the in-phase equatorial stretches of $CH_3GeH[Co(CO)_4]_2$ would account for

TABLE THREE. Carbonyl Stretches of Involatile Fractions (cm^{-1})

Involatiles (a)		$CH_3GeCo_3(CO)_{11}$	$PhGeCo_3(CO)_{11}$
A	B	(b)	(c)
2105w	2105w	2105m	2104w
2095m			
2085s	2082s	2082s	2082s
2070w			
2065w	2064w sh		
2055s	2056s	2056s	2056s
2045w	2047w sh	2046sh	2044w
2030vs	2038vs	2030s	2036s
2020s sh		2020/5m	2025m
shoulders to	2017m		2014m
2000	2009m	2007w	
	2003w sh		
	1998w	1998w	1998w
1850w	1849w	1850m	1850w
1835w	1837w	1838w	1835w sh

(a) A = sample showing 8.75τ doublet and 8.07τ singlet
B = sample showing only 8.07τ singlet

(b) In hexane, ref 1

(c) In cyclohexane, ref 2.

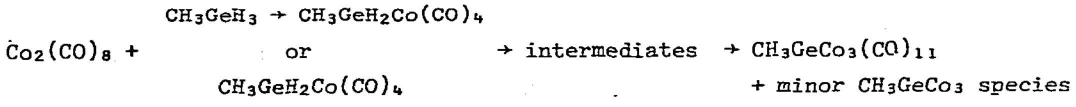
the 2095cm^{-1} band (compare Table Two), and its strong absorptions are expected in the 2030-2020cm^{-1} region. The alternative, $CH_3GeH[Co_2(CO)_7]$, is expected to show a medium-strong bridging mode about 1840cm^{-1}. While not conclusive, the balance of evidence favours the 8.75τ species being $CH_3GeH[Co(CO)_4]_2$. The 8.60τ methyl doublet, which appears when $Co_2(CO)_8$ is not in excess, may then be tentatively identified as the heptacarbonyl.

Assignment of the weak singlets is pure speculation. However it is noted that the 8.4τ species appears early in the CH_3GeH_3 reactions while the 8.2τ compound is only seen after longer standing: this may indicate $CH_3Ge[Co(CO)_4]_3$ and $CH_3GeCo_3(CO)_9$ respectively.

Discussion

Halide Reactions. The work reported here involved short reaction times and work-up at room temperature and below. These conditions yield mono- and di-(cobalt-tetracarbonyl) derivatives. Etzrodt and Schmid[1] reacted CH_3GeCl_3 with $NaCo(CO)_{11}$ (1:3) under more vigorous conditions (finally at 65°C for 3h) and recovered 80% $CH_3GeCo_3(CO)_{11}$. Thus it appears that mono-, di- or tri- substitution can be obtained all under fairly mild conditions, and the small yield of $CH_3GeCo_3(CO)_4$ from our reaction of $CH_3GeCl[Co(CO)_4]_2$ is reasonable. However there are indications, albeit slight, that the open species $CH_3Ge[Co(CO)_4]_3$ forms at room temperature. Thus the undecacarbonyl may arise as the first condensation step.

Hydride Reactions. Three hypotheses about the course of the CH_3GeH_3 reaction are compatible with the observations:- one, that substitution is stepwise in succession from CH_3GeH_3 to $CH_3GeCo_3(CO)_{11}$: the second, that $CH_3GeH_2Co(CO)_4$ and a $GeCo_2$ species form in separate reactions (more likely for $CH_3GeH(Co_2(CO)_7])$ and each reacts to form $CH_3GeCo_3(CO)_{11}$: the third, that the $GeCo_2$ species forms first and disproportionates. It seems reasonably clear that when $CH_3GeH_2Co(CO)_4$ is the starting material, the $GeCo_2$ species form(s) first and $CH_3GeCo_3(CO)_{11}$ follows but the mixture cannot be converted entirely whatever the reactant ratio. On the other hand, the report[4] of about 50% yield of $CH_3SiH_2Co(CO)_4$ from CH_3SiH_3 and $Co_2(CO)_8$ could indicate the third path. Further work, especially directed to the identity of the various di-substituted species, is needed to clarify these details. However, the main picture is clear



$$Co_2(CO)_8 + \begin{array}{c} CH_3GeH_3 \rightarrow CH_3GeH_2Co(CO)_4 \\ \text{or} \\ CH_3GeH_2Co(CO)_4 \end{array} \rightarrow \text{intermediates} \rightarrow \begin{array}{l} CH_3GeCo_3(CO)_{11} \\ + \text{ minor } CH_3GeCo_3 \text{ species} \end{array}$$

It is interesting that CH_3GeH_3 yields the carbonyl-bridged species $CH_3[Co(CO)_4]Ge\ [Co_2(CO)_7]$ directly in reaction at room temperature, analogous to the reaction[13] of GeH_4 with $Co_2(CO)_8$ which gives $Ge[Co_2(CO)_7]_2$. In contrast, CH_3GeX_3 and GeX_4[13] with $NaCo(CO)_4$ give only small yields of fully-substituted species at room temperature but there is evidence that the products include the non-bridged $CH_3Ge[Co(CO)_4]_3$ and $Ge[Co(CO)_4]_4$ species. For both $CH_3GeCo_3(CO)_{11}$ and $GeCo_4(CO)_{14}$, the carbonyl bridged species eliminate CO to give the enneacarbonyl cluster $RGeCo_3(CO)_9$ (R = CH_3[1] or $Co(CO)_4$[13]). The possible condensation of the open species is already indicated[1,13] and is being further explored, although it is resisted[14] for tin and lead analogues.

Experimental

Manipulations were carried out using a vacuum line or under nitrogen and spectroscopic measurements were made as described in earlier[5,6] work. Commercial CH_3GeCl_3 contained dimethyl contaminant which could not be entirely removed. However, the dimethyl products could be readily identified and their contribution to spectra allowed for. A different source (Laramie Chemical Co.) provided pure CH_3GeBr_3.

CH_3GeCl_3 was stirred for 15 minutes at room temperature in THF with $NaCo(CO)_4$ (1:1 mole ratio). The solvent was removed and the residues extracted with hexane. A pale-yellow, air sensitive solid was sublimed from the extract at room temperature. It has a chemical shift of 8.75τ in C_6H_6 and an infrared spectrum (Table One – absorptions of ∿5% $(CH_3)_2GeClCo(CO)_4$ allowed for) compatible with $CH_3GeCl_2Co(CO)_4$. Reaction in Et_2O was very similar.

$CH_3GeCl_2Co(CO)_4$ (formed as above) was reacted with excess $NaCo(CO)_4$ for 15 minutes at room temperature in Et_2O. A similar work-up, below or at room temperature, gave a dark yellow species with a chemical shift of 8.64τ in C_6H_6. This was a little less air-sensitive than the dichloride. The infrared spectrum (Table Two) can be assigned on the basis of $CH_3GeCl[Co(CO)_4]_2$. The mass spectrum shows no P^+ but $(P\text{-}nCO)^+$ are prominent with relative intensities 30:44:15:37:30:100:63:85 for n=1 to 8 respectively. Other significant ions were $CH_3GeCo_2^+$(19), $ClGeCo_2^+$(26), $GeCo_2^+$(16), $CH_3GeClCo^+$(9), CH_3GeCo^+(20), $ClGeCo^+$(8), $GeCo^+$(17) and Co_2^+(20). A minor crop showed some anomalous intensities in the infrared spectrum, especially at 2014cm^{-1}, and its mass spectrum showed an additional weak family of ions $CH_3GeCo_3(CO)_x^+$ for x = 0 to 11.

$CH_3GeCl[Co(CO)_4]_2$ reacted under similar conditions with excess $NaCo(CO)_4$ showed largely unchanged starting material and some $Co_4(CO)_{12}$. A small amount of product had infrared bands at 2105, 2056, 1848 and 1836cm^{-1}.

CH_3GeBr_3 reacted under similar conditions in THF with 1:1 $NaCo(CO)_4$ gave 63% pale-yellow methyldibromogermyltetracarbonylcobalt, $CH_3GeBr_2Co(CO)_4$ [Br% found 39.03, 38.62 calc. 38.10 : m.pt. 78–80°C in a sealed tube]. This sublimes at 10°C, is unchanged after several weeks in N_2, but reacts slowly in air. Reaction in Et_2O was similar but formed a small amount of $CH_3GeBr[Co(CO)_4]_2$ in addition. The chemical shift is 8.43τ(C_6H_6), and the infrared spectrum is given in Table One. The mass spectrum shows no parent but $(P\text{-}nCo)^+$ have relative intensities 26:100:80:38 for n = 1,2,3,4. The $Br_2GeCo(CO)_x^+$ series has 1:6:20:32 for x = 3,2,1,0 : $CH_3GeBrCo(CO)_x^+$ is 1:5:13 for x = 2,1,0 : $BrGeCo(CO)_x^+$ is 0.3:2:13 for x = 2,1,0. Other ions are CH_3GeCo^+(8), $GeCo^+$(10), $CH_3GeBr_2^+$(1), CH_3GeBr^+(1), CH_3Ge^+(62), Br_2Ge^+(1), $BrGe^+$(27), Ge^+(5).

$CH_3GeBr_2Co(CO)_4$ and excess $NaCo(CO)_4$ similarly yielded the pale orange monobromide $CH_3GeBr[Co(CO)_4]_2$ [Br found 15.55%, calc. 15.68% m.pt. 75–77°C in sealed tube). The product sublimes above 30°C, reacts slowly in air, and is less soluble in alkanes than is $CH_3GeBr_2Co(CO)_4$. The chemical shift in benzene is 8.12τ. The carbonyl modes are included in Table Two. The mass spectrum shows similar features to the chloro-analogue with $(P\text{-}nCO)^+$ = 0:20:40:23:33:25:75:60:100 for n = 0 to 8 respectively. A weak series $BrGeCo_2(CO)_x^+$ is seen with relative intensities 6:10:5:3:4:35 for x = 5 to 0. Other ions were $CH_3GeCo_2^+$(9), $GeCo_2^+$(14), $CH_3GeBrCo(CO)^+$(10), $CH_3GeBrCo^+$(15), CH_3GeCo^+(23), $BrGeCo^+$(13), $GeCo(CO)^+$(4), $GeCo^+$(27) and Co_2^+(22).

$CH_3GeBr[Co(CO)_4]_2$ plus excess $NaCo(CO)_4$ at room temperature largely returned starting material. A hexane extract of the mixture showed the following carbonyl stretching modes in addition to starting material and cobalt carbonyls(cm^{-1}) : 2104w, 2081m, 2042w, 2023(?), 2014vs, 2000w sh, compare[12] $CH_3Sn[Co(CO)_4]_3$ 2101w, 2079s, 2040w, 2028w sh, 2020s, 2010s and 1992w sh.

Methylgermyltetracarbonylcobalt, *$CH_3GeH_2Co(CO)_4$*. To an anion sample, prepared from $Co_2(CO)_8$(312mg, 0.92mmole) by reduction with sodium amalgam, was added $MeGeH_2Br$ (271mg, 1.60mmole) and 2ml dry ether. The mixture was shaken at room temperature for 15 minutes and then fractionated. Small amounts of $MeGeH_3$, $HCo(CO)_4$ and unreacted $MeGeH_2Br$ (all identified by i.r. spectra) were recovered with the ether. $MeGeH_2Co(CO)_4$ (182mg, 0.70mmole, 44% based on $MeGeH_2Br$ added) was found in the −45° and −63°C traps. In other runs, yields ranged from 37 to 45%. THF may be used as solvent but is more difficult to separate.

The pure product is colourless but rapidly turns through yellow and orange to dark red-brown, especially in the light or on warming. However, although the colour change is very marked, the rate of decomposition at 20°C is only a few percent an hour. Vapour pressure measurements are vitiated by the decomposition, but the values measured of 5mm at 0°C and 12mm at 22°C give some indication of the handling properties.

Refractionated *methylgermyltetracarbonylcobalt* was characterised spectroscopically. In $SiCl_4$ solution, the ^1H n.m.r. spectrum shows a triplet at 9.16τ (intensity 3), a quartet at 5.67τ (intensity 2) and $^3J = 3.5$Hz. The vibrational spectrum is in Table One. In the mass spectrum, the parent ion envelope showed m/e = 264 to 256 containing 75%P, 15%P-H, and 10%P-2H ($H_5C_5O_4GeCo$ requires m/e = 264 for ^{76}Ge and 258 for ^{70}Ge). The fragmentation pattern was dominated by $CH_3GeH_xCo(CO)_n^+$ ions with relative intensities 3:13:27:24:38: for n = 4,3,2,1,0 respectively. x = 2>1>0 for n = 4,3 and x = 0>1>2 for n = 2,1,0. $GeH_xCo(CO)_n^+$ ions were all present but weak except for n = 1 (10%) and n = 0 (35%). For these x = 0 dominates but x = 3 is clear, showing H transfer. $CH_3GeH_x^+$ and GeH_x^+ were strong but variable, suggesting some decomposition in the spectrometer, cf[6]

$GeH_3GeH_2Co(CO)_4$. $HCo(CO)_n^+$ and $Co(CO)_n^+$ ions were found for all n but are weak.

$\underline{CH_3GeH_2Co(CO)_4 + HgCl_2}$ (1:1 mole ratio) was followed by ^1H n.m.r. and reacted smoothly at room temperature initially yielding CH_3GeH_2Cl. $CH_3GeH_2Co(CO)_4$ was completely consumed after 48h., forming 73% CH_3GeH_2Cl, 26% CH_3GeHCl, and 1% CH_3GeCl_3 : the latter mixture continued to redistribute. From the intensities, 98% of the methyl protons originally in $CH_3GeH_2Co(CO)_4$ appeared in the methylhalogermanes.

$\underline{\text{With } Mn(CO)_5^-}$. $CH_3GeH_2Co(CO)_4$ (52.4mg, 0.20 mmol) was added to excess $NaMn(CO)_5$ in THF. After 15 min. reaction, repeated refractionation yielded pure[11] $CH_3GeH_2Mn(CO)_5$ (46.9mg, 0.17 mmol, 85%). No reaction occurred in pentane or in absence of a solvent.

$\underline{CH_3GeH_3 \text{ plus } Co_2(CO)_8}$. Preliminary experiments showed that reaction at room temperature was very rapid: for example, the ^1H nmr spectrum of a 1:2 mixture showed no further change after 5 minutes when all the CH_3GeH_3 was consumed leaving mainly $HCo(CO)_4$ (21.4τ) and a singlet at 8.07τ.

At −20°C, a number of reactions (ranging from 2:1 to 1:2 ratios), followed by ^1H n.m.r. in $SiCl_4$ solution, showed a consistent pattern of changes. Initially, the signals were very degraded suggesting a paramagnetic intermediate. Indeed, in one run where too much $Co_2(CO)_8$ was added, the signals degraded every time shaking brought more $Co_2(CO)_8$ into solution. When the signals could be resolved (ca 1h at −20°) there were present $HCo(CO)_4$, $CH_3Co(CO)_4$ and species giving a triplet at 9.19τ, (J = 3.3Hx, second component at 5.7τ), a doublet at 8.77τ (J = 2.8Hz, second component detected at a later stage at 4.84τ), a singlet at 8.40τ and a singlet at 8.08τ. As reaction proceeded, the main change was the increase in the 8.08τ singlet. Thus with 10% CH_3GeH_3 reacted the ratios of triplet : doublet : 8.4τ singlet to 8.08τ singlet were 6:10:2:9 and, at 80% reaction, 3:3.5:trace:10. Further weak signals appeared in the later stages, the most consistent being a second doublet at 8.60τ and a singlet at 5.43τ. Although these main features were found consistently, the proportions when the paramagnetic stage had passed were variable with sometimes the doublet and sometimes the triplet being more pronounced. Other minor signals appeared in some runs only. No consistent pattern of these changes with reaction ratio could be discerned.

After completed runs, the n.m.r. tube was opened and the volatiles removed. The involatile fraction showed only the 8.07τ singlet and solutions in cylohexane showed almost identical infrared spectra to those observed from the product of the $CH_3GeH_2Co(CO)_4$ reaction with $Co_2(CO)_8$-cf. sample B, Table Three.

$CH_3GeH_2Co(CO)_4$ plus $Co_2(CO)_8$. The ^1H n.m.r. spectrum of $CH_3GeH_2Co(CO)_4$ (47.6 mg, 0.18 mmol) and $Co_2(CO)_8$ (60.9 mg, 0.18 mmol), dissolved in $SiCl_4$, was observed at temperatures ranging from -40° to 0°C. Again signal resolution was very poor in the early stages. Reaction proceeded steadily with the consumption of $CH_3GeH_2Co(CO)_4$ and the formation first of a species (8.79τ doublet, 4.52τ quartet, J = 2.2Hz) which was later consumed giving major (8.09τ singlet) and minor (8.42τ singlet) products. Throughout the reaction, $HCo(CO)_4$ was also produced (21.5τ singlet). After 1½h, the temperature was raised to 0°C and all changes ceased after 2½h at 0°C. The composition of the final mixture (based on intensities) was unreacted $CH_3GeH_2Co(CO)_4$ 20%, doublet species 20%, 8.42τ species 8%, 8.09τ species 50% while 80% of the reacted hydrogen remained as $HCo(CO)_4$. Further runs followed a similar course. A ratio of 0.15 mmol $CH_3GeH_2Co(CO)_4$ to 0.1 mmol $Co_2(CO)_8$ formed species with doublets at 8.75τ and 8.60τ at -40°, but only after 3h. at -40° and raising the temperature to 0°C at the rate of 10° per 0.5h did the 8.07τ singlet appear. After 7 days at 0°C, this sample contained unreacted $CH_3GeH_2Co(CO)_4$: doublet species : 8.07τ species in the ratio 3:2:1. The ^1H n.m.r. spectrum of the separated volatiles showed the 8.60τ doublet together with $CH_3GeH_2Co(CO)_4$.

When the ratio was 0.05 mmol $CH_3GeH_2Co(CO)_4$ to 0.1 mmol $Co_2(CO)_8$, only the 8.75τ doublet appeared in the first hour at -30°C, after another hour the 8.05τ singlet was present and finally, after 18h at 0°C, the doublet, the 8.05τ singlet, two other weak singlets at 8.42τ and 8.22τ, and $HCo(CO)_4$ were present. Incondensible gas (0.12 mmol) was found when the tube was opened. Volatiles were separated and showed $CH_3GeH_2Co(CO)_4$ plus a weak 8.46τ signal together with a peak at 9.82τ assigned as CH_3GeH_3.

The infrared spectra of various samples from the involatile products of these runs are given in Table Three.

Mass spectra were run on extracts from the CH_3GeH_3 and $CH_3GeH_2Co(CO)_4$ reactions which showed only the 8.07τ singlet. The principal ions were assigned as (relative intensities in brackets) : $CH_3GeCo_3(CO)_n^+$ [11:13:40:38:13:50:100:62:53:74:70:50 for n = 11 to 0 respectively]; $GeCo_3(CO)_n^+$ for n = 8,7,5 to 0 [all very weak except n = 2(1), n = 1(5), n = 0(60)]; $CH_3GeCo_2(CO)_n^+$ for n = 1(8), n = 0(43) together with Co_3^+(4), Co_2^+(9), Co^+(7), CH_3GeCo^+(10), $GeCo^+$(15) and $Co(CO)^+$(6). These agree closely, though with some variations in intensity, with the reported[1] mass spectrum of $CH_3GeCo_3(CO)_{11}$ and with the features[2] of $PhGeCo_3(CO)_{11}$.

Acknowledgements

We thank the NZUGC for scholarships (B.W.L.G. and R.F.G.) and for grants to purchase the n.m.r. and infrared spectrometers. We are grateful to Dr. P. Holland, (Ruakura Agricultural Centre) for mass spectra and to Dr. M. Taylor (Auckland University) for Raman measurements.

References

1 G. Etzrodt and G. Schmid, *J. Organometallic Chem.*, 169 (1979), 259.

2 R. Ball, M.J. Bennett, E.H. Brooks, W.A.G. Graham, J. Hoyano, and S.M. Illingworth, *Chem. Commun.*, (1970) 592.

3 E.H. Brooks and W.A.G. Graham, *Abstracts 4th International Conference on Organometallic Chemistry* (1969) A2.

4 S.K. Gondal and A.G. MacDiarmid, *Inorg. Nucl. Chem. Letters,* 5 (1969) 413.

5 R.D. George, K.M. Mackay and S.R. Stobart, *J. Chem. Soc. Dalton,* (1972) 974.

6 F.S. Wong and K.M. Mackay, *J. Chem. Soc. Dalton,* (1978) 1752.

7 R.F. Gerlach, B.W.L. Graham, and K.M. Mackay, *J. Organometallic Chem.,* 118 (1976) C23: B.W.L. Graham, *D. Phil. Thesis, Waikato* (1973).

8 D.J. Patmore and W.A.G. Graham, *Inorg. Chem.,* 6 (1967) 137.

9 G.C. van der Berg and A. Oskam, *J. Organometallic Chem.* 78 (1974) 357 and references therein.

10 E.E. Ernstbrunner and M. Kilner, *J. Chem. Soc. Dalton* (1975) 2598.

11 B.W.L. Graham, K.M. Mackay, and S.R. Stobart, *J. Chem. Soc. Dalton* (1975) 475.

12 D.J. Patmore and W.A.G. Graham, *Inorg. Chem.* 7(1968)771; 5(1966)2222.

13 R.F. Gerlach, K.M. Mackay, and B.K. Nicholson, *J. Organometallic Chem.* submitted : R.F. Gerlach, B.W.L. Graham, K.M. Mackay, 9th International Conference on Organometallic Chemistry (1979) P3T.

14 G. Schmid, *Angew. Chem. Int. Edn* 17 (1978) 392.