Transition-metal Carbonyl Derivatives of the Germanes. Part II.[1] Germylpentacarbonylmanganese

By **R. D. George, K. M. Mackay, and S. R. Stobart,*†** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Reaction of bromogermane with $NaMn(CO)_5$ in ether or tetrahydrofuran gives germylpentacarbonylmanganese in up to 86% yield. Both $GeH_3Mn(CO)_5$ and $GeD_3Mn(CO)_5$ have been prepared and physical properties, i.r., Raman, n.m.r., and mass spectra are reported; although a molecular symmetry of only C_s is expected, the vibrational spectrum closely follows selection rules predicted assuming local C_{3v} and C_{4v} symmetry at Ge and Mn respectively, and an assignment is proposed on this basis.

GERMANIUM–MANGANESE bonds are well-established[2] in derivatives of organo- or halogeno-germanes, but until our recent preliminary report[3] of germylpentacarbonylmanganese, $GeH_3Mn(CO)_5$, the only similar derivative of germane itself was $GeH_2[Mn(CO)_5]_2$. This complex[4] was isolated in 95% yield by direct reaction of monogermane on manganese carbonyl hydride, and interestingly no evidence for the formation of the corresponding mono- or tri-substituted germanes was found. Much more recently a related digermane, $GeH_3GeH_2Mn(CO)_5$ has been reported[5] by one of us. The silane derivative $SiH_3Mn(CO)_5$ has also been described.[6]

Analysis of the vibrational spectrum of $GeH_3Co(CO)_4$ was facilitated by its relatively high molecular symmetry;[1] however, the greater stability of $GeH_3Mn(CO)_5$ towards photochemical and thermal decomposition allows it to be handled much more easily, and a fuller study of its properties should therefore be possible.

EXPERIMENTAL

Techniques.—Manipulations were carried out on a conventional vacuum line with taps and joints lubricated with Apiezon 'N' grease. Ethers were dried over sodium and distilled from $LiAlH_4$. The sodium used was highly purified by continuous by-pass filtration of the liquid and was made available by courtesy of Dr. R. J. Pulham of this department: if such an exotic source of sodium is not accessible, the metal should be thoroughly freed from organic contaminants. I.r., Raman, ^1H n.m.r., and mass spectra and vapour pressures were measured as reported[1] earlier.

Preparation.—$NaMn(CO)_5$ was prepared from $Mn_2(CO)_{10}$ (891 mg; 2·28 mmol) and an excess of 5% sodium amalgam by shaking in dry diethyl ether. The amalgam was removed and the bulk of the ether was pumped off from the dark green solution. Germyl bromide (702 mg, 4·51 mmol) was condensed in and the mixture was allowed to warm to room temperature, when the green colour lightened and sodium bromide was deposited. After 15 min, when no further change could be discerned, the volatile products were fractionated through traps held at −45, −125, and −196 °C. Monogermane (9·2 mg, 0·12 mmol) was found in the liquid nitrogen trap and *germylpentacarbonylmanganese* (902 mg, 3·33 mmol, 74%) was held at −45 °C. In other successful runs, yields varied in the 55—80% range and tetrahydrofuran was also found to be a satisfactory solvent. Occasionally up to 50% of the germanium appeared as GeH_4 and only traces of the product were

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† *Present address:* Department of Chemistry, Queen's University, Belfast, BT9 5AG.

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found. Recent work[7] has shown that $GeH_3Mn(CO)_5$ reacts with solid NaOH or NaOEt forming 50—80% GeH_4 together with a little digermane. The occasional failure of the preparation is therefore attributed to the effect of alkaline impurities introduced from contaminated sodium.

In preliminary experiments, $Cl_3GeMn(CO)_5$ was treated with $LiAlH_4$ in dry Et_2O or with $NaBH_4$ in a THF/MeOH mixture. The reaction mixture became yellow and a trace of hydrogen was formed, but in each case the only volatile product detected other than the solvents was a little monogermane.

[$^2H_3$]*Germylpentacarbonylmanganese* was prepared on a 2·5 mmol scale from GeD_3Br and $NaMn(CO)_5$ in ether.

Characterisation. For the germylpentacarbonylmanganese, there was found C = 22·3%, H = 1·4: calc. for $C_5H_3O_5GeMn$: C = 22·2%, H = 1·1%. Further characterisation was provided by the accurate mass determination of the families of parent ion peaks $^{12}C_5{}^nH_3{}^{16}O_5{}^mGe^{55}Mn$ (n = 1 or 2: m = 70, 72, 73, 74, 76) in the mass spectra, where agreement of *ca.* 8 p.p.m. between observed and calculated values was obtained.

The ^1H n.m.r. resonance, measured in benzene solution, was a singlet at τ 6·72.

Handling properties. $GeH_3Mn(CO)_5$ is a white solid melting at 23·8 ± 0·3 °C. The vapour pressure is *ca.* 4 mmHg at room temperature and thus the compound may be readily handled in a vacuum line. Between 32 and 81 °C, vapour pressures follow the equation $\log p$ (mmHg) = $-2300/T + 8{\cdot}3$ giving an extrapolated boiling point of 150 °C. Slow decomposition occurs at higher temperatures so that these figures are approximate. The pressure rose 1·0 mmHg during 1 h at 60·5 °C and slight yellowing of the liquid was observed. After 4 h, 3·4 mmHg pressure remained after freezing in liquid nitrogen. In a further experiment, a sample in a sealed glass tube showed only a trace of incondensable gas after 4 h at 100 °C in the dark, suggesting a mainly photochemical reaction at 60 °C. A sample passed through a tube at 220 °C completely decomposed.

Reactions. When air (60 cmHg pressure) was admitted to a sample of $GeH_3Mn(CO)_5$ at 4 mmHg pressure in an i.r. gas cell, CO, CO_2, and GeH_4 were formed slowly as the only volatile products: *ca.* 50% of the sample had reacted after 72 h and decomposition was complete within a week.

A sample reacted rapidly with triethylamine to give a soft, orange solid with a very broad carbonyl stretch at 1940 cm^{-1}. The mull decomposed in air and i.r. bands due to $Mn_2(CO)_{10}$ appeared. Reaction of the orange solid with dry HBr formed triethylammonium bromide but no $HMn(CO)_5$ was observed.

A sample treated with an excess of dry HCl in a sealed glass tube at 60 °C for 5 h yielded 10% unchanged $GeH_3Mn(CO)_5$ and a cream-coloured solid part of which melted at 75—85 °C and part at 140 °C. The i.r. spectrum of the solid showed carbonyl bands together with absorptions at 868s, 755s, 712s, 705s, and 360 cm^{-1} s.

RESULTS AND DISCUSSION

Reaction between bromogermane and sodium pentacarbonylmanganese proceeds according to equation (1) to give in high yield germylpentacarbonylmanganese, $GeH_3Mn(CO)_5$. The failure to produce this or any other Ge–Mn derivative of the related coupling reaction using

$$GeH_3Br + NaMn(CO)_5 \longrightarrow GeH_3Mn(CO)_5 + NaBr \quad (1)$$

GeH_3K and $Mn(CO)_5Cl$ has been reported elsewhere by Massey *et al.*;[4] likewise, our preliminary attempts at the reduction of $Cl_3GeMn(CO)_5$ have been unpromising, even though under similar experimental conditions $H_2Ge[Fe(C_5H_5)(CO)_2]_2$ was obtained[8] from its dichlorogermanium analogue.

Reactions between halogenogermanes and other anionic metal carbonyls have yielded germyl-cobalt,[1] -iron,[9] and -rhenium[10] complexes and also[5] GeH_3GeH_2-$Mn(CO)_5$. This route may therefore be regarded as a useful general approach to the preparation of metal-carbonyl substituted germanes, and in addition several silane analogues have been thus obtained from silyl halides.

The investigation of some preliminary reactions of $GeH_3Mn(CO)_5$ allows an initial comparison with $GeH_3Co(CO)_4$. Markedly higher thermal stability and resistance to oxidation by air are evident for the manganese complex, the former presumably accounting for its synthesis in up to 86% yield[11] compared with only 48% achieved[1] for the cobalt compound. In contrast, although a 2 : 1 reaction of Et_3N with $GeH_3Mn(CO)_5$ is indicated, the resultant adduct is much less stable than the $GeH_3Co(CO)_4,2L$ species examined.[1] This is in agreement with the conclusion, reached by Aylett,[12] that $SiH_3Co(CO)_4$ is a stronger Lewis acid than its manganese analogue. Reaction with HCl yields carbonyl complexes whose i.r. spectra show bands attributable to Ge–Cl stretching and Ge–H bending modes, indicating reaction (2), similar to that observed[6]

$$GeH_3Mn(CO)_5 + xHCl \longrightarrow GeH_{3-x}Cl_xMn(CO)_5 + xH_2 \quad (2)$$

for $SiH_3Mn(CO)_5$, and in contrast to the cleavage of the Ge–Co bond in $GeH_3Co(CO)_4$. A detailed examination of further reactions is presently in progress.[13]

Mass Spectrum.—Mass spectra measured for $GeH_3Mn(CO)_5$ and $GeD_3Mn(CO)_5$ were fully consistent with one another and with the assignments given in Table 1, which also contains peak intensity data for the hydride. Conspicuous features are the high proportion of the ion current carried by fragments containing both metal atoms, the families of ions arising from loss of CO groups, the strong tendency of ions of the type $GeH_xMn(CO)_y{}^+$ to retain all three hydrogen atoms, and the occurrence of hydridomanganese rearrangement ions. These characteristics are similar to those found[1] for germyltetracarbonylcobalt. One unusual feature is the

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relatively low intensity of ions $GeH_xMn(CO)_3^+$ compared with other $GeH_xMn(CO)_y^+$ families, observed for both hydride and deuteride; this coincides with the identification of $GeH_xMn(CO)_3^{2+}$ as the most abundant doubly-charged ions in the spectra. Loss of oxygen to give carbide-like ions is a common feature in the mass spectra of metal carbonyl derivatives; here ions due to several such species containing Ge as well as Mn are apparent.

TABLE 1

Mass spectrum of $GeH_3Mn(CO)_5$

			Ratio of Hydrogens[b]			
m/e	Assignment	Relative intensity[a]	$x = 3$	$x = 2$	$x = 1$	$x = 0$
275—266	$GeH_xMn(CO)_5^+$ [c]	22·3	10·0	2·2	0·4	—
247—237	$GeH_xMn(CO)_4^+$ [c]	42·0	10·0	0·9	1·3	0·3
218—209	$GeH_xMn(CO)_3^+$	9·3	10·0	0·7	4·3	2·1
202—197	$GeH_xMn(CO)_2C^+$?	0·7				
196	$HMn(CO)_5^+$	0·6				
195	$Mn(CO)_5^+$	0·6				
190—181	$GeH_xMn(CO)_2^+$	27·8	10·0	1·4	1·8	0·8
168	$HMn(CO)_4^+$	0·1				
167	$Mn(CO)_4^+$	0·7				
162—153	$GeH_xMn(CO)^+$	33·0	10·0	4·9	3·2	2·7
145—137	GeH_xMnC^+	0·9				
140	$HMn(CO)_3^+$?					
139	$Mn(CO)_3^+$	0·4				
134—125	GeH_xMn^+	100	8·4	1·2	10·0	6·4
112	$HMn(CO)_2^+$	0·6				
111	$Mn(CO)_2^+$	5·9				
109—104·5	$GeH_xMn(CO)_3^{2+}$	1·1				
95—90·5	$GeH_xMn(CO)_2^{2+}$?	0·5				
84	$HMn(CO)^+$	1·7				
83	$Mn(CO)^+$	9·6				
79—70	GeH_x^+	7·2	—	0·7	2·9	10·0
78	$HMnC^+$?					
67	MnC^+	0·1				
56	HMn^+	0·2				
55	Mn^+	33·1				
28	CO^+	d				

[a] Summed over $x = 0, 1, 2, 3$ and over Ge isotopes where appropriate. [b] Relative to strongest component of family = 10·0. Approximate values only, through overlap of peaks due to isotopes of Ge. [c] Peaks at 275 and 247 arise from ^{13}C. [d] Strong peak but includes N_2^+.

Metastable peaks confirm successive loss of CO as an important fragmentation route: process (3) is followed

$$GeH_xMn(CO)_5^+ \longrightarrow GeH_xMn(CO)_4^+ + CO \quad (3)$$
$$(m^* = 221, 219, 217)$$

by similar decomposition of $GeH_xMn(CO)_4^+$ and $GeH_xMn(CO)_3^+$, with $m^* \approx 191$ and 164 respectively. A further series of metastables at $m^* = 136—138$ may arise from (4). Fragmentation thus occurs mainly by

$$GeH_xMn(CO)_5^+ \longrightarrow Mn(CO)_5^+ + GeH_x \quad (4)$$

stepwise loss of CO from the relatively highly abundant parent ion family. Other processes, including those involving fission of the Ge–Mn bond, are of only minor importance.

Vibrational Spectrum.—I.r. and Raman spectra are listed in Table 2, together with tentative assignments which are examined more fully below.

Although the most likely configuration for the $GeH_3Mn(CO)_5$ molecule belongs to the point group C_s, the observed vibrational spectrum above 400 cm^{-1} largely obeys the selection rules predicted for a local symmetry of C_{3v} for the GeH_3 group and of C_{4v} for the $Mn(CO)_5$ group, and is discussed on this basis. In particular a number of i.r. bands have conspicuously type-*A* gas-phase contours, each having a prominent *Q* branch and noticeably weak *P* branch, and have polarised Raman counterparts, as expected for vibrations of species a_1 under C_{nv} symmetry.

GeH, GeD *Modes*.—The vibrations of the GeH_3 group are represented by $2a_1 + 3e$ for C_{3v} symmetry. The a_1 and e stretching modes are readily assigned in the case of the deuteride, and show an unusually large frequency separation of *ca*. 33 cm^{-1}. Assignment is less easy in the case of the hydride, but two gas-phase i.r. features not present in the deuteride spectrum, at 2063 and 2040 cm^{-1}, can be tentatively ascribed to e and a_1 ν(GeH) respectively. The symmetric germyl deformation (a_1) gives rise to a strong and characteristically type-*A* i.r. band at 818 cm^{-1}, dropping in frequency to 581 cm^{-1} for $GeD_3Mn(CO)_5$. The remaining e modes are most obvious in the solid-state i.r. spectrum measured for the hydride, with deformation and rocking vibrations assigned at 880 and 508 cm^{-1}, but a distinct though weak gas-phase i.r. band at 610 cm^{-1} can be assigned to $\delta_{asym}(GeD_3)$.

CO *Stretching Modes*.—The gas-phase i.r. spectra are dominated by the extremely strong absorptions due to the carbonyl stretching vibrations. These divide into species $2a_1 + b_1 + e$, assuming local C_{4v} symmetry, the b_1 mode being i.r.-inactive but allowed in the Raman effect. Following assignments for $SiH_3Mn(CO)_5$ [6] and

$HMn(CO)_5$,[14] as well as for a number of other pentacarbonylmanganese derivatives,[15] the i.r. band well to high frequency of the main absorption and showing PQR structure (2114 cm^{-1}) is attributed to the a_1 equatorial stretching mode. Corresponding Raman bands in both hydride and deuteride are strongly polarised, supporting this conclusion. The strongest i.r. absorption, centred at *ca.* 2020 cm^{-1}, also shows PQR structure and is assigned to the other a_1 vibration, with the related e mode lying under the same contour. This is confirmed by examination of the Raman spectra, where a low-frequency shoulder on the main band which does not appear to be polarised separates into a medium-weak band at 2000 cm^{-1} on cooling to the solid phase. This feature may thus be ascribed to the e mode, phase-shifted out of coincidence with the a_1 band. The strongest Raman intensity is found at 2035 cm^{-1}; this is then assigned to the b_1 mode, with some (polarised) contribution from the a_1 GeH stretch in the hydride.

In the i.r. spectrum of $HMn(CO)_5$, two strong bands both showing PQR structure and lying very close together at 2029 and 2020 cm^{-1} have been assigned [14] to the e and a_1 carbonyl stretches. Our proposed assignment parallels this, rather than attributing structure of the strongest carbonyl band to a separation of the two vibrations, as has been suggested [6] for $SiH_3Mn(CO)_5$. Identification of the strong Raman band at 2035 cm^{-1} as the b_1 carbonyl stretch is consistent with the assignments made for both $HMn(CO)_5$ and $SiH_3Mn(CO)_5$, where the b_1 frequencies were 2041 and 2036 cm^{-1} respectively.[6,14]

Other Modes.—In the region below 800 cm^{-1}, in addition to GeH_3 or GeD_3 modes, are found the remaining vibrations of the $GeMn(CO)_5$ framework. The very strong i.r. absorptions, centred near 660 cm^{-1} and split into two components, are attributable [15] to two of the Mn–C–O bands, probably $a_1 + e$. The polarised Raman bands at 473 and 409 cm^{-1} are assigned respectively as the a_1 Mn–C axial and equatorial stretches. The former is the more intense in the i.r. spectrum and the latter is prominent in the Raman spectrum as expected from the form of the displacements. In the $SiH_3Mn(CO)_5$ spectrum, polarisation of the weak Raman band at 476 cm^{-1} was not observed [6] and it was tentatively assigned as an e mode. Reassignment as an a_1 vibration would be consistent not only with this work but also with vibrational assignments for $HMn(CO)_5$ [14]

TABLE 2

Vibrational spectra of $GeH_3Mn(CO)_5$ and $GeD_3Mn(CO)_5$ (cm^{-1})

$GeH_3Mn(CO)_5$			$GeD_3Mn(CO)_5$		
I.r. (gas)	I.r. (solid)	R [a](liquid)	I.r. (gas)	R [a](liquid)	Tentative description
2117R 2114Q 2111P } m	2110s	2111vs(p)	2112ms	2109s(p)	νCO(eq), a_1
2063m,br					νGeH(e?)
2040sh	2020sh				(νGeH, a_1)?
		2034vs(p)		2040s 2034s }	νCO, $a_1 + b_1(R)$
2022R 2019Q 2016P? } vvs	1980vvs,br 1960sh	2005sh	2023R 2017P } vvs	2000m	νCO, a_1 (*I.r.*) $+e$ (*I.r.*, *R*)
1981m	1945sh		1979m		$\nu^{13}CO$
1975w					
			1490m	1480sh	νGeD, e
			1460R 1457Q 1454P } ms	1458s(p)	νGeD, a_1
	885sh				
	877m	880m			δGeH_3, e
821R 818Q 815P } s	808 804 } vs	810mw			δGeH_3, a_1
			745vw		($\delta GeHD_2$)
685w,sh	725w	757vw	735vw		
672m 663vs }	650vvs	649vvw	667s 659vs }		$\delta MnCO$, $a_1 + e$
			610w	613w	δGeD_3, e
			581vs	585vw	δGeD_3, a_1
	508m				ρGeH_3, e
474m	470s	473w(p)	475mw		νMnC(ax)a_1
	410w	409vvs(p)		413vs(p)	νMnC(eq.)a_1
		219vs(p)		220vs(p)	νMnGe, a_1
		132w,sh			
		110vvs,br(p) 92sh?		106vvs(p)	skeletal deformations

Overtones and combinations, $GeH_3Mn(CO)_5$ (I.r. solid): 2960, 2580, 2505, 2440, 2405, 2360, 1208, 1095, 1075, 1028, 971, 912, 723, 695, 608, 550.

[a] Polarised bands indicated, (p).

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and $ClMn(CO)_5$.[15] The frequency of 409 cm^{-1} for a_1 equatorial Mn–C stretching is very close to that of 408 cm^{-1} found [14] in $HMn(CO)_5$. The difference between these values and that of 431 cm^{-1} for a similar band in the Raman spectrum of $SiH_3Mn(CO)_5$ [6] may be due to interaction between the two a_1 modes in the latter, as seems to be the case for $ClMn(CO)_5$.[15]

A strong, sharp, and polarised Raman band at 219 cm^{-1} for the hydride has a counterpart at 220 cm^{-1} in the spectrum of the [$^2H_3$]-compound, and is confidently assigned to the Ge–Mn stretching vibration (a_1). We have observed the corresponding band in $Cl_3GeMn(CO)_5$ at 235 cm^{-1}, where interaction with ν(Ge–Cl) is likely, and a similar shift occurs for the analogous cobalt complexes, from 228 cm^{-1} in $GeH_3Co(CO)_4$ [1] to 240 cm^{-1} in $GeCl_3Co(CO)_4$.[16]

The remaining bands above 200 cm^{-1} are weak and show no distinctive contours or polarisation properties. They will include three further e modes and two b_1 modes in the Raman effect. No detailed assignment is attempted. It must be emphasised that Mn–C stretches, Mn–C–O bends and probably GeD deformations and GeH(D) rocks are all likely to mix and the descriptions given in Table 2 are not intended to exclude this.

Finally, the skeletal deformations are represented by the Raman bands near 100 cm^{-1}. For $HMn(CO)_5$, the only a_1 skeletal mode was assigned [14] at 77 cm^{-1} while e modes were indicated at 106 and 120 cm^{-1}. The massive band at 110 cm^{-1} is therefore likely to include CMnC and CMnGe bending contributions and its polarisation is the only clear instance in the spectrum of the following of C_s selection rules rather than those of the assumed higher local symmetries.

Conclusion.—The vibrational and mass spectra relate closely to those of $GeH_3Co(CO)_4$,[1] and also $SiH_3Mn(CO)_5$;[6] germylpentacarbonylmanganese is considerably more stable both thermally and chemically than the analogous cobalt complex, and this is paralleled by the silyl analogues.

Assignment of the vibrational spectrum of manganese carbonyl hydride by Edgell *et al.*[14] has shown that for this molecule it is unnecessary to assume a symmetry lower than C_{4v}. The vibrational analysis given above for $GeH_3Mn(CO)_5$, and also shown to be applicable for $SiH_3Mn(CO)_5$, suggests that approximations based on local symmetry are valid for related metal carbonyl derivatives of lower symmetry, provided that extensive mixing of vibrational fundamentals is not likely. A similar approach to the spectroscopic assignment of the substituted tin derivatives $X_3SnMn(CO)_5$ (X = Cl, Br, Me or Ph) has recently been used by Onaka.[17]

[2/506 *Received, 6th March*, 1972]

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