Transition-metal Carbonyl Derivatives of the Germanes. Part V.* Chemistry of Pentacarbonylmanganese Derivatives of Germane and Methylgermane

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The replacement chemistry of the Ge–H bonds in two germylmanganese carbonyl complexes, $[\mathrm{Mn(CO)_5GeH_3}]$ (I) and $[\mathrm{Mn(CO)_5GeH_2Me}]$ (II), has been investigated and related to that found for the unsubstituted hydrides germane and methylgermane. Pentacarbonylmethylgermylmanganese (II) has not been previously reported, and its full characterization using ^{1}H n.m.r., vibrational, and mass spectroscopic methods is described.

PRELIMINARY investigation of the reactivity of the germyl group when linked to a transition metal in carbonyl complexes has indicated that whereas germanium–metal bond cleavage is predominant for cobalt [1] and iron [2] compounds, in the case of pentacarbonyl-manganese [3] and -rhenium [4] derivatives substitution at germanium is possible leaving the intermetallic bond intact. A similar pattern of behaviour has been found for analogous silicon compounds.[5] We report in this paper the results of a study of the substitution chemistry of the GeH_3 group bonded to manganese, in $[\mathrm{Mn(CO)_5GeH_3}]$ (I), and in the new compound $[\mathrm{Mn(CO)_5GeH_2Me}]$ (II) in which substitution of the methylgermyl group can readily be followed using ^{1}H n.m.r. spectroscopy.

Using for comparison results obtained previously or by conducting appropriate experiments, this has allowed the manner in which the chemistry of germane and of methylgermane is affected by metal substitution to be investigated.

RESULTS AND DISCUSSION

The complex (II) was synthesized by the well established [6] alkali-metal halide elimination reaction (1). The yield of purified material was 69%, comparable with

$$\mathrm{MeGeH_2Br} + [\mathrm{Mn(CO)_5}]^- \longrightarrow [\mathrm{Mn(CO)_5GeH_2Me}] + \mathrm{Br}^- \quad (1)$$

that achieved [3] for (I); isolation of (II) was facilitated by the use of diethyl ether as solvent for the reaction. The product is a colourless liquid which quickly becomes pale yellow during handling using high-vacuum techniques. The ^{1}H n.m.r. spectrum is first order at 60 MHz, with average chemical shifts of τ 9·32 (CH_3) and τ 6·30 (GeH_2), and a coupling constant $^3J_{\mathrm{H-H}}$ of 4·0 Hz, resembling those for unsubstituted systems such as methylgermane [7] ($\tau_{\mathrm{C}H}$ 9·71, $\tau_{\mathrm{Ge}H}$ 6·55; $^3J = 4{\cdot}3$ Hz) and methyldigermane [8] ($\tau_{\mathrm{C}H}$ 9·79, $\tau_{\mathrm{Ge}H}$ 6·42; $^3J = 4{\cdot}3$ Hz) and comparable with τ 9·38 in $CDCl_3$ for $[\mathrm{Mn(CO)_5GeMe_3}]$ and τ 6·72 in C_6H_6 for (I).[3,9]

In the mass spectrum of (II), a medium-intensity parent ion family is accompanied by dominance of fragments arising from CO loss to give $[\mathrm{Mn(CO)}_y\mathrm{GeH}_x\mathrm{Me}]^+$ showing the typical [4] alternation of intensity with y; ions resulting from Ge–C bond fission form a much weaker series. Rearrangement processes involving transfer of hydrogen forming $[\mathrm{Mn(CO)}_y\mathrm{GeH_3}]^+$ as well as $[\mathrm{Mn(CO)}_y\mathrm{H}]^+$, and more prominently of methyl to give $[\mathrm{MnCH_3}]^+$ and $[\mathrm{MnCH_2}]^{+\cdot}$, were also observed. Loss of hydrogen from germanium was important only for the ion fragments towards the lower m/e range. These features parallel the behaviour of (I) [3] and of $[\mathrm{Mn(CO)_5GeMe_3}]$,[9] and like the former, for (II), fragments containing both metal atoms carry *ca.* 75% of the total ion current.

In its vibrational spectrum, (II) closely resembles (I) in the wavenumbers, intensities, and symmetry properties of fundamentals due to the pentacarbonylmanganese group, following predictions based on local C_{4v} symmetry for the latter. The methyl rocking and GeH_2 bending modes overlap in the 877 and 838 cm^{-1} contours, and other GeH_2 vibrations are occluded by the strong CO and MnC modes. The Ge–C stretch is assigned to the 583 cm^{-1} i.r. absorption with a feeble Raman counterpart, polarization properties of which have not been determined. The much more intense and strongly polarized Raman shift at 220 cm^{-1} is attributed to the Ge–Mn stretching vibration, found at 219 cm^{-1} in (I).[3]

In a reaction which is much more rapid in the presence of tetrahydrofuran, (I) is decomposed by sodium hydroxide or ethoxide to give germanes and involatile residues. Reaction of this type is probably significant when impure sodium is used as a starting material in synthesis of (I) *via* a route analogous to equation (1); lowered yields of product are accompanied by conversion of germyl bromide into germane, and this may be a general feature of related syntheses where varying amounts of germane (or silane) have often been observed.[1-5]

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* Part IV is ref. 4.

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[4] K. M. Mackay and S. R. Stobart, *J.C.S. Dalton*, 1973, 214.

[5] B. J. Aylett and J. M. Campbell, *J. Chem. Soc.* (*A*), 1969, 1910, 1917; B. J. Aylett, J. M. Campbell, and A. Walton, *ibid.*, p. 2110.

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Mixing of (I) with a five-fold excess of ammonia in the gas phase for 20 min at ambient temperature leaves the complex unchanged, in remarkable contrast with the silyl analogue from which after only 1 min under the same conditions quantitative formation of $[Mn(CO)_5H]$ was observed, most of the silicon appearing as $(SiH_3)_2NH$. Isolation of the latter compound suggests that the known very low stability of germyl(amino)-species may account for the difference in reactivity between the two complexes. Formation of an orange involatile adduct between (I) and NEt_3 has already been reported;[3] with diethylamine in an n.m.r. tube, (I) yields a rust-coloured solid insoluble in an excess of base, so that a chemical shift for the adduct could not be obtained. In pyridine, however, (I) gives a clear lemon-yellow solution showing two new signals, at τ 6·71 and 5·17. This is consistent with an equilibrium represented by equation (2), the τ 6·71

$$[Mn(CO)_5GeH_3] + nC_5H_5N \rightleftharpoons [Mn(CO)_5GeH_3]\cdot nC_5H_5N \quad (2)$$

resonance being due to uncomplexed (I) with that at low field due to a soluble adduct. This is supported by the fact that co-ordination of pyridine to silyl and germyl tetracarbonylcobalt complexes has been found to be weak,[1,10] and by the reported shift to lower field of the silyl resonance in $[Mn(CO)_5SiH_3]$ on formation of $[Mn(CO)_5SiH_3]\cdot 2py$.[10]

Both (I) and (II) proved to be soluble in tetrachlorosilane but no reaction could be detected, so that this medium is a very suitable one in which to follow substitution by n.m.r. methods. Methylgermane was also inert to $SiCl_4$ while digermane underwent a very slow reaction giving digermanyl chloride to the extent of *ca.* 5% in 13 days.[11] Only with $[Fe(CO)_4(GeH_3)_2]$ and $[Fe(CO)_4(MeGeH_2)_2]$ have significant changes been observed in silicon tetrachloride.[12]

The reaction of (I) in carbon tetrachloride was rapid and complete, so that the only products identified were $CHCl_3$ and $[Mn(CO)_5GeCl_3]$. A much slower reaction occurred between (II) and CCl_4 in equimolar ratio, consistent with stepwise chlorination [equation (3)]

$$[Mn(CO)_5GeH_2Me] \xrightarrow{CCl_4} [Mn(CO)_5GeHClMe] \longrightarrow [Mn(CO)_5GeCl_2Me] \quad (3)$$

accompanied by production of both $CHCl_3$ and CH_2Cl_2. When no further change could be detected, scission of 92% of the H from Ge in (II) was accounted for by the total amount of $CHCl_3$ and CH_2Cl_2 which were present in a 10 : 1 ratio. Although a reaction involving chloroform was occurring, there remained unchanged Ge–H bonds and $CHCl_3$ in the final mixture, in which the relative proportions of the germanes were (II) 22%, $[Mn(CO)_5GeHClMe]$ 39%, and $[Mn(CO)_5GeCl_2Me]$ 39%. When CCl_4 was present in excess, as in the HCl reaction, all of (II) was consumed but there still remained unchanged Ge–H in the species formulated as $[Mn(CO)_5GeHClMe]$. In this resistance to complete chlorination by CCl_4 (II) behaves differently from (I) but resembles $MeGeH_3$.

Halogenation as in equation (3) was also observed on treatment of (II) with $GeCl_4$, and although slower than with CCl_4 did proceed to complete conversion into $[Mn(CO)_5GeCl_2Me]$. This is in contrast to the behaviour of methylgermane, where much more extensive reaction occurs with CCl_4 than with $GeCl_4$, and of (I) which in $GeCl_4$ gave a complex n.m.r. spectrum in which the only strong signal was at τ 4·26 thought to arise from $[Mn(CO)_5GeH_2Cl]$. The latter assignment is substantiated by the observation that in equimolar proportions with tin(IV) chloride in $SiCl_4$ solution slow but complete disappearance of the resonance due to (I) occurred during 1 h with a concomitant increase in intensity of a new signal at τ 4·11. We identify this with a reaction of the type (4) which has been reported elsewhere,[13] involving reduction of the tin halide to the divalent state.

$$RGeH_3 + SnCl_4 \longrightarrow RGeH_2Cl + HCl + SnCl_2 \quad (4)$$

In these reactions, polysubstitution where it occurs is clearly stepwise; dichloro-species do not appear until a significant concentration of the corresponding monochloro-derivatives is present. No evidence for Ge–Mn bond cleavage was encountered.

Substitution and cleavage of (II) occur with Br_2, the former predominating [equation (5)]. Minor quantities of $MeGeHBr_2$, $MeGeH_2Br$, and $[Mn(CO)_5GeHBrMe]$

$$[Mn(CO)_5GeH_2Me] \xrightarrow{Br_2} [Mn(CO)_5GeBr_2Me] + MeGeBr_3 \quad (5)$$

were detected, despite the presence of a small proportion of unchanged bromine. This reaction compares with that between bromine and methylgermane, where equimolar proportions give[14] $MeGeH_2Br$ under carefully controlled conditions while with an excess of bromine polybromo-species are also formed although without complete reaction of all Ge–H bonds. By contrast, digermane reacts[11] with cleavage of the Ge–Ge and all Ge–H bonds in each molecule attacked, even at low temperature and with a deficit of bromine. The balance between substitution and cleavage is further illustrated by the bromination of $[Mn(CO)_5GePh_3]$ which gives[15] $[Mn(CO)_5GeBr_3]$ in dibromoethane solution but results in metal–metal bond cleavage in hydrocarbon solvents.

All of our observations are consistent with HX

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(X = Cl[3] or Br) reacting as in equation (6) {as did[5]

$$[\mathrm{Mn(CO)_5GeH_3}] + n\mathrm{HX} \longrightarrow [\mathrm{Mn(CO)_5GeH}_{3-n}\mathrm{X}_n] + n\mathrm{H_2} \quad (6)$$

HCl with $[\mathrm{Mn(CO)_5SiH_3}]$}, where excess HX does not lead to complete halogenation. This is similar to the uncatalysed reaction with methylgermane, although the latter is slower and results in little polysubstitution. In $\mathrm{CCl_4}$ solution, (II) reacted with twice its molar equivalent of hydrogen chloride such that about half the Ge–H bonds were chlorinated by HCl, half with $\mathrm{CCl_4}$, and 8% remained unsubstituted.

With mercuric chloride in $\mathrm{CCl_4}$, reaction (7) occurred where the quantity of chloroform produced indicates that only one Cl per $\mathrm{HgCl_2}$ is involved and no free

$$\mathrm{(II)} + 2\mathrm{HgCl_2} \xrightarrow{\mathrm{CCl_4}} \{\mathrm{Mn(CO)_5GeHClMe}\} \longrightarrow [\mathrm{Mn(CO)_5GeCl_2Me}] + \mathrm{Hg_2Cl_2} + \mathrm{CHCl_3} + \tfrac{1}{2}\mathrm{H_2} \quad (7)$$

mercury is formed. In an inert solvent, the overall reaction between (II) and mercuric chloride was (8),

$$\mathrm{(II)} + \mathrm{HgCl_2} \longrightarrow [\mathrm{Mn(CO)_5GeCl_2Me}] + \mathrm{Hg} + \mathrm{H_2} \quad (8)$$

but again stepwise substitution with $[\mathrm{Mn(CO)_5GeHClMe}]$ as intermediate was evidenced by the fact that metallic mercury was not detected until the dichloro-species started to form.

In these reactions, reduction to mercurous chloride may occur as in equation (9); an analogous step could lead from $\mathrm{Hg_2Cl_2}$ to the Hg observed in reaction (8),

$$2\mathrm{HgCl_2} \longrightarrow 2[\mathrm{HHgCl}] \longrightarrow \mathrm{H_2} + \mathrm{Hg_2Cl_2} \quad (9)$$

or alternatively this might be formed from the unstable[16] $\mathrm{HgH_2}$. With $\mathrm{HgI_2}$, where the apparent slowness of the reaction was probably due to poor contact between the reagents, similar behaviour is observed to give a product whose i.r. spectrum is consistent with the presence of $[\mathrm{Mn(CO)_5GeH}_{3-x}\mathrm{I}_x]$ species. No cleavage of Ge–Mn bonds by $\mathrm{HgX_2}$ (X = Cl or I) was encountered, in contrast to the ready metal–metal bond scission described previously[1,5] for silyl and germyl tetracarbonylcobalt derivatives.

The reaction of (II) with $\mathrm{PCl_3}$ resembled those with the Group IVB halides but was very much slower. The initial phosphane product may well be $\mathrm{PHCl_2}$, decomposition to hydrogen and lower phosphorus halides accounting for the yellow solid with a single broad i.r. absorption. Here (II) is distinctly more active than the germanes ($\mathrm{MeGeH_3}$ or $\mathrm{Ge_2H_6}$) which are hardly affected by $\mathrm{PCl_3}$ and show only a slow and limited degree of substitution with $\mathrm{PBr_3}$. Preliminary experiments with $\mathrm{PF_3}$ suggested mainly CO displacement from (II) but with tentative evidence for Ge–F bond formation. The use of $\mathrm{BBr_3}$ as a selective brominating agent in germane chemistry has been described by Drake *et al.*[17] However, with (II) evidence for metal–metal bond cleavage as well as polybromination was obtained.

In liquid $\mathrm{SO_2}$ at ambient temperature, a solution of (I) became yellow during 30 min; on pumping off the excess it was found to have taken up one molecular equivalent of $\mathrm{SO_2}$ forming a bright yellow adduct [equation (10)]. Analogous behaviour of methyl metal–carbonyl complexes has been thoroughly documented

$$[\mathrm{Mn(CO)_5GeH_3}] + \mathrm{SO_2} \longrightarrow [\mathrm{Mn(CO)_5GeH_3}]\cdot\mathrm{SO_2} \quad (10)$$

by Wojcicki *et al.*[18] and interpreted as insertion of $\mathrm{SO_2}$ to give a sulphinate linkage. I.r. bands at 1195 and 1070 $\mathrm{cm^{-1}}$ for the product isolated here point to an identical type of structure, $[\mathrm{GeH_3{\cdot}S(O)_2{\cdot}Mn(CO)_5}]$.

While $[\mathrm{Mn(CO)_5GeCl_2Me}]$ was recovered and characterized by analytical as well as n.m.r. methods, the monochloro-complex $[\mathrm{Mn(CO)_5GeHClMe}]$ was identified only by its ^{1}H n.m.r. spectrum which, like that of (II), was first order. That this assignment is reasonable is illustrated by the n.m.r. parameters for chloro-substituted germanes collected in Table 1: the trends in chemical shifts and coupling constants for the chloromethylgermylmanganese compounds are clearly similar to those resulting from chlorination of methylgermane. N.m.r. data for species formulated as $[\mathrm{Mn(CO)_5GeH}_{2-x}\mathrm{Br}_x\text{-}\mathrm{Me}]$ (x = 1 or 2) fit into a similar pattern.

TABLE 1

^{1}H N.m.r. parameters

Compound	τ (C*H*) [a]	τ (Ge*H*) [a]	^3J(H–H)/Hz
$\mathrm{MeGeH_3}$	9·68	6·56	4·3
$\mathrm{MeGeH_2Cl}$	9·23	4·69	3·1
$\mathrm{MeGeHCl_2}$	8·83	3·21	1·6
$\mathrm{MeGeCl_3}$	8·35		
$[\mathrm{Mn(CO)_5GeH_2Me}]$	9·33	6·30	4·0
$[\mathrm{Mn(CO)_5GeHClMe}]$	8·83	4·01	3·1
$[\mathrm{Mn(CO)_5GeCl_2Me}]$	8·54		
$[\mathrm{Mn(CO)_5GeH_3}]$		6·58	
$[\mathrm{Mn(CO)_5GeH_2Cl}]$		4·11	

[a] Mean values found in this work, in $\mathrm{CCl_4}$ or $\mathrm{SiCl_4}$ solution.

TABLE 2

Fragment ion abundances * $[\mathrm{Mn(CO)_5GeH_2Me}]$

	y					
	0	1	2	3	4	5
$[\mathrm{Mn(CO)}_y\mathrm{GeH}_x\mathrm{CH_3}]$	100	12	20	14 (*a*)	33	10
$[\mathrm{Mn(CO)}_y\mathrm{GeH}_x]^+$ (*c*)	49 (*b*)	7	4	3·5 (*a*)	7 (*a*)	4
$[\mathrm{Mn(CO)}_y\mathrm{CH_3}]^+$ (*d*)	7	Weak	N.o.	Weak	N.o.	Weak
$[\mathrm{Mn(CO)}_y\mathrm{H}]^+$	5	2	0·6	3	0·6	0·4
$[\mathrm{Mn(CO)}_y]^+$	38	8	4	2	1	0·3
$[\mathrm{CH_3GeH}_x]^+$	24 (*a*)					
$[\mathrm{GeH}_x]^+$ (*c*)	5					

* Intensities normalized to $[\mathrm{MnGeH}_x\mathrm{CH_3}]^+ = 100$ of ions with $m/e > 50$, summed over x where appropriate. For all families $x = 2 \gg x = 1 > x = 0$ except for (*a*) where $x = 0 > x = 2 > x = 1$ and (*b*) where $x = 0 > x = 1 > x = 2$. (*c*) In these families, ions with $x = 3$ are observed forming up to 12% of the total family intensity. (*d*) Also $[\mathrm{MnCH_2}]^+$ (7), $[\mathrm{MnCH}]^+$ (v weak), $[\mathrm{MnC}]^+$ (v weak).

Summary.—With hydrogen halides, mercuric halides, Group IV tetrachlorides, and phosphorus(III) chloride,

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(I) and (II) show only Ge–H substitution with no evidence for cleavage of Ge–C, Ge–Mn, or Mn–C–O linkages. The general pattern of reaction is closely related to that for $MeGeH_3$ or Ge_2H_6, though differences emerge in relative activity of certain reagents; for example CCl_4 compared with $GeCl_4$ or PCl_3. Furthermore, while the latter pair result in only slow chlorination all Ge–H bonds are eventually replaced, the faster reaction with CCl_4 leaving unsubstituted Ge–H. Although some scission of Ge–Mn (but not Ge–C) bonds was encountered in the reactions of (II) with Br_2 or BBr_3, a significant proportion of the products corresponded to substitution of Ge–H, in direct contrast to the reaction between digermane and bromine. Addition of nitrogen-containing bases or of SO_2 to (I), together with its degradation by hydroxide or ethoxide, represent reactions in which Ge–Mn bond cleavage predominates.

EXPERIMENTAL

Manipulations were carried out using a standard high-vacuum system or under dry nitrogen gas in a glove-box. N.m.r. spectra were measured in sealed tubes using a JEOL C-60HL spectrometer relative to internal Me_4Si or benzene, usually with external lock at 30 °C. Mass spectra were run on vapour-phase samples with a Varian CH7 instrument. Vibrational spectra were recorded as before [3,4] or with Shimadzu IR-27G or Beckmann IR-20A spectrometers, while the Raman spectrum of (II) was obtained from a sealed capillary sample on the Spex instrument at the Victoria University of Wellington (Ar ion laser, from 514·5 nm).

Synthesis and Properties of (II).—$[Mn_2(CO)_{10}]$ (814 mg, 2·05 mmol) was shaken in dry THF (15 ml) with an excess of 2% sodium amalgam for 60 min. The amalgam was removed, the ether volume reduced to 2 ml, and CH_3GeH_2Br (368 mg, 2·17 mmol) was condensed onto the anion suspension. The mixture was shaken for 15 min after which the volatiles were fractionated to give: $MeGeH_3$ (trace) at −196 °C; THF at −127 °C; *pentacarbonylmethylgermylmanganese* (II) at −45 °C. After refractionation, (II) was found in 69% yield (413 mg, 1·55 mmol) while other runs in THF or Et_2O gave yields in a range down to 45%. When freshly purified, (II) is a colourless liquid with vapour pressures of 21·6 at 15 and 35·5 mmHg at 25 °C, readily turning pale yellow but without other signs of decomposition over 30—60 min at room temperature; however, decomposition is significant at 50 °C so that an extrapolation to the boiling point is unreliable. In the mass spectrum, the molecular ion family was found at m/e = 288, 286, 285, 284, and 282, corresponding to $^{12}C_6{}^1H_5{}^{16}O_5{}^nGe^{55}Mn^+$ for n = 76, 74, 73, 72, and 70. Major fragment ions are listed in Table 2, where the species have been arbitrarily assigned to the most likely formulae for observed m/e values.

In the vibrational spectrum of (II), the following bands (cm^{-1}) were recorded: I.r. (gas) 2963w, 2926w, 2877w, 2107m, 2029vs, 2018vs, 1985w, 1460w, 1080w, 1030w, 877w, 838s, 695sh, 670s,sh, 660s, 609wbr, 583m, 482m; Raman (liquid) 2106(pol)s, 2031(pol)s, 2012s, 881w, 582w, 429s,sh, 416(pol)s, 220(pol)s, 169w, 109vs,br.

$[Mn(CO)_5GeH_3]$.—*Basic impurities.* Compound (I) was prepared as described [3] previously in yields of 59—73%. However, in early experiments yields of 0—10% were found and up to 95% GeH_4 based on the GeH_3Br formed. Subsequent preparation of (I) and (II) used vacuum-distilled sodium, but initially unpurified metal was the starting material. Test experiments indicated basic impurities; $[Mn(CO)_5GeH_3]$ plus THF condensed onto dry NaOEt or dry NaOH had completely decomposed after 15 min at room temperature, and GeH_4 corresponding to 25—30% of the Ge was recovered. In the absence of THF, (I) reacted slowly during 18 h with NaOEt yielding 20% uncondensable gas, $GeH_4 + Ge_2H_6$ accounting for 30% Ge, no unchanged (I), and a solid containing Ge and Mn. In absence of ether, no decomposition was observed over NaOH for 36 h at room temperature while at 50 °C, *ca.* 12% uncondensable gas was found but no germanes. Finally, (II) containing only a trace of THF showed only slow and partial decomposition to GeH_4 plus Ge_2H_6 over NaOH and unchanged (II) was recovered after 30 min. Addition of more THF led to rapid and complete decomposition.

Reactions.—Compounds (I) *and* (II) *plus* $SiCl_4$. The ^1H n.m.r. spectra of solutions of (I) or of (II) in $SiCl_4$ showed no change after 3 days in the dark, nor after a further day in daylight, at room temperature. In time however slight decomposition occurred but led to no signals which could be firmly assigned to substituted products. $MeGeH_3$ in a similar experiment also showed no sign of reaction while Ge_2H_6 gave weak signals due [11] to GeH_3GeH_2Cl after *ca.* 2 weeks at room temperature.

Compound (II) *plus* CCl_4. Compound (II) (0·13 mmol) and CCl_4 (0·13 mmol) dissolved in $SiCl_4$ showed after 1 h at 30 °C a new weak doublet at τ 8·83 (J = 3·0 Hz) together with a $CHCl_3$ signal at τ 2·72. The spectrum of (II) became weaker and these signals increased, and after 3·5 h a corresponding quartet τ 3·95, J = 3·0 Hz, together with a singlet at τ 8·52 were clear. The signals due to (II) then decreased further; the intensity of multiplets due to the intermediate reached a maximum and then decreased with the τ 8·52 and $CHCl_3$ singlets steadily increasing. Overnight, colourless crystals formed in the tube, the solution yellowed somewhat, and a new weak signal attributable to CH_2Cl_2 appeared at τ 4·83. No significant changes occurred during the next 3 weeks.

$MeGeH_4$ *plus* CCl_4. A solution of $MeGeH_3$ (0·8 mmol) in CCl_4 (12 mmol) reacted steadily during 4 h to give a mixture containing unchanged $MeGeH_3$ (τ 6·58, τ 9·65, J = 4·3 Hz, 2% of original), $MeGeH_2Cl$ (τ 4·68, τ 9·12, J = 3·1 Hz, 8%), $MeGeHCl_2$ (τ 3·17, τ 8·70, J = 1·6 Hz, 30%), $MeGeCl_3$ (τ 8·35, 60%), and $CHCl_3$ (τ 2·77, 98% of reacted H).

Compound (II) *plus* HCl *in* CCl_4. Compound (II) (0·35 mmol) plus HCl (0·70 mmol) were sealed up with CCl_4 (*ca.* 10 mmol). The signal due to (II) declined steadily to 10% during 50 min and, more slowly, to zero during 100 min. The HCl signal (τ 5·37) decreased but not to zero. A doublet at τ 8·87 and quartet at τ 4·07, J = 3·3 Hz, increased to a maximum at 45 min and then decreased to 10% of the total at 100 min and 8% at 3 h. A singlet, τ 8·54, appeared after the multiplets had built up and increased to a maximum at 100 min when the signal suddenly degraded and solid precipitated. A signal at τ 2·85 due to $CHCl_3$ had appeared within 5 min and increased steadily throughout. Little change occurred after precipitation and, at this point, the $CHCl_3$ signal accounted for 47% of the hydrogen which had reacted.

Compound (II) *plus* $GeCl_4$. In a similar experiment,

(II) dissolved in $GeCl_4$ showed no new signals during the first 40 min. The sample was then left overnight in the dark at room temperature when a crystalline solid had formed and the solution was yellow. Signals due to (II) had disappeared, giving a doublet (τ 8·87) and a quartet (τ 4·02) with $J = 3{\cdot}0$ Hz, a singlet (τ 8·55) and $GeHCl_3$ (τ 2·50). After a further 5 days, more solid had deposited and only the τ 8·55 singlet remained together with $GeHCl_3$. The appearance of weak singlets at τ 3·50 and 4·90 assigned as GeH_2Cl_2 and GeH_3Cl was the only change after a further 14 days.

The tube was opened, and the solid separated and washed with $GeCl_4$. It was soluble in acetone and alcohol and the bulk of it sublimed at 10^{-2} mmHg at 45 °C to clear white crystals with Cl content 20·6% ($C_6H_3O_5GeMnCl_2$ requires 20·3%). The i.r. spectrum and assignment was: (cm^{-1}) 3200—100w,br (νCH), 2195m and 1998s,br (νCO), 1231w (δCH_3), 790m (ρCH_3), 657sh and 642s,br ($\delta MnCO$), 591w (νGeC), 456m (νMnC), and 355w,br ($\nu GeCl$). All the data are consistent with the τ 8·55 singlet arising from $[Mn(CO)_5GeCl_2Me]$.

$MeGeH_3$ *plus* $GeCl_4$. After 3 weeks, the only new signals from a sample of methylgermane in $GeCl_4$ were very weak multiplets (τ 4·68 and 9·23) due to *ca.* 2% formation of $MeGeH_2Cl$. A solution of $MeGeH_2Cl$ in $GeCl_4$ showed a quartet at τ 4·70, a triplet at τ 9·25, $J = 3{\cdot}1$ Hz, and no change with time.

Compound (II) *plus* Br_2. Compound (II) reacted with an excess of Br_2 in $SiCl_4$ solution in a rapid reaction to yield (i) a singlet at τ 8·75 accounting for 50% of the total intensity, (ii) $MeGeBr_3$ at τ 8·18, 30% of total, (iii) weak signals from $MeGeHBr_2$ (τ 8·60, $J = 2{\cdot}0$ Hz) and $MeGeH_2Br$ (τ 9·13, J *ca.* 3 Hz), and (iv) a doublet at τ 9·07, $J = 2{\cdot}0$ Hz, accounting for *ca.* 10% of the total. With time a weak singlet at τ 8·35 appeared and grew slowly and is assigned to $MeGeBr_2Cl$ arising from exchange with the solvent. After the initial reaction was over, the weak bromine colour remaining did not appreciably change with time.

Compound (I) *plus* HBr. In 36 h in the dark at room temperature, (I) (0·16 mmol) reacted with an excess of HBr to give H_2 (*ca.* 0·3 mmol), and white needle-like crystals. Part of the solid melted at 94—96 °C and part at 153—154 °C (*cf.* $[Mn(CO)_5GeBr_3]$, m.p.[15] 165—166°) and qualitative tests indicated Br, Mn, and Ge. The solid was insoluble in n-heptane and soluble in THF, acetone, and benzene. The i.r. spectrum showed absorptions assigned to the $Mn(CO)_5$ moiety at 2103ms, 2060—vvs,br, 638sh, 654ms, 634s,br, and 452m. In addition, the GeMn stretch was found at 218 cm^{-1}, $\nu GeBr$ at 261ms,br cm^{-1} and GeH or GeH_2 deformations at 858w, 730w, and 396vw cm^{-1}.

$MeGeH_3$ *plus* HX. Methylgermane reacts in a sealed tube at several atmospheres pressure, or in the presence of traces of mercury and tap-grease below 1 atm, with a moderate excess of either HCl or HBr in a slow reaction which yields $MeGeH_2X$ with only small amounts of less volatile species.

Compound (II) *plus* $HgCl_2$ (2 : 1 *ratio*). Compound (II) (0·06 mmol) and $HgCl_2$ (0·03 mmol) were sealed in CCl_4 solution and the n.m.r. spectrum followed at room temperature. A rapid reaction occurred with complete conversion of (II) into a species giving a singlet at τ 8·47 in 20 min. This may be identified with $[Mn(CO)_5GeCl_2CH_3]$ and an intermediate giving a weak doublet at τ 8·79, $J = 3{\cdot}2$ Hz, is presumably the monochloride. Chloroform (τ 2·75) was also formed and accounted for 75% of the hydrogen initially bonded to germanium. Qualitative tests on the solid remaining after removal of volatiles were negative for Hg^{II} and confirmed Hg^{I}.

Compound (II) *plus* $HgCl_2$ (1 : 1). Compound (II) (0·19 mmol) was added to a $SiCl_4$ solution of $HgCl_2$ (0·20 mmol), the mixture allowed briefly to liquefy to mix the reactants, and then held in the n.m.r. spectrometer probe at −60 °C. About 5% reaction occurred in the brief mixing period with no further change at −60 °C. Reaction started slowly at −30 °C and proceeded for 75 min when 30% of (II) was consumed. The temperature was raised to 0 °C where 78% of (II) was consumed after 20 min and the reaction slowed. The products were the same as in the tetrahalide studies, identified as (a) $[Mn(CO)_5GeHClMe]$ and (b) $[Mn(CO)_5GeCl_2Me]$. Only (a) was found during the time at −30 °C and increased to form 71% of the mixture after the 20 min at 0 °C. At this point, (b) formed *ca.* 7% of the mixture, metallic mercury was present, and gas was evolved. After a further 6 h at room temperature the system contained 4% (II), 74% (a), and 22% (b). Three days later, (II) was completely consumed leaving 78% (a) and 22% (b). After 6 weeks in daylight, a white solid had precipitated and only $[Mn(CO)_5GeCl_2Me]$ remained. At this stage the tube was opened and the solid recovered had an identical i.r. spectrum to that found in the $GeCl_4$ reaction.

Compound (I) *plus* HgI_2. A preliminary experiment between (I) (0·7 mmol) and HgI_2 (1·4 mmol) in absence of solvent gave H_2, some unchanged (I) and unchanged HgI_2, together with an orange solid (27·2 mg) which sublimed at 40 °C and 10^{-4} mmHg. The i.r. spectrum of this solid showed bands at 2095m, 2060w, 2015s, 1992m,sh, 1987m,sh, 720w,br, 645sh, 638s, and 440w cm^{-1}.

Compound (II) *plus* PCl_3. Compound (II) (0·22 mmol) and excess PCl_3 (0·66 mmol), dissolved in $SiCl_4$, were found to react extremely slowly. After 5 days, 75% of (II) remained, the tube was coated with an orange-brown solid, and signals assigned to $[Mn(CO)_5GeHClMe]$ (10%, τ 8·83, $J = 3{\cdot}5$ Hz) and $[Mn(CO)_5GeCl_2Me]$ (15%, τ 8·53) were found. After seven months in daylight, only $[Mn(CO)_5GeCl_2Me]$ and HCl (τ 5·43 very weak) remained and 0·2 mmol incondensible gas was found when the tube was opened. A white solid, with spectrum identical to the $[Mn(CO)_5GeCl_2Me]$ above, was sublimed out of the sample. This left an orange-brown residue insoluble in hydrocarbons, acetone, and water and with only one broad band *ca.* 460 cm^{-1} in its i.r. spectrum.

Germanes plus PX_3. $MeGeH_3$ Did not react with an excess of PCl_3 and showed only *ca.* 5% conversion into $MeGeH_2Br$ with the more reactive PBr_3 during 3 months. A sample of Ge_2H_6 dissolved in PCl_3 yellowed a little in artificial light and rather more in daylight but no signals of Ge_2H_5Cl were detected. Reaction of Ge_2H_6 with PBr_3 gave during 10 days 12% conversion into Ge_2H_5Br, plus possibly some 1,2-$Ge_2H_4Br_2$, and a thick yellow deposit.

Compound (II) *plus* PF_3. In several experiments, (II) was treated in sunlight with an excess of PF_3 in Pyrex tubes. Variable amounts of CO were produced, less than the amounts of PF_3 consumed. The major products were intractable yellow oils giving broad i.r. bands in the 700—850 cm^{-1} region and poorly resolved ^1H n.m.r. signals at τ 8—10.

Compound (II) *plus* BBr_3. An instant reaction was observed in a preliminary study of (II) with an excess of BBr_3 in $SiCl_4$. The n.m.r. spectrum of the product mixture was complex, with broad bands at τ 8·71 and 9·09, and a series of unidentified weak singlets at τ 2·77, 2·92, 7·72, 8·48, 8·54, and 9·16. Strong singlets were assigned to $[Mn(CO)_5GeBr_2Me]$ (τ 8·73) and $MeGeBr_3$ (τ 8·17) and a weak doublet at τ 9·13, J = 1·5 Hz, was possibly due to $[Mn(CO)_5GeHBrMe]$.

Compound (I) *plus* SO_2. Excess of dry SO_2 was condensed onto (I) (62·1 mg, 0·23 mmol) in a pressure take-off tube. On warming to room temperature, the clear solution became yellow and the colour deepened gradually during 30 min. After 1 h the solution was cooled to −45 °C and an excess of SO_2 pumped away. Prolonged pumping at ambient temperature left a bright yellow solid (71·5 mg; 100% conversion into $[Mn(CO)_5GeH_3]\cdot SO_2$ requires 76·5 mg). A further experiment yielded a product the weight of which accounted for 97% formation of the adduct, which was soluble in chloroform and benzene but not in cyclohexane, and which with water evolved H_2S. I.r. ($CHCl_3$ soln.) ν (CO), 2120s, 2040vs, 2028s,sh, and 1968s; (Nujol mull) ν (SO), 1195m and 1070m.

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