Transition-metal Carbonyl Derivatives of the Germanes. Part 18.[1] Tetracarbonylbis(permethylgermyl)iron Compounds $[Fe(CO)_4(GeMe_{3-x}H_x)(GeMe_{3-y}H_y)]$ for x,y = 0—3

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The syntheses of the new mixed-germyl compounds $[Fe(CO)_4(GeH_3)(GeMeH_2)]$, $[Fe(CO)_4(GeH_3)(GeMe_2H)]$, $[Fe(CO)_4(GeMeH_2)(GeMe_2H)]$, $[Fe(CO)_4(GeMeH_2)(GeMe_3)]$, and $[Fe(CO)_4(GeMe_2H)(GeMe_3)]$ have been examined. The tendency to eliminate a methylgermane (derived from the substituted germyl group with the largest number of methyls) and condense to four-membered ring Ge_2Fe_2 compounds increases rapidly with increasing numbers of Me groups. Spectroscopic properties, and the condensation behaviour, were compared with those of known members of the family, including new measurements on the latter. The comparison supports the identifications, even of the very short-lived pentamethyl compound.

Compounds where a carbonyl derivative of a transition metal M is linked to M′ = Si, Ge, Sn, or Pb are a significant subset[2] of the polymetallic compounds containing bonds between M and Main Group elements, M′, which are attracting current interest. When M = Fe, Ru, or Os, very interesting polymetallic compounds have been reported[3] but usually from reactions with variable yields and unpredictable products reflecting the forcing conditions needed. Thus, cleavage of Ge–Me bonds at about 150 °C gave[4] $[\{M(CO)_3(\mu\text{-}GeMe_2)\}_3]$ from $[M(CO)_4(GeMe_3)_2]$ for M = Ru or Os. Similarly, $[Fe_4Ge(CO)_{16}]$ was formed[5] in 4% yield from boiling tetravinylgermane and $[Fe_3(CO)_{12}]$. The scope for a much more directed synthesis is seen in the alternative[6] preparation of this compound.

In contrast, M′–H bonds can often[7] be converted into M′–M bonds under very mild conditions. Because of the wide range of germanium hydrides, this is of particular interest for germanium polymetallics, as in the formation[8] of $[(OC)_5MnGeCo_3(CO)_9]$ from $[Mn(CO)_5(GeH_3)]$ and $[Co_2(CO)_8]$. An especially facile formation of new Ge–Fe bonds was seen[9] in the formation of the four-membered ring species $[\{Fe(CO)_4(GeMe_2)\}_2]$ by elimination of $GeMe_2H_2$ from $[Fe(CO)_4(GeMe_2H)_2]$ in the dark at room temperature. This condensation reaction is important since building the four-membered ring is the first step to further polymetallic complexes. Analogous rings containing Ge–H bonds are also known: $[\{Fe(CO)_4(GeMeH)\}_2]$ from[10] $[Fe(CO)_4(GeMeH_2)_2]$ and $[\{Fe(CO)_4(GeH_2)\}_2]$ from[1,11] $[Fe(CO)_4(GeH_3)(GeMe_3)]$. These, and the bis(permethylgermyl)iron parents, are potentially valuable precursors for polymetallics formed by further self-condensation or by reaction of the Ge–H bonds, as illustrated by the synthesis[1,11] of the multi-ring compound $[Co_4Fe_2Ge_2(CO)_{21}]$ from $[\{Fe(CO)_4(GeH_2)\}_2]$ and $[Co_2(CO)_8]$.

Under the conditions of the condensation or substitution reactions, Ge–Me bonds are inert while Ge–H bonds react. Thus the complexity of the system may be controlled by varying the number of Ge–H bonds. In addition, while the methyl compounds undergo condensation, no such reaction was observed[12] from the parent hydrides $[Fe(CO)_4(GeH_3)_2]$, $[Fe(CO)_4(GeH_3)(Ge_2H_5)]$, or $[Fe(CO)_4(Ge_2H_5)_2]$. This discontinuity between, for example, $[Fe(CO)_4(GeH_3)_2]$ and $[Fe(CO)_4(GeMeH_2)_2]$ is striking compared with the relatively uniform trends usually observed as Me replaces H in germanes.

In this paper we report the preparations of all the compounds with two different $GeMe_xH_{3-x}$ groups (x = 0—3) not already known, and examine their tendency to condense to four-membered ring compounds. Since all the compounds are air-sensitive, and some condense very rapidly, their characterisation depends on spectroscopic properties. Taken with some new measurements on the known compounds, the whole series of digermylmonoiron species containing from zero to six Me groups is available, and comparison within the series adds weight to the evidence from individual compounds.

Results

Syntheses.—The new germyl derivatives were prepared by the route established earlier,[1,11,12] as illustrated in Scheme 1 for $[Fe(CO)_4(GeH_3)(GeMeH_2)]$. A slight deficit of $[Mn(CO)_5]^-$ was used. Since any by-product not only reduces the yield but seriously interferes with the isolation of the product, route (a) is

$$\begin{tikzcd}
{[Fe(CO)_4(GeH_3)_2]} \arrow[d, "(a)"', "(i)\ (ii)"] & \\
{[Fe(CO)_4(GeH_3)(GeMeH_2)]} \arrow[r, "\text{slowly}"] & {GeMeH_3 + [\{Fe(CO)_4(GeH_2)\}]^*} \\
{[Fe(CO)_4(GeMeH_2)_2]} \arrow[u, "(b)", "(iii)\ (iv)"'] \arrow[r] & {GeMeH_3 + 0.5[\{Fe(CO)_4(GeMeH)\}_2]}
\end{tikzcd}$$

Scheme 1. (*i*) $[Mn(CO)_5]^-$, $-[Mn(CO)_5(GeH_3)]$; (*ii*) $GeMeBrH_2$; (*iii*) $[Mn(CO)_5]^-$, $-[Mn(CO)_5(GeMeH_2)]$; (*iv*) $GeBrH_3$. Yields: route (a), 80; (b), 61%. * Plus other products, see text

Table 1. Proton n.m.r. data for the digermyliron tetracarbonyls[a]

Germyls		δ				^3J/Hz	
		GeH_3	GeH_2	GeH	CH_3	$GeMeH_2$	$GeMe_2H$
GeH_3	GeH_3	3.50 (s)					
GeH_3	$GeMeH_2$	3.53 (s)	3.89 (q)		0.51 (t)	3.4	
GeH_3	$GeMe_2H$	3.52 (s)		4.16 (m)	0.51 (d)		3.2
GeH_3	$GeMe_3$	3.47 (s)			0.51 (s)		
$GeMeH_2$	$GeMeH_2$		3.87 (q)		0.49 (t)	3.4	
$GeMeH_2$	$GeMe_2H$		3.93 (q)	4.20 (m)	0.56 (d), 0.62 (t)	3.4	3.2
$GeMeH_2$	$GeMe_3$		3.88 (q)		0.56 (t), 0.55 (s)	3.4	
$GeMe_2H$	$GeMe_2H$			4.17 (m)	0.59 (d)		3.2
$GeMe_2H$	$GeMe_3$[b]			4.2 (br)	0.6 (br), 0.7 (br)		
$GeMe_3$	$GeMe_3$				0.57 (s)		

[a] As 10—20% solutions in C_6H_6 or C_6D_6 at 29 °C. Calibration based on $\delta(C_6H_6) = 7.24$. s = Singlet, d = doublet, t = triplet, q = quartet, and m = septet; usually the five inner lines only were observed. Intensities were in accord with the assignments. [b] See text: unstable species showing broadened signals.

Table 2. Oxygen-17 and ^{13}C chemical shifts for digermyliron tetracarbonyls

Germyls		*cis*-CO		*trans*-CO		CH_3	
		$\delta(^{17}O)$[a]	$\delta(^{13}C)$	$\delta(^{17}O)$[a]	$\delta(^{13}C)$	$\delta(^{13}C)$	Conditions
GeH_3	GeH_3	366.1 (15)	207.3	360.9 (12)	205.9		Neat[b]
GeH_3	$GeMeH_2$	365.5 (30)	208.0	361.3 (10)	206.9	−1.8	Neat[c]
				359.5 (10)	206.4		
$GeMeH_2$	$GeMeH_2$		207.1		205.5	−3.0	*b*, *d*
GeH_3	$GeMe_2H$	365.7	208.2	363.5 (14)	207.2	2.8	Neat[b]
				357.2 (12)	206.0		
$GeMe_3$	$GeMe_3$	355.9 (9)	208.2	355.5 (9)	208.2	7.5	C_6H_{14} at 25 °C
			208.9		208.0	7.5	C_6H_{14} at −20 °C
			208.2		208.2	7.5	C_6H_6 at 10 °C

[a] $W_{\frac{1}{2}}$ Values in parentheses. [b] Relative intensities of *cis* and *trans* signals, 1:1. [c] Relative intensities of the *cis* and the two *trans* signals, 2:1:1. [d] From ref. 10.

preferred and is imperative for the synthesis of $[Fe(CO)_4(GeH_3)(GeMe_2H)]$. Since $[Fe(CO)_4(GeMe_3)_2]$ does not condense, it is the preferred starting material for $[Fe(CO)_4(GeMeH_2)(GeMe_3)]$ and $[Fe(CO)_4(GeMe_2H)(GeMe_3)]$, despite its sensitivity to oxygen and relatively low volatility. The compound $[Fe(CO)_4(GeMeH_2)_2]$ was the starting material for $[Fe(CO)_4(GeMeH_2)(GeMe_2H)]$, but the reaction was difficult.

Products were colourless when pure and were just mobile under vacuum as slightly volatile liquids or subliming solids. All formed brown or green deposits on brief exposure to air. The tendency to condensation and the air sensitivity increased rapidly with increasing number of Me groups. The characterisation depends on spectroscopic properties, and on the reactions of the more stable species. For the more reactive compounds, identification is not conclusive.

Spectroscopic Properties.—It was possible to measure ^1H n.m.r. spectra for all the compounds, and these data are listed in Table 1 along with those for the previously reported[1,9–13] members of the series. The chemical shifts fall into narrow ranges characteristic of each substituent group, thus δ(GeH) moves about 0.3 p.p.m. to low field for each added methyl. Even ^3J is consistently 0.2 Hz less for the $GeMe_2H$ group than for $GeMeH_2$, although this difference is only marginally significant. While methylgermanes from the condensation reactions appear rapidly in the spectra of the less stable polymethyl compounds, the intensities, multiplicities, and chemical shift patterns of the initial signals are entirely consistent with the formulations. Even the broad, poorly resolved bands of the worst case, $[Fe(CO)_4(GeMe_2H)(GeMe_3)]$, fit the general pattern.

It was also possible to observe satisfactory ^{13}C and ^{17}O resonances at natural abundance from the two most stable of the new species, $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ and $[Fe(CO)_4(GeH_3)(GeMe_2H)]$. Both the ^{13}C and ^{17}O signals of the CO groups are in the intensity ratio 2:1:1, confirming the earlier assignment[10] of the lower-field ^{13}C signal to the CO groups *trans* to the germane in $[Fe(CO)_4(GeMeH_2)_2]$, and matching the recent assignment[14] demonstrated by proton coupling in $[Fe(CO)_4H_2]$. The measurements, together with similar ones on known compounds, are collected in Table 2. The ^{13}CO shifts trend to higher field with increasing number of Me groups, and the *trans* values change more than the *cis*. The ^{17}O values show the opposite trend as expected from the standard acceptor π model. As the more dispersed ^{17}O values clearly show, the *cis* and *trans* shifts get closer as the number of methyls increases so that for $[Fe(CO)_4(GeMe_3)_2]$, the ^{13}C shifts were separated only at −20 °C.

The i.r. spectrum was measurable for each compound, while Raman studies were possible on the more stable. The assignment for the two most stable compounds, $[Fe(CO)_4(GeH_3)(GeMeHR)]$ (R = H or Me), is shown in detail in Table 3 as an illustration. The data reported in the Experimental section for the other new species may be assigned similarly. Allowing for phase shifts, the vibrations of the complete series[1,9–14] of seven compounds containing from zero to six Me groups now fall into a systematic pattern. The spectrum of $[Fe(CO)_4(GeMe_2H)_2]$ now available in solution, and the correction to the gas-phase CO stretches of $[Fe(CO)_4(GeMeH_2)_2]$, both assist the comparisons.

The CO stretching modes of all the compounds show the

Table 3. Vibrational bands (cm^{-1}) of the more stable products

$[Fe(CO)_4(GeH_3)(GeMeH_2)]$		$[Fe(CO)_4(GeH_3)(GeMe_2H)]$		
I.r. (gas)[a]	Raman (liquid)[b]	I.r. (gas)[a]	Raman (liquid)	Assignment
2 094s, A	2 091s, p	2 099	2 084vs	ν(CO) sym, ax.
		2 094		
		2 060 (sh)		ν(GeH)?
2 034vvs, A		2 040vs, A		
2 017 (sh)	2 023vvs	2 024 (sh)	2 018vvs	ν(CO)
2 012vs		2 020s		
	883m		882	$\delta(CH_3)$
852w		850br (sh)	865	
837ms, A		836s, A		$\delta(GeH_3)$ asym and $\delta(CH_3)$
		821w		
		817w		
811ms, A	813w	807s, A	808m	$\delta(GeH_3)$ sym
	739vw	728w		
691w	703w			GeH_2 wag
		662mw		
626s		628s		δ(FeCO)
619 (sh)				
581w	589m, p		573s	ν(GeC)
b	566m	*b*		
	534w		537mw	$\delta(GeH_3)$
	445s, p		440s	ν(FeC)
	227s[c]		229s	ν(GeFe)

[a] Type A contours had weak *P* and *R* branches appearing as shoulders at 2—4 cm^{-1} from the *Q* branch maximum. The limit to i.r. observations was *ca.* 550 cm^{-1}. [b] In addition, C–H stretches were seen at 2 987w, p and 2 917w, and deformations at 1 283w and 1 059s cm^{-1}. [c] Polarised component?

three- or four-band pattern characteristic of *cis* isomers, with one band 40—50 cm^{-1} above the others, polarised where measured in the Raman, and assigned to the symmetric axial stretch. This band decreases by 5—6 cm^{-1} for each replacement of H by Me, paralleling a decrease in the mean CO stretching by 25 cm^{-1} on going from zero to six Me groups (compare Table 3). The very unstable $[Fe(CO)_4(GeMe_2H)(GeMe_3)]$ probably produced the band at 2 073 cm^{-1}, assignable as the symmetric axial mode from this regular change.

Characteristic bands are found for each of the $GeMe_xH_{3-x}$ groups and frequencies fall in narrow ranges. Thus the prominent GeH_3 symmetric deformation, with a type A contour in the gas phase, occurs consistently at 815 ± 10 cm^{-1}, while the asymmetric mode is at 882—883 cm^{-1} and the rock near 535 cm^{-1}. Similarly, for $GeMeH_2$ and $GeMe_2H$ groups, the Me rocks occur in the 830—880 cm^{-1} range [with $\delta(GeH_2)$], the GeH_2 wag is at 690 cm^{-1}, and Ge–C stretches at 600 ± 20 cm^{-1}.

The GeFe stretching modes give one strong Raman band around 220 cm^{-1} for the two compounds measured, compared with the resolved bands at 229p and 216 cm^{-1} found[14] for $[Fe(CO)_4(GeH_3)_2]$. The band of $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ at 225 cm^{-1} changes shape during polarisation measurements and probably has the symmetric mode 1—2 cm^{-1} above the antisymmetric one. Vibrations of the $Fe(CO)_4$ unit occur consistently around 630 and 440 cm^{-1} while heavy-atom bends give very strong Raman bands around 100 cm^{-1}.

The germane eliminated in the condensation completely dominated the mass spectra of the compounds with three or more methyl groups. The spectra of $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ and $[Fe(CO)_4(GeH_3)(GeMe_2H)]$, like those previously reported,[9,10,12–14] show a weak parent ion, a dominant $[P - n\text{CO}]^+$ series, and weaker families arising from loss of Me and of germyl. Ions retaining Fe + 2Ge carried the bulk of the ion current. Together with published data, this suggests that the ease of methyl loss increases in the order $GeMeH_2 < GeMe_2H < GeMe_3$.

Condensation Reactions.—When monitored by ^1H n.m.r. spectroscopy the principal reaction observed for $[Fe(CO)_4(GeH_3)(GeMe_2H)]$ is that shown in equation (1), R = Me, which parallels those of $[Fe(CO)_4(GeMeRH)_2]$ for R = Me[9] or H.[10] There was a secondary product, which is interpreted as the singly bridged compound formed as shown in equation (2), which represents a competitive route leading to a minor open by-product.

$$\begin{tikzcd}
2[\mathrm{Fe(CO)_4(GeH_3)(GeMeRH)}] \arrow[r] \arrow[d] & 2\mathrm{GeMeRH_2} + [\{\mathrm{Fe(CO)_4(GeH_2)}\}_2] \quad (1) \\
\mathrm{GeMeRH_2} + [\{\mathrm{Fe(CO)_4(GeH_3)}\}_2\mathrm{GeMeR}] \quad (2) &
\end{tikzcd}$$

The ratio of path (1) to path (2) at three-quarters completion was 3:1. In the 7-d reaction, the starting material had disappeared and the major signals were from $GeMe_2H_2$, the singly bridged product, and the cyclic species, $[\{Fe(CO)_4(GeH_2)\}_2]$ although this is relatively insoluble and had largely precipitated. All other by-products formed were present as traces only.

For $[Fe(CO)_4(GeH_3)(GeMeH_2)]$, the reaction was very slow with 70% unaltered starting material in benzene solution after 84 d and 57% recovered from a neat sample after 122 d. The most prominent product was $GeMeH_3$ but there was no evidence for ring products up to 84 d. It is probable that equation (1) had proceeded only to the first condensation stage and, together with equation (2), gave the two possible singly bridged species. On longer standing, or on gentle heating, $[(H_3Ge)(OC)_4FeGeH_2Fe(CO)_4(GeMeH_2)]$ closed to $[\{Fe(CO)_4(GeH_2)\}_2]$, completing equation (1). Elimination of GeH_4 was minor in solution but amounted to 12% of the $GeMeH_3$ for the pure liquid in the sealed sample. After 2 y at room temperature in benzene all the $[Fe(CO)_4(GeH_3)$-

$(GeMeH_2)]$ had reacted but $[\{Fe(CO)_4(GeH_2)\}_2]$ was only a minor component in solution. Extraction and concentration of involatiles gave samples with spectroscopic properties appropriate to a mixture of the ring compounds $[\{Fe(CO)_4(GeH_2)\}_2]$ and $[\{Fe(CO)_4\}_2(\mu\text{-}GeH_2)(\mu\text{-}GeMeH)]$, with a small amount of $[\{Fe(CO)_4(GeMeH)\}_2]$. The solid from the neat-liquid experiment gave similar species. Thus the ring-closure steps may be assisted by concentration. The very slow condensation appears to allow time for the rare elimination of GeH_4 from the GeH_3 groups to form rings containing μ-GeMeH.

The condensations of $[Fe(CO)_4(GeH_3)(GeMe_3)]$ and of $[Fe(CO)_4(GeMeH_2)(GeMe_3)]$ were so rapid that they dominated the chemistry and prevented the isolation of pure samples. No separate study of the condensation was possible, but the products found in the preparations were $GeMe_3H$ and the known compounds[9,10] $[\{Fe(CO)_4(GeMeR)\}_2]$ for R = H or Me respectively. By-products occurred to only a very minor extent.

The condensation of $[Fe(CO)_4(GeMeH_2)(GeMe_2H)]$ was slower, but still fast enough to cause problems in the separation. Both $GeMe_2H_2$ and $GeMeH_3$ were observed, in a ratio of *ca.* 10:1. The handling problems make any further conclusion very tentative but there was modest evidence for the formation of $[\{Fe(CO)_4(GeMeH)\}_2]$ together with one or both of $[\{Fe(CO)_4\}_2(\mu\text{-}GeMe_2)(\mu\text{-}GeMeH)]$ and $[\{Fe(CO)_4(GeMe_2)\}_2]$.

The products. Reactions analogous to (1), to give the ring compound with the maximum number of hydrogens, were the principal condensations observed. Thus the main products were the known compounds $[\{Fe(CO)_4(GeR_2)\}_2]$ with $R_2 = H_2$[1,11] (**A**), MeH[10] (**B**), or Me_2[9] (**C**). In addition, there were four secondary products which have not been separated from (**A**)—(**C**), but which are reasonably indicated by the spectroscopic characteristics listed in the Experimental section. Two of these new compounds are likely to be the rings with two different GeR_2 groups, $[\{Fe(CO)_4\}_2(\mu\text{-}GeH_2)(\mu\text{-}GeMeH)]$ (**D**) from $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ and $[\{Fe(CO)_4\}_2(\mu\text{-}GeMeH)(\mu\text{-}GeMe_2)]$ (**E**) from $[Fe(CO)_4(GeMeH_2)(GeMe_2H)]$. A number of spectroscopic properties of (**D**) and (**E**) form a series with those of (**A**)—(**C**). This is illustrated by the CO vibrations. The highest-frequency CO mode is attributed to the b_u stretch of the axial CO groups in the D_{2h} molecules (**A**) and (**C**) and to the corresponding vibration of the lower-symmetry species. This is separated by about 30 cm^{-1} from the remaining bands and the wavenumber decreases systematically with the number of Me groups: 2 067 for (**A**), 2 063 for (**D**), 2 059 for (**B**), 2 056 for (**E**), and 2 052 cm^{-1} for (**C**). The remaining three allowed CO modes tend to give one very strong band or two close ones, with extra weak modes for the lower symmetries, but again there is a systematic shift to lower wavenumbers along the series. Thus the pattern of the five spectra reinforces the attribution of the mixed germylene compounds (**D**) and (**E**). The n.m.r. and mass spectra are also compatible.

The singly bridged condensation products of equation (2) are indicated for the first time. The evidence is mainly from the ^1H n.m.r. spectra, but is partly supported by the measurement of the germanes formed. Each species shows an additional ^1H signal appropriate to the bridging group (GeMeH or $GeMe_2$ respectively) together with a second GeH_3 signal very close to that of the starting material, and with the appropriate intensity ratios where the spectra were reasonably clear. The GeH_3 environments in the starting material and the singly bridged compound would obviously be very similar.

Reactions with Covalent Halides.—The two compounds containing a GeH_3 group were sufficiently stable to condensation to allow exploration of their reactions with $SiCl_4$, CCl_4, and HCl for comparison with earlier[9,12,15] work. As before, reactions were followed by ^1H n.m.r. spectroscopy and $SiCl_4$ reacted more slowly than did CCl_4. The monomethyl compound was least reactive, and the first step was clear, equation (3) (E = C or Si). The preference for reaction at the

$$[Fe(CO)_4(GeH_3)(GeMeH_2)] + ECl_4 \longrightarrow [Fe(CO)_4(GeH_3)(GeMeClH)] \quad (3)$$

$GeMeH_2$ group parallels the faster reactions of $[Fe(CO)_4(GeMeH_2)_2]$[15] compared with $[Fe(CO)_4(GeH_3)_2]$.[12] However, the next observation was the formation of $GeMeClH_2$, suggesting the condensation reaction (4), in contrast to the

$$2[Fe(CO)_4(GeH_3)(GeMeClH)] \longrightarrow 2GeMeClH_2 + [\{Fe(CO)_4(GeH_2)\}_2]\ (\mathbf{A}) \quad (4)$$

$[Fe(CO)_4(GeH_2Cl)(GeH_2R)]$ compounds (R = H or GeH_3)[12] where condensation gave GeH_3R and $[\{Fe(CO)_4(GeHCl)\}_2]$.

For the slow $SiCl_4$ reaction, equations (3) and (4) account for all the observations up to 29 d and 21% completion of reaction. Thereafter $GeMeH_3$ appears at the expense of $GeMeClH_2$ but the total of $GeMeH_3$ and $GeMeClH_2$ matches the consumption of starting material up to 47% reaction. While the condensation of the starting material, equation (2), would produce $GeMeH_3$, these observations suggest that the main source of methylgermane is chlorine exchange of $GeMeClH_2$. In the later stages of the $SiCl_4$ reaction, and in the faster CCl_4 reaction, GeH_4 is evolved and further reactions occurred which were not investigated. It is clear that the initial reaction of $SiCl_4$ and CCl_4 is substitution at $GeMeH_2$, followed by condensation which eliminates $GeMeClH_2$ and not GeH_4.

For HCl, in contrast to $[Fe(CO)_4(GeH_3)_2]$,[12] a simple monosubstitution stage was not recognised. The early products resulted from both substitution and Fe–Ge cleavage and included $[Fe(CO)_4(GeClH_2)H]$, $[Fe(CO)_4(GeMeClH)H]$, $GeMeClH_2$, and $GeClH_3$, together with $[Fe(CO)_4(GeH_3)H]$ as a minor product in the early stages. Further changes occurred after all the HCl had been consumed, including the appearance of signals appropriate to $[Fe(CO)_4(GeMeCl_2)H]$ and a later major change with solids precipitating and many new signals. Thus the initial products continue to interact and the system is extremely complex.

With $[Fe(CO)_4(GeH_3)(GeMe_2H)]$ the condensations of equations (1) or (2) are fast enough to interfere significantly with interpretation of the halogen substitutions. Reactions with $SiCl_4$ or CCl_4 were too fast for the monosubstitution product to be recognised, and $GeMe_2ClH$ and $[\{Fe(CO)_4(GeH_2)\}_2]$ appeared rapidly, presumably by steps parallel to those of equations (3) and (4). However, the proportion of $GeMe_2ClH$ was higher than this scheme requires, and extra n.m.r. signals were present suggesting polychlorination and condensation to form ring compounds such as $[\{Fe(CO)_4(GeClH)\}_2]$. Signals from $GeMe_2H_2$, GeH_4, and from GeH_2Cl and $GeMe_2$ groups were also seen, indicating both equations (1) and (2) and halogenation of these products. In the reaction with HCl, signals assigned to hydrides and to halogenated products show similar reactions to the monomethyl compound. Products included $[Fe(CO)_4(GeMe_2Cl)H]$ while the high proportion of $GeMe_2ClH$ and the probable presence of $[Fe(CO)_4(GeCl_2H)H]$ suggest even more extensive halogenation.

Discussion

Preparations and Characterisation.—By using $[Mn(CO)_5]^-$ to remove one GeR_3 group from $[Fe(CO)_4(GeR_3)_2]$, new mixed-germyl compounds $[Fe(CO)_4(GeR_3)(GeR'_3)]$ have been synthesised, completing the series[9,10,12,13,16] where GeR_3 and GeR'_3 include all the possible permutations of H and Me. The compounds increase rapidly in air-sensitivity and tendency to condense, *cf.* equation (1), as the number of methyl groups increases. Condensation is more rapid in the presence of preparation by-products than for the pure compound, which increases the difficulty of handling the more substituted species. Where alternative preparations exist, $[Fe(CO)_4(GeH_3)_2]$ is much the preferred starting material, followed by $[Fe(CO)_4(GeMe_3)_2]$. Preparations starting from $[Fe(CO)_4(GeMeH_2)_2]$ always contained its condensation product, $[\{Fe(CO)_4(GeMeH)\}_2]$.

Of the new compounds, $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ was most stable and gave acceptable spectra with all the available techniques. In spectroscopic properties, and in its reactions with covalent halides, it fits nicely between the two most stable known species, $[Fe(CO)_4(GeH_3)_2]$[12,14] and $[Fe(CO)_4(GeMeH_2)_2]$.[10,15] In accord with earlier[12,15] observations, initial substitution by $SiCl_4$ or CCl_4 is at the $GeMeH_2$ group, followed by a ready condensation with elimination of $GeMeClH_2$. There was no clear evidence for a second chlorine substitution at the unreacted GeH_3, in contrast[15] to the situation with $[Fe(CO)_4(GeMeH_2)_2]$, but the lower reactivity clearly allows the condensation to supervene. In later stages, $GeMeClH_2$ acts as a halogenating agent. The cleavage of Fe–Ge by HCl, to give Fe–H compounds, also parallels earlier work. Later stages of these reactions were complex and not investigated further.

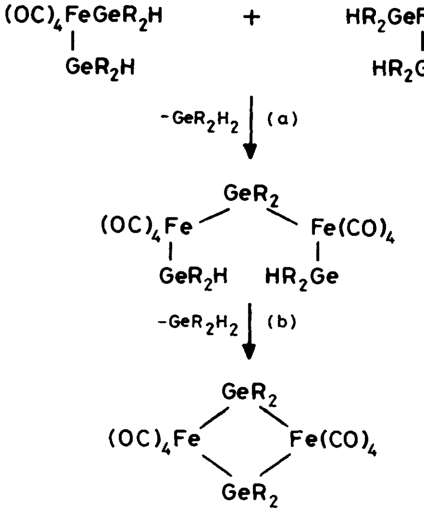
For the somewhat more reactive $[Fe(CO)_4(GeH_3)(GeMe_2H)]$, the spectroscopic evidence was also largely complete and satisfactory. The longer experiments did show $GeMe_2H_2$ and condensation products, but not enough to obscure the data. In the reactions with halides, initial substitution probably gave $[Fe(CO)_4(GeH_3)(GeMe_2Cl)]$ but the evidence was only from its condensation products $GeMe_2ClH$ and $[\{Fe(CO)_4(GeH_2)\}_2]$ resulting from a fast reaction. The faster reactions, and the evidence that the main site for initial substitution was the $GeMe_2H$ group, are again as expected. Hydrogen chloride gave substitution and cleavage as before.

Thus, from their spectroscopic and chemical properties, all these iron compounds containing zero to two Me groups may be regarded as consistently established. For the tri-, tetra-, and penta-methyls the evidence is increasingly more scanty but the provisional identifications are reasonable, particularly in falling into a consistent pattern with the more stable species as far as ^1H n.m.r. and i.r. observations are concerned.

Condensation Reactions.—Under similar conditions in the dark, the condensation tendency is illustrated by the following observations for $[Fe(CO)_4(GeR_3)(GeR'_3)]$. This comparison

GeR_3	GeR'_3	
GeH_3	GeH_3 or Ge_2H_5	No condensation[12]
GeH_3	$GeMeH_2$	11% $GeMeH_3$ after 54 d
$GeMeH_2$	$GeMeH_2$	18% $GeMeH_3$ after 7 d
GeH_3	$GeMe_2H$	22% $GeMe_2H_2$ after 36 h
GeH_3	$GeMe_3$	45% $GeMe_3H$ after 2 d[1,11]
$GeMeH_2$	$GeMe_2H$	10% $GeMe_2H_2$ and 1% $GeMeH_3$ after 3 h
$GeMe_2H$	$GeMe_2H$	95% $GeMe_2H_2$ after 4 d
$GeMeH_2$	$GeMe_3$	60% $GeMe_3H$ after 80 min
$GeMe_2H$	$GeMe_3$	60% $GeMe_2H$ after 15 min
$GeMe_3$	$GeMe_3$	No condensation

has to be seen in broad terms and somewhat exaggerates the accelerating effects of Me groups since the only data available for the less stable compounds apply to preparation mixtures. Pure compounds are less reactive. Thus, when isolated and free of preparation residues, $[Fe(CO)_4(GeMeH_2)_2]$ gave 22% $GeMeH_3$ after 25 d,[8] while $[Fe(CO)_4(GeMe_2H)_2]$ gave 26% $GeMe_2H_2$ after 3 d.[9]



Scheme 2. R_2 = Me_2 or MeH

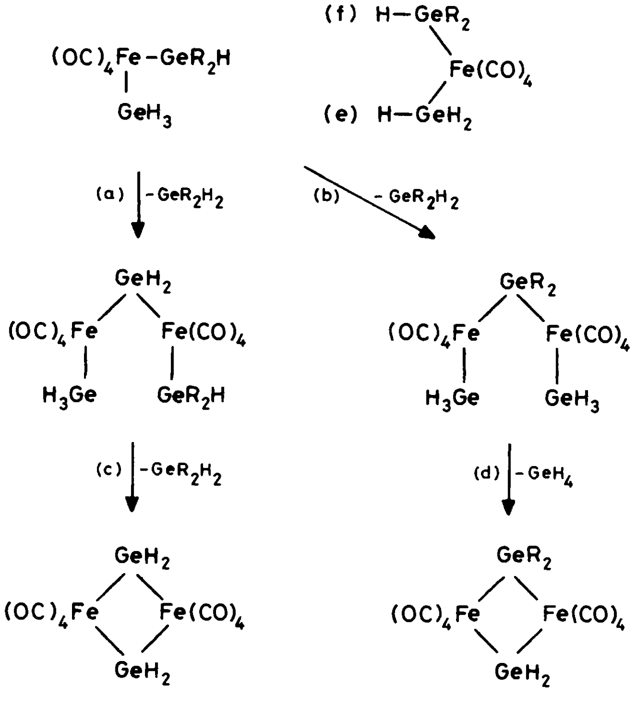
Despite this reservation, it is clear that (*i*) condensation is more rapid as the number of methyl groups increases, (*ii*) the hydride with the largest number of methyls is preferentially produced where there is a choice, (*iii*) there is no evidence for Me transfer and $GeMe_4$ was not formed, and (*iv*) elimination of GeH_4 usually does not occur and is a minor, slow, process when seen. The principal condensation was by equations corresponding to (1), to form the four-membered ring compounds $[\{Fe(CO)_4(GeR_2)\}_2]$ as the commonest products ($R_2 = H_2$ when GeH_3 groups were present, MeH when the least-substituted group was $GeMeH_2$, and Me_2 otherwise). In these reactions, carried out in the dark or in subdued lighting, the substituted $Fe_2(CO)_9$ species $[Fe_2(CO)_7(GeR_2)_2]$ were never more than very minor products.

The early suggestion[9] that condensation proceeded *via* an intramolecular elimination of hydride and formation of a germylene intermediate $Fe(CO)_4GeR_2$ must be abandoned in the light of the much more extended series of observations reported here. Instead, the observations may be rationalised in terms of an intermolecular reaction with subsequent ring closure. For compounds with both germyl groups the same, this follows Scheme 2.

Steps (a) and (b) make up equations analogous to (1). Since the two GeR_2H groups in the intermediate resulting from the condensation (a) are held in contiguous positions, it is reasonable that the closure step (b) is fast in cases where the germane elimination is facile.

For compounds with two different germyl groups there are in general three possible ways in which the first condensation step may occur. If, however, one group is $GeMe_3$, there can be no elimination of $GeMe_4$ between the $GeMe_3$ groups of the two molecules, reducing the alternatives to two. Similarly, if one group is GeH_3 the elimination of GeH_4 is not observed. The simplest mixed germyls are therefore $[Fe(CO)_4(GeR_2H)(GeMe_3)]$ which eliminate $GeMe_3H$ twice in steps entirely analogous to those of Scheme 2 to yield $[\{Fe(CO)_4(GeR_2)\}_2]$ for all three cases $R_2 = H_2$, MeH, or Me_2. For $[Fe(CO)_4(GeH_3)(GeMe_3)]$ the reaction is clean and controllable but for $R_2H = MeH_2$ or Me_2H, the condensations are so fast that the starting materials cannot be isolated. These last two species are also very sensitive to oxygen.

For $[Fe(CO)_4(GeH_3)(GeR_2H)]$, with $R_2H = MeH_2$ or Me_2H, reaction occurs slowly and alternative pathways are



Scheme 3. R_2 = MeH or Me_2

possible as indicated in Scheme 3. For [Fe(CO)$_4$(GeH$_3$)(GeMe$_2$H)], path (a) which corresponds to equation (1) is the preferred route but path (b) is also followed giving rise to the singly linked [(H$_3$Ge)(OC)$_4$FeGeMe$_2$Fe(CO)$_4$(GeH$_3$)].

Steric and statistical grounds would favour the GeMe$_2$H + GeH$_3$ elimination contact of (a) over the GeMe$_2$H + GeMe$_2$H one of (b). Only traces of GeH$_4$ were seen, and then only in the last stages, so that the final closure step (d) is, at most, occurring very slowly and alternative GeH$_4$ eliminations to give more complex products are not precluded. On the other hand, there was no clear evidence for the singly linked product of (a), so that the closure (c) is still fast.

In contrast, in the much slower reaction of [Fe(CO)$_4$(GeH$_3$)(GeMeH$_2$)] (R_2 = MeH) the steps (a) and (b) proceed so sluggishly that both singly linked species accumulate. The ring closure (c) does occur but only on stimulation by gentle heating or concentration, or after prolonged standing. This reaction is so prolonged that there is evidence for ring closure (d), both from modest GeH$_4$ elimination and in the spectroscopic evidence for the mixed-bridge ring.

The remaining compound, [Fe(CO)$_4$(GeMeH$_2$)(GeMe$_2$H)], is potentially the most complex since condensation between each of the three possible pairs of germyls is possible. Unfortunately, the system is sufficiently reactive that the parent could not be freed from the condensation products of the starting materials. The condensation could not therefore be followed in detail but there is clear evidence to suggest that all three possible ring compounds [{Fe(CO)$_4$(GeMeH)}$_2$], [{Fe(CO)$_4$}$_2$(GeMeH)(GeMe$_2$)], and [{Fe(CO)$_4$(GeMe$_2$)}$_2$] were formed.

This bimolecular condensation in two steps is the conservative rationalisation of the observations. The overall reaction to form the four-membered ring compounds according to equations analogous to (1) is established. The three rings where the two germaniums are equivalent, [{Fe(CO)$_4$(GeR$_2$)}$_2$] for R_2 = Me_2,[9] MeH,[10] or H_2[1,11] are established by previous work and their identification is further supported by the reactions and properties reported here.

The evidence for the two stages is more limited. It consists first of evidence (from n.m.r., carbonyl vibrations, and some extent from mass spectroscopy) of two of the mixed-bridged rings, [{Fe(CO)$_4$}$_2$(GeMeH)(GeR$_2$)] for the cases R_2 = H_2 and Me_2. Properties interpolate as expected. Secondly, there is evidence, limited to n.m.r. observations in mixtures, for the two singly bridged species [(H$_3$Ge)(OC)$_4$FeGeR$_2$Fe(CO)$_4$(GeH$_3$)], R_2 = Me_2 or MeH, and there is an indication of [(H$_3$Ge)(OC)$_4$FeGeH$_2$Fe(CO)$_4$(GeMeH$_2$)] persisting in the condensation of [Fe(CO)$_4$(GeH$_3$)(GeMeH$_2$)].

None of the observations precludes more complex products and it is perfectly possible that longer open chains, with backbones such as Ge–Fe–Ge–Fe–Ge–Fe–Ge, may form, especially in the slower reactions.

The preliminary study of the mixture [Fe(CO)$_4$(GeH$_3$)$_2$] plus [Fe(CO)$_4$(GeMe$_3$)$_2$] also supports the bimolecular route. Neither condenses on its own but GeMe$_3$H was rapidly formed in the mixture, along with [{Fe(CO)$_4$(GeH$_2$)}$_2$]. Further minor products and slow changes were indicated, but the main reaction is nicely explained as a bimolecular condensation according to Scheme 3, path (a).

The ultimate cause of the observed eliminations may well be the entropy change rather than the enthalpy change. Since the starting materials and products in each condensing system contain the same number of Ge–H, Ge–Me, and Ge–Fe bonds, in configurations of comparable geometry, the most significant contribution to the driving force may well be the entropy gain in forming the volatile germane, increasing in the order $GeH_4 < GeMeH_3 < GeMe_2H_2 < GeMe_2H$.

This study establishes [Fe(CO)$_4$(GeH$_3$)(GeMeH$_2$)] and [Fe(CO)$_4$(GeH$_3$)(GeMe$_2$H)] as sufficiently stable to join [Fe(CO)$_4$(GeH$_3$)$_2$],[12,14] [Fe(CO)$_4$(GeMeH$_2$)$_2$],[10,15] and [Fe(CO)$_4$(GeH$_3$)(GeMe$_3$)][1,11] as usable precursors to polymetallic species. The best paths to the Ge–H containing rings, also precursors, are to [{Fe(CO)$_4$(GeH$_2$)}$_2$] from [Fe(CO)$_4$(GeH$_3$)(GeMe$_3$)] and to [{Fe(CO)$_4$(GeMeH)}$_2$] from [Fe(CO)$_4$(GeMeH$_2$)$_2$] or from [Fe(CO)$_4$(GeMeH$_2$)(GeMe$_3$)]. There is no useful route as yet to rings containing two different GeR$_2$ groups as these were indicated only in mixtures where they were not dominant components. The H$_3$Ge–Fe–GeR$_2$–Fe–GeH$_3$ species (R_2 = MeH or Me_2) would also be valuable once their isolation is worked out. As shown by the preceding paper,[1] interesting polymetallic species may result from such precursors and further reactions are being investigated.

Experimental

Compounds were handled on a vacuum line or under nitrogen. N.m.r. spectra were run in C_6H_6 or C_6D_6 on JEOL C60HL (^1H) and FX 90Q instruments. Standards were: external CDCl$_3$ taken as 77.1 p.p.m. for ^{13}C at 22.6 MHz, external H_2O for ^{17}O at 12.2 MHz, and external GeCl$_4$ taken as 30.9 p.p.m. (with respect to GeMe$_4$) at 30.09 MHz. Infrared spectra were run on a Perkin-Elmer 180, Raman spectra on a JASCO R300, and mass spectra on a Varian CH5 instrument.

Preparations.—Known compounds. Reported preparations[9,10] were improved by reducing the contact time with [Fe(CO)$_4$]$^{2-}$ to 15—20 min and recycling unreacted halogenogermane. The compound [Fe(CO)$_4$(GeMeH$_2$)$_2$] resulted in 42% yield with the proportion of condensation products reduced[10] to 11%. The ^1H n.m.r. spectrum (Table 1) showed small solvent shifts from the earlier values[10] in CS$_2$. The reported[10] gas-phase i.r. carbonyl stretches are in error and were remeasured as 2 089m (a_1 axial), 2 030vs (b_2 axial + a_1 equatorial), 2 007s, (b_1 equatorial), and 1 985w cm^{-1} (^{13}CO). The rest of the gas-phase spectrum, and the full solution and solid-state spectra, agreed with earlier[10] values.

Use of CH_2Cl_2 as solvent markedly improved the yield[9] of $[Fe(CO)_4(GeMe_2H)_2]$ to 17%. The risk of halogenation makes this solvent inappropriate for the compounds of lower methyl content. The larger yield allowed the determination of the CO stretching i.r. bands in hexane solution at 2 073m, 2 007s, and 1 988s cm^{-1}. These show phase shifts of about 20 cm^{-1} compared with the reported[9] complex solid-film measurements. Bands due to the condensation product $[\{Fe(CO)_4(GeMe_2)_2\}]$ grew in rapidly at 2 052s, 2 025 (sh), and 2 001vs cm^{-1}. The ^1H n.m.r. values (Table 1) show small solvent shifts, and the rest of the spectroscopic data agree with earlier[9] values.

The compound $[Fe(CO)_4(GeMe_3)_2]$ was similarly prepared in up to 70% yield and its properties agreed with those reported earlier.[13] The ^{13}C and ^{17}O n.m.r. spectra, together with those of $[Fe(CO)_4(GeH_3)_2]$, were measured for comparison with the new species (Table 2).

Tetracarbonylgermyl(methylgermyl)iron, $[Fe(CO)_4(GeH_3)(GeMeH_2)]$. After $[Fe(CO)_4(GeH_3)_2]$ (1 271 mg, 3.98 mmol) and $Na[Mn(CO)_5]$ {from $[Mn_2(CO)_{10}]$ (731 mg, 1.87 mmol)} in Et_2O (4 cm^3) had reacted for 20 min, all volatiles were removed including unreacted $[Fe(CO)_4(GeH_3)_2]$ (37 mg, 0.1 mmol) and $[Mn(CO)_5(GeH_3)]$ (929 mg, 3.44 mmol, 92%). To the white-orange anion was added $GeBrMeH_2$ (599 mg, 3.53 mmol) in pentane. The mixture was shaken for 15 min, volatiles were removed, and the products collected by prolonged pumping at diffusion pump vacuum through pre-weighed U-traps, changed at intervals. First recovered was $[Fe(CO)_4(GeH_3)_2]$ (*ca.* 121 mg, 0.38 mmol), followed by the compound identified below as $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ {total 913 mg, 2.74 mmol, 80% based on $[Mn(CO)_5(GeH_3)]$}. Extraction of the pale yellow involatile residue with cyclohexane gave a fraction with i.r. bands at 2 067ms, 2 063s, 2 026 (sh), 2 017vs, 642m, and 619 cm^{-1}, suggesting mixed cyclic products. Among the volatiles removed with pentane were $GeMeH_3$, which was not separated, together with minor amounts of $[Mn(CO)_5(GeH_3)]$ and $[Fe(CO)_4(GeRH_2)H]$ (R = Me or H), indicated by their i.r. spectra.

In further runs, the recovery of $[Mn(CO)_5(GeH_3)]$ was better than 90% and more thorough removal of this raised yields towards 90%. One preparation started with $[Fe(CO)_4(GeMeH_2)_2]$ (and with $GeBrH_3$ added to the anion). The recovery of $[Mn(CO)_5(GeMeH_2)]$ was only 61% with a product yield below 50%.

The spectroscopic properties are consistent with the formulation of the product as *cis*-tetracarbonylgermyl(methylgermyl)iron. In the mass spectrum (*m/z* values), the parent-ion envelope P^+ occurred at 340—323w {$C_5H_8Fe^{76}Ge_2O_4$ requires 340, intensity pattern matches 2Ge, overlapping with $[P - nH]^+$ for n = 1—5 but all weaker than P^+}. Fragment ions observed were $[P - nCO]^+$ for n = 1(s), 2(ms), 3(s), or 4(s), $[P - Me - nCO]^+$ for n = 0(w), 1(w), 2(m), 3(m), or 4(vs), $[P - MeGeH_x - nCO]^+$ for n = 2(m), 1(m), or 0(m), $[P - GeH_x - nCO]^+$ for n = 1(m) or 0(m), $[Fe(CO)_x]^+$ for x = 4(m), 3(s), 2(s), or 1(w), together with $[GeCH_x]^+$(s) and $[GeH_x]^+$(s).

N.m.r. observations are listed in Tables 1 and 2, while the vibrational data and assignments are shown in Table 3. After the Raman spectrum was run, an i.r. spectrum showed additional shoulders at 2 099, 2 012, and 836 cm^{-1} but these were weak indicating only slight decomposition. A Raman spectrum in benzene solution was similar to that given in Table 3, but lacked evidence for the weak bands at 1 243, 1 059, 703, and 566 cm^{-1}.

$[Fe(CO)_4(GeH_3)(GeMe_2H)]$. A similar preparation using $[Fe(CO)_4(GeH_3)_2]$ (3.82 mmol), $[Mn(CO)_5]^-$ (2.82 mmol), and $GeMe_2ClH$ (2.87 mmol) gave, on prolonged pumping through cooled traps, a mixed fraction containing $[Fe(CO)_4(GeH_3)_2]$ plus $[Fe(CO)_4(GeH_3)(GeMe_2H)]$ (in 1:5.3 molar ratio by ^1H n.m.r. intensities) followed by pure $[Fe(CO)_4(GeH_3)(GeMe_2H)]$. The overall yield was 1.96 mmol (69% based on $GeMe_2ClH$). The compound $GeMe_2H_2$ was identified in the solvent fraction but not isolated. In other runs, up to 52% $[\{Fe(CO)_4(GeH_2)\}_2]$ was recovered matching a reduction to 13% in the yield of $[Fe(CO)_4(GeH_3)(GeMe_2H)]$. After each handling operation, a small amount of $GeMe_2H_2$ was formed and an involatile residue remained. Checks before and after established that the main component was always the original material.

With this reservation, *tetracarbonyl(dimethylgermyl)germyliron* was characterised spectroscopically: parent-ion envelope at *m/z* 354—338vw {$C_6H_{10}Fe^{76}Ge_2O_4$ requires 354, intensity pattern appropriate to 2Ge, overlapping with $[P - nH]^+$ ions}. CO And CH_x were both readily lost giving $[P - nCO]^+$ for n = 3(m), 2(ms), 1(s), or 0(s), $[P - Me - nCO]^+$ for n = 0(vw), 1(vw), 2(w), 3(m), or 4(s), together with $[Fe_2Ge_2H_x]^+$ (vs, base peak), $[Fe(CO)_nGeH_x]^+$ for n = 2(ms), 1(s), or 0(s); loss of GeH_x is rarer with only $[FeGeCH_x]^+$(m). The remaining fragments above m/z = 70 were $[Fe(CO)_x]^+$ for x = 4(s), 3(s), 2(s), or 1(s), $[GeCH_xO]^+$(m), $[GeCH_x]^+$(s), and $[GeH_x]^+$(m). The *cis* configuration was shown by the n.m.r. data (Tables 1 and 2).

The i.r. and Raman frequencies are listed in Table 3. At the end of the Raman run the sample was coloured and ^1H n.m.r. spectroscopy indicated 15% $GeMe_2H_2$ and some cyclic products. Because of this decomposition, polarisation measurements were not made: Raman shifts of condensation products were too weak to observe.

Unstable species. While the remaining three compounds were much less stable there is reasonable evidence that the preparations followed the expected course.

(*a*) $[Fe(CO)_4(GeMeH_2)(GeMe_2H)]$. The standard anion preparation, allowing only 10 min contact to reduce side reactions, yielded $[Mn(CO)_5(GeMeH_2)]$ (0.92 mmol, 53%) from $[Fe(CO)_4(GeMeH_2)_2]$ (1.73 mmol). The compound $GeMe_2ClH$ (2.02 mmol) was allowed to react in pentane for 12 min with the orange-red anion. Volatiles, consisting of $GeMe_2H_2$, $GeMeH_3$ (trace), pentane, and a little $[Mn(CO)_5(GeMe_xH_{2-x})]$ (x = 1 or 2), were removed then prolonged pumping gave a colourless oil mixed with a less volatile white sublimate. The i.r. spectrum from volatiles above this mixture showed the presence of germylmanganese species which could be removed only with substantial sacrifice of iron compounds. Extraction of the involatile residues with hexane yielded an orange-red mixture (together with more white sublimate) whose i.r. spectrum showed the presence of the same mixture of cyclic products discussed below.

For the slightly volatile product fraction, the strongest signals in the ^1H n.m.r. spectrum (Table 1) are consistent in position, multiplicity, and intensity with those of $[Fe(CO)_4(GeMeH_2)(GeMe_2H)]$. Additional weak signals were found at δ 4.19 (spt, *J* 3.2) and 3.96 (q, *J* 3.4 Hz) together with extra shoulders on the CH_3 signals. These shifts are close to those of $[Fe(CO)_4(GeMe_2H)_2]$ and $[Fe(CO)_4(GeMeH_2)_2]$ respectively (Table 1) and are much less likely to arise from $[Mn(CO)_5(GeMe_2H)]$ (δ 4.17, spt, *J* 3.6 Hz) and $[Mn(CO)_5(GeMeH_2)]$ (δ 3.79, q, *J* 3.8 Hz).

When the ^1H n.m.r. spectrum was remeasured on samples after handling (*e.g.* for i.r.), additional strong singlets at δ 1.41 and 4.37 were present which do not match those of any of the cyclic condensation products.

When a ^{13}C n.m.r. spectrum was run in C_6H_6 there were two pairs of shifts (matched by intensities) (**A**) at δ 208.2 and 206.4 and (**B**) at 208.5 and 207.2. A ^1H n.m.r. spectrum showed that the sample contained $GeMe_2H_2$, and triplets at δ 0.5 and 0.9, *J* 3.5 Hz, indicated $GeMeH_2$ groups were present. These may arise from $[Fe(CO)_4(GeMeH_2)_2]$ (**A**, with *ca.* 1 p.p.m. shifts from the ^{13}C values in the literature[10]) and $[Fe(CO)_4(GeMeH_2)(GeMe_2H)]$ (**B**).

The i.r. spectrum in hexane–cyclohexane solution was measured with rapid scans showing ν(CO) (cm^{-1}) at 2 077m, 2 058w, 2 010s, 1 998 (sh), and 1 991vs. Condensation products can account for the band at 2 058 cm^{-1} and part of that at 1 998 cm^{-1}. Pale yellow residues left after transferring the product gave i.r. bands at 2 059 (sh) (**B**), 2 056vs (**E**), 2 053s (**C**), 2 021w (sh), 2 016w (sh), 2 006m (sh) (**B**), 2 003 (sh), 2 001vs (**E**), 1 991m (**C**), 1 970vw, 1 964vw, 624m, and 613s cm^{-1}. These values, together with the mass spectra of various samples, are compatible with a mixture of $[\{Fe(CO)_4(GeMe_2)\}_2]$ (**C**), $[\{Fe(CO)_4\}_2(GeMe_2)(GeMeH)]$ (**E**), and $[\{Fe(CO)_4(GeMeH)\}_2]$ (**B**). The labelled pairs are the strong in- and out-of-phase axial stretches, while the unlabelled bands at 2 021, 2 016, and 2 003 cm^{-1} represent the weaker equatorial modes.

$[Fe(CO)_4(GeMeH_2)(GeMe_3)]$. The compound $[Fe(CO)_4(GeMe_3)_2]$ (3.7 mmol) and $K[Mn(CO)_5]$ (2.8 mmol) in Et_2O gave $[Mn(CO)_5(GeMe_3)]$ (*ca.* 1.4 mmol, *ca.* 50%) after 15 min. All volatiles were removed by pumping for 6 h. In 10 min after addition of $GeMeClH_2$ (1.2 mmol) in hexane to the deep wine-red anion the colour changed through orange to green. Removal of volatiles, containing $GeMe_3H$, left a greenish oil and a grey solid.

A green solution of $[Fe(CO)_4(GeMeH_2)(GeMe_3)]$ in benzene gave the ^{1}H n.m.r. data shown in Table 1, together with singlets at δ 0.29, 0.44, and 0.48 which did not change on standing. The initial spectrum also showed $GeMe_3H$ [δ 0.18 (d) and 4.10 (m), *J* 3.2 Hz; *ca.* 3%], a little $[\{Fe(CO)_4(GeMeH)\}_2]$ (δ 1.10, d, *J* 3.4 Hz) and a weak singlet, δ 1.24. After 80 min, these three made up 60, 15, and 4% respectively of the total methyl intensity.

A yellow solution of $[Fe(CO)_4(GeMeH_2)(GeMe_3)]$ turned green before the i.r. spectrum was run. Bands at 2 074mw, 2 021w (sh), and 1 998s cm^{-1} decreased and those at 2 067w and 2 015ms cm^{-1} grew in over 15 min. These, and the green colour, probably reflect reaction with oxygen. Also present throughout were the CO stretches of $[\{Fe(CO)_4(GeMeH)\}_2]$ at 2 060m and 2 008s while a weak absorption at 2 044 cm^{-1} may be ν(GeH) of $GeMe_3H$. Only ions from $[\{Fe(CO)_4(GeMeH)\}_2]$ were observed in attempts to record the mass spectrum.

$[Fe(CO)_4(GeMe_2H)(GeMe_3)]$. In a similar preparation, the waiting time was reduced by extracting unreacted $[Fe(CO)_4(GeMe_3)_2]$ from the anion with hexane rather than using prolonged pumping. The compound $GeBrMe_2H$ was allowed to react with the pink anion for 10 min giving a pale orange solution. After volatiles were removed, the product was pumped directly into a U-trap with an attached n.m.r. tube giving an oily yellow liquid whose ^{1}H n.m.r. spectrum showed rather broad maxima as listed in Table 1. After 15 min, about 60% of the sample had been converted into $GeMe_3H$ plus $[\{Fe(CO)_4(GeMe_2)\}_2]$, which was the only species seen in the i.r. spectrum. Extraction of the reaction residues yielded more $[\{Fe(CO)_4(GeMe_2)\}_2]$.

Condensation Reactions.—Changes with time in the ^{1}H n.m.r. spectra of 0.2—0.3 mmol of each of the stable species in C_6H_6 gave the most detailed information about their condensation. The products from sealed, neat-liquid, samples left in the dark were also examined. In these experiments the germanes were conveniently recognised from the ^{73}Ge shifts: GeH_4, −296.8; $GeMeH_3$, −206.9 (δ_C −11.6); and $GeMe_2H_2$, −125.3 (δ_C −6.2) together with ^{1}H shifts and appropriate intensities and multiplicities.

$[Fe(CO)_4(GeH_3)(GeMeH_2)]$. (*a*) The first product detected in the ^{1}H n.m.r. spectrum was $GeMeH_3$ after 7 d at room temperature. At 10 d, a doublet (δ 1.02, *J* 3.4 Hz) was detectable and much later seen to overlap with a second one of about one quarter the intensity at δ 1.05, *J ca.* 4.5 Hz. Based on methyl signal intensities, the ratio of the starting material to $GeMeH_3$ to the sum of the doublets changed with time: 99.5 : 0.5 : trace at 11 d; 90 : 8 : 2 at 22 d; 85 : 11 : 3 at 54 d; and 70 : 20 : 10 at 84 d when GeH_4 (*ca.* 1%) was also detected.

After a total of 100 d plus 24 h at 30 °C, the tube was opened and the $GeMeH_3$ removed. Re-examination of the spectrum of the solution showed a singlet at δ 3.52, about 0.01 p.p.m. to high field of the GeH_3 resonance of $[Fe(CO)_4(GeH_3)(GeMeH_2)]$. With the doublet at δ 1.02, the intensities are appropriate for $[\{Fe(CO)_4(GeH_3)\}_2GeMeH]$. The involatile, insoluble products from the tube formed yellow crystals and showed i.r. and mass spectra compatible with a mixture of $[\{Fe(CO)_4(GeH_2)\}_2]$ (**A**) with $[\{Fe(CO)_4\}_2(GeH_2)(GeMeH)]$ (**D**) and $[\{Fe(CO)_4(GeMeH)\}_2]$ (**B**). There were three strong series of ions each showing loss of eight CO groups, corresponding to fragments containing two, one, and zero Me groups. The CO stretching bands occurred at 2 067m (**A**), 2 063s, 2 059m (**B**), 2 026m (**A** and **B**), 2 017vs (**A**), and 2 011vs cm^{-1} (**B**). The bands for (**D**) are tentatively assigned as 2 063 cm^{-1}, together with contributions from those at 2 017 and 2 011 cm^{-1}.

(*b*) *Sealed tube.* From a neat sample (98 mg, 0.29 mmol), 57% (56 mg, 0.17 mmol) was recovered unchanged after 122 d in the dark. There were formed $GeMeH_3$ (9 mg, 0.09 mmol), GeH_4 (*ca.* 0.7 mg, 0.01 mmol), incondensable gases (0.04 mmol), and an involatile orange-red oil (*ca.* 32 mg). The i.r. spectrum of the oil in cyclohexane showed CO stretches at 2 067m (**A**), 2 063s, 2 060ms (**B**), 2 024m (**A** and **B**), 2 018s (**A**), 2 010vs, and 2 008s cm^{-1} (**B**), and with (**E**) as above. The variation in composition allows the band at 2 010 cm^{-1}(**E**) to be resolved from that at 2 008 cm^{-1} (**B**).

(*c*) *Sealed n.m.r. tube.* A sample in C_6H_6 was held for 2 y and showed $GeMeH_3$, GeH_4 $[\{Fe(CO)_4(GeH_3)\}_2GeMeH]$ [δ(^{1}H) 3.70 (s), 3.34 (m), and 1.0 (d), *J ca.* 2.9 Hz; δ(^{13}CH$_3$) 5.7], a ^{1}H singlet at δ 3.14 which may be from $[\{Fe(CO)_4(GeH_2)\}_2]$, and a new ^{73}Ge resonance at δ −214.8, a region appropriate for one Me substituent and, with ^{1}H signals at δ 3.23 and 0.915, indicating a methyldigermane (^{73}Ge resonance not observed from Ge bonded to transition metals).

$[Fe(CO)_4(GeH_3)(GeMe_2H)]$. The n.m.r. experiment showed more than 20% reaction in 36 h when $GeMe_2H_2$ (22%), $[\{Fe(CO)_4(GeH_2)\}_2]$ [6%, δ(GeH$_2$) 3.29 (s)], and a third product [*ca.* 1%, δ(CH$_3$) 1.0] were present. After 6 d, the reaction was 44% complete, while after 35 d the mixture contained starting material (24%), $GeMe_2H_2$ (50%), $[\{Fe(CO)_4(GeH_2)\}_2]$ (20%), and the third product (7%). Signals from the last were now clear [δ(CH$_3$) 1.01 (s), δ(GeH) 3.49 (s), relative intensities 1 : 1] and compatible with $[\{Fe(CO)_4(GeH_3)\}_2GeMe_2]$. There were also weak singlets (< 1%) at δ 3.46 (?), 3.10 (GeH$_4$), and 1.09 (?).

A second sample, held for 1 week, allowed a fuller n.m.r. examination and contained $GeMe_2H_2$, signals attributable to $[\{Fe(CO)_4(GeH_3)\}_2GeMe_2]$ [δ(H) 3.50 and 0.74, δ(^{13}CH$_3$) 11.1, δ(^{13}CO) 207.5], and a weak signal from $[\{Fe(CO)_4(GeH_2)\}_2]$ which had partly precipitated. Any GeH_4 was too scanty to be observed, and the starting material had completely reacted.

$[Fe(CO)_4(GeMeH_2)(GeMe_2H)]$. A small liquid sample showed little change after 2 h in the dark at 0 °C. When benzene was added (*ca.* 10% solution), the ^{1}H n.m.r. spectrum showed the presence of 10% $GeMe_2H_2$ after 3 h, together with $GeMeH_3$ (trace) and overlapping methyl signals indicating a mixture of cyclic products at δ $1.06 > 1.02 \approx 1.00 > 1.09$ (decreasing relative intensity).

The compounds $[Fe(CO)_4(GeMeH_2)(GeMe_3)]$ and $[Fe(CO)_4(GeMe_2H)(GeMe_3)]$ condensed so rapidly during their preparations that no further study was made.

Reactions with Representative Chlorides.—Reactions with $SiCl_4$, CCl_4, and HCl have been reported[12,15] for the germyl, digermanyl, and methylgermyl tetracarbonyliron compounds, where the progress of the reaction was followed by ^1H n.m.r. spectroscopy. The reactions described below showed the same characteristic changes in δ and *J* on chlorine substitution. They were carried out on the 0.1-mmol scale in C_6H_6 in n.m.r. tubes.

(*a*) $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ *plus* $SiCl_4$. A 1:1 mixture reacted only slowly and the colour deepened to yellow-orange over 91 d. The compound $[Fe(CO)_4(GeH_3)(GeMeClH)]$ was detectable after 4 d and $GeMeClH_2$ after 10 d. After 20 d the solution consisted of starting material (79%), $[Fe(CO)_4(GeH_3)(GeMeClH)]$ (12%), and $GeMeClH_2$ (9%), and solid was present. Later, $GeMeH_3$ and GeH_4 also appeared in that order, giving solution ratios of these five species of 68:17:3:12:2 after 47 d and 53:20:2:24:5 after 91 d.

(*b*) $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ *plus* CCl_4. The compound CCl_4 (in 2:3 ratio) reacted more quickly than $SiCl_4$ but the first stages were similar giving an orange solution after 2 d composed of 92% starting material, 5% $[Fe(CO)_4(GeH_3)(GeMeClH)]$, 25% $GeMeClH_2$, and 1% $GeMeH_3$ but with three additional very weak singlets in the δ(GeH) region. A white-orange solid started to precipitate after 3 d and the composition changed to $[Fe(CO)_4(GeH_3)(GeMeH_2)]$:$[Fe(CO)_4(GeH_3)(GeMeClH)]$:$GeMeClH_2$:$GeMeH_3$:$GeH_4$:$GeCl_2H_2$ in the ratio 80:11:3:4:1:1 after 3 d, 73:12:3:7:2:1 [plus extra minor δ(Me) signals as well as δ(GeH) ones] after 5 d, 61:16:4:7:7:1 after 22 d, 48:18:3:15:9:3 after 31 d, and 47:13:2:17:14:3 after 40 d (all these last with five to six minor signals). After 80 d, the signals at the positions of the starting material appeared to split and the ratio was 27 (both sets):6:3:26:21:16.

In reactions (*a*) and (*b*) the initial $[Fe(CO)_4(GeH_3)(GeMeClH)]$ [δ(GeH_3) 3.30 (s); δ(CH_3) 0.93 (d), *J* 2.5 Hz, ratio 1:1, δ(GeH) *ca.* 6 and obscured by solvent δ(^{13}CH)] showed an upfield shift of the unsubstituted GeH_3 of 0.23 p.p.m. relative to the starting material. Similar, but smaller shifts in unsubstituted GeH_x signals were observed[12,15] in earlier studies. For $GeMeClH_2$ [δ(CH_3) 0.23 (t), δ(GeH_2) 5.05 (q), *J* 2.6 Hz, ratio 1.57:1], the chemical shifts were up to 0.5 p.p.m. different from reported[17] values in CS_2.

(*c*) $[Fe(CO)_4(GeH_3)(GeMeH_2)]$ *plus* HCl. This reaction, in 1:1 ratio, was fast giving starting material:$GeClMeH_2$:$[Fe(CO)_4(GeMeClH)H]$:$GeClH_3$:$[Fe(CO)_4(GeClH_2)H]$:$[Fe(CO)_4(GeH_3)H]$ in the ratio 73:10:4:5:5:3 after 1 d, 44:19:10:12:12:3 after 2 d, 16:28:16:19:18:4 after 4 d (yellow colour), and 11:32:16:19:18:3 after 6 d. At this point the HCl signal was near zero and $[Fe(CO)_4(GeMe_2Cl)H]$ (19%) had appeared. The starting materials and $[Fe(CO)_4(GeH_3)H]$ had disappeared after 12 d leaving in solution 39% $GeMeClH_2$, 23% $GeClH_3$, 15% $[Fe(CO)_4(GeMeClH)H]$, 18% $[Fe(CO)_4(GeClH_2)H]$, and 3% $[Fe(CO)_4(GeMeCl_2)H]$. After 40 d the ratio of these components had changed only marginally to 37:25:14:17:3. After 84 d, an orange solid had precipitated and a very complex mixture of signals was present. In this, the proportions in solution were $GeMeClH_2$ (25), GeH_4 (16), $[Fe(CO)_4(GeMeClH)H]$ (8), and $[Fe(CO)_4(GeH_3)H]$ (3). The rest of the intensity arose from unidentified species: δ 0.40 (s) (13%), 1.00 (s) (11%), 1.06 (d, *J* 2.2) (8%), 1.48 [d, *J* 5.4 (?)] (6%), 4.61 (q, *J* 4.5 Hz) (6%), and further weak singlets in the Me region.

Additional compounds were attributed; $[Fe(CO)_4(GeMeClH)H]$ [δ(H) −10.56 (s), δ(CH_3) 0.90 (d), *J* 2.5 Hz, ratio 1:3 with δ(GeH) obscured]; $[Fe(CO)_4(GeClH_2)H]$ [δ(H) −10.74, δ(GeH_2) 5.62]; $[Fe(CO)_4(GeH_3)H]$ [δ(H) −10.10 (s), δ(GeH_3) 3.63 (s)]; and $[Fe(CO)_4(GeMeCl_2)H]$ [δ(H) −10.24 (s), δ(CH_3) 1.22 (s)].

(*d*) $[Fe(CO)_4(GeH_3)(GeMe_2H)]$ plus CCl_4. The reaction (1:1) was fairly rapid with a yellow colour and products appearing within 1 d. Species present were starting material:$GeMe_2H_2$:$GeMe_2ClH$:$[\{Fe(CO)_4(GeH_3)\}_2GeMe_2]$:$[\{Fe(CO)_4\}_2(GeCl_2)(GeH_2)]$:$[\{Fe(CO)_4(GeH_2)\}_2]$:$GeH_4$:$[\{Fe(CO)_4\}_2(GeCl_2)(GeMe_2)]$:$[\{Fe(CO)_4\}_2(GeMe_2)(GeClH)]$ in the ratio 86:5:4:3:2:0:0:0:0 after 1 d, 65:8:15:3:9:0:0:0:0 after 2 d, 30:11:36:3:15:2:2:0:0 after 5 d, 12:12:50:5:8:8:3:1:2 after 20 d, and trace:15:55:7:2:10:5:3:3 after 34 d.

(*e*) $[Fe(CO)_4(GeH_3)(GeMe_2H)]$ *plus* HCl. This mixture (2:3) reacted quickly and was pink within 1 d and orange in 34 d. Components identified appeared in the ratios starting material:$GeMe_2ClH$:$[Fe(CO)_4(GeMe_2Cl)H]$:$[Fe(CO)_4(GeH_3)H]$:$GeClH_3$:$[Fe(CO)_4(GeClH_2)H]$:GeH_4:$GeMe_2Cl_2$:$[Fe(CO)_4(GeH_2)]$ of 83:11:1:4:trace:0:0:0:0 after 1 d, 48:20:8:5:8:11:0:0:0 after 2 d, 1:41:15:22:7:11:2:trace: trace after 16 d, 0:41:13:0:0:0:13:23:6 together with five new singlets (all weak) at (δ) 1.40, 3.25, 3.36, 4.53, and 5.42 after 34 d.

(*f*) $[Fe(CO)_4(GeH_3)_2]$ *plus* $[Fe(CO)_4(GeMe_3)_2]$ *in* C_6H_6. In a preliminary experiment this mixture showed, after 17 h, $GeMe_3H$ [δ(GeH_3) 4.23, δ(CH_3) 0.5 (d), *J* 2.9 Hz, δ($^{13}CH_3$) −3.2, δ(^{73}Ge) −57], $[\{Fe(CO)_4(GeH_2)\}_2]$ [δ(^{13}CO) 208.5 and 204.7, δ(GeH_2) 3.66 (s)], and minor products represented by δ(H) 3.43 (s), δ(^{13}C) 6.2, 4.7, and 4.0. There was little change on longer standing.

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References

1 S. Anema, J. A. Audett, K. M. Mackay, and B. K. Nicholson, preceding paper.

2 W. A. Hermann, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 56; K. M. Mackay and B. K. Nicholson, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, 1982, vol. 6, p. 1043.

3 A. Bonny, *Coord. Chem. Rev.*, 1978, **25**, 229.

4 J. Howard and P. Woodward, *J. Chem. Soc. A*, 1971, 3648.

5 A. Batsanov, L. Rybin, M. Rybinskaya, and Y. T. Struchkov, *J. Organomet. Chem.*, 1983, **249**, 319.

6 D. Melzer and E. Weiss, *J. Organomet. Chem.*, 1983, **255**, 335.

7 W. A. Herrmann, C. Hecht, E. Herdtweck, and H-J. Kreuper, *Angew. Chem., Int. Ed. Engl.*, 1987, **27**, 132.

8 J. A. Christie, D. N. Duffy, K. M. Mackay, and B. K. Nicholson, *J. Organomet. Chem.*, 1982, **226**, 165.

9 A. Bonny and K. M. Mackay, *J. Chem. Soc., Dalton Trans.*, 1978, 722.

10 A. Bonny and K. M. Mackay, *J. Chem. Soc., Dalton Trans.*, 1978, 506.

11 S. G. Anema, K. M. Mackay, L. C. McLeod, B. K. Nicholson, and J. M. Whittaker, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 759.

12 A. Bonny, K. M. Mackay, and F. S. Wong, *J. Chem. Res.*, 1985, (*S*) 40; (*M*) 558.

13 A. Bonny and K. M. Mackay, *J. Organomet. Chem.*, 1978, **144**, 389.

14 S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1972, 2442.

15 A. Bonny and K. M. Mackay, *J. Chem. Soc., Dalton Trans.*, 1978, 1569.

16 K. H. Whitmire and T. R. Lee, *J. Organomet. Chem.*, 1985, **282**, 95.

17 J. E. Drake, R. T. Hemmings, and C. Riddle, *J. Chem. Soc. A*, 1971, 600; 1970, 3359.

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