Transition-metal Carbonyl Derivatives of the Germanes. Part 6.† The Methylgermyl Iron Carbonyl System

By **Alan Bonny** and **Kenneth M. MacKay**, School of Science, University of Waikato, Hamilton, New Zealand

The synthesis and spectroscopic characterization of *cis*-[Fe(CO)$_4$(GeMeH$_2$)$_2$] (1) are described. This compound is converted into [{Fe(CO)$_4$(GeMeH)}] (2) and GeMeH$_3$ in the dark. However, its light-assisted reactions are more rapid and result in minor quantities of more condensed clusters.

We have reported[1] that tetracarbonylbis(dimethylgermyl)iron, [Fe(CO)$_4$(GeMe$_2$H)$_2$], undergoes a ready condensation reaction to form the cyclic compound [{Fe(CO)$_4$(GeMe$_2$)}$_2$] and this, in turn, can lose CO to form the enneacarbonyldi-iron analogue [Fe$_2$(CO)$_7$(GeMe$_2$)$_2$]. In contrast, the unsubstituted germane derivative [Fe(CO)$_4$(GeH$_3$)$_2$] was isolated and manipulated[2] with no apparent indication of the analogous condensation. Interest therefore focuses on the methylgermyl derivative whose synthesis and behaviour are reported here. In the parallel manganese species [Mn(CO)$_5$(GeMe$_n$H$_{3-n}$)] the methylgermyl compound behaves[3] very similarly to the germyl derivative.

EXPERIMENTAL

Manipulations and measurements were made as described previously,[1,3] except that ^{13}C n.m.r. spectra were recorded using a Nicolet T.T. 14 Fourier-transform instrument at 15.1 MHz.

Preparation of Tetracarbonylbis(methylgermyl)iron (1).—Starting materials were prepared as before,[1] with higher yields (based on Ge) being obtained when a deficit of the germyl halide was used. In one reaction Na$_2$[Fe(CO)$_4$] prepared from [Fe(CO)$_5$] (11.2 mmol) and Na (23.0 mmol) was treated in pentane with a total of 16.10 mmol of GeBrMeH$_2$ over 6 d at room temperature. The product was periodically separated in a trap at −5 °C and the pentane and unchanged GeBrMeH$_2$ were returned to the reaction vessel. The overall percentage yield of product was 44.3% (3.567 mmol) and it was noted that the rate of formation slowed as the reaction proceeded. As found for the synthesis of [Fe(CO)$_4$(GeMe$_2$H)$_2$],[1] CO was produced in the initial stages only (0.07 mmol was produced after the first 15 min). Methylgermane (1.9 mmol) was recovered from the volatiles and [{Fe(CO)$_4$(GeMeH)}$_2$] (2) (0.12 mmol) was sublimed from the reaction vessel. The total recovery of initial germanium was 58%. Other runs with total reaction times of 5—15 min produced 20—40% yields. The product (1) is a clear liquid which soon turns yellow and is only just volatile at room temperature. In the mass spectrum the molecular-ion family was found at m/e 338—354 and was weak [P^+ at m/e 342—354 for the Ge$_2$ combinations 140—152 respectively (germanium has five naturally occurring isotopes of nominal masses 70, 72, 73, 74, and 76)]. The main component of the molecular family is $[P - \mathrm{H}]^+$ which is five times more intense than the parent, while $[P - 2\mathrm{H}]^+$, $[P - 3\mathrm{H}]^+$, and $[P - 4\mathrm{H}]^+$ were respectively 0.7, 1.2, and 0.3 times the intensity of the parent ion. The family arising from loss of a methyl group is *ca.* 1.2 times more intense than family, at m/e 338—350 and the families arising from carbonyl loss are very much more intense. These fragment ions are listed in Table 2.

The ^{1}H and ^{13}C n.m.r. spectra are consistent with the formulation of (1) and parameters are given in Table 3. The observation of the two ^{13}CO resonances of equal intensity establishes that the compound exists in the *cis* configuration. The vibrational spectrum is also consistent with *cis*-[Fe(CO)$_4$(GeMeH$_2$)$_2$] (Table 4) and exhibits strong Raman bands for Fe–Ge stretching at 210 (asym) and 225 cm^{-1} (sym) in the order observed[2] for [Fe(CO)$_4$(GeH$_3$)$_2$].

From some preparation runs, a sample was also isolated

---

† Part 5 is ref. 3.

[1] Part 7, A. Bonny and K. M. MacKay, *J.C.S. Dalton*, 1978, in the press.

[2] S. R. Stobart, *J.C.S. Dalton*, 1972, 2442.

[3] B. W. L. Graham, K. M. MacKay, and S. R. Stobart, *J.C.S. Dalton*, 1975, 475.

at −22 °C which gave the ^{1}H n.m.r. spectrum [τ 20.13 (s, intensity 1), 9.27 (t, 3), and 6.18 (q, intensity 2) (^3J 3.8 Hz) expected for $[Fe(CO)_4(GeMeH_2)H]$. This species was unstable and not studied further.

Condensation Reactions of (1).—Preliminary experiments established that, in total darkness, (1) slowly evolved $GeMeH_3$ and minor quantities of CO, while depositing a yellow solid. In contrast, even in subdued lighting, the proportion of CO was much higher in the initial stages, H_2 was formed as well, and the reaction mixture became dark red-brown. Data from the preliminary reactions [(ii)—(iv)] are collated in Table 1 together with data for two reactions which were examined in more detail for the limiting cases of total darkness and strong illumination. For the former case [reaction (i) in Table 1] the yellow solid remaining in the reaction vessel was identified as (2) by ^{1}H n.m.r., i.r., and mass spectrometry. Data are collated in Tables 3, 5, and 6. From the reaction under strong illumination [(v)] the red residues were more complex. The ^{1}H n.m.r., i.r., and mass spectra of the residues showed the presence of unchanged (1) and (2), together with signals from smaller amounts of several other compounds. In the ^{1}H n.m.r. spectrum new resonances were observed (in 12% C_6H_6 in CS_2 as solvent) at τ 9.12 and 9.01 [both doublets, J(HH′) 2.4 Hz], *ca.* 8.89(br), 8.87, 8.67(br), and 8.58. The i.r. spectrum showed a new set of absorptions which are mainly attributable to $[Fe_2(CO)_7(GeMeH)_2]$ (3) and are listed in Table 7. Mass spectra were recorded for a sample of the residues at probe temperatures from 25 to 110 °C. At 25 °C a weak spectrum attributable to $[\{Fe(CO)_4(GeMeH)\}_2]$ was obtained. With the probe at 65 °C additional series of weak to very weak envelopes up to *m/e* 917 were observed. As the probe temperature was further increased these higher envelopes appeared to remain at the same relative intensity. These envelopes were very broad and are attributable to Ge_x-containing fragments ($x > 4$). One possible assignment for the highest envelope is $[Fe_4(CO)_{12}\,{}^{284-296}Ge_4Me_4]^+$ (*m/e* 904—916) and the other envelopes could be attributed to ions arising from CO and/or CH_x loss down to $[Fe_4Ge_4C_2H_x]^+$.

TABLE 1

Condensation reactions of (1)

Reaction	Conditions	Time	Amount (μmol) (1) Consumed	GeMeH$_3$ evolved	CO,H$_2$ evolved
(i)	Total darkness	2 d	114 [a]	67	0.8, 0
		7 d		97	1.7, 0
		25 d		128	3.4, 0
(ii)	Total darkness (sealed tube)	3 months	343	322	22, 0
(iii)	Subdued lighting	7 d	86	18	41, 14
		22 d		93	52, 17
(iv)	Laboratory light, 55 °C	78 h	251	203	119, 0
(v)	Strong illumination [b]	0.25 h	*ca.* 135	22	2.2, 1.8
		4.5 h		46	100, 79
		8 h		141	149, 119

[a] 438 μmol of (1) was contained in a trap which was painted black and enclosed within a black plastic bag in a darkened laboratory. 324 μmol of (1) was recovered after 25 d. [b] 250 μmol of (1) was irradiated at 350 nm in a thin-walled (0.5-mm) Pyrex tube. The $GeMeH_3$ evolved was shown by i.r. and mass spectrometry to contain *ca.* 10% $GeMe_2H_2$, 1% $Ge_2Me_2H_4$, and 0.5% $GeMe_3H$. Part of the uncharged portion of (1) was recovered from the vessel (65 μmol) but a further fraction remained, estimated at *ca.* 50 μmol from the ^{1}H n.m.r. signal intensity.

TABLE 2

Mass spectrum of $[Fe(CO)_4(GeMeH_2)_2]$. Values quoted are relative intensities summed over all values of x

n	$[Fe(CO)_nGe_2C_2H_x]^+$	$[Fe(CO)_nGe_2CH_x]^+$	$[Fe(CO)_nGeCH_x]^+$	$[Fe(CO)_nGeH_x]^+$	$[Fe(CO)_n]^+$
4	4	7			3
3	100	8	trace	31	3
2	46	14	*ca.* 5	8	4
1	18	10	27	17	8
0	64	71	28	34	5

Other ions below *m/e* 50 were: $[FeGe_2H_x]^+$ 40; $[GeCH_x]^+$ 29; $[GeH_x]^+$ 8; $[Fe(CO)H]^+$ 1; $[FeH]^+$ 1.

TABLE 3

N.m.r. data for (1) and (2)

Compound	τ (CH$_3$) [a]	τ (GeH$_2$) [a]	^3J/Hz	Solvent
(1)	9.30	6.20	3.9	SiCl$_4$
	9.27	6.22	3.8	CS$_2$
	δ(^{13}CO)$_{ax.}$	δ(^{13}CO)$_{eq.}$	δ(^{13}CH$_3$)	
	207.1	205.5	−3.0	neat [b]
	τ(CH$_3$) [c,d]	τ(GeH) [c]	^3J/Hz	
(2)	8.84	6.33	3.4	12% C$_6$H$_6$ in CS$_2$
	8.81	6.23	3.4	

[a] These signals were in the ratio 3 : 2. Spectra recorded at −70 °C were identical. [b] Sample sealed in 5-mm tubing and run at 27 °C in a 10-mm tube with $CDCl_3$ for lock. J(HGe^{13}C) 7.7, J(H^{13}C) 129 Hz. Minor broadening of the ^{13}CO resonances was observed in the coupled spectrum due presumably to J(HGeFe^{13}C). Compare [4] $[Fe(CO)_4(GeMe_3)_2]$ in CD_2Cl_2 solution at 223 K : δ(^{13}CO)$_{ax.}$ 208.94, δ(^{13}CO)$_{eq.}$ 207.15, and δ(^{13}CH$_3$) 6.96 p.p.m. [c] These signals were in the ratio 3 : 1. [d] Compare τ 8.85 for $[\{Fe(CO)_4(GeMe_2)\}_2]$.[1]

The residue from a run under weak illumination [reaction (iii)] showed, as well as (2), polygermanium envelopes in the mass spectrum up to *m/e* 1 020 (probe temperature 80 °C). The highest envelope had *m/e* 1 006—1 020 and was followed at intervals of 28 *m/e* units by 15 similar envelopes. These could be tentatively assigned to the families $[Fe_5(CO)_nGe_5Me_4]^+$ (n = 0—11), $[Fe_4(CO)_nGe_5Me_4]^+$ (n = 0 or 1), and $[Fe_3Ge_5Me_4]^+$ or to similar combinations involving the overall loss of two ^{56}Fe plus 11 CO units. There followed four more envelopes at intervals of *m/e* 14—16 which could

---

[4] L. Vancea, R. K. Pomeroy, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1976, **98**, 1407.

TABLE 4

Vibrational spectrum (cm^{-1}) of (1)

Infrared			Raman	
Gas	Liquid	Solid	Liquid	Tentative assignment
	3 002w		2 988w,br	ν(CH)
	2 946w			
2 119m (sh)		2 102w (sh)		
2 101s	2 086vs	2 084vs	2 086p,m	$\nu(CO)_{ax.}\ a_1$
			2 040w (sh)	ν(GeH)
2 042vs	2 017vs	2 017vvs	2 014s	$\nu(CO)_{ax.}\ b_2 + \nu(CO)_{eq.}\ a_1$
2 020m	1 991vvs	1 981vvs	2 009vs	$\nu(CO)_{eq.}\ b_1$
1 985w (sh)	1 965w (sh)	1 956w (sh)		$\nu(^{13}CO)$
	1 467w	1 416w	1 420vw	$\delta_{asym}(CH_2)$
	1 415m			
	1 237m	1 238w	1 240m	$\delta_{sym}(CH_2)$
		1 097vvw		
			1 060w	
	1 019w	1 024vvw		
	961w			
873 (sh)	874s	878s	880p,w	$\delta(GeH_2)\ a_1$
846s	836vs	839vs		$\delta(GeH_2)\ b_1$ plus $\rho(CH_3)$ modes
837vs	825vs	822vs		
829s				
683m	696s	691s	700vvw	GeH_2 wag, in and out of phase
639w	643s	644m	658vvw	
		617vvs		
604s	607vvs	610s	620vw	$\delta(FeCO)\ a_1$
		600 (sh)	591p,m	$\nu(GeC)\ a_1 + b_2$
580s	573s	n.o.	583m	
535vw	525w		539m	δ(FeCO), ν(FeC), δ(HGeMe)
485vw	470w		490p,vw	
440vw	432m		448p,m	$\nu(FeC)\ a_1$
	408w			
400vw	390vvw			
225w	n.o.		225p,s	$\nu(GeFe)\ a_1$
211w			210dp,s	$\nu(GeFe)\ b_1$
n.o.			113vs (sh)	ν(CFeGe) and $\delta(C_2Fe)$
			103vvs	
			58vw	$\delta(Ge_2Fe)$

n.o. = Region not observed.

correspond to the loss of the four Me groups leaving $[Fe_3Ge_5]^+$.

Reaction (iv) of Table 1 produced a red residue shown by mass and i.r. spectra to comprise mainly (2). However, the mass spectrum at a probe temperature of 65 °C showed a series of weak single peaks at *m*/*e* 572, 544, and 516 which could be attributed to fragments of the type $[Fe_n(CO)_{20-2n}C - m(CO)]^+$ (n = 4 or 5, m = 0 — 2). At a probe temperature of 85 °C a series of very weak higher envelopes were observed which coincided with the stronger envelopes found at higher temperatures for the residues from the reaction of (1) under strong irradiation.

TABLE 5

Infrared spectra (cm^{-1}) of $[\{Fe(CO)_4(GeMeR)\}_2]$ compounds in C_6H_{12} solutions

R		
Me [a]	H	Assignment
	2 067vw	ν(GeH)
	2 063vw	
2 052vs	2 060vs	$\nu(CO)_{ax.}(b_{2u},a_u,a_1)$ [b]
2 048vw(sh)	2 055vw(sh)	$\nu(^{13}CO)$
2 030vw,br	2 035vw,br	
	2 022mw	ν(CO) in-phase C_{2v}
	2 018vw	
2 001vvs	2 011.5vs	$\nu(CO)_{eq.}(b_{3u},b_u,b_2)$ [b]
	2 008vvs	$\nu(CO)_{ax.}(b_{1u},b_u,a_1)$ [b]
1 993w(sh)	2 002vw(sh)	$\nu(CO)_{eq.}(b_{2u},a_u,b_1)$ [b]
1 978w	1 981vvw	$\nu(^{13}CO)$
1 964w	1 972vw	
1 949w		
796mw		$\rho(CH_3)$
	662vw	δ(GeH)
625ms	623m	δ(FeCO)
614s	613ms	
	603mw [c]	
	507vvw [c]	
	523vw	
	514vw	
430vw		ν(FeC)

[a] Ref. 1. [b] Assignments are listed for the cases when R = Me (D_{2h}) or R = H (C_{2h} and C_2) respectively. [c] ν(GeC) could contribute to one of these absorptions.

RESULTS AND DISCUSSION

From the reaction of $Na_2[Fe(CO)_4]$ with $GeBrMeH_2$, $[Fe(CO)_4(GeMeH_2)_2]$ (1) is produced in 20—45% yields. Evidence was also obtained for the formation of $[Fe(CO)_4(GeMeH_2)H]$ in some runs. Thus the methylgermyl system resembles the GeH_3 species [2] and contrasts with the $GeMe_2H$ system [1] where further condensation proceeded very readily. On the other hand, there is evidence in the recovery of 1—2% $[\{Fe(CO)_4(GeMeH)\}_2]$ and *ca.* 10% $GeMeH_3$ that a minor amount of condensation is occurring during the preparations.

Spectroscopic Properties of (1).—The mass spectrum is summarized in Table 2. The parent ion is relatively weak and the principal fragmentation is stepwise loss of CO groups. About 64% of the ion current is carried by ions of the $FeGe_2$ families and a further 25% is carried by ions containing one Ge and one Fe, proportions which are very close to the 57 and 26% reported [2] for $[Fe(CO)_4$-

$(GeH_3)_2]$. The parent ion loses H_2 and CH_x readily, but otherwise methyl loss is minor until most of the CO groups have gone. The only rearrangement ions observed are the very weak FeH species. With room-temperature sampling, no sign of higher-molecular-weight ions from condensation products was observed, in marked contrast [1] to the dimethylgermyl system.

TABLE 6

Principal fragments in the mass spectrum of (2)

	$[Fe_2(CO)_nGe_2C_2H_x]^+$			$[Fe_2(CO)_nGe_2CH_x]^+$							
		x			x						
n	m/e	8	6	m/e	6	5	4	3	2	1	0
8	506—520w	5	10	492—504w	10	2	2	0	0	0	0
7	478—492vs	10	0	464—476vw	10	2	2	0	0	0	0
6	448—464s *	10	1	435—447w	0	5	2	10	0	0	0
5	420—434s *	0	10	406—418vw	0	0	10	10	5	0	0
4	392—406s *	0	10	378—390vw	5	2	2	2	2	0	1
3	364—378vvs *	0	10	350—363w	0	4	10	3	5	0	0
2	336—350vvs *	0	10	323—335w	0	2	10	5	0	0	0
1	308—322ms *	0	10	295—310mw	5	2	0	10	0	0	0

	$[Fe_2Ge_2C_yH_x]^+$		$[FeGe_2C_yH_x]^+$	
y	m/e	x	m/e	x
2	280—294vs	6 only	226—238w	6 only
1	264—279vvs	3,2,1,0 as 8 : 10 : 2 : 2	208—220ms	2,1,0 as 10 : 10 : 10
0	250—264vvs	0 only	194—206ms	0 only

All the other ions were weak to very weak apart from m/e 100—107m $\{[GeC_2H_x]^+$ (x = 6 and 5 as 10 : 3)$\}$ and 84—91mw $\{[GeCH_x]^+$ (x = 3 and 2 as 10 : 2)$\}$. The only other CO-containing fragments were $[Fe(CO)Ge_2CH_3]^+$, $[Fe_2(CO)GeCH_x]^+$, and $[Fe(CO)GeH_x]^+$. A metastable ion at m/e 431 supports the step: $[Fe_2(CO)_7Ge_2C_2H_8]^{+\cdot} \xrightarrow{-CO} [Fe_2(CO)_6Ge_2C_2H_8]^{+\cdot}$.

* Doubly charged ions (all weak to very weak) were found for these fragments.

Both ^1H and ^{13}C n.m.r. data were obtained and are shown in Table 3. The ^1H n.m.r. values for (1) follow trends now established for methyl-substituted germyl-metal carbonyls [1] (see Table 1 of ref. 1). The ^{13}C n.m.r. spectrum shows that any averaging of the axial and equatorial CO groups is slow on the n.m.r. time scale at room temperature, unlike *cis*-$[Fe(CO)_4(GeMe_3)_2]$ where a slow-limit spectrum was obtained [4] only on cooling to 223 K.

TABLE 7

Comparison of i.r. spectra (cm^{-1}) assigned to $[Fe_2(CO)_7(GeMeR)_2]$ compounds in C_6H_{12} solution

R		
H	Me [a]	Assignment [b]
2 057m(sh)	2 056.8m	$\nu(CO)[a_1(1)]$
2 033.2s		$\nu(GeH)$
2 028.2s	2 025.7vs	$\nu(CO)[b_1(1)]$
	2 020.2(sh)	$\nu(^{13}CO)$
c	1 995.5s	$\nu(CO)(b_2)$
	1 978vs	$\nu(CO)[a_1(2)]$
	1 972vw(sh)	$\nu(CO)[b_1(2)]$
ca. 1 962w(sh)	1 954w	$\nu(^{13}CO)$
1 930vw,br	*ca.* 1 942vw	
1 853mw	1 842s	$\nu(\mu CO)(a_1)$
	839w	
780w,br	786w	$\rho(CH_3)$
	721w	
ca. 603	600ms	
591w(sh)	594m(sh)	
568vw(sh)	584vw(sh)	$\delta(FeCO)$ $\nu(GeC)$
	555vw	
	525w	
	490w	$\nu(FeC)$

[a] Ref. 1. [b] Assignments in the 2 000 cm^{-1} region are those for the C_{2v} $[Fe_2(CO)_7(GeMe_2)_2]$ compound, except for the band at 2 033.2 cm^{-1}. However, as discussed further in the text, the $\nu(CO)$ absorptions of $[Fe_2(CO)_7(GeMeH)_2]$ are assigned to analogous vibrations. [c] This region was obscured by strong absorptions due to (1) and (2).

Vibrational data further support a C_{2v} geometry for (1). Assignment of the spectrum in Table 4 follows earlier discussion [2] of $[Fe(CO)_4(GeH_3)_2]$. The following points deserve mention. (*i*) Assignment of the highest-frequency carbonyl band as $\nu(CO)_{ax.}$ (a_1) is firm. Force-constant calculations for $[M(CO)_4(M'X_3)_2]$ complexes [5] are consistent with $k_{ax.} > k_{eq.}$ but the order of the two modes $\nu(CO)_{ax.}$ (b_2) and $\nu(CO)_{eq.}$ (a_1) is not definitely established. (*ii*) As found [2] for $[Fe(CO)_4(GeH_3)_2]$ the relatively strong symmetric deformation modes of the GeH_x group show two clear components, which can be assigned as the in- and out-of-phase combinations of the modes of the individual germyl groups. Thus, the pair of bands at 693 and 643 cm^{-1} is assigned as the two combinations of the GeH_2 wags corresponding to the wagging frequency at 700 cm^{-1} in the spectra [3,6] of $[Mn(CO)_5(GeMeH_2)]$ and $[Co(CO)_4(GeMeH_2)]$. A similar effect in the scissors mode would be obscured by the methyl rocks. (*iii*) The Raman spectrum shows a strong polarized band at 225 cm^{-1} assigned as the symmetric Fe–Ge stretch, and the antisymmetric mode occurs at 210 cm^{-1}, strong but depolarized. Weak bands were observed in the far-i.r. spectrum of the gas at these frequencies. Thus, the spectrum of (1) repeats the uncommon ordering of symmetric stretch above antisymmetric stretch that was reported [2] for the $[Fe(CO)_4(GeH_3)_2]$ analogue.

---

[5] J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 1215; F. T. Delbeke, E. G. Claeys, G. P. Van der Kelen, and Z. Eeckhaut, *J. Organometallic Chem.*, 1970, **25**, 213; R. K. Pomeroy, R. S. Gay, G. O. Evans, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1972, **94**, 272.

[6] B. W. L. Graham, D.Phil. Thesis, Waikato, 1973.

Spectroscopic Properties of (2).—The ^1H n.m.r. parameters of (2) are included in Table 3. The intensities of the two sets of methyl doublets and germyl quartets are consistent with approximately equal proportions of C_{2v} and C_{2h} isomers at room temperature. Two methyl resonances (also separated by 0.03 p.p.m.) were observed in the ^1H n.m.r. spectrum of $[\{Fe(CO)_4(SnMePh)\}_2]$.[7] The 0.5 p.p.m. shift to lower field for the methyl resonance of (2) from that of (1) is the same as between $[Fe(CO)_4(GeMe_2H)_2]$ and $[\{Fe(CO)_4(GeMe_2)\}_2]$,[1] and similar also to the difference between the bridging and terminal methylgermyl resonances of $[\{Ru(CO)_3(GeMe_2)(GeMe_3)\}_2]$.[8] The reduction in ^3J(HCGeH) value from compound (1) to (2) is similar to the trend found for polymetallation in cobalt derivatives of methylgermane.[6]

The i.r. data are discussed assuming approximately equal proportions of C_{2h} and C_{2v} isomers on the basis of the ^1H n.m.r. evidence. Vibrations involving in-phase coupling between modes of the two $Fe(CO)_4$ units are formally forbidden in the i.r. in the C_{2h} isomer as in the D_{2h} compound $[\{Fe(CO)_4(GeMe_2)\}_2]$, and although formally allowed in the C_{2v} isomer of (2) are likely to involve near-zero dipole changes since neither electronic nor mechanical coupling between the two $Fe(CO)_4$ groups is likely to be significantly changed by the relative orientation of the GeMeH units. Thus we expect only four modes of significant intensity for each isomer of (2); these modes will be of very similar energy in the two isomers and hence a spectrum similar to that of $[\{Fe(CO)_4(GeMe_2)\}_2]$ is expected, with possibly some broadening or slight splitting due to corresponding modes of the two isomers. The stronger ν(CO) absorptions of (2) are thus attributed to vibrations analogous to those of $[\{Fe(CO)_4(GeMe_2)\}_2]$,[1] and the only other absorption of significant intensity (2 022 cm^{-1}) is assigned to an in-phase mode of the C_{2v} isomer.

Other points requiring comment in the assignments of Table 5 are as follows. (*i*) No absorptions were found between 2 063 and 2 067 cm^{-1} for $[\{Fe(CO)_4(GeMe_2)\}_2]$, and one of these is a candidate for ν(GeH) in the isomers of (2). (*ii*) The two absorptions at 1 981 and 1 972 cm^{-1} are asigned to out-of-phase $\nu(^{13}CO)$ modes. (*iii*) The relative intensities and positions of the three absorptions at 603—623 cm^{-1} make them candidates for δ(FeCO) modes. (*iv*) The band at 662 cm^{-1} is rather high to be attributed to a δ(FeCO) mode and is instead attributed to a deformation involving the germyl hydrogen. The GeH deformation mode for $GeBrMe_2H$ has been reported at 669 cm^{-1}.[9] (*v*) The absorptions at 514—570 cm^{-1} are too high in frequency for ν(FeC) modes and are therefore assigned to δ(FeCO) modes with ν(GeC) arising at 570 or 603 cm^{-1} [*cf.* $(GeMeH_2)_2$ has ν(GeC) at 582 cm^{-1}, *i.e.* coupling between the two GeMe groups is not apparent [10]].

The mass spectrum is quite similar to that reported for $[\{Fe(CO)_4(GeMe_2)\}_2]$.[1] Specifically: (*i*) both the P^+ and $[P - CH_x]^+$ ions are relatively weak; (*ii*) the major portion of the ion current is carried by fragments containing the four metal atoms, in this case $[Fe_2(CO)_n(GeMeH_x)]^+$ (n = 0—7) and $[Fe_2Ge_2C_yH_x]^+$ (y = 0 or 1); and (*iii*) CH_x loss is limited until all the CO groups have been removed.

Assignment of I.r. Spectrum to (3).—One of the new products from the strongly illuminated self-reaction of (1) is tentatively identified as $[Fe_2(CO)_7(GeMeH)_2]$ (3) by comparison of the new i.r. absorptions observed for the photolysis residues with the spectrum assigned to $[Fe_2(CO)_7(GeMe_2)_2]$.[1] Compound (3) would be expected to adopt C_{2v} or C_s structures {*cf.* C_{2v} only for $[Fe_2(CO)_7(GeMe_2)_2]$} and hence a more complicated i.r. spectrum is possible than for the dimethylgermyl compound. However, it is probable that the ν(CO) region will be similar for both structures. Only a partial spectrum for (3) is available at present [because of the strong superimposition of bands due to (1) and (2), especially in the 1 990—2 020 cm^{-1} region], and a less detailed assignment of the spectrum is possible.

(*i*) The pattern of bands observed for (3) in the 1 850—2 060 cm^{-1} region is very similar to that reported for $[Fe_2(CO)_7(GeMe_2)_2]$. This applies particularly to the bands at 2 057, 2 028.2, and 1 853 cm^{-1}, for which analogous assignments can be made. (*ii*) The strong band at 2 033.2 cm^{-1} is a candidate for a ν(GeH) mode {no band was observed in this region for $[Fe(CO)_7(GeMe_2)_2]$}. (*iii*) The band at 780 cm^{-1} matches that at 786 cm^{-1} found for $[Fe_2(CO)_7(GeMe_2)_2]$ and hence a similar assignment $[\rho(CH_3)]$ is proposed. (*iv*) Since no analogous absorption was found for $[Fe_2(CO)_7(GeMe_2)_2]$, the weak band at 673 cm^{-1} is assigned to a δ(GeH) vibration [*cf.* δ(GeH) assigned at 662 cm^{-1} for (2), see Table 5]. (*v*) Absorptions found between 568 and 603 cm^{-1} can be assigned to δ(FeCO) and ν(FeC) modes.

Compound (3) could also be a candidate for the weaker doublet resonances observed in the methyl region of the ^1H n.m.r. spectrum for the same residues.

The Condensation Reactions.—In the dimethylgermyl system, rapid condensation of $[Fe(CO)_4(GeMe_2H)_2]$ to the cyclic compound $[\{Fe(CO)_4(GeMe_2)\}_2]$ occurred [1] during the preparation and under most handling conditions. For the methylgermyl analogue such dominant condensation was not observed, although it is a side reaction during the preparation, and (1) is sufficiently stable to be adequately characterized. However, there is a slow reaction in the dark where (1) is converted into (2) and $GeMeH_3$ is eliminated. A much faster reaction is observed in the light, but this is more complex and forms other products as well as (2).

When (1) was held at room temperature in the complete absence of light, 22% of the sample was converted into (2) in 25 d. This is much slower than the condens-

---

[7] T. J. Marks and G. W. Grynkewich, *J. Organometallic Chem.*, 1975, **91**, C9; *Inorg. Chem.*, 1976, **15**, 1307.

[8] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 2874.

[9] G. K. Barker, J. E. Drake, and R. T. Hemmings, *Canad. J Chem.*, 1974, **52**, 2622.

[10] R. D. George and K. M. MacKay, *J. Chem. Soc. (A)*, 1969, 2122.

ation of $[Fe(CO)_4(GeMe_2H)_2]$ which had gone to completion in 15 d.[1] A small amount of CO was also formed, increasing in proportion to the $GeMeH_3$ as the reaction proceeded, which indicates a small contribution from a second reaction, probably of the initially formed (2). Apart from this, the product (2), unchanged (1), and $GeMeH_3$ were the only species observed. Compounds (1) and (2) do not separate cleanly, but the evidence here is compatible with (1) as the major dark reaction, and

$$2[Fe(CO)_4(GeMeH_2)_2] \longrightarrow [\{Fe(CO)_4(GeMeH)\}_2] + 2GeMeH_3 \quad (1)$$

this is exactly analogous to the dark reaction observed[1] in the dimethylgermyl system.

Under illumination, the reaction of compound (1) is much faster. About 50% of the sample had reacted in 8 h at room temperature, with the main limitation being apparently the accumulation of reaction product on the surface. Both $GeMeH_3$ and (2) were found, so that reaction according to equation (1) occurs, but both CO and H_2 were found in increasing amounts as the reaction proceeded. There is evidence for reaction (2), also analogous to one proposed for the dimethylgermyl system, since the i.r. spectrum gave clear indications of

$$[\{Fe(CO)_4(GeMeH)\}_2] \longrightarrow [Fe_2(CO)_7(GeMeH)_2] + CO \quad (2)$$

compound (3). Compounds of the type $[Fe_2(CO)_7(M'R_2)_2]$ ($M'R_2 = GeMe_2$,[1] $SnBu_2$,[7] or SnMePh[7]) have been reported from the photolyses of $[\{Fe(CO)_4(M'R_2)\}_2]$. Here, however, part of the CO together with the H_2 and the small amounts of di- and tri-methyl germanes must arise from further condensation to higher-molecular-weight products, which are probably responsible for the red or orange colours observed. These are also indicated by the mass spectra of the reaction residues run at higher probe temperatures which indicate the presence of Fe_4Ge_4 and Fe_4Ge_5 clusters. It is reasonable to postulate that (2) and (3) may not only eliminate CO but also lose H_2 or germanes from the GeMeH units to give more condensed clusters.

By comparison with $[Fe(CO)_4(GeMe_2H)_2]$, it is much easier to prepare and manipulate $[Fe(CO)_4(GeMeH_2)_2]$ since reaction (1) occurs less readily, presumably because the GeMeH group is less effective in bridging two iron atoms. However, when reaction (1) does occur in the dark there is evidence for a very slow formation of (3) by reaction (2), again a situation that parallels the dimethylgermyl system. Under illumination, not only do reactions (1) and (2) occur readily but more highly condensed products form, whereas there is little indication of these in the dimethylgermyl system.

We thank the New Zealand University Grants Committee and the Williams Georgetti Trust for the award of scholarships (to A. B.) and for grants to purchase the C60-NL and P.E. instruments, and Dr. P. Holland of the Ruakura Agricultural Centre for facilities to record mass spectra.

[7/1336 *Received, 25th July,* 1977]