Transition-metal Carbonyl Derivatives of the Germanes. Part 7.† Properties of Complexes containing Dimethylgermyliron Carbonyl Groups and their Interconversion

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The complex $[Fe(CO)_4(GeMe_2H)_2]$ (1) is unstable with respect to condensation to $[\{Fe(CO)_4(GeMe_2)\}_2]$ (2) eliminating $GeMe_2H_2$. In the light, or very slowly in the dark, (2) loses CO and is probably converted to $[Fe_2(CO)_7(GeMe_2)_2]$ (3). The i.r., ^{1}H n.m.r., and mass spectra of these complexes are reported.

In earlier papers in this series we reported reactions of the Ge–H bond in transition-metal-carbonyl-substituted germanes. Since the Ge–Me bond is relatively unreactive and the properties of $[M(CO)_x(GeMe_nH_{3-n})]$ are expected to be very similar in the series $n = 0$—2, it is often convenient to work with methylgermyl or dimethylgermyl derivatives as well as with the parent germyl compounds. This approach has been useful for the $Mn(CO)_5$ family [1-3] and for $Co(CO)_4$ species.[3,4] Thus when we set out to study the reactions of $[Fe(CO)_4(GeH_3)_2]$, first prepared by Stobart,[5] we intended to conduct parallel studies on $[Fe(CO)_4(GeMeH_2)_2]$ and on $[Fe(CO)_4(GeMe_2H)_2]$. However, we found that, while the monomethylgermyl derivative could be prepared [6] in *ca.* 40% yield by the path used [5] for the parent germyl and was indeed similar in behaviour, the dimethylgermyl analogue could not be isolated under similar conditions. The reason for this anomaly is discussed here and involves the relation between $[Fe(CO)_4(GeMe_2H)_2]$ (1) and the polynuclear species $[\{Fe(CO)_4(GeMe_2)\}_2]$ (2) and $[Fe_2(CO)_7(GeMe_2)_2]$ (3).

Complex (2) has been prepared previously [7,8] by the reaction between $GeMe_2Cl_2$ and $Na_2[Fe(CO)_4]$. It may be presumed to have the planar Fe_2M_2 ring structure found crystallographically [9,10] for $[\{Fe(CO)_4(GeEt_2)\}_2]$ and $[\{Fe(CO)_4(SnMe_2)\}_2]$. Related complexes are also known [11] with one or two $(GeMe_2)_2$ groups in place of $GeMe_2$. Complex (3) has been only briefly mentioned [12a] as a secondary product found during the preparation of $[Fe_2(CO)_6(\mu\text{-}GeMe_2)_3]$ by heating $GeMe_2H_2$ with $[Fe_3(CO)_{12}]$ at 65 °C. However, the similar reaction of $GePh_2H_2$ at 90 °C yielded the phenyl analogue of (3) whose structure [13] has been determined. The silicon analogue [14] of (3) and various tin [15] species $[Fe_2(CO)_7(SnRR')_2]$ are also known.

EXPERIMENTAL

Manipulations and measurements were made as described previously [2] except that i.r. measurements used a Perkin-Elmer 180 spectrometer. The amount of H_2 in incondensable fractions was checked by comparing the filament currents on a V.G. Micromass 602C mass-ratio spectrometer with those observed for standards. The lower limit of detection was much less than 1% H_2 in the fraction.

Preparation of Tetracarbonylbis(dimethylgermyl)iron, (1).—The salt $Na_2[Fe(CO)_4]$ was prepared by the reaction of purified sodium with a slight excess of $[Fe(CO)_5]$ at -63 °C in liquid ammonia. The off-white to pale brown solid was pumped overnight to remove all traces of ammonia, then $GeBrMe_2H$ was added together with dry pentane. A number of attempts {under conditions which yielded 40—50% $[Fe(CO)_4(GeH_3)_2]$ or $[Fe(CO)_4(GeMeH_2)_2]$ in analogous reactions} failed to produce (1). Eventually, $Na_2[Fe(CO)_4]$ prepared from $[Fe(CO)_5]$ (12.8 mmol) and Na (21.7 mmol) was treated with a marked deficit of $GeBrMe_2H$ (1.56 mmol)

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in pentane (5 cm^3) in the dark at 20 °C. After 15 min, 0.08 mmol of CO was formed, volatiles were fractionated, and (1) (0.04 mmol) was collected at -5 °C. The pentane and unchanged $GeBrMe_2H$ were returned to the reaction vessel. No more CO was formed but, after 1 h, another 0.08 mmol of (1) was recovered, giving a total yield of 8% based on the $GeBrMe_2H$ consumed. Dimethylgermane (0.08 mmol) was isolated from the volatiles, and $[\{Fe(CO)_4(GeMe_2)\}_2]$ (0.04 mmol) was sublimed from the involatile residue. These three species correspond to 26% of the initial $GeBrMe_2H$. Other runs carried out in the dark with short contact times but higher ratios of $GeBrMe_2H$ yielded up to 6% $[Fe(CO)_4(GeMe_2H)_2]$. In each case CO was formed during the initial stages only.

The product (1) is a colourless liquid, which soon turns yellow, and is only just volatile at room temperature. Gas-phase i.r. and gas-sampled mass spectra show only $GeMe_2H_2$. In i.r. solution cells, or in contact with the mass spectrometer solid-sampling probe, self-reaction of (1) was rapid and spectra of (2) and/or (3) (see below) were obtained. By condensing the sample directly on to a KBr plate cooled by liquid nitrogen it was possible to observe the i.r. spectrum of the solid free from any reaction product apart, possibly, from $GeMe_2H_2$. The spectrum is complex and shows changes on cautious annealing suggesting that the solid is disordered, but it is compatible with the product being (1). Vibrations of the methyl groups occurred at 2 980w, 2 915w, 1 415w, 1 231mw, 874mw, 853w(sh), 842s, and 823w(sh) cm^{-1}; the GeH deformation is at 758mw, the GeC stretches at 586w and 574ms, FeCO bending modes at 643w(sh), 623w(sh), and 609vvw, and the FeC stretch at 444mw cm^{-1}. The carbonyl-stretching region shows bands at 2 094mw, 2 078s *, 2 073s, and a very intense broad band with prominent maxima at 1 991 *, 1 977, and 1 966 * with a number of shoulders up to 2 054 cm^{-1}. On annealing, the maxima marked with an asterisk weaken, and many of the minor shoulders are smoothed out.

Providing the handling was carried out in subdued lighting, the ^1H n.m.r. spectrum of (1) could be obtained with no extraneous signals, and without changes occurring over a few hours. The sample was sealed. The data are included in Table 1 and distinguish (1) from $GeBrMe_2H$ whose reported [16] parameters are $\tau(CH_3)$ 9.06, τ(GeH) 4.75, and ^3J 2.73 Hz.

Condensation of (1).—(*i*) *In the dark.* In a blackened vessel, in the absence of solvent, and in contact with glass and Teflon only, (1) slowly evolved $GeMe_2H_2$ (identified [17] by ^1H n.m.r., i.r., and mass spectra) together with trace amounts of CO but no H_2. Gases were fractionated, collected using a Topler pump, and measured in a gas burette. Complex (1) (75.3 mg, 0.201 mmol) gave, after 7 d at room temperature, $GeMe_2H_2$ (0.182 mmol) and CO (0.001 36 mmol). After 15 d the total yields were $GeMe_2H_2$ (0.198 mmol) and CO (0.004 33 mmol). The yellow solid remaining showed ^1H n.m.r., i.r., and mass spectroscopic characteristics of $[\{Fe(CO)_4(GeMe_2)\}_2]$ (2). In addition, there were weak n.m.r. singlets at τ 8.78 and 8.88, and very weak carbonyl modes (see Table 3), compatible with the presence of *ca.* 5% $[Fe_2(CO)_7(GeMe_2)_2]$ (3).

(*ii*) *In the preparation of* (1). Dimethylgermane was found in all the preparations of (1), and samples of a yellow solid with i.r. bands at 2 050s and 2 000vs cm^{-1}, characteristic of (2), could be sublimed from the residues. The amounts were considerably in excess of those expected from condensation of (1) in the time available.

TABLE 1

Hydrogen-1 n.m.r. parameters for germylmetal carbonyls

		N.m.r.				
Complex	R	$\tau(CH_3)$	$\tau(GeH_x)$	^3J/Hz	Solvent	Ref.
$[Fe(CO)_4R_2]$	GeH_3		6.45		CS_2	*a*
	$GeMeH_2$	9.27	6.22	3.8	CS_2	*a*
	$GeMe_2H$	9.36	6.02	3.4	CS_2	*a,b*
	$GeMe_3$	9.39			CS_2	*a*
$[Mn(CO)_5R]$	GeH_3		6.58		CS_2	2
	$GeMeH_2$	9.33	6.30	4.0	CCl_4	2
	$GeMe_2H$	9.3	5.8	3.6	$SiCl_4$	3
	$GeMe_3$	9.38				*c*
$[Co(CO)_4R]$	GeH_3		6.31		C_6D_6	*d*
	$GeMeH_2$	9.16	5.67	3.2	CCl_4	*e*
	$GeMe_2H$	9.04	5.1	3.2	$SiCl_4$	3
	$GeMe_3$	9.41			C_6H_6	*f*

[a] Measured, or remeasured, in this work. [b] Containing 12% C_6H_6. [c] R. A. Burham and S. R. Stobart, *J.C.S. Dalton*, 1973, 1269. [d] Value corrected from that given in ref. 1: F. S. Wong, Waikato, 1976. [e] B. W. L. Graham, D. Phil. Thesis, Waikato, 1973. [f] G. F. Bradley and S. R. Stobart, *J.C.S. Dalton*, 1974, 264.

(*iii*) *In solution.* A solution of (i), 7% in a 8 : 1 mixture of CS_2 and C_6H_6, was sealed in an n.m.r. tube and exposed only to subdued laboratory lighting. New signals were detected after 18 h, and these increased in intensity with time at the expense of (1): a singlet at τ 8.85 matched the signal from other samples of (2) in this solvent, and compares with a literature [8] value of τ 8.70 in benzene. The second species was $GeMe_2H_2$ [τ 9.74(t) and 6.35(spt), J 3.8 Hz], and a third species at τ 9.56 (s) was unidentified. After 3 d the relative molar concentrations were 54 (1), 15 (2), 26 ($GeMe_2H_2$), and 4% of the species at τ 9.56 (assuming a $GeMe_2$ molecule); after 7 d the composition was 32 (1), 22 (2), 38 ($GeMe_2H_2$), and 8% of the species at τ 9.56. This sample was then exposed to bright sunlight for 10 min; the orange contents of the tube turned brown and a brown solid was precipitated. The major change in the n.m.r. signals was a marked diminution of (2) and the appearance of new singlets at τ 9.02 and 9.13.

Mass Spectrum of $[\{Fe(CO)_4(GeMe_2)\}_2]$ (2).—A yellow, resublimed, sample of (2) was placed on the gold cup of the solid-sample insertion probe of the mass spectrometer with all the handling in subdued light in an argon atmosphere. Spectra were run with probe temperatures of 25 and 50 °C. Values are shown in Table 2.

Stability and Effect of Light on (2).—At room temperature in the dark, samples of (2) evolved CO very slowly, to the extent of *ca.* 5 mol % in 2 weeks. In a Pyrex tube in sunlight, or on irradiation with blue light, initial CO evolution was fast but then slowed as the solid turned brown. For example, a sample of (2) (17.7 mg, 0.032 7 mmol) evolved CO as follows: 3 mol % in 10 min; 10 mol % in 65 min; accumulating to 0.010 1 mmol (31 mol %) in 19 h. Further amounts of 0.007 8, 0.003 9, and 0.001 2 mmol were evolved in three successive 17-h periods. In 3 d a total of 0.024 6 mmol of CO, *ca.* 0.75 mol per mol of (2), had

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formed. The only other volatile products found were a trace amount of $[Fe(CO)_5]$ and *ca.* 0.5% $GeMe_3H$. The reaction mixture was dissolved in cyclohexane, and its i.r. spectrum is given in Table 3. A sample gave a poor broad n.m.r. signal centred at *ca.* τ 8.87.

Attempts to Record the Mass Spectrum of (1).—Even after prolonged pumping, the mass spectrum of a gaseous sample of (1) gave only the ions expected from $GeMe_2H_2$ and, later, weak ions from $[Fe(CO)_5]$. These species must arise from decomposition within the manifold. A sample of (1) was dissolved in cyclohexane and placed in the gold cup of the solid-sampling probe, handling under argon. The solvent was removed under a stream of argon and spectra were recorded at probe temperatures of 25 and 50 °C (Table 4).

TABLE 2

Principal fragments (*m*/*e* values) in mass spectrum of (2)

n	$[Fe_2(CO)_n$-$(C_4H_x)Ge_2]^+$	x: 12	x: 10	$[Fe_2(CO)_n$-$(C_3H_x)Ge_2]^+$	x: 10	x: 9	x: 8
8	546—536w	10	0	531—521w	0	10	0
7	520—504vs	10	1	504—494m	10	0	0
6	492—478vs	10	0	476—465m	5	8	10
5	462—451m	10	3	448—436mw	5	5	10
4	436—420s	10	1	420—408w	5	5	10
3	408—394vvs	10	0	392—376w			
2	380—364s	10	3	364—352w	10	5	10
1	352—336s	10	5	335—325w	0	10	0
0	324—310s	10	0	308—294m	0	5	10
				(x = 7,6 also)			

$[Fe_2(C_2H_6)Ge_2]^+$ 292—280m
$[Fe_2(CH_x)Ge_2]^+$ 278—264vs (x = 3,2,1,0 as 7 : 10 : 3 : 3)
$[Fe_2Ge_2]^+$ 264—250s

Ions with fewer than four metal atoms were all weak or very weak apart from $[Fe(CH_x)Ge_2]^+$ (ms), $[FeGe_2]^+$ (mw), $[Fe(C_3H_x$-$Ge]^+$ (m), and $[FeGe]^+$ (m). Only three ions of lower *m*/*e* contained CO and all were weak: $[Fe(CO)_3C_2H_6]^+$, $[Fe(CO)(CH_x)Ge]^+$, and $[Fe(CO)GeH_x]^+$. Metastable ions were observed at *m*/*e* 460, 376, and 348.

TABLE 3

Carbonyl-stretching modes (cm^{-1}) for mixed samples of (2) and (3)

$[\{Fe(CO)_4(GeMe_2)\}_2]$ 100% [a]	$[\{Fe(CO)_4(GeMe_2)\}_2]$ 95%	$[\{Fe(CO)_4(GeMe_2)\}_2]$ 25%	$[Fe_2(CO)_7$-$(SiMe_3)_2]$ [b]	Assignment [c]
	2 057vw(sh)	2 056.8m	2 063m	(3) *q*
2 053.1	2 052.5vs	2 053s		(2) b_{2u} ax.
	2 048vw(sh)	2 048vw(sh)		(2) ^{13}CO
			2 043ms	
	2 025w(sh)	2 025.7vw	2 032vs	(3) *s*
		2 020w(sh)		(3) *t*
	2 009w(sh)	2 007vw(sh)		(2)
2 000.4	2 001vvs	2 001vvs		(2) b_{3u} eq.
(1 996.1) [d]				(2) b_{1u} ax.
	1 999.5w(sh)	1 995.5s	2 004vs	(3) *u*
(1 983) [d]	1 993w(sh)			(2) b_{2u} eq.
	1 978w	1 978vs	1 983vs	(3) *v*
		1 972vw(sh)		(3) *w*
	1 964w			(2) ^{13}CO
		1 954w		(3) *x*
	1 949w			(2) ^{13}CO
		1 942vw		(3) *y*
		1 842s	1 843s	(3) μ-CO

[a] Ref. 7. [b] Ref. 14. [c] Assignments for (3) are lettered according to the system of G. Bor, *J. Organometallic Chem.*, 1975, **94**, 181. [d] Resolved [7] in Et analogue though not in Me species.

Oxidation or Transformation of (2).—In a conventional solution cell, in contact with KBr, stainless steel, and Teflon, the spectrum of a sample of (2) showed the following new bands after 5 d: 2 092w, 2 070vw, 2 040m, 2 022ms, 2 014vw(sh), 2 009w(sh), 1 987m, 1 909mw,vbr, 760w, 746mw, and 642 mw cm^{-1}.

TABLE 4

Relative intensities of fragment ions from $[Fe_2(CO)_n(Ge_2Me_4)]$

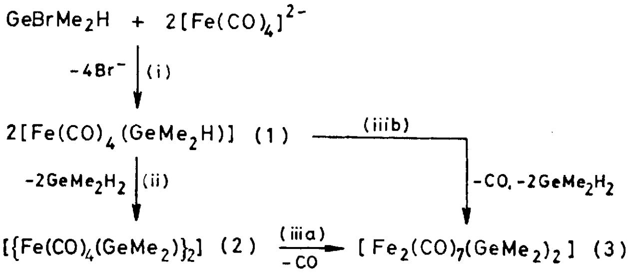
	n: 8	7	6	5	4	3	2	1	0
$[Fe_2(CO)_n$-$(Ge_2Me_4)]^+$									
a	w	vs	vs	m	s	vvs	s	s	s
b	vvw	ms	s	m	ms	vvs	s	vvs	vs
$[Fe_2(CO)_n$-$(Ge_2Me_3)]^+$									
a	w	m	m	mw	w	w	w	w	m
b	vvw	m	m	m	w	w	mw	s	s
			$[Fe_2(Ge_2Me_2)]^+$			$[Fe_2(Ge_2Me)]^+$		$[Fe_2Ge_2]^+$	
a			m			vs		s	
b			s			vvs		vs	

Each sample was measured using the solid-insertion probe at 25 °C. Intensities are of the total envelope, including H-loss species.

[a] Sublimed sample of (2). [b] Evaporated from (1).

RESULTS AND DISCUSSION

These observations on the dimethylgermyl–iron carbonyl system may be rationalised in terms of the Scheme. Reaction (i), the standard route to germyl-metal complexes, yielded 0—8% (1) whereas the GeH_3 or $GeMeH_2$ analogues of (1) are formed in 20—60% yield. The low recovery of (1) arises, at least in part, from the readiness of the condensation reaction (ii) under the conditions of these preparations.



SCHEME

Because (ii) and possibly (iiib) predominate the characterisation of (1) is only partial. The most direct evidence for the formulation of (1) is the ^1H n.m.r. spectrum where changes due to condensation are not seen for the first 12—15 h in subdued lighting. The parameters given in Table 1 distinguish (1) from $GeBrMe_2H$ and also from a possible $GeMe_2H$–O product. The absence of a high-field singlet excludes $[Fe(CO)_4(GeMe_2H)H]$. Allowing for solvent effects, the trends in chemical shift and *J* values follow the pattern of those observed in the manganese and cobalt systems. The i.r. spectrum of solid (1), deposited through a short-path glass jet on a cold plate, is compatible with the formulation as $[Fe(CO)_4(GeMe_2H)_2]$, and is distinct from other possibilities such as a mixture of $GeMe_2H_2$ and

[$Fe(CO)_5$]. All the other techniques used produced only $GeMe_2H_2$ or a sample containing (2) as the major component. Further, indirect, evidence that the initial product of reaction (i) is indeed (1) comes from the observations on reaction (ii) which is very close to being stoicheiometric for neat (1) and is the major reaction of (1) in solution.

Judging by the production of $GeMe_2H_2$ and CO and postulating the latter to arise from reaction (iiia) or (iiib), the conversion of (1) follows reaction (ii) with 99% specificity to 90% completion in 7 d and is 97% complete (97.5% specific) after 15 d. As the proportion of CO increases in the second week, reaction (iiia) seems a more likely source of CO than (iiib).

In a sealed tube with intermittent exposure to laboratory lighting a sample of (1) in CS_2 solution reacts basically according to equation (ii). The reaction is relatively slow, being two-thirds complete in 7 d. However, the system is more complex than the reaction of (1) in the absence of solvent. While (2) is formed according to equation (ii), there is a deficit of $GeMe_2H_2$, the ratio of $GeMe_2H_2$ to (2) being 1.7 : 1. If the signal at τ 9.56 may be identified as a $GeMe_2$ species, then the sum of the $GeMe_2H_2$ and τ 9.56 intensities is very close to twice that of the signal from (2). Possibilities for the species at τ 9.56 are a sulphide arising from a side reaction with the solvent, or an oxygen species possibly derived from the carbonyl group. The effect of bright sunlight on the solution containing 22% (2) and 32% (1) plus the other reaction products was mainly on (2). The products formed from (2) in this experiment were not identified, but appear to be different from (3), giving ^1H n.m.r. signals at *ca.* τ 9.1.

Although the above examples of reaction (ii), with purified (1) and in the dark or subdued light, proceed slowly, in all other circumstances (1) appears to react rapidly. This is the case in the course of the preparation of (1), when handling in contact with gold or stainless steel, and generally in strong light. Under these conditions, either or both of $GeMe_2H_2$ and (2) were recognised. Thus it appears that the difficulties in isolating (1) lie in the ready occurrence of reaction (ii), and perhaps of (iiia), under most handling conditions.

[$\{Fe(CO)_4(GeMe_2)\}_2$] (2).—A pure sample of (2), kept in the dark at room temperature, very slowly evolves CO while a much faster evolution occurs in the light. This reaction slows as the surface becomes covered with reaction product. Thus a sample of (2) can be obtained nearly pure by sublimation and handling in subdued light. Since (2) is a known complex [7,8] its identity can be established and additional spectroscopic properties are reported. The conversion of (2) in the light into (3), [$Fe_2(CO)_7(GeMe_2)_2$], by reaction (iiia) is indicated but complete conversion does not occur.

Kahn and Bigorgne [7] reported all the four CO stretches expected in the i.r. for [$\{Fe(CO)_4(GeEt_2)\}_2$]. The methyl analogue showed [7] two prominent bands, at 2 053s and 2 000vs cm^{-1}, similar to the Marks and Newman [8] values of 2 061s and 2 007vs cm^{-1}. For (2), we observe bands at 2 052.5 vs and 2 001vvs with a weak shoulder at 1 993 cm^{-1} which could be the b_{2u} equatorial mode (D_{2h} point group). In addition there were characteristic lower-energy absorptions at 796mw (CH_3 rock), 625ms, and 614s (FeCO bends) and 430vw cm^{-1} (FeC stretch). When a sample was allowed to stand in a stainless-steel solution cell slow changes occurred in the i.r. spectrum. The new bands do not fit the spectrum [18] of $(GeMe_2O)_x$. One possibility is a cyclic oxide containing the Ge–O–Ge unit as found [19] for [$\{Fe(CO)_2(C_5H_5)(GeMe_2)\}_2O$] or [$\{Fe(CO)_4(GePh_2)\}_2O$], reported [20] to be formed from [$Fe_2(CO)_7(GePh_2)_2$]. A species of this type could also account for the signal at τ 9.1.

The mass spectrum of (2) has not previously been reported and is summarised in Table 2 for a sublimed sample shown by i.r. to be >98% pure. The parent-ion envelope is relatively weak. It is reported that no parent ion was observed [12] for [$\{Fe(CO)_4(GePh_2)\}_2$] while [$\{Ru(CO)_4(SnMe_2)\}_2$] also shows [21] a very weak parent ion. The major portion of the ion current is carried by fragments [$\{Fe(GeMe_2)\}_2(CO)_n$]$^+$ ($n = 0$—7) together with [$Fe_2(C_yH_x)Ge_2$]$^+$ species ($y = 0$—3). The ions observed are compatible with a scheme wherein stepwise loss of CO is the easiest process (supported by metastables for $n = 7 \longrightarrow 6$, $4 \longrightarrow 3$, and $3 \longrightarrow 2$) accompanied by minor paths where H_2 or CH_x ($x = 2$—4) are lost from [$Fe_2(CO)_n(GeMe_2)_2$]$^+$. Once all the CO groups are gone, all the four methyl carbons may be lost, but paths leading to loss of Ge or Fe are minor. This scheme differs from that [21] of [$\{Ru(CO)_4(SnMe_2)\}_2$] where methyl loss occurs readily after loss of the first four CO groups.

[$Fe_2(CO)_7(GeMe_2)_2$] (3).—The product formed from (2) by loss of CO is provisionally identified as (3). No i.r. absorptions attributable [12b] to [$Fe_2(CO)_6(\mu\text{-}GeMe_2)_3$] were observed. This species was not obtained pure, but was a major component of the photolysis of (2) in the absence of solvent and of the reaction of (1) in the mass spectrometer. The carbonyl region of the i.r. spectrum of the photolysis product is compatible with a mixture of 75 (3) and 25% (2). Further aid to the assignment is given by a comparison with a sample containing 5 (3) and 95% (2). The frequencies are listed in Table 3. The least certain assignment is that of *w*, the weak b_1 mode ν_5 which is assigned to the slight shoulder on *v*. The bridging carbonyl mode is clear at 1 842 cm^{-1}. In addition to the carbonyl modes, bands were observed at 839w, 786w, and 721w (methyl rocks), and 600ms, 594m(sh), 584vw(sh), 555vw, 525w, and 490w which include Ge–C stretches and FeCO bending.

The ^1H n.m.r. resonance of (3) is tentatively assigned [12b,14] to the weak singlets at τ 8.77 and 8.88 in the

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spectrum of the product from the dark reaction of (1). This would correspond to the 5% or so of (3) formed together with (2).

The mass spectrum of a sample of (1), introduced in solution on to the solid insertion probe, is similar to that observed for (2) but the octacarbonyl ions were very much weaker, and there were clear differences in the relative intensities of the other Fe_2Ge_2-containing ions. This suggests that both (2) and (3) form under these conditions, possibly *via* equation (iiib) as well as (iiia).

It is concluded that the simplest rationalisation of the observations reported is that reactions (ii) and (iiia) occur quantitatively, or nearly so, under the conditions studied. There is also the possibility of (iiib). There is little evidence for reaction to higher-molecular-weight species: no polygermanium ion was seen. The relatively easy isolation [5,6] of the GeH_3, $GeMeH_2$, and $GeMe_3$ analogues of (1) suggests that reaction (ii) occurs most readily in the dimethylgermyl–iron carbonyl system. One similar reaction reported [22] is that of $[Fe(CO)_4(SnMe_3)_2]$ going to $SnMe_4$ plus $[\{Fe(CO)_4(SnMe_2)\}_2]$ on heating at 140 °C. If we postulate an initial step (iia) with a GeR_2 intermediate, then for the $GeMe_3$ analogue

$$[Fe(CO)_4(GeMe_2H)_2] \longrightarrow GeMe_2H_2 + [Fe(CO)_4(GeMe_2)] \quad \text{(iia)}$$

to react involves breaking a relatively strong Ge–CH_3 bond while the other hydride analogues would involve the less-stable GeH_2 or GeMeH intermediates. Further, these latter species would form analogues of (2) with Ge–H bonds which could be susceptible to further germane elimination and condensation.

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