Transition-metal Carbonyl Derivatives of the Germanes. Part III.[1] Germyl(carbonyl)iron Complexes

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Reaction between chlorogermane and $Na_2Fe(CO)_4$ in n-butane affords digermyltetracarbonyliron, $(GeH_3)_2Fe(CO)_4$ (I) and monogermylhydridotetracarbonyliron, $GeH_3(H)Fe(CO)_4$ (II) together with $H_2Fe(CO)_4$ (III). Germyl-(cyclopentadienyl)dicarbonyliron, $GeH_3Fe(C_5H_5)(CO)_2$ (IV) can be obtained similarly from $NaFe(C_5H_5)(CO)_2$. Physical properties, i.r., Raman, ^1H n.m.r., and mass spectra of (I) and (II) are consistent with their fomulation as monomeric, *cis*-octahedral structures, allowing assignment of vibrational spectra in terms of C_{2v} and C_s symmetry respectively. Gas-phase i.r. data for (III) in the range 4000—350 cm^{-1} are also reported and partially assigned. Reaction of (I) with HCl gives (II) in 46% yield; interaction of solid (I) with $HgCl_2$ results in Ge–Fe bond cleavage with the formation of GeH_3Cl, GeH_4, and HCl.

Recognition of the dimeric nature of the organotin-iron complexes $R_2SnFe(CO)_4$ and their organolead analogues [2,3] has led to continuing interest [4] in the chemistry of carbonyl derivatives of iron, ruthenium, and osmium in which there are Group IVB–metal bonds. The readiness with which polynuclear cluster compounds are formed through reaction of mononuclear metal-carbonyl species with organo-Group IVB derivatives has been established during recent work,[5] but the properties of simpler compounds containing only one transition-metal atom have received less attention. Volatile silyliron complexes falling into the latter category have been reported by Aylett,[6] and also by Amberger.[7] More recently, however, Nasta and MacDiarmid [8] have formulated trimethylsilyl derivatives of empirical composition $(Me_3Si)_2Fe(CO)_4$ and $Me_3Si(H)Fe(CO)_4$ as siloxy- or carbonyl-bridged dimers, and have further suggested that related complexes hitherto assumed to be monomeric may possess analogous structures. Here, the preparation of the volatile germane derivatives $(GeH_3)_2$-$Fe(CO)_4$ and $GeH_3(H)Fe(CO)_4$ is reported, together with that of $GeH_3Fe(C_5H_5)(CO)_2$; physical and spectroscopic properties of the germyl(tetracarbonyl)iron compounds

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[3] R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 3833.

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[6] B. J. Aylett, J. M. Campbell, and A. Walton, *J. Chem. Soc.* (*A*), 1969, 2110.

[7] E. Amberger, E. Mühlhofer, and H. Stern, *J. Organometallic Chem.*, 1969, **17**, P5.

[8] M. A. Nasta and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 1971, **93**, 2813.

confirm that they are monomeric, and are analogues of the silyliron complexes described by Aylett and co-workers.[6] A preliminary account of one aspect of this work has been published.[9]

EXPERIMENTAL

Manipulations were carried out as described earlier.[1] Mass spectra were also obtained as reported previously,[1] i.r spectra were measured using Perkin-Elmer 457 and Grubb-Parsons Spectromajor spectrometers and ^{1}H n.m.r. spectra with a Varian A60-D instrument. The Raman spectrum of $GeH_3(H)Fe(CO)_4$ was recorded on a Cary 81 spectrometer with laser excitation at 632·8 nm (He–Ne laser), and that of $(GeH_3)_2Fe(CO)_4$ similarly and also using a Cary 83 instrument operating at 488·0 nm (Ar ion laser). Under the latter conditions photochemical decomposition of the sample was encountered but could be curtailed by unfocussing the laser beam at the sample point.

$Na_2Fe(CO)_4$ was prepared as a buff, very air-sensitive powder by reduction of either $Fe(CO)_5$ or $Fe_3(CO)_{12}$ using sodium in liquid ammonia; $NaFeC_5H_5(CO)_2$ was obtained through the action of 5% sodium amalgam on $[FeC_5H_5(CO)_2]_2$ in tetrahydrofuran solution. Chlorogermane was prepared by reaction of GeH_4 with HCl in the presence of aluminium chloride.[10] Commercial n-butane was used without further purification.

Preparation of Digermyltetracarbonyliron and Germylhydridotetracarbonyliron.—In a typical preparation, chlorogermane (474·2 mg, 4·23 mmol) and n-butane (*ca.* 4 ml) were condensed onto $Na_2Fe(CO)_4$ [prepared from $Fe(CO)_5$, 1·1 ml, 8·25 mmol]. After shaking at 0 °C for 15 min, volatile products were pumped through traps held at −22, −46, −63, and −196 °C, yielding *digermyltetracarbonyliron* (276·1 mg, 0·77 mmol, 37%) at −22°, *germylhydridotetracarbonyliron* (93·1 mg, 0·38 mmol, 9%) at −46°, and some *dihydridotetracarbonyliron*, condensed at −63°. Butane, unchanged GeH_3Cl and some GeH_4 were recovered at −196°. In other experiments the use of longer reaction times led to the formation of more $H_2Fe(CO)_4$ and lowered the yield of the germyliron complexes.

Characterisation.—*Digermyltetracarbonyliron* (Found: C, 15·1; H, 1·8. Calc. for $C_4H_6FeGe_2O_4$: C, 15·05; H, 1·9%). *Germylhydridotetracarbonyliron* was characterised by exact mass determination of ions from the parent family $^{12}C_4{}^1H_x{}^{56}Fe^mGe^{16}O_4$ (x = 4, 3, or 2: m = 70, 72, 73, 74, or 76) in the mass spectrum, to within the accuracy reported earlier.[1] Mass spectra and also vibrational spectroscopy support the formulation of both these complexes as monomers. *Dihydridotetracarbonyliron* was characterised by its handling properties and by gas-phase i.r. spectroscopy. The ^{1}H n.m.r. data measured for the two germyl(carbonyl)iron complexes are given in Table 1.

Handling Properties.—$(GeH_3)_2Fe(CO)_4$ is a colourless, readily-sublimable crystalline solid melting at 71 °C and with a vapour pressure at 22° of 0·8 mmHg. $GeH_3(H)Fe(CO)_4$ is a colourless volatile liquid, melting at *ca.* −30 °C and with a vapour pressure of 3·5 mmHg at 22°. Both compounds may conveniently be handled in a high vacuum system; the digermyliron complex rapidly becomes pale yellow in daylight, but decomposition is slight and resublimation leaves only traces of involatile material.

A sample of freshly sublimed $(GeH_3)_2Fe(CO)_4$ in a sealed glass tube was completely colourless after 66 h in the dark at 20° but became yellow within 5 min on exposure to normal daylight. A further sample (72 mg, 0·23 mmol) was heated in a break-seal tube at 75°. After 27 h the only change was a slight yellowing of the liquid and the temperature was increased to 112°: the sample rapidly became orange and then deep reddish brown, with the formation of a dark brown mirror on the walls of the tube. After 4·5 h, fractionation yielded incondensable gas (1·99 ml at s.t.p., 0·09 mmol) assumed to be hydrogen [no ν(CO), i.r.], GeH_4 (4·5 mg, 0·06 mmol) and unchanged $(GeH_3)_2Fe(CO)_4$ (38·4 mg, 0·13 mmol). A viscous dark red residue remained. Solid $(GeH_3)_2Fe(CO)_4$ rapidly turned brown on exposure to air; after 30 min some complex could be recovered by sublimation *in vacuo* leaving dark involatile residues.

After 3 days at 20° in a 100 ml closed bulb, $GeH_3(H)Fe(CO)_4$ (32·1 mg, 0·13 mmol) had deposited a brown mirror on the walls of the bulb. Attempted recovery afforded incondensable gas as the only volatile component.

Reaction of $(GeH_3)_2Fe(CO)_4$ *with* HCl.—Gaseous HCl (*ca.* 2·0 mmol) was condensed onto $(GeH_3)_2Fe(CO)_4$ (90·4 mg, 0·28 mmol). On warming to room temperature the solid complex slowly reacted to give a pale orange liquid phase. After 90 min fractionation yielded $GeH_3(H)Fe(CO)_4$ (32·1 mg, 0·13 mmol), held in a trap at −45°. Condensation of volatiles in a further trap at −127° gave no other GeH species; the excess HCl contained some GeH_4, identified by i.r. spectroscopy. Extraction of the orange residue gave a small amount of an unidentified orange-red carbonyl derivative (i.r., KBr disc: 2110s, 2065vs, 600vs, 465m, 455m, and 350m cm^{-1}).

Reaction of $(GeH_3)_2Fe(CO)_4$ *with* $HgCl_2$.—$(GeH_3)_2Fe(CO)_4$ (41·4 mg, 0·13 mmol) was condensed onto a large excess of dry, powdered $HgCl_2$. At room temperature the mixture slowly turned dark grey; after 15 min volatile products were unchanged starting complex (23·8 mg, 0·07 mmol), GeH_3Cl (3·8 mg, 0·03 mmol) and a mixture of GeH_4 and HCl, all identified by i.r. spectroscopy.

Preparation of Germyl(cyclopentadienyl)dicarbonyliron.—Chlorogermane (360·0 mg, 3·20 mmol) was condensed into a solution of an excess of $Na[(C_5H_5)Fe(CO)_2]$ in tetrahydrofuran. After 2 h at room temperature, vigorous pumping through a fractionation line yielded *germylcyclopentadienyldicarbonyliron*, (*ca.* 50% based on GeH_3Cl) held at 0 °C as a yellow, air-sensitive solid. Sublimation onto a probe cooled to −78° gave waxy, bright yellow plates, m.p. 81—82°, characterised by i.r. and n.m.r. spectroscopy: i.r., 2960s, 2930vs, 2860s, 2025s, 2000s, 1970vs, 1460s, 1380m, 875w, 830w, 808s, 636m, 590s, 525w cm^{-1}; n.m.r. τ 5·20, *5·00* (C_5H_5); 6·73, *3·07* (GeH_3). (Table 1.)

Attempted Reaction between Monogermane and Dihydridotetracarbonyliron.—GeH_4 (35·5 mg, 0·46 mmol) Was sealed off with $H_2Fe(CO)_4$ (*ca.* 2 mmol) and n-butane (*ca.* 2 ml). After warming the contents of the reaction tube to −10°, followed by two weeks at −15°, volatile material was fractionated; no incondensable gas had been formed and an essentially quantitative recovery of starting materials was made.

RESULTS AND DISCUSSION

Treatment of a suspension of disodium tetracarbonylferrate in n-butane with germyl chloride at 0 °C affords a mixture of digermyltetracarbonyliron, $(GeH_3)_2Fe(CO)_4$ and monogermylhydridotetracarbonyliron, $GeH_3(H)Fe(CO)_4$ in *ca.* 4 : 1 ratio. This reaction is analogous to the

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[9] S. R. Stobart, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 219.

[10] L. M. Dennis and P. R. Judy, *J. Amer. Chem. Soc.*, 1929, **51**, 2321.

preparation of silyliron complexes from iodosilane reported by Aylett,[6] although in the latter case a much smaller proportion of the monosubstituted hydrido-derivative was obtained. The overall conversion of GeH_3Cl to germyliron complexes of *ca.* 46% is rather lower than that achieved in the silane system, monogermane and dihydridotetracarbonyliron appearing as additional products in varying yields depending on reaction conditions. The two germyl(carbonyl)iron complexes are readily separated by fractional condensation, and can easily be distinguished from one another by vapour-phase i.r. spectroscopy, the 750—900 cm^{-1} region (GeH_3 deformations) being characteristic (Figure 1).

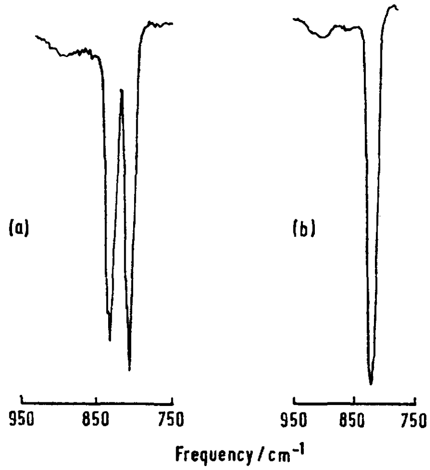

FIGURE 1 Gas-phase infrared spectra of (a) $(GeH_3)_2Fe(CO)_4$ and (b) $GeH_3(H)Fe(CO)_4$

Like other germyl(metal-carbonyl) derivatives [1,11,12] both compounds can conveniently be handled in a high-vacuum system, although $(GeH_3)_2Fe(CO)_4$ rapidly acquires a yellow colour under normal conditions by a reaction which is clearly photochemical, resembling the behaviour [11] of $GeH_3Co(CO)_4$. By contrast the digermyl complex is much more stable thermally than the cobalt compound, 53% being recovered after 4·5 h at 112 °C. Similarly, $GeH_3(H)Fe(CO)_4$ is considerably more thermally stable than $H_2Fe(CO)_4$ and can be handled at room temperature without significant decomposition.

Reaction between $(GeH_3)_2Fe(CO)_4$ and dry HCl at 20 °C affords a 46% yield of $GeH_3(H)Fe(CO)_4$, showing that the latter is considerably more resistant to attack by HCl than the digermyl complex. An analogous reaction has been reported [8] for $(Me_3Si)_2Fe(CO)_4$, and with HCl traces of $SiH_3(H)Fe(CO)_4$ were formed [6] from $(SiH_3)_2Fe(CO)_4$. No evidence for the formation of chlorogermane as a cleavage product was found during this reaction although some monogermane was detected. Similarly, following a solid–solid interaction between $(GeH_3)_2Fe(CO)_4$ and $HgCl_2$, little GeH_3Cl was observed, GeH_4 and HCl apparently being formed preferentially; 58% of the digermyl complex was recovered after contact for 15 min at 20°.

For comparative purposes, the formation of monogermyl(cyclopentadienyl)dicarbonyliron, $GeH_3Fe(C_5H_5)(CO)_2$ was investigated. The waxy, bright yellow product resembles the disubstituted germane $GeH_2[Fe(C_5H_5)(CO)_2]_2$ reported by Stone and co-workers,[13] rather than the germyl(carbonyliron) complexes. Spectroscopic properties of this compound are being further examined in conjunction with preparation of Group VIA analogues. Attempted low-temperature reaction between germane and $H_2Fe(CO)_4$ gave no evidence for formation of Ge–Fe bonds although GeH_4 reacts directly with $HMn(CO)_5$ at room temperature.[14]

The ^1H n.m.r. chemical shift data for the three germyl-iron derivatives are collected in Table 1. All resonances were sharp singlets, suggesting the existence in solution of only one isomer for each of the tetracarbonyliron complexes although variable temperature measurements would be required to confirm this. The GeH shifts all lie in the middle of the range τ 6·13—7·20 found for related complexes with germanium–transition metal bonds [13,15] and the high-field resonance at τ 19·87 for the Fe–H proton in $GeH_3(H)Fe(CO)_4$ is also in the expected region and is near that reported [16] for

TABLE 1

^1H n.m.r. data [a] for germyl(carbonyl)iron complexes

	τ(GeH_3) [b]	τ(FeH)	τ(C_5H_5)
$(GeH_3)_2Fe(CO)_4$	6·50		
$GeH_3(H)Fe(CO)_4$	6·65 (*3·00*)	19·87 (*1·00*)	
$GeH_3Fe(C_5H_5)(CO)_2$	6·73 (*3·07*)		5·20 (*5·00*)

[a] In $CDCl_3$ solution at 35 °C, relative to internal TMS; relative intensities in parenthesis. [b] τ Values virtually unaltered in C_6D_6 solution.

TABLE 2

Vibrational spectrum of $(GeH_3)_2Fe(CO)_4$ (cm^{-1})

I.r. (gas)	Raman (solid)	Tentative description
2101s	2099s	νCO ($a_1^{(2)}$)
2060s,sh		νGeH?
2042vvs	2042vs	νCO ($a_1^{(1)} + b_1$)
2022vs	2023s,sh	νCO (b_2)
1954w		ν^{13}CO
890w	890w	δGeH_3 ($2b_1 + b_2$)
	870vw	
838*R* 835*Q* } vs 831*P*		δGeH_3 (a_1)
812*R* 809*Q* } vs 805*P*		δGeH_3 (a_1)
728w		δFeCO?
628vs		δFeCO (a_1)
	436vs (p) *	νFeC (a_1)
	229vs (p) *	νGeFe (a_1)
	216m (dp) *	νGeFe (b_1)
	105vvs	δCFeC + δCFeGe

* Cyclohexane solution: p, polarised; dp, depolarised.

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[11] R. D. George, K. M. Mackay, and S. R. Stobart, *J.C.S. Dalton*, 1972, 974.

[12] K. M. Mackay and S. R. Stobart, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 687.

[13] N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1130.

[14] A. G. Massey, A. J. Park, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1963, **85**, 2021.

[15] J. E. Bentham, S. Cradock, and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1971, 587.

[16] W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 4.

$Cl_3Si(H)Fe(CO)_4$. For the compound $Me_3Si(H)Fe(CO)_4$ for which a dimeric structure has been proposed no high-field resonance attributable to τ(Fe*H*) was detected.[8]

Table 3

Vibrational spectrum of $GeH_3(H)Fe(CO)_4$ (cm^{-1})

I.r. (gas)	Raman [a] (liquid)	Tentative description
2115s	2109s (p)	νCO (a')
2052*R* 2049*Q* vvs 2043*P*	2035vs (p)	νCO (a')
2039vvs		νCO ($a' + a''$)
2018m	2000m,sh	νCO
1970w		ν^{13}CO
1885vw	1878m (p)	νFeH (a')
1200vw		
1110w		
900w	882w	δGeH_3 ($a' + a''$)
825*R* 821*Q* vs 818*P*	818vw	δGeH_3 (a')
755m		δFeCO
732*R* 728*Q* vs 726*P*		δFeH (a')
623vs		δFeCO
596s		δFeH (a'')
570m		δFeCO
500w,br		ρGeH_3 ($a' + a''$)
468w		νFeC ($a' + a''$)
	432vs (p)	νFeC (a')
	412s (p)	νFeC (a')
	226vs (p)	νGeFe (a')
	102vvs (p)	δCFeC + δCFeGe

[a] Polarised bands indicated (p)

Table 4

Infrared spectrum of $H_2Fe(CO)_4$ (cm^{-1})

I.r. (gas) *	Tentative assignment
2127w (*RQP*)	νCO ($a_1^{(2)}$)
2110vw	ν^{13}CO
2060vvs (*RQP*)	νCO ($a_1^{(1)} + b_1 + b_2$)
2035vs,sh	
2020vs	
1985w (*RQP*)	ν^{13}CO
1895vw	νFeH ($a_1 + b_1$)
885vw	
840vw,br	
818w	
800s (*RQP*) [a]	δFeH_2 (a_1, ' scissor ')
760m [a]	δFeCO
700sh	
693s [a]	δFeH_2 (b_2, ' twist '?)
642vs [b]	δFeCO
618s (*RQP*) [b]	δFeCO
585m [a]	δFeH_2 (b_1, ' wag '?)
545vw	
520w	
477m	νFeC (a_1,ax)
428m	νFeC (a_1,eq)

* 10 mmHg pressure, 10 cm KBr cell.

[a] Intensity decreased after *ca.* 10 min at 15°. [b] Intensity increased after *ca.* 10 min at 15°.

No coupling could be resolved between the two types of proton in $GeH_3(H)Fe(CO)_4$ at 35 °C. Both $(GeH_3)_2Fe(Co)_4$ and $GeH_2(H)Fe(CO)_4$ were unaffected by $CDCl_3$ over 24 h in sealed n.m.r. tubes, unlike pentacarbonylmanganese-substituted germanes where chlorination occurs rapidly at Ge under similar conditions.[17]

Vibrational Spectra.—The i.r. and Raman spectra of $(GeH_3)_2Fe(CO)_4$ and $GeH_3(H)Fe(CO)_4$ are given in Tables 2 and 3, while the gas-phase i.r. spectrum of $H_2Fe(CO)_4$ is listed in Table 4. The assignments included in the Tables are tentative and are discussed further below. Although the spectra possess some common features, the two germyl complexes belong to different symmetry Point Groups and are therefore considered separately.

Digermyltetracarbonyliron.—For a *cis*-octahedral configuration, $(GeH_3)_2Fe(CO)_4$ has C_{2v} symmetry, while the *trans*-arrangement is a C_{2h} system, assuming staggered GeH_3 groups (not D_{4h} as suggested[6,18,19] elsewhere). Under C_{2v} selection rules, the four carbonyl stretching vibrations are expected to be of species $2a_1 + b_1 + b_2$, all of which are allowed both in the i.r. and in the Raman; the two Ge–Fe stretching modes, of symmetry species $a_1 + b_1$, should both appear in the Raman spectrum. By contrast, C_{2h} symmetry predicts that only one carbonyl stretching mode (b_u) of $a_g + 2b_g + b_u$ will be i.r. active and likewise only the a_g Ge–Fe stretch would be Raman active, the b_u mode being allowed only in the i.r. From these considerations, it is clear that both in the vapour and solid states the observed spectra (Table 2) are consistent with a *cis*-configuration, and they are therefore interpreted in terms of C_{2v} symmetry. On this basis the 45 vibrational fundamentals simplify to the representation $15a_1 + 8a_2 + 12b_1 + 10b_2$ but it is obvious from Table 2 that all are not observed and consequently only a partial assignment is possible.

The 2000 cm^{-1} region is complicated by uncertainty as to the position of the Ge–H stretching modes, one of these possibly giving rise to a strong shoulder at 2060 cm^{-1} in the gas-phase i.r., but following earlier assignments[6,18] the high-frequency absorption at 2101 cm^{-1} is attributed to the axial a_1 CO stretch, with the b_2 mode at lowest frequency (2022 cm^{-1}) and the other two CO stretching vibrations each contributing to the very strong bands at 2042 cm^{-1} in both i.r. and Raman spectra. Strong bands at 628 cm^{-1} in the i.r. and 436 cm^{-1} in the Raman effect are the only features which can be assigned to FeCO bending and FeC stretching modes, thus giving the spectra a deceptively simple appearance when compared with those of $GeH_3Co(CO)_4$[11] and $GeH_3Mn(CO)_5$.[1]

The other characteristic region of the i.r. spectrum is 750—900 cm^{-1}, where two strong absorptions of equal intensity are found (Figure 1a). For C_{2v} symmetry, deformations of the GeH_3 groups account for six vibrations of species $2a_1 + a_2 + 2b_1 + b_2$: the type-A contours of these prominent bands allows them to be assigned to the two a_1 modes, the remaining i.r.-active vibrations being accounted for by the much weaker broad band at high frequency. Although similar i.r. spectra have been observed for several disilyl compounds[6,20] including $(SiH_3)_2Fe(CO)_4$, where the incidence of two strong bands due to SiH_3 deformations was taken

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[17] S. R. Stobart, unpublished observations.

[18] O. Kahn and M. Bigorgne, *J. Organometallic Chem.*, 1967, **10**, 137.

[19] J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2758.

[20] E. A. V. Ebsworth, R. L. Taylor, and L. A. Woodward, *Trans. Faraday Soc.*, 1959, **55**, 211; C. Glidewell and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1969, 350.

as evidence for a *cis*-geometry,[6] no analogous separation of GeH_3 modes has previously been found. Thus $(GeH_3)_2E$ (E = O, S, Se, or Te) all show only one strong i.r. band [21] although the derivatives of the three heavier elements have skeletal interbond angles approaching 90°. Only for the lower-symmetry species $(GeH_2)_2EH$ (E = P or As) have spectra which begin to resemble that of $(GeH_3)_2Fe(CO)_4$ been observed,[22] but a detailed assignment was not attempted. For the digermyliron complex, with the assumption that both the i.r. bands are due to a_1 vibrations, that at 809 cm^{-1} would be expected to be a symmetric GeH_3 deformation, the corresponding asymmetric a_1 mode occurring at higher frequency (835 cm^{-1}).

FIGURE 2 Raman spectrum of $(GeH_3)_2Fe(CO)_4$

In the Raman spectrum, two bands at 216 and 229 cm^{-1} can be assigned to Ge–Fe stretching vibrations. That at higher frequency is the more intense (Figure 2) and is polarised, and therefore originates from the a_1 fundamental, the b_1 mode giving rise to a weaker, depolarised band as expected. The observation of ν_{sym}(MM'M) at higher frequency than ν_{asym}(MM'M) is the reverse of the situation found for polygermanes and silicon–germanium hydrides.[23] Likewise, although relatively few metal–metal stretching frequencies have been reported for main group-transition element systems, symmetric modes have nearly always been found at lower energy than the corresponding asymmetric vibrations. For example, two Raman bands have been observed [24] in the spectrum of $GeH_3GeH_2Mn(CO)_5$, at 205 and 273 cm^{-1} and similarly there are two bands in the Raman spectrum [25] of $H_2Ge[Mn(CO)_5]_2$, at 200 and 226 cm^{-1}; in each case, the low-frequency band is much the stronger, is polarised and is attributable to the symmetric metal–metal stretch. A similar situation is found [26,27] for bis(metalcarbonyl)-mercury complexes like $Hg[Co(CO)_4]_2$, but an exception is provided by $(XHg)_2Fe(CO)_4$, X = Cl or Br, where spectra closely resembling that shown in Figure 2 have been observed.[27] Apart from the obvious stereochemical relationship between these complexes and $(GeH_3)_2Fe(CO)_4$, no rationalisation of these observations seems possible at present.

It is also of interest further to compare the spectra of $(XHg)_2Fe(CO)_4$ and related compounds [6,27] with that of $(GeH_3)_2Fe(CO)_4$ in the CO stretching region. Bradford *et al.*[27] have constructed a figure relating νCO frequencies to effective electronegativity of R in $R_2Fe(CO)_4$. Fitting to this relationship of the frequencies of i.r. bands assigned to the $a_1^{(2)}$, $a_1^{(1)} + b_1$, and b_2 carbonyl stretching modes for $(MH_3)_2Fe(CO)_4$ (respectively at 2092, 2040, and 2021 cm^{-1} for M = Si [6] and 2101, 2042, and 2022 cm^{-1} for M = Ge) allows the relative effective electronegativities of the SiH_3 and GeH_3 groups to be estimated; the resulting order for this property is $Cl > Br > I > SiCl_3 > GeH_3 \approx SiH_3 > HgCl > HgBr > HgI > HgMe$.

Monogermylhydridotetracarbonyliron.—Both *cis*- and *trans*-octahedral structures for $GeH_3(H)Fe(CO)_4$ belong to the Point Group C_s so that deciding between the two configurations on the basis of the vibrational spectrum is more difficult than for $(GeH_3)_2Fe(CO)_4$, but the appearance of more than two i.r.-active carbonyl stretching modes suggests a local symmetry at Fe of C_s rather than D_{4h} or C_{4v}, implying a *cis*-arrangement. A similar structure has been proposed for $SiH_3(H)Fe(CO)_4$ and related silyl(metal-carbonyl) hydrides.[6,16] As in the case of the digermyliron compound, not all of the 36 fundamentals $(22a' + 14a'')$ can be distinguished (Table 3).

All four predicted carbonyl stretching vibrations are present in the i.r. spectrum, although again a contribution in this region from the Ge–H stretches is expected. The Fe–H stretch is barely detectable in the gas-phase i.r. but a medium intensity polarised band at 1878 cm^{-1} in the Raman spectrum can be assigned to this a' mode. The symmetric GeH_3 deformation gives rise to a characteristic strong i.r. absorption at 821 cm^{-1} (Figure 1b), very similar in appearance to those observed for other volatile germyl–metal complexes [1,11,12] and close in frequency to the mean of the two bands observed for $(GeH_3)_2Fe(CO)_4$.

The region below 800 cm^{-1} is complex, with five prominent i.r. bands, two of which must contain contributions from FeH bending modes $(a' + a'')$. By comparison with related systems the assignments shown in Table 3 can be tentatively proposed. In the Raman spectrum, the single intense band *ca.* 430 cm^{-1} observed for $GeH_3Co(CO)_4$, $GeH_3Mn(CO)_5$, and $(GeH_3)_2Fe(CO)_4$ is here replaced by two strong bands at 412 and 432 cm^{-1}. Since both are polarised, they are assigned as two a' FeC stretching modes, possibly with different stereo-

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chemical relationships to the GeH_3– and H– ligands, the other two FeC stretches ($a' + a''$) being observed in the i.r. at 468 cm^{-1}. The Ge–Fe stretching vibration (a') is found as a strong polarised Raman band at 226 cm^{-1}, close to the a_1 Ge–Fe mode in $(GeH_3)_2Fe(CO)_4$. The remaining Raman band at 102 cm^{-1} resembles that in $(GeH_3)_2Fe(CO)_4$ and other germyl(carbonyl) metal complexes[1,11] and is assigned to a mixture of skeletal deformations.

Dihydridotetracarbonyliron.—Due to the low thermal stability of $H_2Fe(CO)_4$ little information is available regarding its vibrational spectrum. Gas-phase i.r. data recorded during the course of this work are listed in Table 4. The presence of more than one i.r.-active carbonyl stretching mode confirms a *cis*-dihydrido-configuration (C_{2v} symmetry) as reported earlier;[6,28] however, previous work has been confined to the region above 690 cm^{-1} and the results have not been discussed. In the lower frequency range (550—800 cm^{-1}) the observed spectrum resembles those of $HMn(CO)_5$[29] and $GeH_3(H)Fe(CO)_4$: there are six strong absorptions, four of which decrease in intensity with time and thus probably involve contributions from FeH bending modes. Three such modes are predicted, of species $a_1 + b_1 + b_2$. The strong band at 800 cm^{-1} showing PQR structure can be assigned to the a_1 (' scissor ') FeH_2 bend, since in other $-MH_2$ systems this type of vibration characteristically gives rise to bands well separated to high frequency.[30] Assignment of the other two FeH_2 bends [the b_1 (' wag ') and b_2 (' twist ') modes] is much less certain as the relative positions of similar vibrations in main-group metal dihydrido-derivatives and related compounds are well known to be very variable,[30,31] but by comparison with the spectra of $MH_3(H)Fe(CO)_4$ (M = Si[6] or Ge) the bands at 693 and 585 cm^{-1} probably arise mainly from these fundamentals as suggested in the Table. One other notable feature is the extremely low intensity of the absorption at 1895 cm^{-1} due to the two FeH stretching modes ($a_1 + b_1$).

Mass Spectra.—Mass spectral data for $(GeH_3)_2Fe(CO)_4$ and $GeH_3(H)Fe(CO)_4$ are listed in Supplementary Publication No. SUP 20544 (2 pp.).* For digermyltetracarbonyliron, the very weak parent-ion family contrasts sharply with the relatively high parent-ion abundances observed[1,11] for monogermyl(carbonyl) complexes of cobalt and manganese. In common with these latter, however, decomposition *via* successive elimination of CO is indicated, with a high proportion of ion current carried by polymetallic fragments. Thus where for $GeH_3Co(CO)_4$ and $GeH_3Mn(CO)_5$ respectively, 77 and 79% of ions contained both Ge and Co or Mn, here 57% belong to Ge_2Fe families and a further 26% contain Fe and one Ge atom. These features are illustrated by the relatively high abundance of $Ge_2H_xFe(CO)_3^+$ ions, arising from process (1) combined with the absence of a family due to $GeH_xFe(CO)_4^+$, (2).

$$\begin{tikzcd}
 & Ge_2H_xFe(CO)_3^+ + CO \quad (1) \\
Ge_2H_xFe(CO)_4^+ \arrow[ur] \arrow[dr, "\times" marking] & \\
 & GeH_xFe(CO)_4^+ + GeH_x \quad (2)
\end{tikzcd}$$

Likewise, the strongest family of ions is here $Ge_2H_xFe^+$, similar to the GeH_xM^+ (M = Co or Mn) base-peak multiplets found for the monogermyl compounds. One other feature is the significant and near-equal intensities of all the peaks for $Fe(CO)_n^+$ ions (n = 0—4); in the case of the Co and Mn complexes, related ions increased markedly in abundance for low values of n, from *ca.* zero at n = 4 or 5. The only doubly charged ions detected in the spectrum of $(GeH_3)_2Fe(CO)_4$ were $Ge_2H_xFe(CO)_2^{2+}$.

For germylhydridotetracarbonyliron significant differences are evident. Ions containing both metal atoms account for only about 35% of the total ion-current, the base-peak multiplet being that due to GeH_x^+. $Fe(CO)_n^+$ fragments are very much more abundant than for $(GeH_3)_2Fe(CO)_4$, peak intensities remaining roughly equal for all n(0—4). These features may imply a weakening of the metal–metal bond in $GeH_3(H)Fe(CO)_4$ relative to the GeCo, GeMn, and Ge_2Fe systems, but might also be in part due to the lower thermal stability of the former, although the mass spectrometer was operated at only *ca.* 60° in an attempt to avoid thermal decomposition. Little information regarding the stability of the Fe–H bond could be obtained because of the m/e spread of GeH_x-containing families, and ions $HFe(CO)_n^+$ were of only very low abundance.

Nature of the Complexes.—Like their silyl analogues, $(GeH_3)_2Fe(CO)_4$ and $GeH_3(H)Fe(CO)_4$ are of intermediate stability between related germyl–manganese[1] and –cobalt[11] compounds. High volatility and the absence of ions at higher mass than those of the expected parent ions indicate that the complexes are monomeric, and this is confirmed by the absence of any unusual features from the vibrational and ^1H n.m.r. spectra.

There thus appear to be at least three distinct classes of Group-IVB substituted tetracarbonyliron derivatives. The compounds $(MH_3)_2Fe(CO)_4$ and $MH_3(H)Fe(CO)_4$ (M = Si or Ge) typify the first and simplest category; the second is represented by $(Me_3Si)_2Fe(CO)_4$ where a dimeric structure apparently arises[8] through formation of Si–O–C linkages and metal–metal bonds; and finally, there is a large group of complexes where more complicated types of structure occur through more extensive metal–metal bond formation.[2,3,5,19]

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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