bulky ligands on the aluminum center. This would have the dual effect of controlling the binding orientation and destabilizing the aluminum dimer, though care must be taken that not so much steric bulk is introduced into the systems that the binding of substrate becomes unfavorable as well. Comparisons of the dimerization and complexation reaction energies of AlH_3 and $Al(CH_3)_3$ suggest that the former reaction is likely to be far more sensitive to steric factors. Note especially that the parent complexes have similar Lewis acidities. Experimental work is in accord with these results.[21]

Conclusions

We find that complexes of simple alkenes with $R_nCl_{3-n}Al$ are stable intermediates. Binding in most cases is predicted to be somewhat less favorable than dimerization, though these results should be viewed with caution. Binding does not significantly affect the C=C bond in ethylene, as evidenced by CC bond distances and CC stretching frequencies. The systems exhibit true olefin-metal complexation. The trends in complex stability follow the trends in the Lewis acidities of the parent $R_nCl_{3-n}Al$ fragments, i.e. $AlCl_3 > AlCl_2CH_3 > AlCl(CH_3)_2 > Al(CH_3)_3$. To first order, there is no electronic preference for orientation of an alkene to aluminum; steric effects are expected to be the controlling factor in determining the regiochemistry of addition. Work is currently in progress in this group to characterize the transition structures linking the intermediates described here and the related insertion products.

Acknowledgment. We appreciate the support of the Academic Computing Centers of Bryn Mawr College and Haverford College. P.R.S. and Y.-M.C. thank Bryn Mawr College and the Charles A. Dana Foundation for fellowship support. M.M.F. thanks Dr. Kerwin Dobbs and John Freeman for many helpful discussions.

Registry No. AlH_3, 7784-21-6; $Al(CH_3)_3$, 75-24-1; $AlCl_3$, 7446-70-0; $AlCl(CH_3)_2$, 1184-58-3; $AlCl_2CH_3$, 917-65-7; $(AlH_3)_2$, 12004-30-7; $[Al(CH_3)_3]_2$, 15632-54-9; $(AlCl_3)_2$, 13845-12-0; $H_3Al\cdots NH_3$, 27710-55-0; $Cl_3Al\cdots NH_3$, 15550-69-3; $H_3Al\cdots H_2C{=}CH_2$, 128660-20-8; $Al(CH_3)_3\cdots H_2C{=}CH_2$, 128660-21-9; $AlCl_3\cdots H_2C{=}CH_2$, 12175-82-5; $AlCl_2CH_3\cdots H_2C{=}CH_2$, 128683-52-3; $AlCl(CH_3)_2\cdots H_2C{=}CH_2$, 128660-22-0; $AlH_3\cdots H_2C{=}CHCH_3$, 128660-23-1.

Supplementary Material Available: Tables of full Cartesian coordinates and total energies for all optimized structures included in this paper (7 pages). Ordering information is given on any current masthead page.

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[21] Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966,** *88,* 2213. Eisch, J. J.; Amtmann, R. *J. Org. Chem.* **1972,** *37,* 3420.

Synthesis of Iron Carbonyl Clusters with Trigonal-Bipyramidal E_2Fe_3 Cores (E = Ge, Si). Crystal Structures of $(\mu_3\text{-GeEt})_2Fe_3(CO)_9$, $[\mu_3\text{-Ge}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$, and $[\mu_3\text{-Si}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$

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The reaction of $RGeH_3$ with $Fe_3(CO)_{12}$ at 50 °C gives low-to-moderate yields of the trigonal-bipyramidal clusters $(\mu_3\text{-GeR})_2Fe_3(CO)_9$ (**3**) together with complexes tentatively identified as $(\mu\text{-GeRH})_2Fe_2(CO)_7$ and $(\mu\text{-GeRH})_3Fe_2(CO)_6$. A superior route to clusters **3** is from $RGeH_3$ and $Fe(CO)_5$ at 140 °C. The corresponding reactions with silanes $RSiH_3$ appear to give similar products, but the lack of stability precluded complete characterization. The stable Si_2Fe_3-core cluster $[\mu_3\text{-Si}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (**5a**) can be prepared in good yield by reacting SiH_4 with $Fe(CO)_5$ and $[Fe(CO)_2Cp]_2$ at 150 °C; the corresponding Ge analogue **5b** is similarly available from GeH_4. X-ray crystal structures are reported for cluster **3** (R = Et; $C_{13}H_{10}Fe_3Ge_2O_9$, $a = 9.341$ (2) Å, $b = 15.264$ (4) Å, $c = 14.216$ (3) Å, $\beta = 91.22$ (2)°, $P2_1/n$, $Z = 4$), for **5a** ($C_{23}H_{10}Fe_5Si_2O_{13}$, $a = 10.020$ (8) Å, $b = 9.914$ (6) Å, $c = 28.07$ (2) Å, $\beta = 92.68$ (7)°, $P2_1/n$, $Z = 4$), and for **5b** ($C_{23}H_{10}Fe_5Ge_2O_{13}$, $a = 10.125$ (3) Å, $b = 10.024$ (3) Å, $c = 28.308$ (9) Å, $\beta = 92.53$ (3)°, $P2_1/n$, $Z = 4$). The E_2M_3 cores are slightly irregular trigonal bipyramids with Ge–Fe ranging from 2.302 to 2.336 Å and Fe–Fe = 2.721–2.742 Å in **3**; in **5a**, Si–Fe = 2.294–2.324 Å (distinctly longer than the external Si–Fe value of 2.251 Å) and Fe–Fe is 2.654–2.687 Å, while in **5b** Ge–Fe = 2.365–2.391 Å (external Ge–Fe = 2.318 Å) and Fe–Fe = 2.717–2.742 Å.

Introduction

Clusters containing a *closo*-E_2M_3 core, where E is a main-group element and M is a transition metal, are relatively rare.[1] In 1988, Whitmire[2] listed only nine examples, of which five were P_2Fe_3 species. Crystallographically established examples where E is a group 14 element are limited to the long-known[3] $[\mu_3\text{-SnCl}_3]_2Pt_3(C_8H_{12})_3$, the sparsely described[4] $[\mu_3\text{-Sn}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (**5c**), and three complexes not in Whitmire's review,[2] $(\mu_3\text{-CF})_2Fe_3(CO)_9$[5] and the pair $[\mu_3\text{-E}\{Re(CO)_5\}]_2Fe_3(CO)_9$ (E = Sn,[6]

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[1] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 56.

[2] Whitmire, K. H. *J. Coord. Chem.* **1988,** *17,* 95.

[3] Guggenberger, L. J. *J. Chem. Soc., Chem. Commun.* **1968,** 512.

[4] McNeese, J. T.; Wreford, S.; Tipton, L. D.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1977,** 390.

[5] Lentz, D.; Brudgam, I.; Hartl, H. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 119.

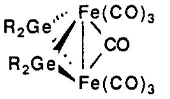
0276-7333/90/2309-2436$02.50/0

Ge[7]) recently reported by Haupt and co-workers.

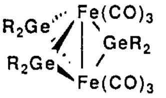
We have previously shown that the group 14 hydrides R_xEH_{4-x} are useful reagents for the synthesis of a wide range of iron[8] or cobalt[9,10] carbonyl clusters. We now report that the hydrides provide useful routes to Si_2Fe_3 and Ge_2Fe_3 trigonal-bipyramidal clusters, adding Si and a second Ge species to the range of group 14 E_2M_3 species and allowing fuller comparisons with other main groups.

Results and Discussion

Preparations. There was no reaction between $MeGeH_3$ and $Fe_3(CO)_{12}$ in pentane up to 30 °C, but at 50 °C reaction was complete after 24 h. The pentane-soluble fraction of the product mixture contained two components that were difficult to separate because of similar solubility and lack of stability toward chromatography. However, the infrared spectra suggested that they were the related complexes **1a** and **2a**, which can be regarded as derivatives of $Fe_2(CO)_9$ in which a μ-GeMeH group has replaced two and three of the bridging carbonyl groups, respectively. The complex **1a** has been previously characterized from the self-condensation reaction of $(MeGeH_2)_2Fe(CO)_4$[12] and is also produced from the reaction of $MeGeH_3$ and $Fe_2(CO)_9$.[13] The structure type **2a** is well established for the fully methylated $(\mu\text{-}GeMe_2)_3Fe_2(CO)_6$.[14]

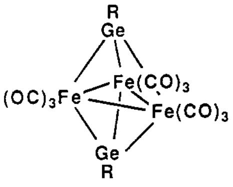


1a, R_2 = MeH
b, R_2 = EtH



2a, R_2 = MeH
b, R_2 = EtH

The remaining fraction was a red product soluble in dichloromethane. This was characterized as the trigonal-bipyramidal cluster **3a** on spectroscopic evidence. The mass spectrum was entirely consistent with this formulation, while a carbonyl-region infrared spectrum showed two intense bands with the same pattern as those found for other trigonal-bipyramidal clusters such as $(\mu_3\text{-}Bi)_2Fe_3(CO)_9$,[15a] $(\mu_3\text{-}As)_2Fe_3(CO)_9$,[15b] and $(\mu_3\text{-}CF)_2Fe_3(CO)_9$.[5]



3a, R = Me
b, R = Et

While the proportion of **3a** to the Fe_2 species **1a** and **2a** was variable and unpredictable, these three products together accounted for essentially all the initial $Fe_3(CO)_{12}$, when a 2.2–10-fold excess of $MeGeH_3$ was used. Thus, within the limits imposed by the inseparability of **1a** and **2a**, all the $Fe_3(CO)_{12}$ was converted, but the factors determining the proportion of **3a** could not be identified, and we were unable to optimize the yield. No **3a** was recovered from one run prolonged for 8 days.

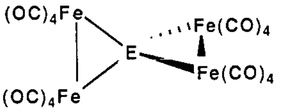
The corresponding reaction of $EtGeH_3$ with $Fe_3(CO)_{12}$ followed the same course, although all of the nonvolatile products were pentane-soluble. An infrared spectrum of the crude mixture suggested **1b**, **2b**, and **3b** were all present. Chromatography gave complete decomposition of any **1b** but allowed the isolation of pure fractions of **2b** (characterized by its mass and infrared spectra) and of **3b**, characterized by spectroscopy and by a crystal structure determination (see below). Again, the yield of **3b** was variable and unpredictable.

The overall reaction of $RGeH_3$ (R = Me, Et) with $Fe_3(CO)_{12}$ therefore can be summarized by eq 1.

$$RGeH_3 + Fe_3(CO)_{12} \rightarrow \underset{\mathbf{1}}{(\mu\text{-}GeRH)_2Fe_2(CO)_7} + \underset{\mathbf{2}}{(\mu\text{-}GeRH)_3Fe_2(CO)_6} + \underset{\mathbf{3}}{(\mu_3\text{-}GeR)_2Fe_3(CO)_9} + H_2 + CO + Fe(CO)_5 \quad (1)$$

As the reaction (1) could not be directed specifically toward **3**, an alternative synthesis was sought.

A mixture of $MeGeH_3$ and excess $Fe(CO)_5$ in hydrocarbon solvent showed no sign of change at 70 °C, but complete reaction occurred at 135 °C over 3 h. The isolated products of the reaction were the previously known[11] pentane-soluble $Ge[Fe_2(CO)_8]_2$ (**4a**) in 20–25% yields and the trigonal-bipyramidal cluster **3a** in 30–50% yields; this is a more efficient and reproducible route to **3** than from $Fe_3(CO)_{12}$. The isolation of **4a** from the system in moderate yield indicates that appreciable cleavage of the Ge–C bond of $MeGeH_3$ is occurring, which is relatively unusual, since experience[8,12] with other reactions of alkylgermanes with metal carbonyls shows that the Ge–C bonds are normally retained in the products. However, the conditions used for these $Fe(CO)_5$ reactions are quite forcing. The fate of the excised methyl group was not determined, but the incondensable gas volume and average molecular weight suggest that CH_4 may have been formed, accounting for part or all of the methyl groups.



4a, E = Ge
b, E = Si

The reaction is therefore

$$MeGeH_3 + Fe(CO)_5 \rightarrow \underset{\mathbf{4a}}{Ge[Fe_2(CO)_8]_2} + \underset{\mathbf{3a}}{(\mu_3\text{-}GeMe)_2Fe_3(CO)_9} + H_2 + CO + CH_4? \quad (2)$$

It is interesting that in unpublished work, probably from the early 1970s and reported in Bonny's review,[16] a hydride reaction gave $(PhGe)_2Fe_3(CO)_9$, tentatively identified as a trigonal bipyramid from its infrared spectrum. The work

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(6) Haupt, H. J.; Gotze, A.; Florke, U. *Z. Anorg. Allg. Chem.* **1988**, *557*, 82.

(7) Haupt, H. J.; Florke, U. *Acta Crystallogr.* **1988**, *C44*, 472.

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(11) Anema, S. G.; Barris, G. C.; Mackay, K. M.; Nicholson, B. K. *J. Organomet. Chem.* **1988**, *350*, 207.

(12) Bonny, A.; Mackay, K. M. *J. Chem. Soc., Dalton Trans.* **1978**, 506.

(13) Anema, S. G. D.Phil. Thesis, University of Waikato, 1989.

(14) Brooks, E. H.; Elder, M.; Graham, W. A. G.; Hall, D. *J. Am. Chem. Soc.* **1968**, *90* 3587.

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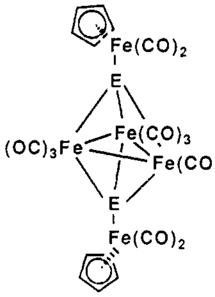
(16) Bonny, A. *Coord. Chem. Rev.* **1978**, *25*, 229 (ref 111).

reported here helps to confirm this pioneering preparation, which presumably occurred via a reaction similar to eq 1 or 2.

The reactions of silanes corresponding to the germanes of eq 1 and 2 were also investigated and appeared to follow the same routes. $RSiH_3$ (R = Me, Et) and $Fe_3(CO)_{12}$ reacted at 50 °C, although 14 days was needed for completion compared with 1 day in the germanium system. An infrared spectrum of the crude products gave carbonyl stretching bands that matched those of the corresponding germanium products, suggesting a mixture of the silicon analogues of **1**, **2**, and **3** had been formed. However, these could not be further characterized since they were much less stable than the germanium compounds and attempted separation led to complete decomposition. Similarly the reaction of $MeSiH_3$ with $Fe(CO)_5$ was complete after 1.5–2 h at 140 °C. Workup gave reasonable yields of $Si[Fe_2(CO)_8]_2$ (**4b**)[11] and a red compound that showed the characteristic two-band infrared spectrum of a trigonal-bipyramidal cluster and so is presumed to be $(\mu_3\text{-SiMe})_2Fe_3(CO)_9$. Further characterization was hampered by ready decomposition, which gave $Fe_3(CO)_{12}$ among other products, so that pure samples could not be obtained. A similar reaction of $PhSiH_3$ with $Fe(CO)_5$ also gave a mixture of **4b** and a product tentatively identified as $(\mu_3\text{-SiPh})_2Fe_3(CO)_9$, but again full characterization was not possible.

An alternative route to trigonal-bipyramidal clusters of type **3** was suggested by the work of Haupt and co-workers,[6,7] who combined $SnCl_2$ (or Ge/$GeCl_4$), $Fe(CO)_5$, and $MnRe(CO)_{10}$ to prepare $[\mu_3\text{-Sn}\{Re(CO)_5\}]_2Fe_3(CO)_9$ (or the Ge analogue). The similar reaction of SiH_4, $Fe(CO)_5$, and $[Fe(CO)_2Cp]_2$ in petroleum ether at 150 °C gave some $Si[Fe_2(CO)_8]_2$ (**4b**) (which is the main product in the reaction of SiH_4 with $Fe(CO)_5$ in the absence of other components[11]) and good yields of a red complex characterized by spectroscopy and by a crystal structure analysis as $[\mu_3\text{-Si}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (**5a**). Although the reaction pathway is unknown, it seems reasonable to propose a sequence involving initial reaction of SiH_4 with $[Fe(CO)_2Cp]_2$ to give $H_3SiFe(CO)_2Cp$, which then reacts with $Fe(CO)_5$ in a way similar to that for $RSiH_3$ discussed above. We note that $H_3SiFe(CO)_2Cp$ reacts with $Co_2(CO)_8$ to give $Cp(CO)_2FeSiCo_3(CO)_9$.[17] In marked contrast to the Si_2Fe_3 clusters with organic groups on the apical silicon atom, the example with $Fe(CO)_2Cp$ groups shows good stability, so full characterization was possible.



5a, E = Si
b, E = Ge
c, E = Sn

The corresponding reaction of GeH_4 with a mixture of $Fe(CO)_5$ and $[Fe(CO)_2Cp]_2$ follows a similar course, giving significant quantities of $Ge[Fe_2(CO)_8]_2$ (**4a**) and moderate yields of red $[\mu_3\text{-Ge}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (**5b**). **5b** has an infrared spectrum barely distinguishable from that of the silicon complex **5a**, and the ^1H and ^{13}C NMR spectra were also very similar. We were unable to observe a ^{29}Si signal from **5a** at the 17.88-MHz frequency available.

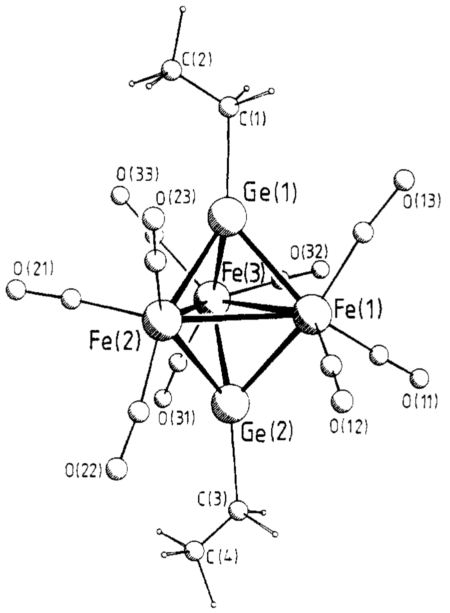


Figure 1. PLUTO diagram of the structure of $(\mu_3\text{-GeEt})_2Fe_3(CO)_9$ (**3a**).

Table I. Selected Bond Lengths and Angles for $(\mu_3\text{-GeEt})_2Fe_3(CO)_9$

	Bond Lengths (Å)		
Fe(1)–Fe(2)	2.721 (4)	Fe(2)–Fe(3)	2.742 (3)
Fe(1)–Fe(3)	2.734 (3)	Fe(2)–Ge(1)	2.324 (3)
Fe(1)–Ge(1)	2.334 (3)	Fe(2)–Ge(2)	2.336 (3)
Fe(1)–Ge(2)	2.308 (3)	Fe(3)–Ge(1)	2.302 (3)
		Fe(3)–Ge(2)	2.323 (3)
	Bond Angles (deg)		
Fe(2)–Fe(1)–Fe(3)	60.4 (1)	Fe(1)–Fe(3)–Fe(2)	59.6 (1)
Fe(2)–Fe(1)–Ge(1)	54.1 (1)	Fe(1)–Fe(3)–Ge(1)	54.4 (1)
Fe(2)–Fe(1)–Ge(2)	54.6 (1)	Fe(1)–Fe(3)–Ge(2)	53.6 (1)
Fe(3)–Fe(1)–Ge(1)	53.3 (1)	Fe(2)–Fe(3)–Ge(1)	54.0 (1)
Fe(3)–Fe(1)–Ge(2)	54.1 (1)	Fe(2)–Fe(3)–Ge(2)	54.2 (1)
Ge(1)–Fe(1)–Ge(2)	94.4 (1)	Ge(1)–Fe(3)–Ge(2)	94.8 (1)
Fe(1)–Fe(2)–Fe(3)	60.1 (1)	Fe(1)–Ge(1)–Fe(2)	71.5 (1)
Fe(1)–Fe(2)–Ge(1)	54.4 (1)	Fe(1)–Ge(1)–Fe(3)	72.3 (1)
Fe(1)–Fe(2)–Ge(2)	53.7 (1)	Fe(2)–Ge(1)–Fe(3)	72.7 (1)
Fe(3)–Fe(2)–Ge(1)	53.3 (1)	Fe(1)–Ge(2)–Fe(2)	71.7 (1)
Fe(3)–Fe(2)–Ge(2)	53.7 (1)	Fe(1)–Ge(2)–Fe(3)	72.4 (1)
Ge(1)–Fe(2)–Ge(2)	93.9 (1)	Fe(2)–Ge(2)–Fe(3)	72.1 (1)

Crystal Structures. The X-ray crystal structure of $(\mu_3\text{-GeEt})_2Fe_3(CO)_9$ (**3b**) was determined to confirm the spectroscopic characterization. The geometry is illustrated in Figure 1, and bond parameters are summarized in Table I. The structure shows the expected near-equilateral triangle of Fe atoms capped on both sides by Ge atoms, each of which is further bonded to an ethyl group. Each of the iron atoms is bonded to three CO ligands, one pointing upward and one downward and the third being nearly in the Fe_3 plane and leaning toward the adjacent iron atom. The distances and angles are such that these last CO ligands should not be regarded as semibridging, although only a small rotation of the Fe_3 triangle would make them so. The Ge–Fe bonds lie in the range 2.301 (3)–2.336 (3) Å (average 2.321 Å), while the Fe–Fe bonds average 2.732 (3) Å.

The structure of the isomorphic molecules $[\mu_3\text{-Si}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (**5a**) and $[\mu_3\text{-Ge}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (**5b**) is shown in Figure 2, and selected bond parameters are given in Table II. The structural characterization of **5a** is the first for a Si_2Fe_3-core cluster. For each, the Fe_3 triangle is capped on each face by the group 14 atom, with

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(17) Kohler, F. H. *Z. Naturforsch.* **1982**, *37B*, 601.

Table II. Selected Bond Lengths and Angles for [μ_3-E{Fe(CO)$_2$Cp}]$_2$Fe$_3$(CO)$_9$ (E = Si (5a), Ge (5b))

Bond Lengths (Å)

	E = Si	E = Ge		E = Si	E = Ge
E(1)–Fe(1)	2.296 (1)	2.367 (2)	Fe(2)–Fe(3)	2.658 (1)	2.719 (2)
E(1)–Fe(2)	2.294 (1)	2.365 (2)	Fe(4)–C(1)	2.099 (3)	2.092 (8)
E(1)–Fe(3)	2.324 (1)	2.391 (2)	Fe(4)–C(2)	2.102 (3)	2.111 (8)
E(1)–Fe(4)	2.246 (1)	2.316 (2)	Fe(4)–C(3)	2.102 (3)	2.124 (8)
E(2)–Fe(1)	2.315 (1)	2.382 (2)	Fe(4)–C(4)	2.100 (3)	2.112 (8)
E(2)–Fe(2)	2.306 (1)	2.380 (2)	Fe(4)–C(5)	2.098 (3)	2.092 (8)
E(2)–Fe(3)	2.301 (1)	2.383 (2)	Fe(5)–C(6)	2.112 (3)	2.101 (8)
E(2)–Fe(5)	2.255 (1)	2.319 (2)	Fe(5)–C(7)	2.103 (3)	2.113 (8)
Fe(1)–Fe(2)	2.687 (1)	2.742 (2)	Fe(5)–C(8)	2.094 (3)	2.115 (8)
Fe(1)–Fe(3)	2.654 (1)	2.717 (2)	Fe(5)–C(9)	2.097 (3)	2.103 (8)
Fe(5)–C(10)	2.109 (3)	2.094 (8)			

Average Bond Lengths

Si–Fe (internal) in **5a**: 2.306
Ge–Fe (internal) in **5b**: 2.378
Sn–Fe (external)[a] in **5c**: 2.48

Si–Fe (external) in **5a**: 2.250
Ge–Fe (external) in **5b**: 2.318
Sn–Fe (internal)[a] in **5c**: 2.53

Bond Angles (deg)

	E = Si	E = Ge		E = Si	E = Ge
Fe(2)–Fe(1)–Fe(3)	60.4 (1)	59.7 (1)	Fe(1)–Fe(3)–Fe(2)	59.6 (1)	60.6 (1)
Fe(2)–Fe(1)–Ge(1)	54.1 (1)	54.6 (1)	Fe(1)–Fe(3)–Ge(1)	54.4 (1)	54.8 (1)
Fe(2)–Fe(1)–Ge(2)	54.6 (1)	54.8 (1)	Fe(1)–Fe(3)–Ge(2)	53.6 (1)	55.2 (1)
Fe(3)–Fe(1)–Ge(1)	53.3 (1)	55.6 (1)	Fe(2)–Fe(3)–Ge(1)	54.0 (1)	54.7 (1)
Fe(3)–Fe(1)–Ge(2)	54.1 (1)	55.3 (1)	Fe(2)–Fe(3)–Ge(2)	54.2 (1)	55.1 (1)
Ge(1)–Fe(1)–Ge(2)	94.4 (1)	97.3 (1)	Ge(1)–Fe(3)–Ge(2)	94.8 (1)	96.6 (1)
Fe(1)–Fe(2)–Fe(3)	60.1 (1)	59.7 (1)	Fe(1)–Ge(1)–Fe(2)	71.5 (1)	70.8 (1)
Fe(1)–Fe(2)–Ge(1)	54.4 (1)	54.6 (1)	Fe(1)–Ge(1)–Fe(3)	72.3 (1)	69.6 (1)
Fe(1)–Fe(2)–Ge(2)	53.7 (1)	54.9 (1)	Fe(2)–Ge(1)–Fe(3)	72.7 (1)	69.7 (1)
Fe(3)–Fe(2)–Ge(1)	53.3 (1)	55.6 (1)	Fe(1)–Ge(2)–Fe(2)	71.7 (1)	70.3 (1)
Fe(3)–Fe(2)–Ge(2)	53.7 (1)	55.2 (1)	Fe(1)–Ge(2)–Fe(3)	72.4 (1)	69.5 (1)
Ge(1)–Fe(2)–Ge(2)	93.9 (1)	97.4 (1)	Fe(2)–Ge(2)–Fe(3)	72.1 (1)	69.6 (1)

[a] Data for **5c** from ref 4.

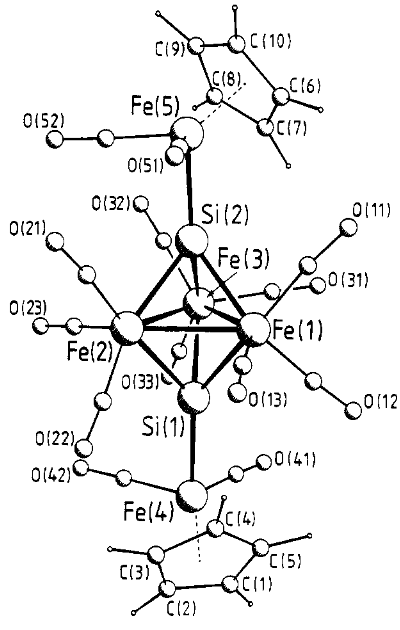

Figure 2. Structure of [μ_3-Si{Fe(CO)$_2$Cp}]$_2$Fe$_3$(CO)$_9$ (**5a**). The structure of the isomorphous [μ_3-Ge{Fe(CO)$_2$Cp}]$_2$Fe$_3$(CO)$_9$ (**5b**) is identical.

a further E–Fe bond to the apical Fe(CO)$_2$Cp group. The terminal CO ligands on the iron atoms adopt the same general arrangement described above for the germanium complex **3b**, suggesting that this is determined by intramolecular rather than crystal-packing interactions. The clusters **5a** and **5b** are the direct analogues of the previously described[4] [μ_3-Sn{Fe(CO)$_2$Cp}]$_2$Fe$_3$(CO)$_9$ (**5c**), and a comparison of bond parameters shows that the average E–Fe bond lengths (both internal and external) increase by 0.07 Å and then by 0.16 Å on passing from the silicon to the germanium to the tin example, exactly as expected on the basis of atomic radii. Similarly, the Fe–Fe bonds increase from 2.666 through 2.726 to 2.792 Å as the capping atom changes from Si to Ge to Sn, reflecting the relative size change. The Ge–Fe and Fe–Fe bond lengths in **5b** are marginally longer than the corresponding values for **3b** (see Tables I and II) but are essentially the same as those for [μ_3-Ge{Re(CO)$_5$}]$_2$Fe$_3$(CO)$_9$, which has Ge–Fe = 2.379 (4) Å and Fe–Fe = 2.719 (4) Å,[7] perhaps because of the different steric requirements of the apical group bonded to the germanium.

For all of the clusters **3b**, **5a**, and **5b** the capping E atoms deviate significantly from the most symmetrical site, possibly reflecting the low symmetry of the apical substituent group but more likely arising from crystal–packing effects.

These preparations establish that the six-skeletal-electron-pair trigonal bipyramid with the E_2M_3 skeleton joins the trigonal-pyramidal EM_3[1,2,18,19] and the square-bipyramidal E_2M_4 species[1,2,9,10,19,20] among the closo structures formed by the group 14 elements (E = Si, Ge). As in the other series, the silicon species are less accessible than the germanium analogues and have a lower range of stability. Although the Sn_2Fe_3 trigonal bipyramid has been characterized in two cases[4,6] (as well as the longstanding Sn_2Pt_3[3]), there are no examples of either *closo*-SnM_3 or *closo*-Sn_2M_4 structures. While this may represent an intrinsic property of the trigonal bipyramids[18] (but contrast ref 21), it also reflects the very limited number of studies so far undertaken. Similar patterns are seen for E = group

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Table III. Summary of Crystallographic Data

	3b	**5a**	**5b**
formula	$C_{13}H_{10}Fe_3Ge_2O_9$	$C_{23}H_{10}Fe_5Si_2O_{13}$	$C_{23}H_{10}Fe_5Ge_2O_{13}$
M_r	622.94	829.73	918.78
color	deep red	deep red	deep red
cryst size, mm	0.40 × 0.40 × 0.10	0.62 × 0.66 × 0.40	0.34 × 0.21 × 0.20
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	9.341 (2)	10.020 (8)	10.125 (3)
b, Å	15.264 (4)	9.914 (6)	10.024 (3)
c, Å	14.216 (3)	28.07 (2)	28.308 (9)
β, deg	91.22 (2)	92.68 (7)	92.53 (3)
V, Å^3	2026.4 (8)	2785 (3)	2870 (1)
T, °C	20	−145	−120
Z	4	4	4
D_{calc}, g cm^{-3}	2.04	1.98	2.13
$F(000)$	1208	1640	1784
μ, cm^{-1}	51	28	47
T_{max}/T_{min}	0.99, 0.36	0.64, 0.34	0.95, 0.65
2θ range, deg	5–52	4–50	3–50
unique data	3987	4453	5036
no. of data $I > 2.5\sigma(I)$	1507	3689	3187
anisotropic atoms	Fe, Ge	Fe, Si, C, O	Fe, Ge, C, O
$R(F)$	0.0597	0.0311	0.0551
$R_w(F)$	0.0580	0.0318	0.0543
p ($w = [\sigma^2(F) + pF^2]^{-1}$)	0.0010	0.0035	0.0011
max Δ/σ	0.6	0.02	0.6

15 or 16 atom.[1,2,18,21,22] In E_2M_3 species, the widest variety of main-group elements, E, is found in the nido 50-electron $E_2Fe_3(CO)_9$ class of compounds, where E = S, Se, and Te[23] or E = RP, RAs, and mixed species with two different E groups.[24] In these compounds, one of the Fe–Fe edges is open. In addition to the group 14 compounds already discussed, the *closo*-E_2M_3 skeleton is found for E = group 15 element in the 48-electron $E_2Fe_3(CO)_9$ species with E = As and Bi,[15] where there is a lone pair on E. This series was recently extended by five crystal structures of phosphorus compounds, reported by Huttner and colleagues,[25] where the outward-pointing lone pair on P coordinates to a 16-electron ML_x fragment in $Fe_3(CO)_9(PML_x)_2$ species. A variety of species with E = P and several permutations of ML_x were made from the trihalide and $Fe_2(CO)_9$, while reaction of the inidene chloride with $Na_2Fe(CO)_4$ gave similar P, As, or Sb compounds. The potential richness of the chemistry is well illustrated by one compound which builds a further four-membered ring on the skeleton by an $Fe_2(CO)_8$ group that links one P to one of the equatorial Fe atoms.[25]

Conclusion. Clusters incorporating a *closo*-E_2Fe_3 core can be prepared by a range of routes starting from the parent silicon and germanium hydrides. The use of $Fe_3(CO)_{12}$ as the iron source allows reactions under mild conditions but leads to a mixture of products that are not readily separated, and the reactions are somewhat variable for reasons that are not yet clear. With $Fe(CO)_5$ as the reagent, reactions must be performed under more forcing conditions, but yields are better and the reactions are reproducible. The germanium-containing clusters are stable and are convenient to handle, whereas the silicon equivalents with alkyl and aryl groups as the apical substituent are sensitive to handling and are difficult to isolate pure. However, good stability is conferred by an $Fe(CO)_2Cp$ apical group. Although it is a relatively rare configuration, the *closo*-E_2M_3 skeleton is now established for E = C, Si, Ge, and Sn in group 14 and for E = P, As, Sb, and Bi in group 15.

Experimental Section

Reactions were carried out in sealed, evacuated glass ampules of about 200-mL capacity, with use of pentane (10 mL) as solvent for the $Fe_3(CO)_{12}$ reactions and petroleum ether (bp 100–130 °C, 5 mL) for the $Fe(CO)_5$ reactions. Reagents, instrumentation, and vacuum-line and Schlenk-line techniques have been described recently elsewhere.[8] Gases incondensable in liquid nitrogen were handled with a Toepler pump. In most reactions these were mixtures of H_2 and CO, and the composition was estimated from the average molecular weight. In the higher temperature runs, where methyl groups were lost, methane may also have been present in the incondensable fraction.

Reaction of $MeGeH_3$ with $Fe_3(CO)_{12}$. $MeGeH_3$ (1.04 mmol) and $Fe_3(CO)_{12}$ (100 mg, 0.20 mmol) showed no visible reaction at room temperature over a 4-week period. After 24 h at 50 °C, the green $Fe_3(CO)_{12}$ was replaced by a red product. The ampule was opened to the vacuum line, and incondensable gases were removed (H_2, 0.47 mmol; CO, 0.24 mmol). Subsequent pumping removed pentane, $Fe(CO)_5$ (identified by an IR spectrum), and unreacted $MeGeH_3$ together. The residue was extracted with pentane (5 × 5 mL) to give a mixture of two compounds tentatively identified as $(\mu\text{-GeMeH})_2Fe_2(CO)_7$ (**1a**; ν(CO) 2092 w, 2059 m, 2032 vs, 2017 m, 2006 vs, 1982 m, 1852 s cm^{-1}) and $(\mu\text{-GeMeH})_3Fe_2(CO)_6$ (**2a**; ν(CO) 2009 vs, 1970 vs cm^{-1}) in a combined yield of 114 mg (0.21–0.23 mmol depending on composition; ca. 70% based on $Fe_3(CO)_{12}$). Careful washing allowed the isolation of part of the **2a**, to the extent of 20–25% of the mixed fraction. The red solid remaining was slightly soluble in CH_2Cl_2 and was shown to be $(\mu_3\text{-GeMe})_2Fe_3(CO)_9$ (**3a**; 29 mg, 0.047 mmol, 24%). Electron probe ratio for Ge:Fe: 2.0:3.1. Infrared spectrum: in CH_2Cl_2, ν(CO) 2013 vs, 1966 m cm^{-1}; in CsI disk, 2009 sh, 1992 vs, 1946 vs, 600 sh, 595 vs, 576 vs, 525 m cm^{-1}. Mass spectrum: highest envelope at m/e 592–601 (P^+); all ions $(P - nCO)^+$ for n = 0–9, $MeGe_2Fe_3(CO)_x{}^+$ for x = 3–0, and $Ge_2Fe_3{}^+$.

The reaction was repeated several times with $MeGeH_3$:$Fe_3(CO)_{12}$ ratios between 2.2:1 and 10:1, giving variable and unpre-

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Table IV. Final Positional Parameters for $(\mu_3\text{-GeEt})_2Fe_3(CO)_9$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Fe(1)	0.1506 (2)	0.1671 (2)	0.3999 (1)	C(13)	0.095 (2)	0.059 (2)	0.400 (1)
Fe(2)	−0.0134 (2)	0.2869 (2)	0.3047 (2)	O(13)	0.072 (2)	−0.017 (1)	0.399 (1)
Fe(3)	−0.0163 (2)	0.2814 (2)	0.4978 (2)	C(21)	−0.164 (3)	0.363 (1)	0.312 (1)
Ge(1)	−0.0997 (2)	0.1735 (1)	0.3972 (1)	O(21)	−0.251 (2)	0.412 (1)	0.314 (1)
C(1)	−0.255 (2)	0.089 (2)	0.388 (2)	C(22)	0.099 (2)	0.351 (2)	0.230 (1)
C(2)	−0.368 (3)	0.101 (2)	0.353 (2)	O(22)	0.158 (2)	0.391 (2)	0.179 (1)
Ge(2)	0.1797 (2)	0.3174 (1)	0.4071 (1)	C(23)	−0.083 (2)	0.221 (1)	0.213 (1)
C(3)	0.337 (3)	0.400 (2)	0.412 (2)	O(23)	−0.124 (1)	0.175 (1)	0.1541 (8)
C(4)	0.378 (4)	0.455 (2)	0.382 (3)	C(31)	0.029 (2)	0.386 (2)	0.549 (1)
C(11)	0.289 (2)	0.154 (1)	0.487 (1)	O(31)	0.060 (2)	0.447 (1)	0.585 (1)
O(11)	0.377 (2)	0.145 (1)	0.541 (1)	C(32)	0.030 (2)	0.222 (1)	0.601 (1)
C(12)	0.254 (2)	0.161 (2)	0.296 (2)	O(32)	0.060 (2)	0.186 (1)	0.6675 (9)
O(12)	0.317 (2)	0.158 (1)	0.230 (1)	C(33)	−0.202 (2)	0.294 (2)	0.516 (1)
				O(33)	−0.320 (2)	0.303 (1)	0.532 (1)

Table V. Final Positional Parameters for $(\mu_3\text{-SiFe(CO)}_2Cp)_2Fe_3(CO)_9$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Si(1)	0.9939 (1)	0.6194 (1)	0.1461 (1)	C(32)	1.0985 (4)	0.8945 (4)	0.2054 (1)
Si(2)	1.2144 (1)	0.8494 (1)	0.1031 (1)	O(32)	1.0523 (3)	0.9810 (3)	0.2255 (1)
Fe(1)	0.9858 (1)	0.8247 (1)	0.1082 (1)	C(33)	1.1573 (3)	0.6353 (4)	0.2220 (1)
Fe(2)	1.1597 (1)	0.6251 (1)	0.0925 (1)	O(33)	1.1571 (3)	0.5653 (3)	0.2546 (1)
Fe(3)	1.1681 (1)	0.7552 (1)	0.1754 (1)	C(41)	0.8564 (4)	0.5497 (5)	0.2276 (1)
Fe(4)	0.8531 (1)	0.4635 (1)	0.1729 (1)	O(41)	0.8540 (3)	0.6048 (4)	0.2627 (1)
Fe(5)	1.3633 (1)	0.9951 (1)	0.0742 (1)	C(42)	0.9953 (4)	0.3617 (4)	0.1854 (1)
C(11)	0.9995 (4)	0.9996 (5)	0.0967 (2)	O(42)	1.0862 (3)	0.2936 (3)	0.1925 (1)
O(11)	0.9961 (3)	1.1142 (4)	0.0905 (2)	C(1)	0.6551 (3)	0.4005 (3)	0.1802 (1)
C(12)	0.8432 (4)	0.8423 (5)	0.1433 (2)	C(2)	0.7272 (3)	0.2983 (3)	0.1570 (1)
O(12)	0.7515 (3)	0.8613 (4)	0.1651 (1)	C(3)	0.7737 (3)	0.3535 (3)	0.1142 (1)
C(13)	0.9051 (4)	0.7723 (4)	0.0539 (1)	C(4)	0.7304 (3)	0.4897 (3)	0.1109 (1)
O(13)	0.8474 (3)	0.7388 (3)	0.0201 (1)	C(5)	0.6570 (3)	0.5187 (3)	0.1517 (1)
C(21)	1.2511 (4)	0.6519 (4)	0.0409 (1)	C(51)	1.2875 (4)	0.9681 (4)	0.0174 (1)
O(21)	1.3091 (3)	0.6586 (3)	0.0064 (1)	O(51)	1.2385 (3)	0.9535 (3)	−0.0197 (1)
C(22)	1.0551 (4)	0.4990 (4)	0.0654 (1)	C(52)	1.4781 (4)	0.8599 (5)	0.0722 (1)
O(22)	0.9928 (3)	0.4175 (3)	0.0461 (1)	O(52)	1.1551 (3)	0.7756 (4)	0.0712 (1)
C(23)	1.2768 (4)	0.5241 (4)	0.1250 (1)	C(6)	1.2930 (3)	1.1937 (3)	0.0836 (1)
O(23)	1.3521 (3)	0.4557 (3)	0.1454 (1)	C(7)	1.3152 (3)	1.1301 (3)	0.1286 (1)
C(31)	1.3424 (4)	0.7855 (4)	0.1851 (1)	C(8)	1.4523 (3)	1.0939 (3)	0.1334 (1)
O(31)	1.4547 (3)	0.7995 (3)	0.1936 (1)	C(9)	1.5148 (3)	1.1352 (3)	0.0915 (1)
				C(10)	1.4163 (3)	1.1969 (3)	0.0607 (1)

Table VI. Final Positional Parameters for $(\mu_3\text{-GeFe(CO)}_2Cp)_2Fe_3(CO)_9$ (5b)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ge(1)	0.9903 (1)	0.6159 (1)	0.1477 (1)	O(32)	1.0535 (8)	0.9812 (9)	0.2266 (3)
Ge(2)	1.2135 (1)	0.8540 (1)	0.1024 (1)	C(33)	1.1583 (9)	0.640 (1)	0.2239 (4)
Fe(1)	0.9816 (1)	0.8254 (2)	0.1091 (1)	O(33)	1.1565 (8)	0.5691 (8)	0.2558 (3)
Fe(2)	1.1575 (1)	0.6250 (2)	0.0920 (1)	C(41)	0.853 (1)	0.534 (1)	0.2304 (5)
Fe(3)	1.1682 (1)	0.7548 (2)	0.1764 (1)	O(41)	0.8524 (8)	0.585 (1)	0.2668 (3)
Fe(4)	0.8492 (2)	0.4544 (2)	0.1752 (1)	C(42)	0.991 (1)	0.353 (1)	0.1865 (4)
Fe(5)	1.3633 (2)	1.0038 (2)	0.0726 (1)	O(42)	1.0819 (9)	0.2859 (9)	0.1938 (3)
C(11)	0.994 (1)	1.000 (1)	0.0974 (5)	C(1)	0.6560 (8)	0.385 (1)	0.1818 (3)
O(11)	0.9873 (9)	1.113 (1)	0.0911 (5)	C(2)	0.7278 (8)	0.290 (1)	0.1560 (3)
C(12)	0.838 (1)	0.844 (1)	0.1440 (5)	C(3)	0.7702 (8)	0.353 (1)	0.1144 (3)
O(12)	0.7477 (8)	0.859 (1)	0.1653 (4)	C(4)	0.7247 (8)	0.487 (1)	0.1145 (3)
C(13)	0.904 (1)	0.772 (1)	0.0551 (4)	C(5)	0.6540 (8)	0.507 (1)	0.1561 (3)
O(13)	0.8470 (8)	0.7361 (9)	0.0216 (3)	C(51)	1.289 (1)	0.976 (1)	0.0153 (4)
C(21)	1.250 (1)	0.653 (1)	0.0411 (4)	O(51)	1.2449 (8)	0.9588 (9)	−0.0223 (3)
O(21)	1.3072 (8)	0.6591 (9)	0.0063 (3)	C(52)	1.479 (1)	0.872 (1)	0.0713 (4)
C(22)	1.054 (1)	0.498 (1)	0.0648 (4)	O(52)	1.5565 (8)	0.787 (1)	0.0698 (3)
O(22)	0.9930 (8)	0.4156 (8)	0.0460 (3)	C(6)	1.2851 (8)	1.1951 (9)	0.0831 (3)
C(23)	1.276 (1)	0.526 (1)	0.1248 (5)	C(7)	1.3127 (8)	1.1338 (9)	0.1277 (3)
O(23)	1.3502 (9)	0.4581 (9)	0.1452 (3)	C(8)	1.4501 (8)	1.1055 (9)	0.1316 (3)
C(31)	1.339 (1)	0.788 (1)	0.1858 (4)	C(9)	1.5075 (8)	1.1492 (9)	0.0894 (3)
O(31)	1.4514 (8)	0.8023 (9)	0.1941 (3)	C(10)	1.4055 (8)	1.2046 (9)	0.0594 (3)
C(32)	1.096 (1)	0.894 (1)	0.2057 (4)				

dictable amounts of **1a**, **2a**, and **3a**. The yields of **1a** plus **2a** varied inversely with that of **3a**, and the latter ranged from a trace to 24%. A more reproducible preparation of **3a** is given below.

Reaction of $EtGeH_3$ with $Fe_3(CO)_{12}$. Similarly, $EtGeH_3$ (2.7 mmol) and $Fe_3(CO)_{12}$ (326 mg, 0.65 mmol), reacted at 50 °C for 48 h, gave incondensable gases (H_2, 1.71 mmol; CO, 0.77 mmol) and a red solution. Removal of solvent gave a red residue that was completely soluble in pentane; an infrared spectrum indicated a mixture of **1b**, **2b**, and **3b**. Chromatography on a short Florasil column led to decomposition of **1b** but gave pure fractions of $(\mu\text{-GeEtH})_3Fe_2(CO)_6$ (**2b**; 100 mg, 18%; Ge:Fe ratio 2.0:3.3; infrared spectrum (pentane) ν(CO) 2007 vs, 1964 vs cm^{-1}; mass spectrum envelopes at *m/e* 580–593 (P^+), all ions $Et_3Ge_3H_3Fe_3(CO)_{6-x}{}^+$ (x = 6–0)) and $(\mu_3\text{-GeEt})_2Fe_3(CO)_9$ (**3b**; 0.051 g, 0.082 mmol, 13%; infrared spectrum (pentane) ν(CO) 2014 vs, 1963 m cm^{-1}; mass spectrum envelopes *m/e* 622–628 (P^+), all ions $Et_2Ge_2Fe_3(CO)_{9-x}{}^+$ (x = 0–9), together with $EtGe_2Fe_3{}^+$ and $Ge_2Fe_3{}^+$; the compound was further identified by a single-crystal X-ray structure determination (see below)). The yield of **3b** was reduced in a 24-h reaction and was zero when a temperature of 70 °C was used.

Reaction of $MeGeH_3$ with $Fe(CO)_5$. $MeGeH_3$ (0.55 mmol) and $Fe(CO)_5$ (3 mL, 23 mmol) were heated at 135 °C for 180 min. When the red solution was cooled, purple-red crystals were deposited, and incondensable gases were measured (2.65 mmol; average M_r 19.4). The solvent, together with unreacted $Fe(CO)_5$ and $MeGeH_3$, was pumped away, leaving a deep red residue. Extraction with pentane (5 × 5 mL) removed $Ge[Fe_2(CO)_8]_2$ (**4a**;[11] 91 mg, 0.12 mmol, 22%). The remaining purple-red solid was $(\mu_3\text{-GeMe})_2Fe_3(CO)_9$ (**3a**; 80 mg, 0.134 mmol, 48% based on $MeGeH_3$) characterized as above. A similar reaction for 2 h at 145 °C gave only 31% of **3a** and a slightly enhanced yield of **4a** (25%).

Reaction of $RSiH_3$ (R = Me, Et) with $Fe_3(CO)_{12}$. The reactions were carried out in a manner analogous to that for the corresponding germanes. Reactions were slower; at least 14 days was needed at 50 °C to discharge the $Fe_3(CO)_{12}$ color. In each case a mixture of products with infrared spectral features appropriate for the silicon analogues of **1**, **2**, and **3** was obtained, but complete decomposition occurred on attempted separation and no definite characterization was possible.

Reaction of $MeSiH_3$ with $Fe(CO)_5$. $MeSiH_3$ (0.55 mmol) and $Fe(CO)_5$ (3 mL, 23 mmol), heated at 140 °C for 90 min, gave purple-red crystals on cooling. Incondensable gases (1.85 mmol; average M_r 19.1) and unreacted $Fe(CO)_5$ and $MeSiH_3$ were removed. The products soluble in petroleum ether were mainly $Si[Fe_2(CO)_8]_2$ (**4b**; 87 mg, 0.125 mmol, 23%), while the remaining red solid was tentatively characterized as $(\mu_3\text{-SiMe})_2Fe_3(CO)_9$ (47 mg, 0.093 mmol, 34%; ν(CO) (CH_2Cl_2) 2016 vs, 1967 m cm^{-1}), but full characterization was hampered by ready decomposition, which gave $Fe_3(CO)_{12}$ among other species. This reaction was reproducible at 140 °C, did not occur at 70 °C, and gave metallic deposits at 220 °C.

Reaction of $PhSiH_3$ with $Fe(CO)_5$. A similar reaction of $PhSiH_3$ with $Fe(CO)_5$ at 150 °C for 120 min gave a red mixture that appeared to contain a mixture of $Si[Fe_2(CO)_8]_2$ (**4b**) and $(\mu_3\text{-SiPh})_2Fe_3(CO)_9$ (ν(CO) 2014 vs, 1965 m cm^{-1}), which could not be readily separated as the solubilities were similar and the latter complex was unstable.

Reaction of SiH_4 with $Fe(CO)_5$ and $[Fe(CO)_2Cp]_2$. A mixture of $Fe(CO)_5$ (3 mL, 23 mmol), $[Fe(CO)_2Cp]_2$ (102 mg, 0.29 mmol), and SiH_4 (0.66 mmol) was heated at 150 °C for 90 min, giving red crystals. Incondensable gases (H_2, 0.98 mmol; CO, 1.90 mmol), unreacted $Fe(CO)_5$ and SiH_4, and solvent were removed. The residue was extracted with pentane (5 × 5 mL) to remove $Si[Fe_2(CO)_8]_2$ (**4b**) together with an unidentified product with ν(CO) 2054 s, 2032 w, 2005 vs, 1952 m, 1773 m cm^{-1} total yield 135 mg. The remaining pentane-insoluble and dichloromethane-soluble product was $[\mu_3\text{-Si}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (**5a**; 162 mg, 0.195 mmol, 67%; infrared spectrum (CH_2Cl_2) ν(CO) 2053 m, 2033 s, 2018 m, 1999 vs, 1948 s, br cm^{-1}; NMR spectra ($CDCl_3$) ^1H δ 5.29 s, ^{13}C δ 85.8 (C_5H_5), 214.7 ($Fe(CO)_3$), and 210.5 ($Fe(CO)_2$); no ^{29}Si signal could be detected with the available instrument; mass spectrum *m/e* 830 ((P)$^+$), all ions $C_{10}H_{10}Si_2Fe_5(CO)_{13-x}^+$ (x = 0–13), other ions 402 (($C_5H_5Si_2Fe_2)^+$), 334 (($Si_2Fe_5)^+$), 279 (($Si_2Fe_4)^+$), 252 (($SiFe_4)^+$)). The compound was further characterized by a single-crystal X-ray structure determination (see below). The reaction was reproducible at similar temperatures and times.

Reaction of GeH_4 with $Fe(CO)_5$ and $[Fe(CO)_2Cp]_2$. Similarly, a mixture of $Fe(CO)_5$ (3 mL, 23 mmol), $[Fe(CO)_2Cp]_2$ (102 mg, 0.29 mmol), and GeH_4 (0.77 mmol), heated at 150 °C for 160 min, also gave red crystals. Unreacted $Fe(CO)_5$ and a trace of GeH_4 were removed with the solvent. The residue was extracted with pentane (10 × 10 mL) to remove $Ge[Fe_2(CO)_8]_2$ (**4a**; 88 mg, 25% based on GeH_4). The remaining solid was extracted with dichloromethane to give $[\mu_3\text{-Ge}\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (**5b**; 91 mg, 35% based on $[Fe(CO)_2Cp]_2$), characterized by spectroscopy and by an X-ray study (see below). Infrared spectrum: (CH_2Cl_2): ν(CO) 2053 m, 2033 s, 2018 m, 1999 vs, 1948 s, br cm^{-1}. NMR spectra ($CDCl_3$): ^1H δ 5.32 s; ^{13}C δ 84.8 (C_5H_5), 214.6 ($Fe(CO)_3$), and 210.0 ($Fe(CO)_2$).

X-ray Crystallography. For all three structures space groups were assigned on the basis of precession photography. Accurate cell dimensions and intensity data were obtained with a Nicolet P3 diffractometer using graphite-monochromated Mo Kα X-rays (0.71069 Å). Crystallographic details are summarized in Table III. Absorption corrections were based on ϕ scans. Hydrogen atoms were included in calculated positions with common temperature factors. Solution (direct methods) and refinement (full-matrix least squares based on *F*) used the SHELXS-86 and SHELX-76 programs.[26] Positional parameters for **3b**, **5a**, and **5b** are given in Tables IV–VI, respectively, and selected bond parameters are given in Table I for **3b** and in Table II for **5a** and **5b**.

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Supplementary Material Available: Tables of thermal parameters, hydrogen atom positions, and all bond lengths and angles for structures **3b**, **5a**, and **5b** (12 pages); structure factor tables for structures **3b**, **5a**, and **5b** (45 pages). Ordering information is given on any current masthead page.

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(26) Sheldrick, G. M. SHELX-76: Program for X-ray Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976; SHELXS-86: Program for Solving Crystal Structures; University of Gottingen: Gottingen, West Germany, 1986.