

Improved syntheses of $M[Fe_2(CO)_8]_2$ ($M = Si, Ge$ or Sn) and the X-ray crystal structure of $Si[Fe_2(CO)_8]_2$

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Abstract

The reaction of MH_4 ($M = Si, Ge$) with $Fe_2(CO)_9$ in hexane gives $Si[Fe_2(CO)_8]_2$ or $Ge[Fe_2(CO)_8]_2$ in 61 or 43% yield, respectively. A reproducible synthesis of $Sn[Fe_2(CO)_8]_2$ from “[$Fe_2(CO)_8$] $^{2-}$ ” and $SnCl_4$ in thf is also described. The X-ray crystal structure of $Si[Fe_2(CO)_8]_2$ shows two mutually perpendicular $SiFe_2$ triangles linked at the common *spiro*-silicon atom, with each iron atom carrying four terminal CO ligands. Average bond lengths are: Fe–Si 2.345(4), Fe–Fe 2.795(3) Å.

Introduction

The synthesis and structure of the cluster $Sn[Fe_2(CO)_8]_2$ (**1c**) was reported in 1967 [1,2]. It was initially prepared in $\leq 16\%$ yield by vigorous reaction of Bu_3SnCl with $Fe(CO)_5$, but could also be isolated in 25% yield from a $SnCl_4$ /“ $Fe(CO)_4$ ” $^{2-}$ system. The germanium analogue $Ge[Fe_2(CO)_8]_2$ (**1b**) was briefly described soon after [3], and then in 1983 was structurally characterised by two groups independently [4,5]. The Russian workers [4] isolated **1b** in 4% yield from a $(CH_2=CH)_4Ge/Fe_2(CO)_9$ reaction, while the German synthesis [5] from $Ge[Mn(CO)_2(MeCp)]_2$ and $Fe_2(CO)_9$ gave 4–8% yields. The silicon analogue $Si[Fe_2(CO)_8]_2$ (**1a**) has also been briefly described in the Russian literature [6]. Very recently the lead analogue $Pb[Fe_2(CO)_8]_2$ (**1d**) has been synthesised in moderate

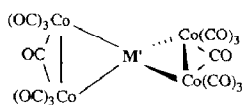


(**1a**, $M' = Si$;

1b, $M' = Ge$;

1c, $M' = Sn$;

1d, $M' = Pb$)



(**2a**, $M' = Si$;

2b, $M' = Ge$)

yields and structurally characterised [7]. Thus the complete set of clusters $M[Fe_2(CO)_8]_2$ for $M = Si, Ge, Sn, Pb$ is known, but the first two members in particular cannot be regarded as being readily available for reactivity studies.

We previously found that the closely related cobalt analogues $M[Co_2(CO)_7]_2$ (2 , $M = Si, Ge$) are useful precursors for higher clusters incorporating main group IV atoms [8–10]. To extend our studies into the iron system we needed to develop better routes to the complexes **1**, and we now describe improved syntheses of **1a–c**. We have also determined the structure of **1a** to allow comparisons between **a–d**.

Experimental

Volatile reagents were handled in a standard vacuum line and other manipulations were performed under nitrogen by standard Schlenk techniques. GeH_4 was prepared by slight modification of published method [11], and SiH_4 [CARE] was produced by $LiAlH_4$ reduction of $SiCl_4$. Chromatography was performed on a Chromatotron (Harrison Research) with silica gel plates.

*Preparation of $Si[Fe_2(CO)_8]_2$ (**1a**)*

$Fe_2(CO)_9$ (0.85 g, 2.34 mmol), SiH_4 (1.0 mmol) and hexane (7 ml) were sealed in a thick-walled 50 ml Pyrex ampoule. After 7 d at $30^\circ C$ the ampoule was opened and the contents transferred to a Schlenk tube and evaporated. The volatile material contained no unchanged SiH_4 , while $Fe(CO)_5$ (20–30% of iron) was found in the hexane fraction. Chromatography of the residue on silica plates, with hexane as eluant gave orange $Si[Fe_2(CO)_8]_2$, (0.43 g, 61% based on silicon). *Infrared*: $\nu(CO)$ (hexane) 2076m, 2050vs, 2030w, 2013m; $\nu(CO)$ (CsI disc) 2109vw, 2080s, 2065m,sh, 2049vs,br, 2028m,sh, 2011vs, 1987s, 1968m. *Raman*: $\nu(CO)$ (solid) 2112s, 2079m, 2051m, 2035w, 2025vs, 2016w, 2006s, 1996m, 1983ms. Mass spectrum: m/z 700 (P^+), all ions $SiFe_4(CO)_n$ $n = 16–0$. The compound was further characterised by an X-ray crystal structure (see below).

Similar procedures with up to a 25% excess of $Fe_2(CO)_9$ gave yields above 55%, while use of $SiH_4/Fe_2(CO)_9$ ratios of 1/2 or less gave 27–32% yields.

*Preparation of $Ge[Fe_2(CO)_8]_2$ (**1b**)*

A 200 ml vessel fitted with a greaseless tap was charged with $Fe_2(CO)_9$ (0.97 g, 2.7 mmol) and hexane (50 ml). The vessel was cooled (77 K), and evacuated on a vacuum line. GeH_4 (0.44 mmol) was condensed in and the mixture was warmed to room temperature in the closed ampoule. The vessel was then immersed in an oil bath at $65^\circ C$ for 15 min, after which the solution was brown-yellow and little solid $Fe_2(CO)_9$ remained. The vessel was re-attached to the vacuum line and incondensable gases removed with a Toepler pump (H_2 0.89 mmol, CO 0.122 mmol). Pumping removed hexane and appreciable amounts of $Fe(CO)_5$ together. The residue was chromatographed, with pentane as eluant, to give, in order of elution, green $Fe_3(CO)_{12}$ (0.20 g, 0.40 mmol), yellow $Ge[Fe_2(CO)_8]_2$ (**1b**), (recrystallised from pentane to give red crystals with properties identical to those in the literature [3–5], 0.14 g, 43%), two minor unidentified species, and an orange compound which appears to be the higher homologue of **1b**, $Ge_2Fe_6(CO)_{23}$ (ca. 10%).

The reaction was repeated with different $\text{GeH}_4/\text{Fe}_2(\text{CO})_9$ ratios, and different conditions but yields were always poorer (e.g. 25 °C for 10 d, 5% of **1b**; 30 °C for 10 d, 10% of **1b**; 50 °C for 8 d, 19% of **1b**).

*Preparation of $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2$ (**1c**)*

(a) *From mixed anions in thf.* On a vacuum line $\text{Fe}(\text{CO})_5$ (1.3 ml, 9.96 mmol) was condensed on to thf (50 ml) over a 1% sodium amalgam. The mixture was stirred for 3 h at room temperature. The resulting red mixture containing $[\text{Fe}_2(\text{CO})_8]^{2-}$, and a suspension of $\text{Na}_2\text{Fe}(\text{CO})_4$ was decanted from the amalgam into SnCl_4 (0.14 ml, 1.19 mmol) in thf (20 ml). The mixture was stirred under N_2 for 18 h, and the volatiles were then pumped away. The residue was extracted with 2×50 ml aliquots of CHCl_3 to give a solution containing **1c** and $[\text{HFe}_3(\text{CO})_{11}]^-$ (by IR). Silica gel was added to the mixture to absorb the ionic product, the solution was filtered, and the silica gel was washed with CH_2Cl_2 (200 ml). The combined filtrates were evaporated to give spectroscopically pure $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2$, 0.60 g, 64% based on Sn.

(b) *From $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$ in thf.* Sodium metal (0.26 g, 11.3 mmol) was dissolved in liquid ammonia (ca. 20 ml, -63°C) on a vacuum line. $\text{Fe}(\text{CO})_5$ (0.64 g, 4.7 mmol) was distilled over in small portions until the blue colour was discharged, giving $\text{Na}_2[\text{Fe}(\text{CO})_4]$. An equivalent of $\text{Fe}(\text{CO})_5$ was added, and the mixture kept at -63°C for 2 h. The ammonia was evaporated and the residue of $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$ dissolved in thf (50 ml). The solution was added to SnCl_4 (0.13 ml, 1.13 mmol) in thf (20 ml) under nitrogen and the mixture stirred for 20 h. Worked-up as described above gave $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2$ (0.14 g, 16% based on Sn).

(c) *From $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{CO})_8]$ in CH_2Cl_2 .* A mixture of SnCl_4 (0.11 g, 0.43 mmol) and $[\text{Et}_4\text{N}]_2[\text{Fe}_2(\text{CO})_8]$ (0.17 g, 0.29 mmol) in CH_2Cl_2 was stirred for 1.5 h then evaporated. The hexane extract of the residue was chromatographed on silica to give $\text{Fe}_3(\text{CO})_{12}$ (0.018 g, 18% of Fe), and $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2$ (0.019 g, 17% of Fe). The hexane-insoluble products contained $[\text{Cl}_3\text{SnFe}(\text{CO})_4]^-$ (identified by IR [14]) and red $[\text{HFe}_3(\text{CO})_{11}]^-$.

The reaction was repeated with 1/1 and 1/2 $\text{SnCl}_4/[\text{Fe}_2(\text{CO})_8]^{2-}$ ratios, but even lower yields of **1c** were obtained.

(d) *From $[\text{Fe}(\text{CO})_4]^{2-}$.* A suspension of essentially white $\text{Na}_2[\text{Fe}(\text{CO})_4]$ in thf (made by sodium–liquid ammonia reduction of $\text{Fe}(\text{CO})_5$) was treated with SnCl_4 . After overnight stirring the reaction was worked up to give only traces of $\text{Sn}[\text{Fe}_2(\text{CO})_8]_2$, along with $\text{Fe}_3(\text{CO})_{12}$ and $[\text{Cl}_3\text{SnFe}(\text{CO})_4]^-$.

*X-ray structure of $\text{Si}[\text{Fe}_2(\text{CO})_8]_2$ (**1a**)*

Red needle-shaped crystals were obtained from CH_2Cl_2 /hexane. Preliminary precession photography showed the crystals to be isomorphous with those of the germanium analogue [4]. Intensity data were obtained on a Nicolet XRD P3 diffractometer using monochromated Mo-K_α X-rays.

Crystal data. $\text{C}_{16}\text{Fe}_4\text{O}_{16}\text{Si}$, M 699.64, monoclinic, space group $P2_1/c$, a 9.655(4) $\text{\AA}$, b 11.933(4) $\text{\AA}$, c 20.695(5) $\text{\AA}$, β 98.47(3)°, U 2358(1) $\text{\AA}^3$. D_c 1.97 g cm^{-3} for $Z = 4$. $F(000)$ 2052, $\mu(\text{Mo-K}_\alpha)$ 26 cm^{-1} , T 23 °C, crystal size 0.44 $\times$ 0.16 $\times$ 0.10 mm. Intensity data in the range $4^\circ < 2\theta < 45^\circ$ were collected using a θ – 2θ scan technique. Absorption corrections were applied based on a series of azimuthal

Table 1

Final positional parameters for $\text{Si}[\text{Fe}_2(\text{CO})_8]_2$

Atom	x	y	z	Atom	x	y	z
Si(1)	0.7022(3)	0.2434(3)	0.3886(2)	O(23)	0.444(1)	0.022(1)	0.3903(6)
Fe(1)	0.7350(2)	0.2317(2)	0.5028(1)	C(24)	0.510(2)	0.408(2)	0.4201(8)
Fe(2)	0.4805(2)	0.2618(2)	0.4213(1)	O(24)	0.519(1)	0.505(1)	0.4154(6)
Fe(3)	0.7783(2)	0.1249(2)	0.3101(1)	C(31)	0.846(2)	0.106(1)	0.2327(8)
Fe(4)	0.8107(2)	0.3573(2)	0.3185(1)	O(31)	0.887(1)	0.090(1)	0.1847(6)
C(11)	0.662(2)	0.239(1)	0.5798(7)	C(32)	0.745(1)	−0.017(1)	0.3320(6)
O(11)	0.619(1)	0.239(1)	0.6269(5)	O(32)	0.727(1)	−0.1071(9)	0.3486(5)
C(12)	0.915(2)	0.203(2)	0.5304(7)	C(33)	0.944(2)	0.112(1)	0.3614(8)
O(12)	1.029(1)	0.189(2)	0.5487(7)	O(33)	1.048(1)	0.098(1)	0.3942(7)
C(13)	0.713(2)	0.083(2)	0.4917(7)	C(34)	0.599(2)	0.139(1)	0.2690(7)
O(13)	0.708(2)	−0.011(1)	0.4864(6)	O(34)	0.487(1)	0.1413(8)	0.2431(5)
C(14)	0.769(2)	0.382(2)	0.5014(7)	C(41)	0.900(2)	0.362(1)	0.2476(8)
O(14)	0.800(2)	0.474(1)	0.5025(6)	O(41)	0.951(1)	0.364(1)	0.2011(5)
C(21)	0.381(1)	0.265(1)	0.4906(7)	C(42)	0.806(2)	0.499(1)	0.3418(8)
O(21)	0.321(1)	0.2662(9)	0.5336(5)	O(42)	0.803(1)	0.591(1)	0.3553(6)
C(22)	0.349(2)	0.281(2)	0.3526(9)	C(43)	0.963(2)	0.343(1)	0.3787(7)
O(22)	0.264(1)	0.295(1)	0.3119(6)	O(43)	1.061(1)	0.3432(9)	0.4184(5)
C(23)	0.464(2)	0.115(1)	0.4052(8)	C(44)	0.635(2)	0.374(1)	0.2752(7)
O(44)	0.524(1)	0.3901(8)	0.2493(5)				

scans. A total of 3076 unique reflexions were collected and those 1581 for which $I > 2\sigma(I)$ were used in all calculations.

The positions of the metal atoms in the isomorphous germanium analogue [4] were used as a starting set, and other atoms were found routinely in subsequent difference maps. In the final cycles of full-matrix least-squares refinement all the atoms were assigned anisotropic temperature factors. The refinement converged at $R = 0.069$ $R_w = 0.058$ where $w = [\sigma^2(F) + 0.0003F^2]^{-1}$, with no final shifts greater than 0.01σ , and with no residual electron density $> 0.6 \text{ e } \text{\AA}^{-3}$. Calculations were performed using SHELX-76 [12]. The final positional parameters are given in Table 1, and bond lengths and angles in Table 2.

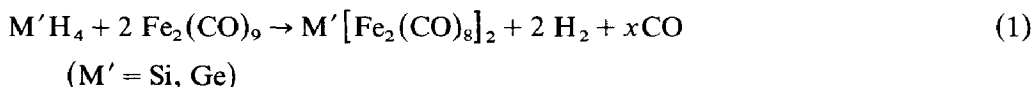
Table 2

Selected bond lengths (Å) and angles (°) for $\text{Si}[\text{Fe}_2(\text{CO})_8]_2$

Si–Fe(1)	2.342(4)	Si–Fe(2)	2.348(4)
Si–Fe(3)	2.352(4)	Si–Fe(4)	2.345(4)
Fe(1)–Fe(2)	2.792(3)	Fe(3)–Fe(4)	2.793(3)
Fe(1)–C(11)	1.83(1)	Fe(1)–C(12)	1.78(1)
Fe(1)–C(13)	1.79(1)	Fe(1)–C(14)	1.82(1)
Fe(2)–C(21)	1.84(1)	Fe(2)–C(22)	1.78(1)
Fe(2)–C(23)	1.79(1)	Fe(2)–C(24)	1.77(1)
Fe(3)–C(31)	1.83(1)	Fe(3)–C(32)	1.79(1)
Fe(3)–C(33)	1.79(1)	Fe(3)–C(34)	1.82(1)
Fe(4)–C(41)	1.81(1)	Fe(4)–C(42)	1.75(1)
Fe(4)–C(43)	1.79(1)	Fe(4)–C(44)	1.81(1)
Fe(1)–Si–Fe(2)	73.1(1)	Fe(3)–Si–Fe(3)	73.0(1)
Si–Fe(1)–Fe(2)	53.6(1)	Si–Fe(2)–Fe(1)	53.4(1)
Si–Fe(3)–Fe(4)	53.4(1)	Si–Fe(4)–Fe(3)	53.6(1)

Results and discussion

The group IV hydride SiH_4 reacts cleanly with $\text{Fe}_2(\text{CO})_9$ in hexane to give the cluster **1a** (eq. 1) in good yields. A quantitative amount of H_2 was evolved, but most



of the CO was found in the by-product $\text{Fe}(\text{CO})_5$. The reaction can be carried out for several days at low temperatures, or for hours at higher temperatures (ca. 65°C) without markedly altering the yields. The reaction stoichiometry is likewise not very critical. The cluster is readily purified by chromatography, since the other, unidentified, product of the reaction is irreversibly absorbed on the silica gel.

In contrast the reaction of GeH_4 with $\text{Fe}_2(\text{CO})_9$ according to eq. 1 is temperamental and optimum yields are only obtained by use of higher temperatures and short reaction times (see Experimental). An excess of the iron carbonyl over the stoichiometric amount is required for reasonable yields, most of the surplus ending up as $\text{Fe}(\text{CO})_5$. Reaction times must be kept to a minimum so that little conversion of $\text{Fe}(\text{CO})_5$ into $\text{Fe}_3(\text{CO})_{12}$ occurs, since the latter cluster can only be separated from the $\text{Ge}[\text{Fe}_2(\text{CO})_8]_2$ product by careful chromatography. Nevertheless, with due attention to detail **1b** can be routinely obtained in yields of ca. 40%, which is a considerable improvement on previous syntheses. In the germanium system a second orange species is produced in 5–10% yields; this appears to be the higher homologue of **1b**, namely $\text{Ge}_2\text{Fe}_6(\text{CO})_{23}$ (cf. the corresponding cobalt carbonyl system [13]). Further details will be published when full characterisation is complete.

The mechanism of formation of the clusters **1a** and **1b** as in eq. 1 is not known, but in view of the common replacement of a $\mu\text{-CO}$ ligand by a $\mu\text{-GeR}_2$ group a stepwise reaction proceeding via $(\mu\text{-GeH}_2)\text{Fe}_2(\text{CO})_8$ can be envisaged.

The corresponding route to the tin cluster **1c** is hampered by the instability of SnH_4 . A recent alternative synthesis, involving oxidation of $\{\text{Sn}[\text{Fe}_2(\text{CO})_8][\text{Fe}(\text{CO})_4]_2\}^{2-}$, gives **1c** in only low overall yields [7], so we attempted to improve the salt elimination method of synthesis [1]. The original report claimed that **1c** could be prepared from SnCl_4 and $[\text{Fe}(\text{CO})_4]^{2-}$ in thf. However, we could only isolate very low yields by this route, using pure $[\text{Fe}(\text{CO})_4]^{2-}$ from Na/ NH_3 reduction of $\text{Fe}(\text{CO})_5$. Further enquiries * revealed that the 1967 studies used “ $[\text{Fe}(\text{CO})_4]^{2-}$ ” from a sodium-amalgam reduction of $\text{Fe}(\text{CO})_5$, which gave a highly-coloured mixture of iron-containing anions including $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Fe}_2(\text{CO})_8]^{2-}$. Using this approach we were able to isolate **1c** in 64% yields, with $[\text{HFe}_3(\text{CO})_{11}]^-$ as the other major product. This suggested that $[\text{Fe}_2(\text{CO})_8]^{2-}$ may be the key anion in the mixture. Accordingly we treated $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$ with SnCl_4 in thf, but **1c** was produced in only 16% yield. A similar reaction of $[\text{Et}_4\text{N}]_2[\text{Fe}_2(\text{CO})_8]$ with SnCl_4 in CH_2Cl_2 gave only 6% of **1c**, together with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Cl}_3\text{SnFe}(\text{CO})_4^-$. Hence the ill-defined mixture of anions produced in Na/Hg reduction of $\text{Fe}(\text{CO})_5$ gives the best results for reasons that are not clear, but may indicate the participation of an intermediate containing both Sn- $\text{Fe}(\text{CO})_4$ and Sn- $\text{Fe}_2(\text{CO})_8$ groups. We note

* We thank Dr. J.D. Cotton for extra details.

that the reaction of $\text{Fe}_2(\text{CO})_8^{2-}$ with Ph_2SnCl_2 does not give rise to SnFe_2 triangular units [15], although reaction with R_2CX_2 does give CFe_2 species [16]. It is reported [7] that GeCl_4 behaves like SnCl_4 , and did not give **1b** when reacted with $[\text{Et}_4\text{N}]_2[\text{Fe}_2(\text{CO})_8]$. There is therefore considerable unpredictability in these salt elimination syntheses, and optimisation of yields requires a largely empirical approach.

The physical and spectroscopic properties of $\text{Ge}[\text{Fe}_2(\text{CO})_8]_2$ have been described before [4,5], and those of the silicon analogue are very similar. Previous workers [1,3–5] have noted that only four carbonyl stretches appear in the infrared spectra of $\text{M}'[\text{Fe}_2(\text{CO})_8]_2$, in place of the seven modes predicted for overall D_{2d} symmetry. It was suggested therefore that the four-band pattern reflected local C_{2v} or C_s symmetry at each iron, and that coupling was minimal. However, the intensity pattern, with the dominance of the second highest frequency, is unlike that of $\text{R}_2\text{Fe}(\text{CO})_4$ compounds [17], and it is unlikely that interaction constants are negligible [18]. These suspicions were confirmed by the Raman spectrum of the silicon compound **1a**, where 10 out of the predicted 11 modes [$3 A_1 + B_1 + 3 B_2 + 4 E$, with A_2 inactive] are resolved. Similarly, a sample in a CsI disc shows five major bands and two resolved shoulders in the infrared. Strong infrared bands generally have weak Raman counterparts. Thus the $\text{Fe}(\text{CO})_4$ units do interact and the vibrations must be treated as a whole.

For comparison with the published structures of $\text{M}'[\text{Fe}_2(\text{CO})_8]_2$, $\text{M}' = \text{Ge}$ [4,5], Sn [2] and Pb [7], we have carried out an X-ray determination of $\text{Si}[\text{Fe}_2(\text{CO})_8]_2$.

The cluster consists of two near-orthogonal SiFe_2 triangles sharing a mutual apex at the silicon atom (Fig. 1). Each Fe atom carries four terminal CO ligands. The silicon complex is isomorphous with the germanium analogue, but not with the tin or lead species. All four structures are, however, very similar, and the main bond parameters are compared in Table 3. The obvious changes are a decrease in the $\text{M}'\text{--Fe}$ and in the $\text{Fe}\text{--Fe}$ bond lengths, and an increase in the $\text{Fe}\text{--M}'\text{--Fe}$ angle with

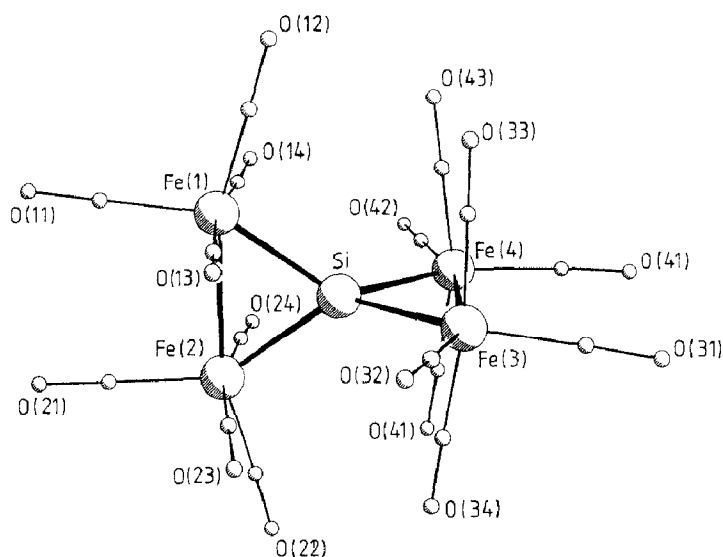


Fig. 1. The structure of $\text{Si}[\text{Fe}_2(\text{CO})_8]_2$ (**1a**).

Table 3
Structural features of clusters with a *spiro-M'M₄* core ^a

	Si[Fe ₂ (CO) ₈] ₂	Ge[Fe ₂ (CO) ₈] ₂	Sn[Fe ₂ (CO) ₈] ₂	Pb[Fe ₂ (CO) ₈] ₂	Si[Co ₂ (CO) ₇] ₂	Ge[Co ₂ (CO) ₇] ₂
M'-M (Å)	2.347	2.40	2.54	2.620	2.288	2.361
M-M (Å)	2.792	2.825	2.87	2.901	2.528	2.56
M-M'-M (°)	73	72	69	67	67	66
Dihedral angle (°) ^b	89	89	87	87	81	84
Reference	This work	4	2	7	8	9

^a Average values given; M' = Si, Ge, Sn or Pb; M = Fe or Co. Sn[Co₂(CO)₇]₂ does not exist. ^b Between M'M₂ triangles. Covalent radii are (Å): Si 1.17, Ge 1.22, Sn 1.40, Pb 1.44.

a decrease in the radius of the group IV element. The $\text{Si}[\text{Fe}_2(\text{CO})_8]_2$ cluster is compact, with $\text{CO} \cdots \text{CO}$ interactions between the two halves of the molecule similar to those between CO ligands on adjacent iron atoms. However, these are not sufficient to cause significant deviations from regular geometry, since the individual SiFe_2 triangles are symmetrical, and the dihedral angle between them is 89.4° . This contrasts with the situation for $\text{Si}[\text{Co}_2(\text{CO})_7]_2$ (**2a**) [9], in which there are two fewer CO ligands to accommodate but where the constraints of the bridging carbonyl ligand lead to less efficient packing, with concomitant distortions of the metal framework and a dihedral angle about the *spiro* silicon atom well removed from 90° (Table 3). The ease with which the two halves pack together may explain why replacement of one CO of triply-bridged $\text{Fe}_2(\text{CO})_9$ gives rise to the non-carbonyl-bridged $\text{Fe}_2(\text{CO})_8$ units of **1**, rather than to the isomer with two bridging CO groups. The absence of bridging carbonyls in clusters **1** allows the lengthening of the Fe–Fe bond (cf. $2.523 \text{ \AA}$ in $\text{Fe}_2(\text{CO})_9$ [19]) to accommodate the large group IV atom without too severe Fe–M'–Fe angular strain. For the related *spiro* cobalt carbonyl clusters (**2**) a non-carbonyl-bridged isomer is not possible, and this probably accounts for the non-existence of the Sn or Pb analogues of **2**. A *spiro* Sn or Pb atom would be too large to complete a triangle with two cobalt atoms already bridged by a carbonyl ligand. Finally, the Fe–C bond lengths in **1a** fall into three distinct groups; the four *trans* to the silicon atom are the longest, ($1.83(1) \text{ \AA}$), the eight *trans* to other carbonyls are intermediate ($1.80(1) \text{ \AA}$), and those opposite the Fe–Fe bonds are the shortest ($1.78(1) \text{ \AA}$).

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