

Synthesis and structures of doubly bridged bis(cyclopentadienyl) tetracarbonyl diiron complexes

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Abstract

A series of doubly bridged bis(cyclopentadienyl) tetracarbonyl diiron complexes (**7–13**) have been synthesized by the reaction of the corresponding ligand (**1–6**) with Fe(CO)₅ in refluxing xylene. It is unusual that the reaction of ligand (GeMe₂)(GeMe₂)(C₅H₄)₂ (**3**) with Fe(CO)₅ gave the complex (GeMe₂)[(η⁵-C₅H₄)Fe(CO)]₂(μ-CO)₂ (**10**) as the main product which lost the GeMe₂, only a small amount of the expected product (GeMe₂)₂[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**9**) was obtained. The molecular structures of **9** and (SiMe₂SiMe₂)₂[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**13**) have been determined by X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fe–Fe bond; Doubly bridged complexes; Cyclopentadienyl; Metal carbonyl

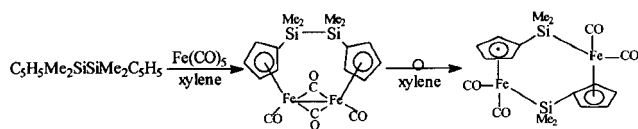
1. Introduction

Considerable attention has been focused on the synthesis and chemical behavior of a variety of bridged dinuclear metal–metal bonded transition-metal complexes [1–4]. These systems are suitable for studying interactions between two metal reaction sites that are in close proximity. In particular, we have been interested in bridged bis(cyclopentadienyl) tetracarbonyl diiron complexes in which two cyclopentadienyl ligands are linked together by certain alkyl or silyl groups [5–11]. We recently reported a novel rearrangement of the Si–Si and Fe–Fe bonds in a tetramethyldisilane-bridged

bis(cyclopentadienyl) dinuclear iron complex (Me₂SiSiMe₂)[(η⁵-C₅H₄)Fe(CO)]₂(μ-CO)₂ (Scheme 1) [12]. An alternative mechanism was subsequently proposed based on detailed investigation of the rearrangement stereospecificity, reaction intermediate, and cross-over reactions [13,14]. In order to study the reactivity of silicon- or germanium-containing doubly bridged analogues, we have synthesized a series of doubly bridged bis(cyclopentadienyl) tetracarbonyl diiron complexes **7–13**.

2. Experimental

Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon before use. THF and xylene were distilled from sodium/benzophenone ketyl and purged with argon atmosphere prior to use. ¹H-NMR spectra were obtained on a BRUKER AC-P200 spectrometer using CHCl₃ (δ: 7.24 ppm) as an internal standard. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Infrared spectra



Scheme 1.

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were obtained as KBr disks and recorded on a Nicolet 5DX FTIR spectrometer.

2.1. Preparation of

$(\text{SiMe}_2)(\text{SiMe}_2)[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**7**)

A solution of 3.8 g (15.6 mmol) of $(\text{SiMe}_2)(\text{SiMe}_2)(\text{C}_5\text{H}_4)_2$ (**1**) [15] and 2.7 ml (20 mmol) of $\text{Fe}(\text{CO})_5$ in 30 ml of xylene was refluxed for 12 h. After the removal of the solvent under reduced pressure, the residue, which was dissolved in a minimum of CH_2Cl_2 was chromatographed on an alumina column. Elution with petroleum ether– CH_2Cl_2 (1:1) developed a dark green band that afforded 1.11 g (24%) of **7** as dark green crystals. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$, δ ppm): 5.11 (s, 4H, C_5H_3), 4.86 (s, 2H, C_5H_3), 0.56 (s, 6H, SiCH_3), 0.45 (s, 6H, SiCH_3). IR (cm^{-1}): (ν_{co}) 1978 (s), 1944 (s), 1766 (s).

2.2. Preparation of

$(\text{SiMe}_2)(\text{GeMe}_2)[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**8**)

43 ml of *n*-BuLi (1.35 M, 58 mmol) hexane solution was added to the solution of 5.5 g (29 mmol) of $\text{C}_5\text{H}_5\text{SiMe}_2\text{C}_5\text{H}_5$ [16] in 100 ml of THF under 0°C . The mixture was stirred for 1 day at room temperature to give a white suspension of dilithium salts. To the suspension, 7.6 g (29 mmol) of Me_2GeBr_2 was added slowly. After stirring for 2 days at room temperature the solvents were removed under reduced pressure. The residue was extracted with pentane and the solvent was removed again. The residue was distilled under reduced pressure. The fraction of b.p. $120\text{--}140^\circ\text{C}/0.5$ mm Hg was collected to give 6.1 g of crude product. After recrystallization from pentane 4.2 g (50%) of $(\text{SiMe}_2)(\text{GeMe}_2)(\text{C}_5\text{H}_4)_2$ (**2**) was obtained as colorless crystals, m.p. $82.5\text{--}83.5^\circ\text{C}$. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$, δ ppm): 6.79 (s, 2H, C_5H_4), 6.69 (s, 2H, C_5H_4), 6.53 (s, 2H, C_5H_4), 4.00 (s, 2H, C_5H_4), 0.71, 0.54, 0.49, 0.35, 0.07, -1.24 (s, s, s, s, s, s, 12H, CH_3).

A solution of 0.8 g (3.0 mmol) of **2** and 1.4 ml (10 mmol) of $\text{Fe}(\text{CO})_5$ in 30 ml of xylene was refluxed for 10 h. Treatment as described above gave 0.33 g (21%) of **8** as dark green crystals, m.p. 226°C (dec.). Anal. Found: C, 42.03; H, 3.45. Calc. for $\text{C}_{18}\text{H}_{20}\text{Fe}_2\text{SiGeO}_4$: C, 42.33; H, 3.55%. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$, δ ppm): 5.22 (s, 2H, C_5H_3), 5.18 (s, 2H, C_5H_3), 5.14 (s, 1H, C_5H_3), 5.13 (s, 1H, C_5H_3), 0.87 (s, 3H, Ge–Me), 0.72 (s, 3H, Ge–Me), 0.58 (s, 3H, Si–Me), 0.41 (s, 3H, Si–Me). IR (cm^{-1}): (ν_{co}) 1765 (s), 1940 (s), 1976 (s).

2.3. Preparation of

$(\text{GeMe}_2)_2[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**9**)

A solution of 1.7 g (5.1 mmol) of $(\text{GeMe}_2)_2(\text{C}_5\text{H}_4)_2$ (**3**) [17] and 1.5 ml (12 mmol) of $\text{Fe}(\text{CO})_5$ in 30 ml of

xylene was refluxed for 10 h. Treatment as described above gave a green band and a red band. The first green band afforded 0.062 g (2%) of **9** as dark green crystals. The red band afforded 0.256 g (11%) of $(\text{GeMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**10**) [18] as deep red crystals. For **9**, m.p. 145°C (dec.). Anal. Found: C, 38.67; H, 3.17. Calc. for $\text{C}_{18}\text{H}_{18}\text{Fe}_2\text{Ge}_2\text{O}_4$: C, 38.94; H, 3.27%. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$, δ ppm): 5.48 (m, 2H, C_5H_3), 5.31 (m, 4H, C_5H_3), 1.02 (s, 6H, Ge–Me), 0.53 (s, 6H, Ge–Me). IR (cm^{-1}): (ν_{co}) 1974 (s), 1939 (s), 1911 (m), 1763 (s), 1731 (m). For **10**, $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$, δ ppm): 5.44 (s, 4H, C_5H_4), 4.97 (s, 4H, C_5H_4), 0.50 (s, 6H, Ge–Me).

2.4. Preparation of

$(\text{CMe}_2)(\text{SiMe}_2\text{SiMe}_2)[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**11**)

The ligand $(\text{CMe}_2)(\text{SiMe}_2\text{SiMe}_2)(\text{C}_5\text{H}_4)_2$ (**4**) was prepared by the reaction of 5.1 g (30 mmol) of $\text{C}_5\text{H}_5\text{CMe}_2\text{C}_5\text{H}_5$ [19] with 60 mmol of *n*-BuLi hexane solution and 5.6 g (30 mmol) of $\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$ [20] using a similar method with ligand **2**. After the removal of the solvents the residue was extracted with hexane. The solution was concentrated to give 8.2 g (95%) of **4** as a light yellow liquid. Ligand **4** was used without further purification.

A solution of 2.0 g (7.0 mmol) of **4** and 2.0 ml (15 mmol) of $\text{Fe}(\text{CO})_5$ in 30 ml of xylene was refluxed for 10 h. Treatment as described above gave 0.054 g (2%) of **11** as dark red crystals, m.p. 244°C (dec.). Anal. Found: C, 49.97; H, 4.76. Calc. for $\text{C}_{21}\text{H}_{24}\text{Fe}_2\text{Si}_2\text{O}_4$: C, 49.60; H, 4.76%. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$, δ ppm): 5.39 (s, 2H, C_5H_3), 5.32 (s, 2H, C_5H_3), 4.95 (s, 2H, C_5H_3), 1.64 (s, 3H, C–Me), 1.41 (s, 3H, C–Me), 0.69 (s, 3H, Si–Me), 0.32 (s, 3H, Si–Me). IR (cm^{-1}): (ν_{co}) 1981 (s), 1954 (s), 1774 (s).

2.5. Preparation of

$(\text{SiMe}_2)(\text{SiMe}_2\text{SiMe}_2)[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**12**)

A solution of 2.3 g (8.0 mmol) of $(\text{SiMe}_2)(\text{SiMe}_2\text{SiMe}_2)(\text{C}_5\text{H}_4)_2$ (**5**) [21] and 2.7 ml (20 mmol) of $\text{Fe}(\text{CO})_5$ in 30 ml of xylene was refluxed for 10 h. Treatment as described above gave 1.31 g (31%) of **12** as dark red crystals, m.p. 225°C (dec.). Anal. Found: C, 45.54; H, 4.70. Calc. for $\text{C}_{20}\text{H}_{24}\text{Fe}_2\text{Si}_3\text{O}_4$: C, 45.81; H, 4.61%. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$, δ ppm): 5.66 (s, 2H, C_5H_3), 5.31 (s, 2H, C_5H_3), 5.21 (s, 2H, C_5H_3), 0.66 (s, 9H, Si–Me), 0.33 (s, 3H, Si–Me), 0.26 (s, 6H, Si–Me). IR (cm^{-1}): (ν_{co}) 1982 (s), 1945 (s), 1769 (s).

2.6. Preparation of

$(\text{SiMe}_2\text{SiMe}_2)_2[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**13**)

A solution of 0.7 g (2.0 mmol) of $(\text{SiMe}_2\text{SiMe}_2)_2(\text{C}_5\text{H}_4)_2$ (**6**) [22] and 1.0 ml (7.0 mmol) of

Table 1
Crystallographic data for complexes for **9** and **13**

	9	13
Formula	C ₁₈ H ₁₈ Fe ₂ Ge ₂ O ₄	C ₂₂ H ₃₀ Fe ₂ O ₄ Si ₄
<i>M</i> (g mol ⁻¹)	555.22	582.52
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>Z</i>	4	4
<i>a</i> (Å)	15.072(3)	14.5440(16)
<i>b</i> (Å)	9.630(2)	12.3070(14)
<i>c</i> (Å)	14.854(3)	15.3357(16)
β (°)	117.57(3)	96.837(2)
<i>V</i> (Å ³)	1911(1)	2725.5(5)
Crystal size (mm)	0.25 × 0.30 × 0.35	0.20 × 0.15 × 0.10
<i>D</i> _{calc} (Mg m ⁻³)	1.930	1.420
<i>F</i> (000)	1096	1208
Temperature (K)	299 ± 1	293(2)
Scan type	ω -2 θ	ω -2 θ
μ (Mo-K α) (mm ⁻¹)	4.5844	1.265 (λ = 0.71073)
θ _{max} (°)	25	26.37
Reflections collected	1862	7742
Independent reflection	1523	2782
Goodness-of-fit	1.25	1.051
<i>R</i> _{int}	0.147	0.0480
Final <i>R</i> and <i>wR</i>	0.066 and 0.065	0.0409 and 0.0921
Maximum residual peak (e Å ⁻³)	1.03	0.352

Fe(CO)₅ in 30 ml of xylene was refluxed for 10 h. Treatment as described above gave 0.173 g (15%) of **13** as dark red crystals, m.p. 260°C (dec.). Anal. Found: C, 45.28; H, 5.16. Calc. for C₂₂H₃₀Fe₂Si₄O₄: C, 45.36; H, 5.19%. ¹H-NMR (CHCl₃-*d*, δ ppm): 5.72 (s, 2H, C₅H₃), 5.23, 5.22 (d, 4H, C₅H₃), 0.55 (s, 12H, Si-Me), 0.19 (s, 12H, Si-Me). IR (cm⁻¹): (ν_{co}) 1985 (s), 1943 (vs), 1760 (s), 1732 (vs).

2.7. Crystallographic studies

Crystals of **9** and **13** suitable for X-ray diffraction were obtained from CH₂Cl₂-hexane solution. All data were collected on an ENRAF-NONIUS CAD-4 diffractometer for **9** and BRUKER SMART 1000 for **13** with graphite monochromated Mo-K α radiation. The empirical absorption correction using the program DIFBAS was applied for **9**. All calculations were performed on PDP11/44 and Pentium MMX/166 computers using the SDP-PLUS or SHELXS-97 program system. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the refinement and calculations of structure factors. Neutral atom scattering factors were taken from the tabulation of Cromer and Waber [23]. A

Table 2
Selected bond distances (Å) and angles (°) for **9**

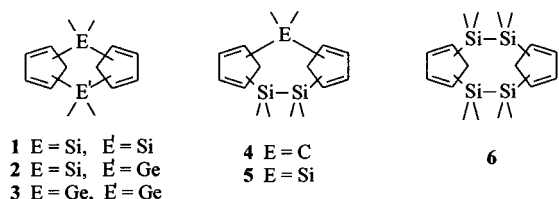
<i>Bond distances</i>					
Fe(1)–Fe(1a)	2.494(2)	Fe(1)–C(11)	2.110(8)	Fe(1)–C(15)	2.113(8)
Fe(1)–C(12)	2.125(12)	Fe(1)–C(13)	2.100(11)	Fe(1)–C(14)	2.121(8)
Ge(1)–C(11)	1.940(7)	Ge(1)–C(15a)	1.940(10)	Ge(1a)–C(15)	1.940(10)
Fe(1)–CEN ^a	1.748	Fe(1)–PL ^b	1.7479		
<i>Bond angles</i>					
Fe(1)–C(2)–Fe(1a)		81.4(4)	C(11)–Ge(1)–C(15a)		97.2(4)
Fe(1)–C(11)–Ge(1)		117.8(4)	Fe(1)–C(15)–Ge(1a)		117.2(4)
Fe(1a)–Fe(1)–CEN		124.8	PL–PLa		69.7

^a CEN, centroid of C(11)–C(15).

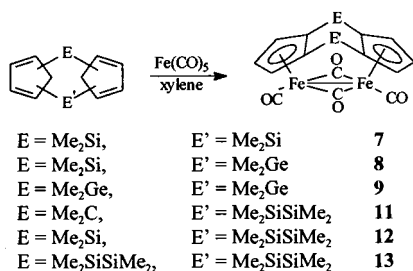
^b PL, plane of C(11)–C(15).

Table 3
Selected bond distances (Å) and bond angles (°) for **13**

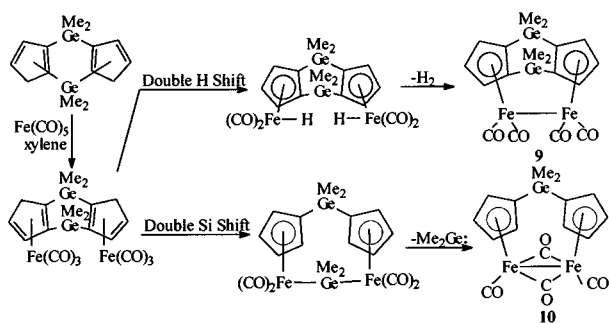
<i>Bond distances</i>					
Fe(1)–Fe(1a)	2.5440(8)	Fe(1)–C(11)	2.167(3)	Fe(1)–C(15)	2.166(3)
Fe(1)–C(12)	2.120(3)	Fe(1)–C(13)	2.100(3)	Fe(1)–C(14)	2.121(3)
Si(1)–Si(2a)	2.3565(12)	Si(2)–Si(1a)	2.3565(12)	C(15)–Si(1)	1.890(3)
Si(2)–C(11)	1.887(3)	Fe(1)–PL	1.7568		
<i>Bond angles</i>					
Fe(1)–C(2)–Fe(1a)		82.64(13)	Si(1)–C(15)–Fe(1)		128.45(14)
Si(2)–C(11)–Fe(1)		131.23(15)	C(11)–Si(2)–Si(1a)		115.42(9)
C(15)–Si(1)–Si(2a)		112.75(9)	PL–PLa		79.74(9)



Scheme 2.



Scheme 3.



Scheme 4.

summary of the crystallographic results is presented in Table 1. Selected bond distances and angles for **9** and **13** are given in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Synthesis of complexes 1–4

Ligands **1–6** were prepared by the reaction of the corresponding bridged cyclopentadiene with *n*-BuLi and the corresponding Me₂SiCl₂, Me₂GeBr₂ or ClMe₂SiSiMe₂Cl using literature methods or analogous methods (Scheme 2).

Ligand **1** reacted with Fe(CO)₅ in refluxing xylene for 10 h to give (SiMe₂)₂[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**7**) in high yield (24%) as dark green crystals (Scheme 3). Siemeling et al. [15] conducted the same reaction in refluxing methylcyclohexane for 44 h and obtained the product **7** in very poor yield (2.2%), showing that the yield is dependent on the reaction temperature, and increasing reaction temperature increases the yield.

The similar treatment of ligand **2** with Fe(CO)₅ also afforded the expected product (SiMe₂)₂(GeMe₂)[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**8**) in high yield (21%) as dark green crystals, which also further indicated that xylene was the suitable solvent for this reaction. While in the methylcyclohexane, even 4 days later, only a small amount of **8** was obtained, and meanwhile, more than 10 kinds of byproducts were produced, but the amount of each was too small to separate.

The reaction of ligand **3** with Fe(CO)₅ gave unexpected results. Complex (GeMe₂)[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**10**) (11%) is the main product which has lost a part of the bridge, i.e. GeMe₂. Only a small amount of expected product (GeMe₂)₂[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**9**) (2%) was isolated as dark green crystals. To explain the experimental results, the following possible mechanisms were suggested. When ligand **3** reacted with Fe(CO)₅, the ligand coordinated with two equivalents of Fe(CO)₅ to form the dinuclear π-complex at first. At this stage, if double hydrogen atoms were shifted, the dinuclear Fe–H intermediate was formed, which through the elimination of hydrogen led to form the diiron complex **9**. If double germyls were shifted, the FeGeMe₂Fe intermediate was formed, which eliminated the GeMe₂ to form the product **10** (Scheme 4). The weaker C–Ge bond and the larger strain in the molecular structures of doubly bridged diiron complexes than the corresponding singly bridged analogues make the second pathway much easier than other cases.

The reaction of ligand **4** with Fe(CO)₅ in the refluxing xylene for 10 h gave complex (CMe₂)(Me₂SiSiMe₂)[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**11**) in very poor yield (2%); while the analogous reaction of ligand **5** afforded complex (SiMe₂)(Me₂SiSiMe₂)[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**12**) in high yield (31%). This maybe because ligand **4** with the carbon and disilicon bridges has a larger twist angle between the Cp ring than ligand **5** with mono and disilicon bridges which might weaken the Fe–Fe bond and lead to polymerization of the units. The reaction of ligand **6** with Fe(CO)₅ gave the normal product (Me₂SiSiMe₂)₂[(η⁵-C₅H₃)Fe(CO)]₂(μ-CO)₂ (**13**) in 15% yield.

The current series of doubly bridged bis(cyclopentadienyl) tetracarbonyl diiron complexes **7–13** have been synthesized because these complexes have the similar structures with (Me₂SiSiMe₂)[(η⁵-C₅H₄)Fe(CO)]₂(μ-CO)₂ which can undergo the thermal rearrangement reaction found by our group [12]. The goal is to test the reactivity of silicon- or germanium-containing doubly bridged analogues concerning the rearrangement of singly bridged bis(cyclopentadienyl) diiron complexes. However, when complex **11**, **12** or **13** was heated in refluxing xylene for 20 h, or even in refluxing decahydronaphthalene for 10 h, no reaction was observed except the decomposition of the starting materials by TLC monitoring. This indicated that complexes **11–13**

cannot undergo the thermal rearrangement reaction between the Si–Si and Fe–Fe bonds. Based on our mechanism for the rearrangement reaction [13,14], iron radicals are formed through the thermal homolysis of Fe–Fe bond upon heating at first, then there is a suitable rotation about the Si–Si bond and concerted (or stepwise) attack of iron radicals at the Si–Si bond to complete the reaction. The suitable rotation along the Si–Si single bond was assumed to be a key requirement of the mechanism. For the doubly bridged bis(cyclopentadienyl) diiron complexes **11**–**13**, even if iron radicals could be formed during heating, they cannot be rotated along the Si–Si bond owing to the rigid structures of the doubly bridged ligands. So the iron radicals

cannot attack at the Si–Si bond to lead the rearrangement reaction. This further verified the mechanism suggested by us from the other aspect.

3.2. Crystal and molecular structures of complexes **9** and **13**

The crystal structures of **9** and **13** were determined by X-ray diffraction. The molecular structure of **9** is presented in Fig. 1. The molecular structure of **9** has C_2 symmetry. The Ge(1) and Ge(1a) atoms deviate from one Cp plane by 0.2179 and 0.2445 Å, respectively. The bridging ligand adopts a bent structure with a flat boat conformation of the central six-membered ring of Ge(1)–C(11)–C(15)–Ge(1a)–C(11a)–C(15a). The Fe–Fe bond is 2.494(2) Å, which is between the Fe–Fe bond length in $(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2$ [2.520 Å] [10]; $\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}_2(\text{CO})_4$ [2.484 Å] [11]. The dihedral angle between the two Cp planes is 69.7°, much smaller than those in $(\text{SiMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2](\mu\text{-CO})_2$ [97.2°] [10] and $(\text{CMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2](\mu\text{-CO})_2$ [109.5°] [11]. This can be attributed to the rigidity of the doubly bridged ligand and the flexibility of these large germanium atoms to accommodate distortions out of the Cp plane.

The molecular structure of **13** is presented in Fig. 2. The molecular structure of **13** also has C_2 symmetry. Si(1), Si(1a), Si(2) and Si(2a) are in a same plane and the eight-membered ring formed by the silicon atoms and bridge head carbon atoms takes a saddle conformation. The Fe–Fe [2.5440(8) Å] and Si–Si bond distances [2.3565(12) Å] are slightly longer than that in single-bridged compound $(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2$ [2.526(2), 2.346(4) Å] [12]. The dihedral angle between the two Cp planes is 79.74°, smaller than in $(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2$ [85.3°] [12] due to the rigidity of the doubly bridged ligand.

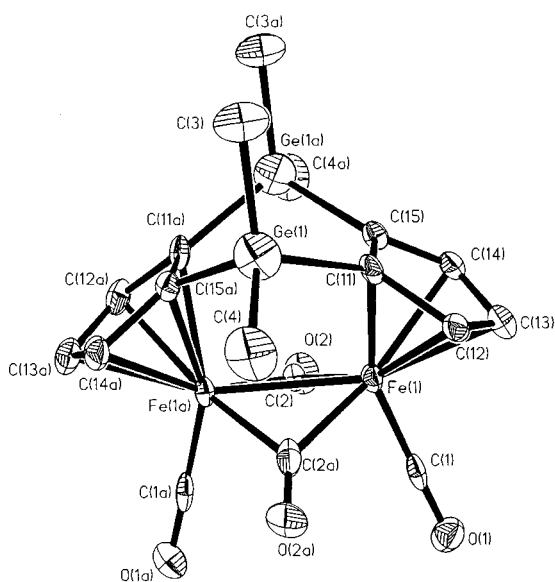


Fig. 1. ORTEP diagram of the molecular structure of $(\text{GeMe}_2)_2[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})_2](\mu\text{-CO})_2$ (**9**).

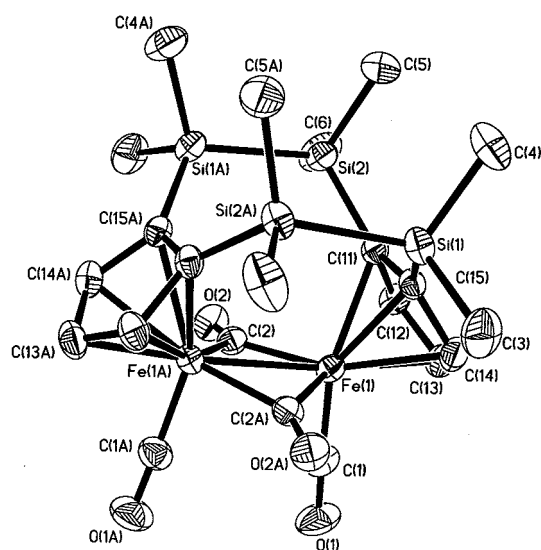


Fig. 2. ORTEP diagram of the molecular structure of $(\text{SiMe}_2\text{SiMe}_2)_2[(\eta^5\text{-C}_5\text{H}_3)\text{Fe}(\text{CO})_2](\mu\text{-CO})_2$ (**13**).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 152351 and 152352 for compounds **9** and **13**, respectively. Copies of this information may be obtained free of charge The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk of www: <http://www.ccdc.cam.ac.uk>).

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