Preliminary communication

Synthesis, characterization, and molecular structure of [(CH$_3$)$_2$C(C$_5$H$_4$)$_2$]Fe$_2$(μ-CO)$_2$(CO)$_2$

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Abstract

[(CH$_3$)$_2$C(C$_5$H$_4$)$_2$]Fe$_2$(μ-CO)$_2$(CO)$_2$ (1) has been synthesized from 2,2-dicyclopentadienyl propane and pentacarbonyliron in 26% yield. The crystal and molecular structure of 1 has been determined by X-ray diffraction. The molecule has the expected carbonyl-bridged structure with a *cis* configuration of the cyclopentadienyl rings. The Fe–Fe distance of 2.484 Å is the shortest one reported to date for ring-bridged dicyclopentadienyl di-iron tetracarbonyl complexes.

Keywords: Carbon monoxide; Cyclopentadienyl; Iron; Nuclear magnetic resonance; X-ray diffraction

Several ring-bridged di-iron tetracarbonyl complexes (Cp′–X–Cp′)Fe$_2$(CO)$_4$ (Cp′ = C$_5$H$_4$) have been reported, e.g. X = –SiMe$_2$– [1,2], –[SiMe$_2$]$_2$– [3], 2,4-B$_5$H$_5$C$_2$[SiMe$_2$]$_2$ [1], –CH$_2$– [4], –[CMe$_2$]$_2$– [5], –[CH(NMe$_2$)]$_2$– [6,7], –Me$_2$SiCH$_2$CH$_2$SiMe$_2$– [8], –Me$_2$SiOSi(C$_6$H$_5$)$_2$OSiMe$_2$– [9], –Me$_2$SiOSi-Me$_2$(C$_6$H$_4$)$_2$SiMe$_2$OSiMe$_2$– [9]. All of these ring-bridged complexes have a *cis* arrangement of the Cp rings, whereas in the case of the non-bridged complex Cp$_2$Fe$_2$(CO)$_4$ (Cp = C$_5$H$_5$) the *cis* and *trans* isomer are in equilibrium [10]. The structures of some of these complexes have been reported [1–3,7] by others, together with those of *cis*- and *trans*-Cp$_2$Fe$_2$(CO)$_4$ [10,11].

In order to expand our investigations of ring-bridged cyclopentadienyl iron–sulfur clusters [12], we synthesized a CMe$_2$-bridged dicyclopentadienyl di-iron tetracarbonyl complex [(CH$_3$)$_2$C(C$_5$H$_4$)$_2$]Fe$_2$(μ-CO)$_2$-(CO)$_2$ (1). The aim is to obtain a deeper insight into the structural constraints on going from SiMe$_2$-bridged to CMe$_2$-bridged species. Therefore, an X-ray structure analysis of 1 has been performed.

2,2-Dicyclopentadienyl propane, prepared by the method of Nifant'ev et al. [13] without further purification, was reacted with Fe(CO)$_5$ in refluxing toluene (Scheme 1). After work-up [14], pure 1 was obtained in 26% yield. In the IR spectrum of 1, two strong absorption bands are observed at 1995 and 1786 cm^{-1}, and one weak absorption band at 1958 cm^{-1}. This is consistent with a *cis*-Fe$_2$(μ-CO)$_2$(CO)$_2$ fragment. In the ^{1}H NMR spectrum one singlet at 1.35 ppm (6H) and an AB pattern at 5.03–5.12 ppm (8H) are observed, corresponding to the two isopropylidene methyl groups and the proximal and distal C$_5$H$_4$ protons respectively. The number of NMR signals reveals that 1 has at least C_{2v} symmetry in solution at room temperature [15].

Slow crystallization of 1 from toluene–hexane mixtures ultimately yielded red, shiny, needle-like single crystals suitable for X-ray diffraction [16]. The unit cell of 1 contains two crystallographically independent molecules, 1a and 1b, with slightly different geometry. Selected interatomic distances and angles for both molecules are given in Tables 1 and 2 respectively. The molecular structure is depicted in Fig. 1. The molecules of 1a and 1b have approximately C_s symmetry in the solid state, the mirror plane containing the bridging carbonyl ligands and the bridging carbon atom C(51). A comparable small deviation from C_s symmetry has been observed for *cis*-Cp$_2$Fe$_2$(CO)$_4$ [11] and (CH$_3$)$_2$-Si(C$_5$H$_4$)$_2$Fe$_2$(CO)$_4$ [1,2].

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Table 1
Selected interatomic distances (Å) for 1

	1a	1b
Fe(11)–Fe(12)	2.4836(6)	2.4838(6)
Fe(12)–C(10)	2.132(3)	2.125(3)
Fe(12)–C(11)	2.124(3)	2.117(3)
Fe(12)–C(12)	2.108(3)	2.097(3)
Fe(12)–C(13)	2.085(3)	2.090(3)
Fe(12)–C(14)	2.119(3)	2.126(3)
Fe(11)–C(30)	2.135(3)	2.126(3)
Fe(11)–C(31)	2.123(3)	2.122(3)
Fe(11)–C(32)	2.092(3)	2.092(3)
Fe(11)–C(33)	2.112(3)	2.114(3)
Fe(11)–C(34)	2.130(3)	2.129(3)
Fe(11)–Cp	1.740(2) [a]	1.740(2) [a]
Fe(12)–Cp	1.734(2) [a]	1.732(2) [a]
Fe(11)–C(54)	1.941(3)	1.919(3)
Fe(11)–C(55)	1.925(3)	1.930(3)
Fe(11)–C(56)	1.750(3)	1.753(3)
Fe(12)–C(54)	1.918(3)	1.918(3)
Fe(12)–C(55)	1.920(3)	1.905(3)
Fe(12)–C(57)	1.756(3)	1.752(3)
O(11)–C(54)	1.170(3)	1.181(3)
O(12)–C(55)	1.179(3)	1.179(3)
O(13)–C(56)	1.152(3)	1.148(3)
O(14)–C(57)	1.149(3)	1.154(4)
C(51)–C(52)	1.530(4)	1.533(5)
C(51)–C(53)	1.541(4)	1.531(5)
Cp–Cp [b]	4.434(3)	4.449(3)

[a] Distance to plane. [b] Distance between centroids.

The C_{2v} symmetry of 1 in solution, as deduced from NMR data (vide supra), is apparently not maintained in the solid state.

The distortion from C_{2v} symmetry can best be seen in the projection view along the Fe–Fe bond (Fig. 2). The bridging group is turned away from the Fe₂(terminal-CO)₂ plane by 13.14(6)° for 1a and 11.59(8)° for 1b. The same effect is found in (CH₃)₂Si(C₅H₄)₂- Fe₂(CO)₄ (13.6°) and other compounds containing (CH₃)₂Si(C₅H₄)₂M₂ fragments [15]. As a consequence, C(51) has moved by 0.68 Å for 1a and 0.60 Å for 1b out of the Fe₂(terminal-CO)₂ plane, and therefore one of the methyl groups (C(52)) lies almost in the Fe₂(terminal-CO)₂ plane. The bridging group turning away from the Fe₂(terminal-CO)₂ plane forces the Cp ligands closer together. The distance between the centroids of the Cp ligands in 1 (4.44 Å) is shorter than in cis-Cp₂Fe₂(CO)₄ (5.02 Å). It is also shorter than in

Table 2
Selected angles (°) for 1

	1a	1b
C(10)–C(51)–C(30)	109.6(2)	109.5(2)
C(52)–C(51)–C(53)	108.7(2)	108.8(3)
C(54)–Fe(11)–C(55)	94.28(12)	94.37(12)
Fe(11)–C(54)–Fe(12)	80.12(11)	80.69(11)
Cp–Cp [a]	109.6(1)	109.3(1)

[a] Angle between least-squares planes.
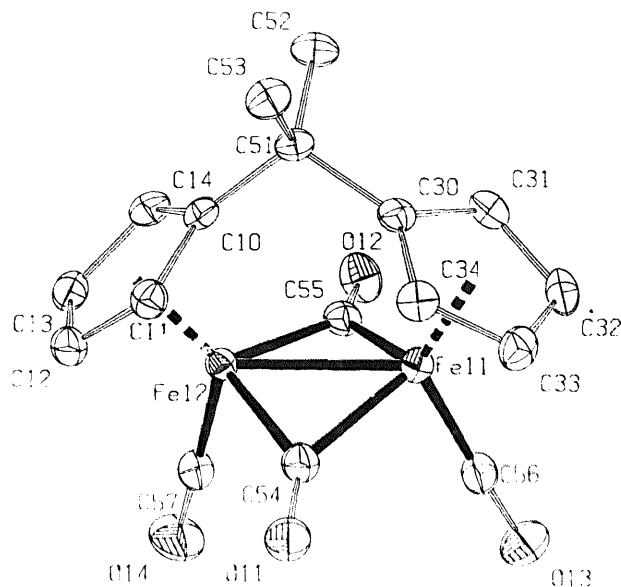
Fig. 1. ORTEP drawing [22] of one of the two independent molecules of Me₂CCp′₂Fe₂(CO)₄ (1) with atom labeling. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at 50% probability.

(CH₃)₂Si(C₅H₄)₂Fe₂(CO)₄ (4.77 Å), which is obviously the result of the smaller atomic radius of the bridging carbon atom compared with silicon, since their position out of the Fe₂(terminal-CO)₂ plane is similar.

Three factors govern the spatial position of the Cp ligands: (i) orientation of the substituents around the bridging atom; (ii) bending of the bridging atom out of the Cp plane; and (iii) rotation of the Cp rings around the Cp–X bond (X = bridging atom). To obtain minimal energy these three factors are carefully balanced.
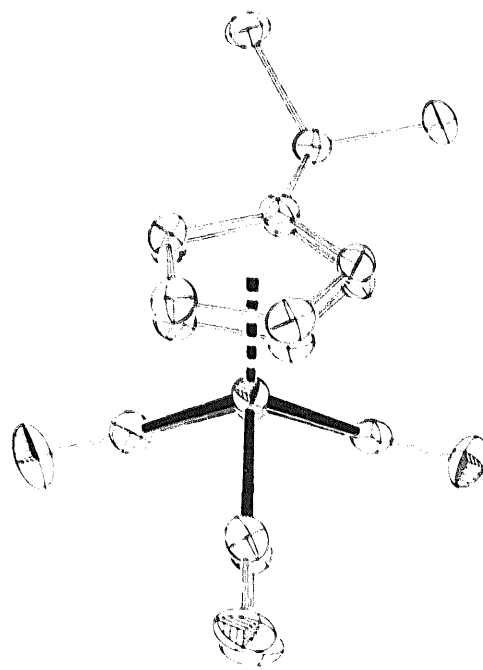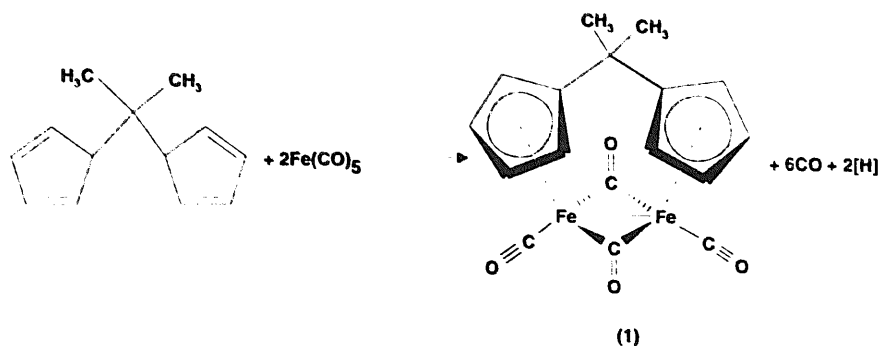

Fig. 2. Side view of 1.

(1)

Scheme 1.

Since deviation from tetrahedral geometry around Si requires less energy than for C, the C–Si–C angles in the structure of $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_4$ vary between $106°$ (C_{Cp}–Si–C_{Cp}) and $114°$ (C_{Me}–Si–C_{Me}), whereas in 1 there is no significant variation in the C–C(51)–C angles ($109.5 \pm 0.8°$). Furthermore, in 1 the bridging atom C(51) lies almost perfectly in the plane of each Cp ring. This is in sharp contrast to $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_4$, where the bridging silicon atom has moved out of the Cp planes towards the Fe_2 axis, thus causing the Cp–Cp angle to be smaller than the C(Cp)–Si–C(Cp) angle. The Cp–Cp angle of $109°$ in 1 is rather large compared with the corresponding angles in complexes without a bridging group (cis-$Cp_2Fe_2(CO)_4$), or with a flexible bridging group (as in $[CH(NMe_2)]_2Cp'_2Fe_2(CO)_4$), which are about $90°$. In $(CH_3)_2Si(C_5H_4)_2Fe_2(CO)_4$ this angle is $97°$, which is intermediate between the optimum $90°$ for unrestricted Cp rings [2] and the $109°$ for ideal tetrahedral geometry around the Si atom. The bond angle constraint around Si is relieved partly by Si moving out of the Cp planes towards the Fe_2 axis [2]. The bridging carbon atom in 1, however, does not move out of the Cp planes, and therefore the Cp–Cp angle has a value close to the perfect tetrahedral geometry of the bridging carbon atom.

The Fe–Fe distance of 2.48 Å in compound 1 is shorter than the Fe–Fe distances found in $(CH_3)_2$-$Si(C_5H_4)_2Fe_2(CO)_4$ (2.51 Å), $R,R/S,S$-$[CH(NMe_2)]_2$-$Cp'_2Fe_2(CO)_4$ (2.50 Å) [7] and R,S-$[CH(NMe_2)]_2Cp'_2Fe_2(CO)_4$ (2.51 Å) [23], and is clearly shorter than the Fe–Fe distance in the non-bridged cis-$Cp_2Fe_2(CO)_4$ (2.53 Å). All Fe–C(carbonyl) and C–O distances in 1 are close to the values found for the other $(Cp'$–X–$Cp')Fe_2(CO)_4$ molecules.

As can be seen in Table 1, the distances between Fe and the Cp carbon atoms in compound 1 vary somewhat. The average distance between the iron atoms and the distal Cp carbon atoms (C(12, 13, 32, 33)) is shorter than the average distance between the iron atoms and the proximal and ipso Cp carbon atoms (C(10, 11, 14, 30, 31, 34)). Five out of eight Fe–C(distal) distances are

significantly shorter than the Fe–C(proximal) and Fe–C(ipso) distances.

Compound 1 shows some interesting structural differences compared with the corresponding $SiMe_2$-bridged and non-bridged derivatives, which could be important for the degree of strain in η^5 cyclopentadienyl-stabilized Fe–S clusters. These effects are currently being investigated.

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[14] All manipulations were carried out under dinitrogen atmosphere using standard Schlenk techniques. To a cooled solution of 3.88 g (22.6 mmol) of $(C_5H_5)_2CMe_2$ in 300 ml of toluene was added 8.94 g (46 mmol) of $Fe(CO)_5$. This mixture was rapidly brought to reflux. After 15 h of reflux, the mixture was evaporated to dryness, yielding a red oil with red crystalline material. The red crystals were washed with hexane and dried in vacuo. The combined dark red colored hexane washings were evaporated to dryness and the residue was recrystallized from toluene–hexane mixture. The resulting red crystalline material

was collected by filtration. The filtrate was purified by column chromatography (SiO_2, toluene/hexane 1:1). The main red fraction was collected, evaporated to dryness and the red residue was recrystallized from toluene–hexane mixtures. Yield (total) 2.32 g (5.8 mmol, 26%). Anal. Found: C, 51.62; H, 3.52. Calc.: C, 51.83; H, 3.58. EI MS: 394 (12%, M^+); 366 (8.6%, [M–CO]$^+$); 338 (19%, [M–2CO]$^+$); 310 (25%, [M–3CO]$^+$); 282 (47%, [M–4CO]$^+$); 226 (100%, [M–4CO–Fe]$^+$). ^1H NMR ($CDCl_3$) 5.12–5.03 (m, 2×4H, C_5H_4) 1.35 (s, 2×3H, CH_3). IR (toluene): 1995 (s); 1958 (w) 1786 (s).

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[16] Crystal data for 1: $C_{17}H_{14}Fe_2O_4$; $M = 393.99$; space group $P2_1/c$ (No. 14); $a = 18.5581(8)$ Å; $b = 12.4211(6)$ Å; $c = 13.7625(6)$ Å; $\beta = 108.033(7)°$; $V = 3016.6(2)$ Å^3; $Z = 8$; $D_{calc} = 1.735$ g cm^{-3}; μ(Mo Kα) = 19.40 cm^{-1}; $T = 208(2)$ K; Mo Kα. The unit cell dimensions were determined from the setting angles of 25 reflections in the range $32° < 2\theta < 38°$. Standard experimental details and computational details are given elsewhere [17]. The positions of the non-hydrogen atoms were found from an automatic Patterson interpretation (PATTY [18]) followed by a phase refinement procedure to expand the fragment (DIRDIF [19]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were initially placed at

calculated positions (C–H 0.93 Å for the cyclopentadienyl and 0.96 Å for the methyl hydrogen atoms respectively) and subsequently refined independently. An additional empirical absorption correction based on $F_o - |F_c|$ was applied using DIFABS [20] on the original unmerged F_o values. The structure was refined by full-matrix least-squares on F_o values using SHELXL [21]. The refinement converged to an R-value of 0.0289, $wR_2 = 0.0569$. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma^2(F_o^2) + (0.0206F_c^2)^2 + 2.35F_c^2]$.

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