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Solid state structure of the (2,4-dimethylpentadienyl)iron dicarbonyl dimer

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Abstract

A solid state structural investigation of the Fe(2,4-dimethylpentadienyl)$(CO)_2$ dimer has revealed a structure quite similar to that of the known *cis* isomer of $[Fe(C_5H_5)(CO)_2]_2$. A lengthening of the Fe–Fe bond by ca. 0.08 Å can be correlated with substantial intramolecular steric crowding.

Pentadienyl ligands have been shown to be capable of imparting both thermal stability and chemical reactivity to their homoleptic metal complexes [1]. Given the rich chemistry associated with (cyclopentadienyl)metal carbonyl compounds [2], one would have to expect that (pentadienyl)metal carbonyl analogs should also prove interesting. In fact, quite unique reaction chemistry has already been observed for a molybdenum complex, in which an unusual trialkylation of a carbonyl ligand was brought about [3]. There are also indications that the structural aspects of such compounds will prove interesting, and these complexes do appear to possess somewhat different structural natures relative to their cyclopentadienyl analogs [4]. Thus, for a recently reported series of $Fe(2,4\text{-}C_7H_{11})(CO)(L)X$ complexes (C_7H_{11} = dimethylpentadienyl; X = I, CH_3, $Fe(2,4\text{-}C_7H_{11})(CO)_2$ for L = CO; X = $C(O)CH_3$ for L = $P(CH_3)_2C_6H_5$), richer conformational behavior was indeed observed for the monometallic complexes, while the observation of a strong ESR signal for the dimeric species suggested that it probably possessed a somewhat weaker Fe–Fe bond than in the related C_5H_5 dimer (the "Fp" dimer) [4]. While the conformational differences could readily be explained [5], it was not clear whether the weaker Fe–Fe bonding might be predominately an electronic or a steric effect. In an attempt to clarify this situation, we have therefore determined the solid-state structure of $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$.

Experimental

Single crystals of $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ were obtained by slowly cooling its concentrated solutions in toluene/hexane mixtures. A crystal of approximate di-

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mensions 0.32 × 0.35 × 0.35 mm was selected and mounted in a glass capillary under nitrogen. Unit cell data were determined from a combination of oscillation photographs and standard Nicolet P$\bar{1}$ software programs. Accurate cell constants were obtained from 15 centered reflections in the range $40° < 2\theta < 46°$, using the Mo-K_α peak at 0.71070 Å. The unit cell parameters are a 8.4945(9), b 16.1118(13), c 13.3728(10) Å, β 99.010(8)°, V 1807.7(3) Å^3 for $Z = 4$ dimeric units. Symmetric θ–2θ scans having a width of 2° were employed, at rates of 1–2 deg/min out to 2θ 52°. Background intensities were estimated using the program CARESS [6]. Three standard reflections were monitored for every 97 reflections, and indicated a net decrease during data collection of 2% in intensity, for which a correction was applied.

A total of 3711 independent reflections were obtained, of which 2836 had $I > 3\sigma(I)$. Calculations were carried out using Strouse's programs [6], and a weighting factor of $w = 1/\sigma(F_o)$ was applied. Absorption effects were treated numerically, for which a range in transmission factors of 0.584–0.639 was obtained. The crystal faces were indexed as (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), and (00$\bar{1}$), while $\mu = 16.15$ cm^{-1}.

Reflections of the type $0k0$ were observed only for $k = 2n$, indicating either space group $P2_1$ or $P2_1/m$. The latter space group was clearly suggested by the

Table 1

Positional parameters for the non-hydrogen atoms of $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$

Atom	x	y	z
Fe(1)	0.22399(5)	0.33107(2)	0.13251(3)
Fe(2)	0.14995(5)	0.66895(2)	0.39877(3)
C(1)	0.3771(4)	0.4299(2)	0.0974(3)
C(2)	0.3031(4)	0.3931(2)	0.0058(2)
C(3)	0.1365(4)	0.3785(2)	−0.0167(2)
C(4)	0.0223(4)	0.3934(2)	0.0470(3)
C(5)	0.0616(4)	0.4321(2)	0.1425(3)
C(6)	0.4058(5)	0.3613(3)	−0.0685(3)
C(7)	−0.1457(5)	0.3627(3)	0.0146(3)
C(8)	0.2870(4)	0.3540(2)	0.2603(3)
C(9)	0.3940(5)	0.2500(0)	0.1301(3)
C(10)	0.0774(5)	0.2500(0)	0.1732(3)
C(11)	0.2797(4)	0.5676(2)	0.4796(3)
C(12)	0.1844(4)	0.6057(2)	0.5431(2)
C(13)	0.0196(4)	0.6218(2)	0.5124(3)
C(14)	−0.0710(4)	0.6076(2)	0.4157(3)
C(15)	−0.0040(5)	0.5691(2)	0.3369(3)
C(16)	0.2619(5)	0.6359(3)	0.6468(3)
C(17)	−0.2406(5)	0.6384(3)	0.3949(4)
C(18)	0.2637(4)	0.6463(2)	0.3034(3)
C(19)	0.3085(5)	0.7500(0)	0.4574(3)
C(20)	0.0266(5)	0.7500(0)	0.3123(3)
O(8)	0.3194(4)	0.3750(2)	0.3437(2)
O(9)	0.5325(4)	0.2500(0)	0.1321(3)
O(10)	−0.0375(4)	0.2500(0)	0.2110(3)
O(18)	0.3376(4)	0.6269(2)	0.2430(2)
O(19)	0.4411(4)	0.7500(0)	0.5002(3)
O(20)	−0.0696(4)	0.7500(0)	0.2382(2)

Table 2

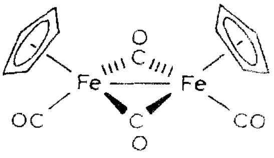
Selected bond distances (Å) and angles (deg) for $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$

Fe(1)–Fe(1′)	2.6125(6)	Fe(1)–C(8)	1.749(3)	C(1)–C(2)	1.417(5)
Fe(2)–Fe(2′)	2.6116(6)	Fe(1)–C(9)	1.951(3)	C(2)–C(3)	1.419(4)
Fe(1)–C(1)	2.154(3)	Fe(1)–C(10)	1.940(3)	C(3)–C(4)	1.408(4)
Fe(1)–C(2)	2.163(3)	Fe(2)–C(18)	1.754(3)	C(4)–C(5)	1.413(5)
Fe(1)–C(3)	2.158(3)	Fe(2)–C(19)	1.950(3)	C(2)–C(6)	1.510(5)
Fe(1)–C(4)	2.153(3)	Fe(2)–C(20)	1.939(3)	C(4)–C(7)	1.508(5)
Fe(1)–C(5)	2.151(3)	C(8)–O(8)	1.156(4)	C(11)–C(12)	1.403(4)
Fe(2)–C(11)	2.162(3)	C(9)–O(9)	1.173(5)	C(12)–C(13)	1.420(5)
Fe(2)–C(12)	2.162(3)	C(10)–O(10)	1.168(5)	C(13)–C(14)	1.416(5)
Fe(2)–C(13)	2.154(3)	C(18)–O(18)	1.142(4)	C(14)–C(15)	1.417(5)
Fe(2)–C(14)	2.164(3)	C(19)–O(19)	1.181(5)	C(12)–C(16)	1.519(5)
Fe(2)–C(15)	2.155(4)	C(20)–O(20)	1.181(5)	C(14)–C(17)	1.508(5)
Fe(1′)–Fe(1)–C(8)	102.22(12)	C(11)–Fe(2)–C(20)	172.73(13)	C(1)–C(2)–C(3)	123.1(3)
Fe(1′)–Fe(1)–C(9)	47.97(9)	C(15)–Fe(2)–C(19)	173.52(14)	C(2)–C(3)–C(4)	127.0(3)
Fe(1′)–Fe(1)–C(10)	47.69(8)	Fe(1)–C(9)–Fe(1′)	84.06(17)	C(3)–C(4)–C(5)	122.3(3)
C(8)–Fe(1)–C(9)	92.51(16)	Fe(1)–C(10)–Fe(1′)	84.63(17)	C(1)–C(2)–C(6)	119.1(3)
C(8)–Fe(1)–C(10)	88.84(17)	Fe(1)–C(8)–O(8)	174.0(3)	C(3)–C(2)–C(6)	117.6(3)
C(9)–Fe(1)–C(10)	93.61(13)	Fe(1)–C(9)–O(9)	137.91(9)	C(3)–C(4)–C(7)	118.7(3)
C(1)–Fe(1)–C(10)	174.14(13)	Fe(1)–C(10)–O(10)	137.58(9)	C(5)–C(4)–C(7)	118.9(3)
C(5)–Fe(1)–C(9)	172.30(14)	C(3)–Fe(1)–C(8)	146.87(15)	C(11)–C(12)–C(13)	122.8(3)
Fe(2′)–Fe(2)–C(18)	101.98(12)	Fe(2)–C(19)–Fe(2′)	84.08(18)	C(12)–C(13)–C(14)	127.2(3)
Fe(2′)–Fe(2)–C(19)	47.96(9)	Fe(2)–C(20)–Fe(2′)	84.66(18)	C(13)–C(14)–C(15)	121.8(3)
Fe(2′)–Fe(2)–C(20)	47.67(9)	Fe(2)–C(18)–O(18)	176.0(4)	C(11)–C(12)–C(16)	119.0(3)
C(18)–Fe(2)–C(19)	90.40(17)	Fe(2)–C(19)–O(19)	137.83(10)	C(13)–C(12)–C(16)	118.1(3)
C(18)–Fe(2)–C(20)	90.80(17)	Fe(2)–C(20)–O(20)	137.58(9)	C(13)–C(14)–C(17)	118.8(4)
C(19)–Fe(2)–C(20)	93.64(14)	C(13)–Fe(2)–C(18)	147.37(15)	C(15)–C(14)–C(17)	119.4(4)

intensity distribution of the data set, and from the Patterson function, which contained a number of major peaks attributable to the presence of a mirror plane. The iron atom locations were determined from the Patterson map. Several near solutions could be obtained for the two iron atom locations, but while most peaks could be accounted for, there was always some discrepancy, until a solution was attempted in which both iron atoms had the same *y* coordinate. This solution resulted in the overlap of a number of various iron–iron vectors, and matched the Patterson map quite well. From this point, the structure solution proceeded routinely, and all remaining non-hydrogen atoms could be located from difference Fourier maps. Except for H(15A) all of the non-methyl hydrogen atoms could be located, and all were placed in positions idealized for $d(C-H) = 0.95$ Å. Hydrogen atom thermal parameters (U) were set to be equal to ca. 0.01 plus the equivalent isotropic U value for the carbon atom to which they were attached. Many of the methyl hydrogen atoms could be found, and all methyl hydrogen atom positions were included based on least-squares fits to tetrahedral geometries. Final refinement, with anisotropic thermal parameters for all non-hydrogen atoms, led to $R = 0.040$ and $R_w = 0.050$. A final difference Fourier map revealed a peak near each iron atom (0.80 and 0.56 e/Å^3), followed by other peaks of 0.20 e/Å^3 or less. Pertinent bonding parameters are provided in Tables 1 and 2. Tables of hydrogen atom parameters, anisotropic thermal parameters, least-squares plane information, Patterson function peaks, and the structure factor tables may be obtained through NAPS. No unusual intermolecular contacts were observed.

Results

The solid-state structure of $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$, **1**, is depicted in Figs. 1 and 2 for both independent dimers. Each dimer is situated on a mirror plane of symmetry which passes through the two bridging carbonyl ligands, and the two dimers are essentially identical, with only minor differences occurring between a few bond angles [7*]. It can be seen that the dimers have adopted a configuration akin to the *cis* isomer of $[Fe(C_5H_5)(CO)_2]_2$ (I) [8]. The Fe–Fe bond distances in **1** are dependent only on the iron atoms' *y* coordinates, and formally average 2.6120(4) Å [9*]. To allow for possible systematic errors, however, a distance of 2.612(1) Å will be assumed. This distance is much shorter than that of 3.138(3) Å in $[Fe(C_3H_5)(CO)_3]_2$, which contains no bridging carbonyl ligands [10], but still significantly longer than the distances of 2.531(2) and 2.534(2) Å observed in the *cis* [8] and *trans* [11] isomers of $[Fe(C_5H_5)(CO)_2]_2$, respectively.



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* This and other references marked with an asterisk indicates a note occurring in the list of references.

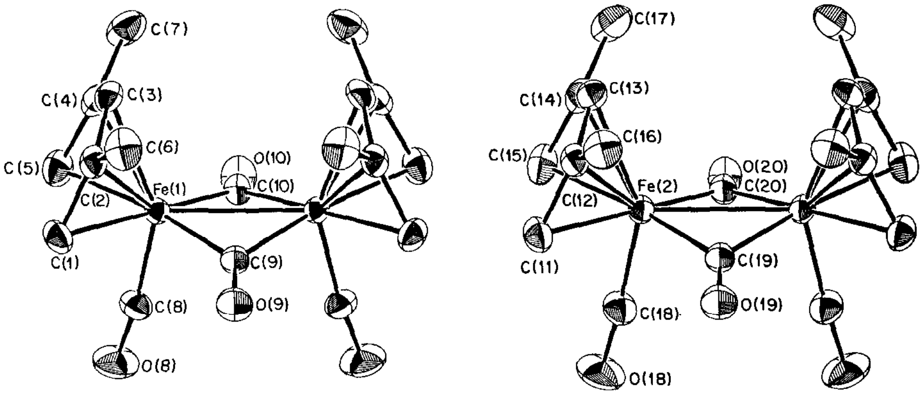


Fig. 1. Perspective views and numbering schemes of the two independent $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ molecules. Each lies on a crystallographic mirror plane.

The pentadienyl ligands are positioned rather symmetrically with respect to the iron atoms. Thus, the average Fe–C(1,5), Fe–C(2,4), and Fe–C(3) bond distances are 2.156(2), 2.160(2), and 2.156(2) Å, respectively, compared to ca. 2.108(2) Å in the C_5H_5 analogs. No distinction can be made between the internal and external pairs of delocalized C–C bonds in the pentadienyl ligands, which average 1.416(2) and 1.412(2) Å, respectively, while the C–CH_3 bond distances average 1.511(3) Å. As has generally been observed, the C–C–C bond angles involving the delocalized carbon atoms become smaller when a methyl group is located on the central atom, in this case by an average of 4.6° (127.1(2) vs. 122.5(2)°) [12].

The pentadienyl ligands are reasonably planar, although the uncharged carbon atoms lie out of the plane by an average of ca. 0.013 Å in a direction toward the iron atom, while the 1,5 and 3 positions are bent out the other way, by averages of 0.004 and 0.018 Å, respectively. The methyl groups are located out of the ligand planes by an average of 0.154 Å toward their iron atoms, corresponding to a bend of 5.8°. Similar bends take place for the central hydrogen atom (0.02 Å, 1°) and the *exo*

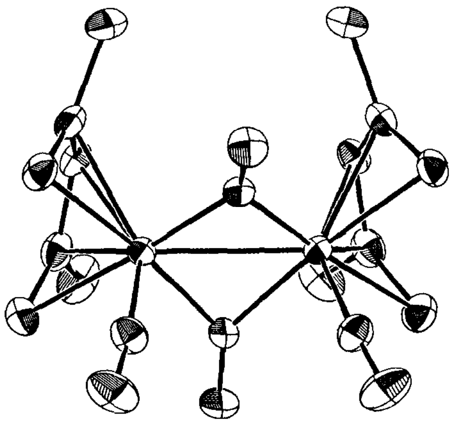


Fig. 2. Alternate view of the first dimer. A rotation around the Fe–Fe bond has been used to orient the terminal CO ligands more toward the viewer.

hydrogen atoms on the terminal carbon atoms (0.25 Å, 15°), while their *endo* counterparts are bent in the opposite direction (0.68 Å, 46°). The iron atoms are situated an average of 1.530 Å away from the pentadienyl ligand planes (cf., ca. 1.745(3) Å for the C_5H_5 analogs).

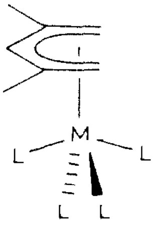
The carbonyl ligands appear normal. The average Fe–C distances are 1.945(2) Å for the bridging carbonyls and 1.752(2) Å for the terminal ones. The respective average C–O distances are 1.176(3) and 1.149(3) Å. The parameters observed in the *cis* and *trans* forms of $[Fe(C_5H_5)(CO)_2]_2$ are statistically indistinguishable, with the exception of the Fe–CO (terminal) distances, which averaged 1.917(4) and 1.910(5) Å, respectively. The observation that the Fe–CO (terminal), Fe–Fe, and Fe–C (pentadienyl) distances are all longer in the pentadienyl complex suggests greatly increased steric congestion (vide infra).

Despite the overall similarity of $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ to *cis*-$[Fe(C_5H_5)(CO)_2]_2$, there are several significant differences. As noted above, increased steric interactions appear to be present in the former complex, for which the angle between the pentadienyl ligand plane perpendicular and the Fe–Fe vector averages 154.3°, compared to only 135.5(3)° for the analogous angle in the latter complex. In this regard, it can be noted that the $CH_3 \cdots CH_3$ interactions between the opposite pentadienyl ligands average only 3.62 Å, compared to an expected van der Waals separation of 4.0 Å [13]. However, the orientations of the carbonyl ligands to one another are similar to those in the *cis* (and *trans*) C_5H_5 dimers [14*]. Thus, the average values for the C(bridge)–Fe–C(bridge) and C(bridge)–Fe–C(terminal) angles are 93.6(1)° and 90.6(1)° for $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$, compared to 96.0(2)° and 90.5(2)°, respectively, for the *cis*-C_5H_5 analog. A slightly greater butterfly angle is observed between the two Fe_2C(bridge) planes of the former, 20.6° vs. 16°, and this is accompanied by a slightly larger Fe′–Fe–C(terminal) angle, 102.1(1)° vs. 100.0(2)°, respectively.

Discussion

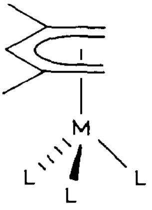
The observation of a reasonably strong ESR signal for $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ in solution suggested that its metal–metal bond should be weaker than that in $[Fe(C_5H_5)(CO)_2]_2$. In accord with this expectation, the Fe–Fe bond distance in the former complex is indeed longer, by ca. 0.08 Å, although it is of course not clear if this represents sufficient weakening of the Fe–Fe bond to bring about the noticeable homolysis of the dimer.

Despite the clear similarity of the observed structure to that of *cis*-$[Fe(C_5H_5)(CO)_2]_2$, such a relationship could not readily be appreciated a priori, even neglecting the possibility of observing the *trans* isomer. Thus, theoretical studies have indicated that M(pentadienyl)L_4 complexes should adopt a configura-



(II)

tion such as II [5,15], from which several potential structures could be derived. It is therefore interesting to note that the locations adopted by the three carbonyl ligands around a given iron atom are quite similar to those adopted in related M(pentadienyl)L_3 structures (III), e.g., Fe(2,4-C_7H_{11})$(CO)_2$I [16*]. It would appear that the Fe–Fe interaction exerts little stereochemical activity, despite the fact that in other mono(pentadienyl) complexes, the locations of the other ligands are generally very well-defined.



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As to the origin of the apparently weaker Fe–Fe bond in [Fe(2,4-C_7H_{11})$(CO)_2]_2$, this clearly seems to be a steric influence. In this dimer, one not only observes a longer Fe–Fe bond, but also significantly longer Fe–C (pentadienyl) and Fe–CO (terminal) bond lengths as compared to either $[Fe(C_5H_5)(CO)_2]_2$ structure. No clearly shorter Fe–C bond distances were observed in the former complex to balance the other, longer bonds. A significant portion of the steric congestion seems to involve the opposing, symmetry-related methyl groups [17*]. Conceivably, an unmethylated pentadienyl ligand might bring about significant less steric interaction [18*,19*] and a shorter Fe–Fe bond. On the other hand, the use of bulkier substituents, such as t-butyl, or the addition of substituents to the 3-position [20*] might significantly destabilize the observed form of the *cis* isomer, so that some other configuration, perhaps *trans*, would be adopted. Such possibilities will be addressed in the future.

Acknowledgements

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14 To a large extent, the only major difference between **1** and the *cis*-C_5H_5 analog involves the greater twist of the pentadienyl ligand by ca. 18.8° relative to the Fe–Fe bond. Thus, while the arrangements of the two $Fe(CO)_2$ units seemed relatively unchanged relative to one another, the 18.8° pentadienyl tilt results in a smaller angle between the pentadienyl ligand perpendicular and the terminal CO ligands (averages of 124.41(3) vs. 103.1°) and a larger angle between the above perpendicular and the bridging CO ligands (averages of 123.2(2) vs. 131.6°).

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16 (a) The angles formed between the pentadienyl perpendicular and the Fe–I and two Fe–CO vectors in $Fe(2,4\text{-}C_7H_{11})(CO)_2I$ are 135.9, 133.3, and 106.7° [16b]. These values are similar to those observed herein [14]. (b) H. Ma, P. Weber, M.L. Ziegler, and R.D. Ernst, Organometallics, 6 (1987) 854.

17 Other possibly important non-bonded contacts take place between the carbonyl and pentadienyl ligands. Each bridging carbonyl engages in close non-bonded contacts with the proximate pentadienyl carbon atoms in the 1 and 2 positions, and with the 2-substituted methyl group. These fall in the respective ranges of 2.86–2.88 Å, 2.93–2.97 Å, and 3.18–3.22 Å. The terminal carbonyls engage in close contacts with the adjacent pentadienyl carbon atoms in the 1,5 positions. These four contacts fall in the range of 2.60–2.71 Å.

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20 Using the observed geometry for the $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ dimer, one can estimate a $CH_3 \cdots CH_3$ separation of only ca. 2.7 Å for opposing 3-methyl substituents.