Journal of Organometallic Chemistry, 321 (1987) 389–395
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SOLID-STATE STRUCTURE OF BIS(2,3,4-TRIMETHYLPENTADIENYL)IRON

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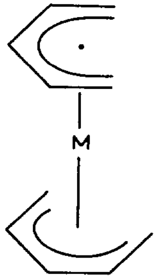
(Received July 28th, 1986)

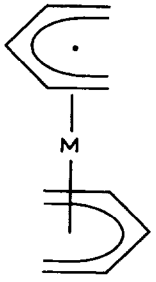
Summary

The solid-state structure of bis(2,3,4-trimethylpentadienyl)iron, $Fe(2,3,4\text{-}C_8H_{13})_2$, has been determined by single crystal X-ray diffraction. The space group is C_i^1-$P\bar{1}$ (No. 2) with unit cell parameters being *a* 9.442(3), *b* 11.212(3), *c* 7.743(3) Å, *α* 101.38(3), *β* 116.29(3), *γ* 89.77(2)°, and *V* 717.3(4) Å^3 for $Z = 2$. Final agreement indices of $R = 0.046$ and $R_w = 0.051$ were obtained for the 1998 unique reflections judged to be above background. Even with substantially increased ligand–ligand repulsions relative to its isomorphous ruthenium analog, the complex has also been found to exist in a distorted *gauche*-eclipsed structure. The average Fe–C bond distance of 2.087(1) Å compares well with the value of 2.089(3) Å in $Fe(2,4\text{-}C_7H_{11})_2$.

Recently we have isolated a series of bis(pentadienyl) complexes for iron [1], ruthenium [2], and osmium [3]. Somewhat surprisingly, each compound to date has adopted the unsymmetric *gauche*-eclipsed conformation, I, rather than the otherwise reasonable *anti*-eclipsed form, II. Structures similar to I have also been adopted by related cyclic species [4]. As it was not clear how great the favorability of the *gauche*-eclipsed conformation might be, an attempt was made for ruthenium to

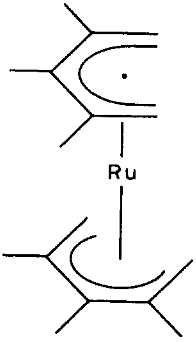


(I)



(II)

destabilize the *gauche*-eclipsed conformation by the use of 2,3,4-trimethylpentadienyl ligand, 2,3,4-C_8H_{13}, which would bring about appreciable intramolecular CH_3-CH_3



(III)

repulsions, as in III. Despite the presence of these interactions, Ru(2,3,4-C_8H_{13})$_2$ was also found to adopt the *gauche*-eclipsed conformation [2]. Since replacement of ruthenium by the smaller iron should further increase the CH_3-CH_3 nonbonded contacts, Fe(2,3,4-C_8H_{13})$_2$ has also been synthesized [5], and subjected to a single crystal X-ray structural investigation which is reported herein.

Experimental

X-Ray diffraction study of Fe(2,3,4-C_8H_{13})$_2$

Single crystals of this compound were obtained by slowly cooling concentrated solutions in pentane. Unit cell data were obtained through a combination of oscillation photographs and Nicolet $P\bar{1}$ software programs, and confirmed by cell reduction. Accurate cell constants and their standard deviations were derived from the least-squares refinement of 14 centered reflections for which $23° < 2\theta < 30°$, using the Mo-$K_{\bar{\alpha}}$ peak at 0.71073 Å. The unit cell parameters were chosen to be analogous to those of the isomorphous ruthenium compound [2] with a 9.442(3), b 11.212(3), c 7.743(3) Å, α 101.38(3), β 116.29(3), γ 89.77(2)°, and V 717.3(4) Å^3 for $Z = 2$. The space group is C_i^1-$P\bar{1}$ (No. 2).

Mo-$K_{\bar{\alpha}}$ radiation was monochromatized using the 002 face of mosaic graphite. θ-2θ scans were employed from 1.0° below the Mo-K_{α_1} peak to 1.0° above the Mo-K_{α_2} peak at a scan rate of 3.0° min^{-1}. A 1.0 mm diameter collimator was used as the crystal edges varied from 0.16 to 0.37 mm. Data were collected out to 45° in 2θ, with total background counting time equal to half the total scan time. The intensities of 5 standard reflections were monitored for every 95 reflections, and did not indicate any substantial changes. All calculations were carried out using the SHELX programs. A correction for absorption was made, for which the transmission factors ranged from 0.728 to 0.861. A total of 2894 reflections were processed, leading to 1998 unique reflections judged to be above background ($I > 2.5\sigma(I)$). These were used in subsequent calculations. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, with the value for w being chosen as $1/(\sigma^2(F) + 0.006(F)^2)$.

Following the location of the iron atom from a Patterson map, all carbon atoms were located from a difference Fourier map, as were most of the hydrogen atoms.

TABLE 1

POSITIONAL PARAMETERS FOR THE NON-HYDROGEN ATOMS OF $Fe(2,3,4\text{-}(CH_3)_3C_5H_4)_2$

Atom	x	y	z
Fe	0.33745(5)	0.29917(4)	0.09749(7)
C(1)	0.5802(5)	0.2978(4)	0.2466(7)
C(2)	0.5061(4)	0.1887(3)	0.2469(6)
C(3)	0.3871(4)	0.1118(3)	0.0769(6)
C(4)	0.3156(5)	0.1443(3)	−0.1096(5)
C(5)	0.3806(6)	0.2437(4)	−0.1473(6)
C(6)	0.5461(6)	0.1603(5)	0.4467(7)
C(7)	0.3207(6)	−0.0054(4)	0.0962(7)
C(8)	0.1624(6)	0.0740(4)	−0.2699(7)
C(9)	0.3402(6)	0.4812(4)	0.0894(8)
C(10)	0.1865(5)	0.4238(4)	−0.0394(6)
C(11)	0.0993(4)	0.3478(3)	0.0131(6)
C(12)	0.1665(4)	0.3123(4)	0.1958(6)
C(13)	0.3107(5)	0.3699(4)	0.3507(6)
C(14)	0.1183(8)	0.4353(5)	−0.2542(9)
C(15)	−0.0635(5)	0.2922(5)	−0.1371(8)
C(16)	0.0851(6)	0.2075(5)	0.2260(8)

The hydrogen atoms were subjected to limited isotropic least-squares refinement in which the C–H bond distances were constrained to be equivalent for a given carbon atom, while all non-hydrogen atoms were refined anisotropically. Final refinement led to agreement indices of $R = 0.046$ and $R_w = 0.051$. A final difference Fourier map revealed no peaks greater than 0.62 e/Å^3. The final positional parameters for the non-hydrogen atoms are presented in Table 1, with the bond distances and angles contained in Table 2. The anisotropic thermal parameters for the non-hydrogen atoms, the parameters for the hydrogen atoms, and some least-squares plane information can be found in Tables 3–5 (supplementary material). No unusual intermolecular contacts were observed.

TABLE 2

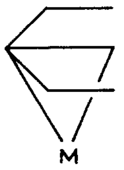
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $Fe(2,3,4\text{-}(CH_3)_3C_5H_4)_2$

Fe–C(1)	2.062(4)	Fe–C(9)	2.055(5)	C(1)–C(2)	1.412(6)	C(9)–C(10)	1.410(6)
Fe–C(2)	2.080(4)	Fe–C(10)	2.083(4)	C(2)–C(3)	1.410(4)	C(10)–C(11)	1.418(7)
Fe–C(3)	2.141(3)	Fe–C(11)	2.147(4)	C(3)–C(4)	1.420(6)	C(11)–C(12)	1.410(6)
Fe–C(4)	2.059(4)	Fe–C(12)	2.061(5)	C(4)–C(5)	1.413(7)	C(12)–C(13)	1.402(5)
Fe–C(5)	2.089(6)	Fe–C(13)	2.088(5)	C(2)–C(6)	1.521(7)	C(10)–C(14)	1.527(8)
				C(3)–C(7)	1.520(6)	C(11)–C(15)	1.497(5)
				C(4)–C(8)	1.513(5)	C(12)–C(16)	1.517(8)

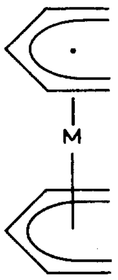
C(1)–C(2)–C(3)	124.3(4)	C(3)–C(4)–C(8)	119.3(4)	C(10)–C(11)–C(15)	119.3(4)
C(1)–C(2)–C(6)	117.2(3)	C(4)–C(3)–C(7)	117.9(3)	C(11)–C(10)–C(14)	118.5(4)
C(2)–C(3)–C(4)	122.7(4)	C(5)–C(4)–C(8)	118.9(4)	C(11)–C(12)–C(13)	121.3(4)
C(2)–C(3)–C(7)	119.1(4)	C(9)–C(10)–C(11)	124.3(4)	C(11)–C(12)–C(16)	120.1(3)
C(3)–C(2)–C(6)	118.2(4)	C(9)–C(10)–C(14)	116.9(5)	C(12)–C(11)–C(15)	118.2(4)
C(3)–C(4)–C(5)	121.7(3)	C(10)–C(11)–C(12)	122.2(3)	C(13)–C(12)–C(16)	118.6(4)

Results and discussion

A perspective view and numbering scheme for Fe(2,3,4-C_8H_{13})$_2$ can be seen in Fig. 1, and pertinent atomic and bonding parameters are contained in Tables 1 and 2. The atoms labelled C(n) ($n = 1$–8) on one ligand are related to the C($n + 8$) atoms by a noncrystallographic C_2 rotational axis. It is clear from the figure that the complex has adopted the same *gauche*-eclipsed conformation as found in the isomorphous Ru(2,3,4-C_8H_{13})$_2$ (I) as well as in Fe(2,4-C_7H_{11})$_2$ (II). One can define the conformation more precisely by the angle formed between two planes, one for each ligand, each plane containing the metal atom as well as the central carbon atom and the midpoint between the two terminal carbon atoms of the pentadienyl ligand, as in IV. The *syn*-eclipsed, V, and *anti*-eclipsed, II, structures will be defined to have conformation angles of 0 and 180°, respectively, so that the ideal value for the *gauche*-eclipsed conformation will be 60°. In fact, the value of 59.7° found for Fe(2,4-C_7H_{11})$_2$ is very close to this. The value for Ru(2,3,4-C_8H_{13})$_2$, however, was found to be a little different at 52.5°, which was attributed to the



(IV)



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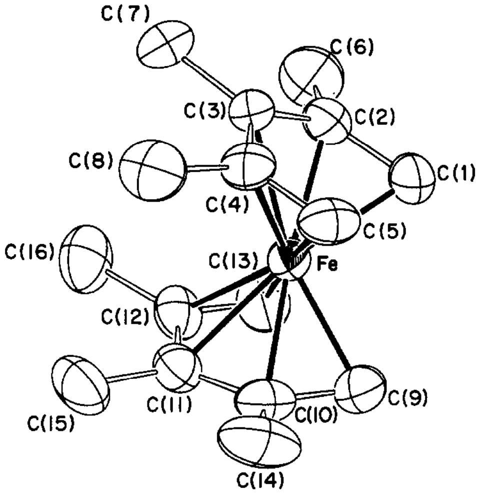
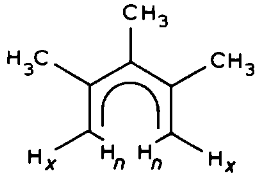


Fig. 1. Perspective view and numbering scheme for Fe(2,3,4-C_8H_{13})$_2$.

presence of two eclipsing CH_3–CH_3 interactions (cf. III). Because iron is substantially smaller than ruthenium, the CH_3–CH_3 interactions should be even more significant in Fe(2,3,4-C_8H_{11})$_2$, conceivably even enough to bring about adoption of the *anti*-eclipsed conformation [6]. While that has not happened here, it was nonetheless expected that the conformation would be at least twisted even more from 60° than was observed for Ru(2,3,4-C_8H_{13})$_2$ [2,7]. Unexpectedly, in the present case the conformation angle is 55.1°, actually closer to the ideal value than was the ruthenium compound [8]. However, there are other distortions which may also serve to relieve the CH_3–CH_3 interactions. In particular, the two pentadienyl ligand planes may bend away from a parallel orientation, which does in fact occur to a greater extent for Fe(2,3,4-C_8H_{13})$_2$ than for Ru(2,3,4-C_8H_{13})$_2$ [9]. Thus, for Ru(2,3,4-C_8H_{13})$_2$, the angle between the ligand planes is 18.2°, while it is 20.4° for Fe(2,3,4-C_8H_{13})$_2$, and only 15.0° for Fe(2,4-C_7H_{11})$_2$ [1]. Possibly this distortion is more effective in relieving the CH_3–CH_3 interactions than is the conformation twist, although there does seem to be an electronic contribution [8].

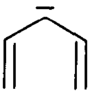
Another reflection of the presence of substantial CH_3–CH_3 interactions may be seen in the extent of bending out of the ligand planes by the mutually eclipsing methyl substituents. In Ru(2,3,4-C_8H_{13})$_2$, the methyl groups in the 2 and 4 positions were tilted out of the ligand plane in a direction toward the metal atom by ca. 9.5°, similar to what has been observed in other metal complexes [10,11]. This bending has been ascribed to an attempt by the large ligand to improve overlap with the metal orbitals [10,12]. The methyl groups in the 3 positions, however, were slightly tilted (2.0°) away from the metal, perhaps in response to the greater tilting by the eclipsing C(8) and C(16) atoms [13,14]. In Fe(2,3,4-C_8H_{13})$_2$, the methyl groups in the 2 and 4 positions are again significantly tilted toward the metal atom (7.2 and 13.7°, respectively), and the methyl groups in the 3 positions are again tilted significantly away from the metal atom (3.2°). In no other structures have we observed such tilting, which is clear evidence of the fact that the CH_3–CH_3 interactions must be repulsive. The *endo* and *exo* hydrogen atoms (see VI) on the terminal carbon atoms are bent out of the ligand plane by respective averages of 42° (range 35–51°) away from, and 19° (range 14–22°) toward, the iron atom. The average values observed for Ru(2,3,4-C_8H_{13})$_2$ were quite similar at 42° and 17°, respectively.



(VI)

The average Fe–C bond distances to the C(n) and C($n+8$) atoms are 2.059(3), 2.081(3), 2.144(3), 2.060(3) and 2.088(4) Å, respectively for $n = 1$–5. The average Fe–C bond distance is 2.087(1) Å, essentially identical to the value of 2.089(3) Å in Fe(2,4-C_7H_{11})$_2$, even with the apparently greater inter-ligand repulsions. It is interesting that in Fe(2,4-C_7H_{11})$_2$ the longest metal–carbon bonds clearly involved the terminal carbon atoms, while for Fe(2,3,4-C_8H_{13})$_2$ it is clear that the longest metal–carbon bonds involve the central carbon atoms. The primary reason for this difference is related to the presence of the extra methyl groups attached to the C(3) and C(11) atoms. In Fe(2,4-C_7H_{11})$_2$, the C(2)–C(3)–C(4) angles averaged 125.5(3)°, significantly larger than the 122.4° value for the C(1)–C(2)–C(3) and C(3)–C(4)–C(5) types of angles, while in the present case a smaller central angle of 122.4(3)° is found, which is more similar to the values found for the C(1)–C(2)–C(3) and C(3)–C(4)–C(5) (and their equivalent) angles [15], which average 122.9(2)°. The contraction of the C(2)–C(3)–C(4) angles in Fe(2,3,4-C_8H_{13})$_2$ relative to Fe(2,4-C_7H_{11})$_2$ will bring the C(1), C(2), C(4), and C(5) atoms into closer proximity to the metal atom, and move the ligand center of mass away from the C(3) atom. In fact, the relative pattern of the metal–carbon bond distances in Fe(2,3,4-C_8H_{13})$_2$ is more similar to that in Ru(2,3,4-C_8H_{13})$_2$, for which the average metal–carbon bond distances were 2.152(7), 2.195(7), 2.258(7), 2.166(8), and 2.172(9) Å for C(1)–C(5) and their respective counterparts. Thus, the relative values of the various metal–carbon bond distances in a given transition metal-pentadienyl complex seem to be at least as dependent on the geometry of the flexible pentadienyl ligand as on anything else (such as electronic influences). An additional effect of this contraction is that the bonded portion of the pentadienyl ligand becomes smaller. This can be seen by comparing the C(1)–C(5) types of nonbonded contacts. Thus, the value of 2.706(9) Å for Fe(2,3,4-C_8H_{13})$_2$ is clearly shorter than the value of 2.785(5) Å for Fe(2,4-C_7H_{11})$_2$ but comparable to that for Ru(2,3,4-C_8H_{13})$_2$, 2.715(9) Å.

The delocalized carbon–carbon bond distances for the pentadienyl ligands average 1.412(2) Å. No significant distinction could be made between the "internal" and "external" distances, which averaged 1.414(3) and 1409(3) Å, respectively. In most other pentadienyl structures, the "external" bond distances tended to be shorter than the "internal" ones due to a contribution by resonance hybrid VII. The C–CH_3 bond distances averaged 1.516(3) Å.



(VII)

Acknowledgement

R.D.E. expresses his appreciation for generous support of this research from the National Science Foundation (CHE-8120683 and CHE-8419271).

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2 L. Stahl and R.D. Ernst, Organometallics, 2 (1983) 1229.

3 L. Stahl and R.D. Ernst, unpublished results.

4 (a) M. Mathew and G.J. Palenik, Inorg. Chem., 11 (1972) 2809; (b) J.R. Blackborow, R.H. Grubbs, K. Hildenbrand, E.A. Koerner von Gustorf, A. Miyashita, and A. Scrivanti, J. Chem. Soc., Dalton Trans., (1977) 2205; (c) H. Schmid and M.L. Ziegler, Chem. Ber., 109 (1976) 125.

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6 (a) The respective C(7)–C(16) and C(8)–C(15) contact distances were found to be 3.556 and 3.536 Å for Fe(2,3,4-C_8H_{13})$_2$. Other possibly significant contacts (in Å) take place between the following

pairs of carbon atoms: C(1,9), 3.059; C(1,13), 3.053; C(2,12), 3.379; C(2,13), 2.969; C(3,12), 3.329; C(4,10), 3.389; C(4,11), 3.332; C(5,9), 3.047; C(5,10), 2.966; C(5,14), 3.206; C(6,13), 3.193. The deviations of one of these contacts to the other pair related by a C_2 rotation average less than 0.006 Å. The Van der Waals radii for carbon atoms and methyl groups are 1.7 and 2.0 Å, respectively [6b]; (b) L. Pauling, 'The Nature of the Chemical Bond', 3rd Ed., Cornell University Press, Ithaca, New York, 1960, Chapter 7.

7 A referee has suggested an alternative (metal-independent) method of calculating the conformation angles. In this approach, five three-atom planes are calculated for each ligand, each involving the two ligand mass centers (determined from the metal-bound carbon atoms only) and one of the five bound pentadienyl carbon atoms. The angle between any two analogous planes is then determined (e.g., CM(1)–CM(2)–C(n) vs. CM(1)–CM(2)–C($n+8$), where $n = 1$–5 for this complex), and an average of the five values determined. For $Fe(2,4\text{-}C_7H_{11})_2$, $Ru(2,3,4\text{-}C_8H_{13})_2$, and $Fe(2,3,4\text{-}C_8H_{13})_2$, the new values become 60.9, 52.2, and 55.8°, respectively. That little difference is observed between the two approaches is due to the fact that the metal atom is located rather symmetrically to the two ligand planes in each complex.

8 (a) Actually, the conformation angle for $Os(2,4\text{-}C_7H_{11})_2$ has recently been determined to be 48.2°, so that the 52.5° value for the $Ru(2,3,4\text{-}C_8H_{13})_2$ complex may actually reflect more of an electronic, rather than steric, trend; (b) M.L. Ziegler, private communication.

9 Least-squares plane data may be found in Table 5 (Supplementary material). The average deviation for the ten metal-bound carbon atoms from their ligands planes is 0.035 Å. C(4) and the related C(12) atom are bent significantly toward the other pentadienyl ligand by ca. 0.065 Å, and this is accompanied by a bend away from them of ca. 0.045 Å by C(3) and C(11). For $Fe(2,4\text{-}C_7H_{11})_2$, $Fe(2,3,4\text{-}C_8H_{13})_2$, and $Ru(2,3,4\text{-}C_8H_{13})_2$, the two ligand planes are tilted in similar fashions. In each case, the carbon atom deviations from the other ligand plane fall in the order of furthest = C(3), C(4), C(5), C(2), and C(1) (closest). The actual average distances (Å) for the two ligands in each respective complex are as follows: 3.23, 3.16, 2.96, 2.89, 2.53 (avg. 2.95); 3.34, 3.24, 2.92, 2.88, 2.41 (avg. 2.96); 3.56, 3.45, 3.15, 3.14, 2.74 (avg. 3.21). However, while the orderings remain constant, some adjustments can be seen. For example, in $Fe(2,4\text{-}C_7H_{11})_2$ the C(3) and C(4) types of atom are closer to the other ligand plane than they are in $Fe(2,3,4\text{-}C_8H_{13})_2$. The situation is reversed, however, for the C(1), C(2), and C(5) types. This trend can again be explained by the eclipsing interactions involving the methyl groups on the C(3) and C(4) atoms.

10 A. Haaland, Acc. Chem. Res., 12 (1979) 415.

11 (a) R.D. Ernst, Struct. Bond. (Berlin), 57 (1984) 1; (b) In this discussion the tilting values have been calculated from the deviation of a given substituent from the ligand least-squares plane, and the C–(substituent) bond distance.

12 R.D. Ernst, Acc. Chem. Res., 18 (1985) 56.

13 In general, 3-methyl substituents do not exhibit the tendency to bend down toward the metal atom to the extent observed for 2 and 4 substituents. In $Mn_3(3\text{-}C_6H_9)_4$, a tilting of only 3.7° was observed [14].

14 M.C. Böhm, R.D. Ernst, R. Gleiter, and D.R. Wilson, Inorg. Chem., 22 (1983) 3815.

15 Methyl substitution at a 2,3, or 4 position has to date invariably led to a contraction of the C–C–C angle around the substituted carbon atom [1,2,11,12,14].