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References

Chen, M.-Q., Liu, J., Mao, Z.-W., Hang, Q.-W. & Tang, W.-X. (1995). *Acta Cryst.* C**51**, 1080–1082.
Graeber, E. J. & Morosin, B. (1981). *Acta Cryst.* A**37**, 233.
Graeber, E. J. & Morosin, B. (1983). *Acta Cryst.* C**39**, 567–570.
Lee, K.-Y. & Coburn, M. D. (1983). *J. Energ. Mater.* **1**, 109–115.
Lieberman, M. L. (1983). *The Deflagration-to-Detonation Transition Project*, pp. 1–72. SAND82–0924. Sandia National Laboratories, New Mexico, USA.
Lieberman, M. L. (1985). *I&EC Prod. Res. Develop.* **24**, 436–440.
Lu, T.-H, Chen, B.-H. & Chung, C.-S. (1993). *Acta Cryst.* C**49**, 1912–1914.
Schlessinger, G. (1960). *Inorganic Synthesis*, Vol. VI, pp. 173–175. New York: McGraw-Hill.
Schlessinger, G. (1962). *Inorganic Laboratory Preparations*, pp. 231–235. New York: Chemical Publishing.
Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1994). *SHELXTL.* Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Dicarbonyl(η^5-cyclopentadienyl)(pyrrolyl-*N*)iron(II)

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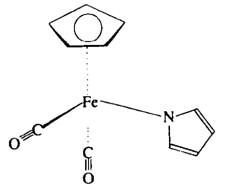
Abstract

The crystal structure of the title compound, [Fe(C_5H_5)(C_4H_4N)(CO)$_2$], shows a discrete molecular structure with a distorted tetrahedral geometry about the Fe atom. The bond angles between the ligands in the tripod and the Fe—Cp$_{\rm centroid}$ vector range from 121.9 to 123.7 (3)°, and the angles between the tripod ligands range from 90.5 (4) to 96.0 (4)°. The mean Fe—C$_{\rm carbonyl}$ and Fe—C$_{\rm Cp}$ distances are 1.776 (4) and 2.098 (16) Å, respectively [Fe—Cp$_{\rm centroid}$ 1.722 (4) Å], and the Fe—N$_{\rm pyrrole}$ distance is 1.962 (3) Å. The Cp and pyrrole rings are both planar (maximum deviations of 0.007 and 0.006 Å, respectively). The rotational orientation of the Cp ring with respect to the tripod ligands is approximately eclipsed with respect to the Fe—N$_{\rm pyrrole}$ bond [N(1)—Fe(1)—Cp$_{\rm centroid}$—C(8) −3.1°]. The dihedral angle between the pyrrole ring and the N(1)—Fe(1)—Cp$_{\rm centroid}$ plane is 73.7°.

Comment

Dicarbonyl(η^5-cyclopentadienyl)(pyrrolyl-*N*)iron(II), (I), was first reported in 1967 (Pauson & Quazi, 1967). The compound displays interesting chemical behavior, including the ability to undergo a reversible 'ring-slip' process to yield azoferrocene (Zakrzewski & Giannotti, 1990). Recently, we have shown that (I) reacts with chemical oxidants to form novel electronically conducting polymers (Martin, Dotson, Litterer, Hanks & Veas, 1996). The reactivity of (I) was explained and the structure of the resulting polymer was predicted based on force-field and semi-empirical quantum mechanical calculations. In this report, we present single-crystal diffraction data which is entirely consistent with our predicted minimum-energy gas-phase structure.



(I)

Compound (I) has the familiar 'three-legged piano-stool' structure (see Fig. 1). The bonding distances and angles for CO and η^5-C_5H_5 (Cp) coordination are similar to those observed in other related complexes. Average values based on a large number of carbon monoxide–iron complexes and cyclopentadienyl–iron complexes are: Fe—C$_{\rm carbonyl}$ = 1.78 (3), C—O = 1.14 (2), Fe—C$_{\rm Cp}$ = 2.08 (3), Fe—Cp$_{\rm centroid}$ = 1.71 (4), and C—C in Cp = 1.40 (3) Å (Orpen *et al.*, 1989). Corresponding values for compound (I) are: Fe—C$_{\rm carbonyl}$ = 1.776 (4), C—O = 1.138 (4), Fe—C$_{\rm Cp}$ = 2.10 (2), Fe—Cp$_{\rm centroid}$ = 1.72 (2), and C—C in Cp = 1.41 (1) Å. The Fe—N$_{\rm pyrrole}$ distance is also within the range of values reported for this type of compound where *X* is a nitrogen ligand [1.961 (4) Å for *X* = 1,2,3-triazole (Antipin *et al.*, 1983), 1.970 (7) Å for *X* = benzimidazole (Nesmeyanov *et al.*, 1977) and 1.956 (3) Å for *X* = phthalimidato (Bukowska-Strzyzewska, Tosik, Woka & Zakrzewski, 1994)].

The gas-phase minimum-energy structure for (I) has been calculated using both *ZINDO* and molecular mechanics methods (Martin *et al.*, 1996), and there is

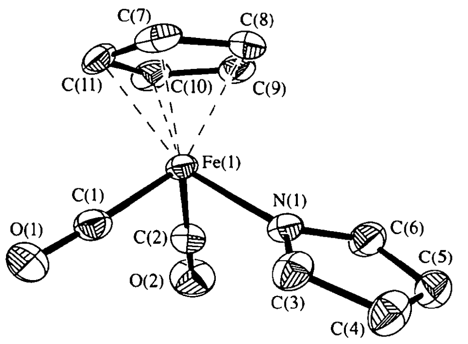


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

good agreement between the results of these two methods. The only major conformational differences between the calculated structure and the observed structure (see Fig. 2) is in the rotational orientation of the Cp ring and in the conformation of the pyrrole ring. In (I), the rotational orientation of the Cp ring with respect to the tripod ligands is approximately eclipsed with respect to the Fe—$N_{pyrrole}$ bond [N(1)—Fe(1)—$Cp_{centroid}$—C(8) is −3.1°]. The dihedral angle between the pyrrole ring and the N(1)—Fe(1)—$Cp_{centroid}$ plane is 73.7°. In the calculated structure, the Cp ring is arbitrarily shown in a nearly staggered rotational conformation with respect to the Fe—$N_{pyrrole}$ bond [N(1)—Fe(1)—$Cp_{centroid}$—C(8) is −29.4°], but there is no one energetically preferred rotational orientation of this group. The pyrrole ring plane of the calculated structure is nearly orthogonal to the N(1)—Fe(1)—$Cp_{centroid}$ plane (dihedral angle of 87.2°). The only significant differences in the distances and angles between the observed and calculated structures for (I) involves the Fe—$C_{carbonyl}$ coordination. The Fe—CO distances are somewhat elongated in the calculated structure (Fe—C = 1.903 Å) and the angle between the two CO groups is considerably smaller (85.8°). Both of these discrepancies indicate that the Fe—CO backbonding is not adequately accounted for in the calculated model.

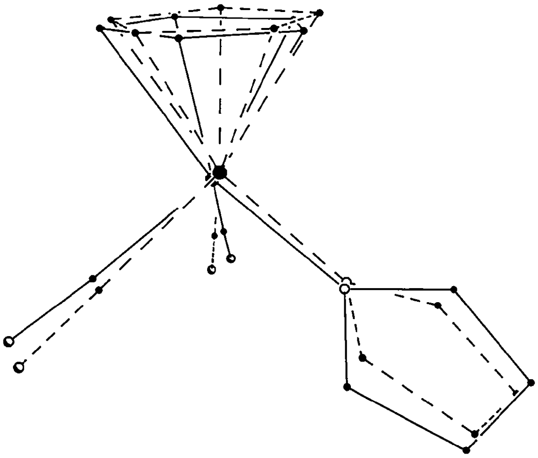


Fig. 2. Comparison of the observed structure of (I) (solid line bonds) with the *ZINDO* calculated structure (dashed line bonds).

Molecules of (I) are discrete moieties, with no close contacts resulting from crystal packing.

Experimental

The title compound was prepared by a modification of a previously developed procedure (Zakrzewski & Giannotti, 1990). In an airless flask, $CpFe(CO)_2I$ (2.45 g, 8.06 mmol) and pyrrole (16.0 ml, 231 mmol) were added to diisopropylamine (40.0 ml, 285 mmol) and 180 ml of toluene (all of the liquid reagents, pyrrole, diisopropylamine and toluene, were freshly distilled). The resulting brown–black solution was then placed in an ice bath, stirred and irradiated with a 500 W tungsten lamp for 5.5 h. The reaction mixture was then removed from the ice bath and flash chromatographed through silica under nitrogen. All but 10 ml of the toluene was then removed *in vacuo*. Methanol (25 ml) was added and all of the solvent was removed *in vacuo* as an azeotrope. The resulting red-brown powder was dissolved in diethyl ether. Crystals were grown by slow evaporation to yield (I) in 62% yield. Spectral data were consistent with reported values (Zakrzewski & Giannotti, 1990; Martin *et al.*, 1996).

Crystal data

$[Fe(C_5H_5)(C_4H_4N)(CO)_2]$
$M_r = 243.04$
Monoclinic
$P2_1/n$
$a = 8.309\ (5)$ Å
$b = 11.420\ (4)$ Å
$c = 10.766\ (4)$ Å
$\beta = 95.48\ (4)°$
$V = 1017.0\ (7)$ Å^3
$Z = 4$
$D_x = 1.587$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 4.68–8.58°$
$\mu = 1.46$ mm^{-1}
$T = 148$ K
Parallelepiped
0.28 × 0.26 × 0.18 mm
Purple

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1991)
$T_{min} = 0.66$, $T_{max} = 0.77$
2025 measured reflections
1786 independent reflections

1300 reflections with $F > 4\sigma(F)$
$R_{int} = 0.017$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = -12 \rightarrow 12$
3 standard reflections every 100 reflections intensity decay: −3.2%

Refinement

Refinement on *F*
$R = 0.032$
$wR = 0.0383$
$S = 1.12$

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

1300 reflections
172 parameters
H-atom positional parameters and *U*'s refined
Extinction correction: none
Scattering factors from Cromer & Waber (1974)

Table 1. *Selected geometric parameters (Å, °)*

Fe(1)—N(1)	1.962 (3)	N(1)—C(3)	1.367 (5)
Fe(1)—C(1)	1.777 (4)	N(1)—C(6)	1.361 (5)
Fe(1)—C(2)	1.774 (4)	C(3)—C(4)	1.375 (5)
Fe(1)—C(7)	2.113 (4)	C(4)—C(5)	1.396 (6)
Fe(1)—C(8)	2.116 (4)	C(5)—C(6)	1.379 (6)
Fe(1)—C(9)	2.090 (4)	C(7)—C(8)	1.398 (5)
Fe(1)—C(10)	2.079 (4)	C(7)—C(11)	1.426 (6)
Fe(1)—C(11)	2.093 (3)	C(8)—C(9)	1.410 (6)
O(1)—C(1)	1.136 (4)	C(9)—C(10)	1.413 (5)
O(2)—C(2)	1.141 (5)	C(10)—C(11)	1.400 (6)
N(1)—Fe(1)—C(1)	94.0 (1)	C(3)—C(4)—C(5)	106.9 (4)
N(1)—Fe(1)—C(2)	90.5 (1)	C(4)—C(5)—C(6)	106.4 (3)
C(1)—Fe(1)—C(2)	96.0 (2)	N(1)—C(6)—C(5)	110.3 (3)
Fe(1)—N(1)—C(3)	127.5 (2)	C(8)—C(7)—C(11)	107.9 (3)
Fe(1)—N(1)—C(6)	126.0 (2)	C(7)—C(8)—C(9)	108.8 (3)
C(3)—N(1)—C(6)	106.5 (3)	C(8)—C(9)—C(10)	107.0 (3)
Fe(1)—C(1)—O(1)	176.9 (3)	C(9)—C(10)—C(11)	109.0 (4)
Fe(1)—C(2)—O(2)	178.5 (3)	C(7)—C(11)—C(10)	107.2 (3)
N(1)—C(3)—C(4)	109.9 (3)		

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined with anisotropic displacement parameters and H atoms were refined isotropically [C—H: 0.87 (2)–0.98 (2) Å; *U*(H): 0.015 (8)–0.055 (13) Å^2].

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1322). Services for accessing these data are described at the back of the journal.

References

Antipin, M. Yu., Aleksandrov, G. G., Struchkov, Yu. T., Belousov, Yu. A., Babin, V. N. & Kochetkova, N. S. (1983). *Inorg. Chim. Acta*, **68**, 229–232.

Bukowska-Strzyzewska, M., Tosik, A., Woka, D. & Zakrzewski, J. (1994). *Polyhedron*, **13**, 1689–1694.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71–98. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Martin, K., Dotson, M., Litterer, M., Hanks, T. W. & Veas, C. (1996). *Synth. Met.* **78**, 161.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nesmeyanov, A. N., Belousov, Yu. A., Babin, V. N., Aleksandrov, G. G., Struchkov, Yu. T. & Kochetkova, N. S. (1977). *Inorg. Chim. Acta*, **23**, 155–162.

Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans. Suppl.* S1–S83.

Pauson, P. L. & Quazi, A. R. (1967). *J. Organomet. Chem.* **7**, 321.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Zakrzewski, J. & Giannotti, C. J. (1990). *Organomet. Chem.* **388**, 175.