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## $\eta$ -Cyclopentadienylcarbonylbis(diphenylphosphino)methaneiron Tetraphenylborate

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**Abstract.** [Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO){[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Pl<sub>2</sub>CH<sub>2</sub>]}]·B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, C<sub>31</sub>H<sub>27</sub>FeOP<sub>2</sub>·C<sub>24</sub>H<sub>20</sub>B<sup>-</sup>, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 20.503 (5), *b* = 15.937 (5), *c* = 13.724 (5) Å, *D*<sub>c</sub> = 1.26 Mg m<sup>-3</sup> for *Z* = 4. An approximate mirror plane bisects the cation. A correlation was shown to exist between Fe–C length and C–O stretching frequency of a number of {Fe(cp)(CO)XY} complexes, including the title compound.

**Introduction.** Attempts to prepare the binuclear Fe complex [Fe(cp)(CO)<sub>2</sub>(SC<sub>2</sub>H<sub>5</sub>)(dppm)]B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> [dppm = bis(diphenylphosphino)methane; cp =  $\eta$ -C<sub>5</sub>H<sub>5</sub>] by refluxing [Fe<sub>2</sub>(cp)<sub>2</sub>(CO)<sub>3</sub>(SC<sub>2</sub>H<sub>5</sub>)]B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> (English, Haines & Nolte, 1975; English, Nassimbeni & Philpott, 1978) with dppm in acetone led to the formation of glossy yellow needles of the title complex. A crystal, 0.07 × 0.07 × 0.15 mm, was used for data collection. Intensities were measured on a four-circle Philips PW1100 diffractometer with graphite-monochromated Mo *K* $\alpha$  radiation ( $\lambda$  = 0.7107 Å) and the  $\omega$ -2 $\theta$  scan mode. 2387 independent reflections were collected of which 1294 unique observed [*I* ±  $\sigma$ (*I*)] reflections were employed in the analysis. No crystal decomposition was observed. Lorentz–polarization but no absorption corrections were applied.

The position of the Fe atom was found from a Patterson map. Peaks corresponding to the two P atoms were present in a difference synthesis based on the Fe atom. Subsequent isotropic refinement followed by difference syntheses revealed the positions of the remaining non-hydrogen atoms; phenyl and cyclopentadienyl rings were treated as rigid perfect polygons with C–C = 1.395 and 1.42 Å respectively (Sheldrick, 1978). Refinement continued with blocked-matrix (two blocks, for the cation and anion, refining in alternate

cycles) least-squares calculations with Fe, P, O and B anisotropic, to an *R* of 0.18.

In the final blocked-matrix refinement, H atom positions were calculated with C–H = 1.080 Å, and geometric constraints were removed from the ring C atoms. Phenyl C atoms were refined isotropically, as were C(1), R5C(2) and R5C(3): attempts to refine these latter three atoms anisotropically resulted in non-positive-definite temperature-factor-matrix determinants. *R* fell to its final value of 0.079 and *R*<sub>w</sub> was 0.059 with a weighting scheme  $w = 1.6397/\sigma^2 F$ .

The final *R* values did not distinguish between the two possible enantiomorphs: *R*<sub>G</sub> (Sheldrick, 1978) for the coordinates given = 0.0528; *R*<sub>G</sub> for the enantiomorph = 0.0542.

The isotropic temperature factors of the H atoms of the phenyl groups bound to the P and B atoms, the cyclopentadienyl group and methylene group were refined as three single variables and converged to *U* = 0.15 (2), 0.03 (2) and 0.07 (5) Å<sup>2</sup> respectively. No peak >0.4 e Å<sup>-3</sup> appeared in a difference map based on all atoms and the average shift/error in the last two cycles was in no case >0.1. Scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). Final positional parameters for the non-hydrogen atoms are given in Table 1.\* Fig. 1 shows the structure of the cation and the atomic labelling, and Fig. 2 is a stereo pair depicting the somewhat complex packing in this structure, projected on to (001). Tables 2 and 3 list some bond lengths and angles.

\* Lists of structure factors, anisotropic and isotropic thermal parameters and H atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34160 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) of the non-hydrogen atoms (with *e.s.d.*'s)

	x	y	z
Fe	7079 (1)	371 (2)	4695 (2)
P(1)	8065 (3)	804 (3)	5149 (4)
C(2)	7761 (7)	1575 (12)	6032 (14)
P(2)	6911 (3)	1505 (3)	5571 (4)
C(1)	6980 (10)	-265 (11)	5720 (13)
O(1)	6919 (7)	-694 (8)	6386 (10)
R5C(1)	7025 (13)	679 (14)	3218 (15)
R5C(2)	7288 (9)	-131 (13)	3328 (13)
R5C(3)	6825 (11)	-628 (15)	3751 (15)
R5C(4)	6265 (11)	-111 (16)	3928 (16)
R5C(5)	6413 (12)	710 (17)	3574 (19)
R11C(1)	8640 (9)	110 (12)	5774 (14)
R11C(2)	8580 (9)	-737 (12)	5603 (13)
R11C(3)	9097 (10)	-1273 (14)	5969 (15)
R11C(4)	9586 (9)	-944 (13)	6520 (14)
R11C(5)	9604 (10)	-87 (12)	6739 (15)
R11C(6)	9127 (8)	451 (13)	6399 (13)
R12C(1)	8636 (8)	1302 (11)	4323 (13)
R12C(2)	8894 (9)	2091 (11)	4474 (14)
R12C(3)	9382 (9)	2424 (13)	3884 (15)
R12C(4)	9624 (11)	1969 (15)	3135 (17)
R12C(5)	9350 (11)	1158 (15)	2931 (18)
R12C(6)	8868 (10)	830 (14)	3547 (17)
R21C(1)	6703 (10)	2466 (12)	4975 (15)
R21C(2)	7139 (11)	2907 (13)	4393 (15)
R21C(3)	6962 (14)	3613 (16)	3845 (19)
R21C(4)	6338 (12)	3914 (15)	3954 (19)
R21C(5)	5888 (12)	3531 (16)	4481 (19)
R21C(6)	6057 (10)	2772 (12)	4998 (14)
R22C(1)	6383 (9)	1463 (13)	6633 (14)
R22C(2)	6539 (9)	1921 (13)	7456 (15)
R22C(3)	6134 (10)	1876 (12)	8283 (16)
R22C(4)	5577 (10)	1401 (12)	8236 (15)
R22C(5)	5398 (10)	977 (14)	7430 (16)
R22C(6)	5793 (9)	971 (12)	6578 (16)
B	1227 (11)	490 (15)	28 (16)
R1C(1)	537 (9)	1049 (12)	-188 (16)
R1C(2)	400 (9)	1240 (12)	-1178 (15)
R1C(3)	-103 (8)	1786 (11)	-1468 (14)
R1C(4)	-493 (11)	2117 (13)	-788 (18)
R1C(5)	-368 (9)	1955 (12)	148 (17)
R1C(6)	129 (9)	1388 (12)	496 (16)
R2C(1)	1845 (9)	1136 (11)	-110 (15)
R2C(2)	2409 (10)	1107 (13)	492 (16)
R2C(3)	2948 (11)	1673 (13)	345 (17)
R2C(4)	2906 (11)	2291 (13)	-349 (17)
R2C(5)	2394 (10)	2294 (13)	-989 (17)
R2C(6)	1888 (10)	1718 (12)	-823 (15)
R3C(1)	1249 (10)	-315 (13)	-707 (13)
R3C(2)	707 (9)	-832 (12)	-824 (14)
R3C(3)	738 (9)	-1501 (13)	-1486 (14)
R3C(4)	1269 (10)	-1674 (14)	-1969 (14)
R3C(5)	1818 (10)	-1169 (12)	-1881 (14)
R3C(6)	1811 (9)	-498 (13)	-1260 (13)
R4C(1)	1231 (9)	183 (14)	1183 (14)
R4C(2)	1225 (10)	706 (14)	1963 (16)
R4C(3)	1273 (10)	467 (16)	2956 (16)
R4C(4)	1355 (10)	-407 (15)	3159 (17)
R4C(5)	1410 (11)	-945 (15)	2407 (18)
R4C(6)	1345 (9)	-629 (14)	1429 (15)

 Table 2. Relevant bond lengths (with *e.s.d.*'s) (Å)

Fe—P(1)	2.226 (6)
Fe—P(2)	2.198 (6)
Fe—C(1)	1.75 (2)
Fe—C (ring 5) (average)	2.11 (2)
C(1)—O(1)	1.15 (2)
P(1)—C(2)	1.84 (2)
P(2)—C(2)	1.86 (2)
C—C (ring 5) (average)	1.40 (3)
P(1)—R11C(1)	1.83 (2)
P(1)—R12C(1)	1.81 (2)
P(2)—R21C(1)	1.79 (2)
P(2)—R22C(1)	1.82 (2)
C—C (phenyl rings) (average)	1.39 (4)

 Table 3. Relevant bond angles (with *e.s.d.*'s) ( $^\circ$ )

P(1)—Fe—P(2)	74.6 (2)	P(1)—C(2)—P(2)	93.1 (9)
P(1)—Fe—C(1)	93.5 (7)	Fe—P(1)—C(2)	94.8 (5)
P(2)—Fe—C(1)	91.1 (6)	Fe—P(2)—C(2)	95.1 (6)
Fe—C(1)—O(1)	179 (2)		

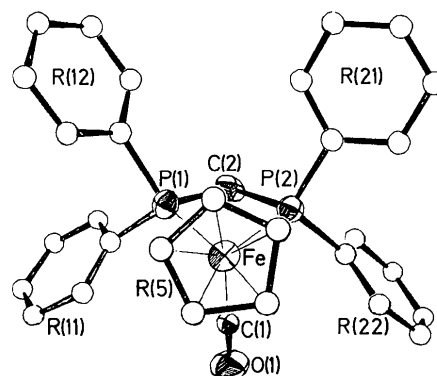


Fig. 1. Perspective view of the cation with atomic and phenyl-ring nomenclature.

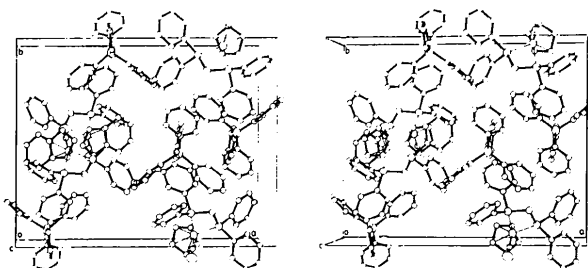


Fig. 2. Stereoscopic view of the unit cell, projected on to (001).

**Discussion.** While the formulation of the title complex as  $[\text{Fe}(\text{cp})(\text{CO})(\text{dppm})]\text{B}(\text{C}_6\text{H}_5)_4$  followed in a straightforward manner from microanalytical, conductimetric

and spectroscopic data, the low value of the infrared C—O stretching frequency [ $\nu(\text{C—O}) = 198.2 \text{ mm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$  solution] of this cationic complex was of some interest. Traditionally, the  $\nu(\text{C—O})$  frequencies of transition-metal carbonyls have been correlated with the degree of overlap between metal *d* orbitals and the  $\pi^*(\text{C—O})$  molecular orbitals (and therefore the metal—C bond distance) (Cotton & Wing, 1965*a,b*).

Table 4. Correlation of Fe—C bond length with C—O stretching frequency

Compound	Number (see Fig. 3)	Bond length (Å)	Residual index	$\nu(\text{CO})$ mm <sup>-1</sup>
Fe(cp)(CO)(CHNCH <sub>3</sub> ) <sub>2</sub> BH <sub>2</sub> ]	1	1.718 (17) <sup>a</sup>	0.113 <sup>a</sup>	195.0 <sup>b</sup>
[Fe(cp)(CO)(dppm)]B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	2	1.745 (18) <sup>c</sup>	0.079 <sup>c</sup>	198.2 <sup>c</sup>
Fe(cp)(CO)(CF <sub>3</sub> CNH)(NCCF <sub>3</sub> )	3	1.745 (9) <sup>d</sup>	0.049 <sup>d</sup>	199.6 <sup>e</sup>
Fe(cp)(CO) <sub>2</sub> (C <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )	4	1.754 (5) <sup>f</sup> (av.)	0.060 <sup>f</sup>	200.0 <sup>g</sup>
Fe(cp)(CO) <sub>2</sub> (CH <sub>2</sub> CO <sub>2</sub> H)	5	1.72 (2) <sup>h</sup> (av.)	0.132 <sup>h</sup>	202.6 <sup>h</sup>
Fe(cp)(CO) <sub>2</sub> (SC <sub>2</sub> H <sub>5</sub> )	6	1.751 (5) <sup>i</sup>	0.049 <sup>i</sup>	202.8 <sup>j</sup>
[Fe(cp)(CO) <sub>2</sub> (C <sub>8</sub> H <sub>8</sub> )]SbF <sub>6</sub> *	7	1.84 (5) <sup>k</sup>	0.123 <sup>k</sup>	203.3 <sup>l</sup>
Fe(cp)(CO) <sub>2</sub> [P(CF <sub>3</sub> ) <sub>2</sub> ]	8	1.768 (7) <sup>m</sup> (av.)	0.0480 <sup>m</sup>	204.6 <sup>m</sup>
Fe(cp)(CO) <sub>2</sub> [P(CF <sub>3</sub> ) <sub>2</sub> O]	9	1.780 (7) <sup>m</sup> (av.)	0.0450 <sup>m</sup>	206.2 <sup>m</sup>
Fe(cp)(CO) <sub>2</sub> (C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> )	10	1.74 (2) <sup>n</sup>	0.107 <sup>n</sup>	207.0 <sup>o</sup>
[Fe(cp)(CO) <sub>3</sub> ]PF <sub>6</sub>	11	1.816 (6) <sup>p</sup> (av.)	0.083 <sup>p</sup>	212.0 <sup>o</sup>

(a) Butler & Enemark (1973), (b) Treichel, Stenson & Benedict (1971), (c) this work, (d) Bottrill, Goddard, Green, Hughes, Lloyd, Taylor & Woodward (1975), (e) King & Pannell (1968), (f) Goddard, Howard & Woodward (1974), (g) Green & Mole (1968), (h) Ariyaratne, Bierrum, Green, Ishaq, Prout & Swanwick (1969), (i) English, Haines & Nassimbeni (1978), (j) Ahmad, Bruce & Knox (1966), (k) Churchill & Fennessey (1970), (l) Ehntholt, Emerson & Kerber (1969), (m) Barrow & Sim (1975), (n) Redhouse (1974), (o) Bruce & Redhouse (1971), (p) Gress & Jacobson (1973), (q) Busetto & Angelici (1968).

\* Compound decomposed rapidly.

The correlation is an inverse one and, as yet, no theoretical relationship has been shown to exist between the force constant of the C—O bond and the metal—C or C—O bond energy. However, the  $\nu(\text{C—O})$  frequency does seem to be a sensitive measure of the electron density at the metal atom in these complexes. This in turn is influenced by both the electron-donating powers of the other ligands bound to the metal, and the total charge on the complex.

In the title complex the  $\nu(\text{C—O})$  band occurs in the same region as peaks of other, neutral {Fe(cp)(CO)} complexes with strongly electron-donating ligands. This suggests that the overall charge in such complexes plays only a secondary part in determining the amount of metal *d*-orbital— $\pi^*(\text{C—O})$ -orbital overlap [although overall charge has been shown by English, Haines & Nassimbeni (1978) to have an effect].

Fig. 3 shows a graph of  $\nu(\text{C—O})$  frequencies [the highest  $\nu(\text{C—O})$  band in those cases where more than one band is present] exhibited by a number of complexes containing the {Fe(cp)(CO)} moiety against the Fe—C length. (Data are given in Table 4.) In the majority of the complexes a surprisingly good correlation exists between the two parameters. Long, Alway & Barnett (1978) reported a similar correlation between Mössbauer effect, chemical isomer shift and carbonyl stretching force constant. The secondary effect of overall charge is well emphasized by the position of the point representing the title complex on the curve.

All calculations were performed on the University of South Africa's Burroughs B6800 computer with the *SHELX* (Sheldrick, 1978) program system.

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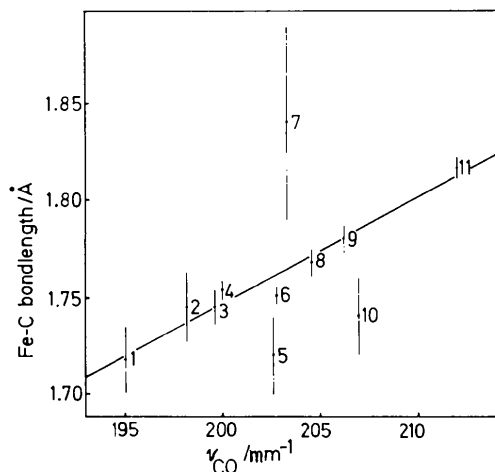


Fig. 3. Fe—C lengths for [Fe(cp)(CO)XY] complexes vs C—O stretching frequencies. Data are given in Table 4.

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## Structure of (–)<sub>589</sub>Bis[(1*R*,2*R*)-1,2-cyclohexanediamine](3,3'-dimethyl-2,2'-bipyridine)cobalt(III) Bromide Diperchlorate Monohydrate

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**Abstract.** [Co(C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>)<sub>2</sub>]<sup>3+</sup>.Br<sup>-</sup>.2ClO<sub>4</sub><sup>-</sup>.H<sub>2</sub>O, [C<sub>24</sub>H<sub>40</sub>CoN<sub>6</sub>]<sup>3+</sup>.Br<sup>-</sup>.2ClO<sub>4</sub><sup>-</sup>.H<sub>2</sub>O, *M<sub>r</sub>* = 768.4, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 12.298 (1), *b* = 30.394 (4), *c* = 8.599 (1) Å, *U* = 3214 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.59, *D<sub>x</sub>* = 1.59 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.7107 Å, μ(Mo *K*α) = 2.10 mm<sup>-1</sup>. The final *R* value is 0.052 for 2749 independent reflections collected by X-ray diffractometry. The complex cation, (–)<sub>589</sub>[Co(*R,R*-chxn)<sub>2</sub>(3,3'-dmbpy)]<sup>3+</sup> (chxn: *trans*-1,2-cyclohexanediamine; dmbpy: dimethyl-2,2'-bipyridine), has approximate twofold symmetry, and its absolute configuration can be designated as *A* (λλ,λ-dmbpy).

**Introduction.** When the two H atoms at the 3 and 3' positions of 2,2'-bipyridine are replaced by bulky methyl groups, the two pyridine moieties are no longer coplanar on forming a chelate ring. Thus 3,3'-dmbpy may coordinate to the cobalt(III) ion with a stereospecific conformation depending on the configuration. As part of a series of structure determinations of cobalt(III) complexes containing 3,3'-dmbpy (Sato & Saito, 1978), crystals of (–)<sub>589</sub>[Co(*R,R*-chxn)<sub>2</sub>(3,3'-dmbpy)]Br(ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O were subjected to X-ray structure analysis in order to reveal the conformational details of the complex ion and to establish an empirical

rule relating its absolute configuration and circular-dichroism spectrum. Orange-red plate-like crystals of the title compound were kindly supplied by Dr T. M. Suzuki (Suzuki & Kimura, 1977). Weissenberg photographs showed them to be orthorhombic with the systematic absences *h*00, 0*k*0 and 00*l* for odd indices, determining the space group as *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. For X-ray work a spherical specimen 0.5 mm in diameter was prepared. Intensities and cell dimensions were measured on a Rigaku automated four-circle diffractometer. Data were collected by the ω-scan technique to a maximum 2θ value of 55° with Mo *K*α radiation (λ = 0.7107 Å) monochromated by a graphite plate. Of the 4158 measured unique reflections, 2749 with |*F<sub>o</sub>*| > 3σ(|*F<sub>o</sub>*|) were considered as observed. The intensities were corrected for Lorentz-polarization and absorption effects.

The structure was solved by the heavy-atom method, and refined by block-diagonal least squares with anisotropic thermal parameters for the non-hydrogen atoms. With *R* = 0.068 (*R* = ∑|Δ*F*|/∑|*F<sub>o</sub>*|), all the H atoms appeared in a difference synthesis, except for those of the methyl groups. At this stage the thermal parameter of H(C2) was –3.5 Å<sup>2</sup> and the C(2)–H(C2) distance was 1.25 (7) Å. This unusual result could be accounted