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[*R*-(*R**,*R**)]-(η^5-Cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine-*P*)]-(1-phenylphosphirane-*P*)iron(II) Hexafluorophosphate

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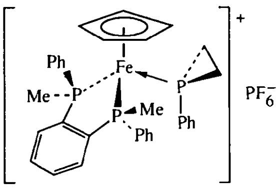
Abstract

The title compound, $[\mathrm{Fe(C_5H_5)(C_8H_9P)(C_{20}H_{20}P_2)]PF_6}$, was obtained by spontaneous resolution of the racemate from acetone/diethyl ether solution. The cationic piano-stool iron(II) complex exhibits pseudo-octahedral coordination geometry, with Fe—P distances of 2.189 (3) and 2.178 (4) Å for the bidentate ligand, and 2.170 (3) Å for the phosphirane ligand. The bond parameters for the phosphirane ligand are in good agreement with those found for related complexes.

Comment

As part of our investigations of iron(II) complexes containing heterocyclic phosphorus and arsenic ligands, the compound (*R**,*R**)-(±)-[(η^5-$\mathrm{C_5H_5}$){1,2-$\mathrm{C_6H_4(PMePh)_2}$}Fe($\mathrm{PhPCH_2CH_2}$)]$\mathrm{PF_6}$, (*R**,*R**)-(1), was prepared by direct synthesis from 1-phenylphosphirane and (*R**,*R**)-(±)-[(η^5-$\mathrm{C_5H_5}$){1,2-$\mathrm{C_6H_4(PMePh)_2}$}-Fe(MeCN)]$\mathrm{PF_6}$ (Bader, Kang, Pabel, Pathak, Willis & Wild, 1995). Orange (*R**,*R**)-(1) crystallized as a conglomerate of enantiomorphic crystals from acetone/diethyl ether solution. The crystal chosen for X-ray structure analysis was found to be the [*R*-(*R**,*R**)] enantiomer of the compound.



[*R*-(*R**,*R**)]-(1)

To our knowledge, this is the first cationic coordination complex of 1-phenylphosphirane to be characterized by X-ray crystallography. The molecular structure of the cation of [*R*-(*R**,*R**)]-(1) is depicted in Fig. 1. The complex has piano-stool geometry, with pseudo-octahedral coordination around the Fe atom. Bond distances and angles within the three-membered phosphirane ring (Table 2) differ little from the corresponding parameters for the neutral complexes [W(CO)$_5$($\mathrm{PhPCH_2CH_2}$)] (Hung, Yang, Gray & Lammertsma, 1993) and *fac*-[Mo(CO)$_3$($\mathrm{PhPCH_2CH_2}$)$_3$] (Kang, Pabel, Willis & Wild, 1994). Bond parameters for the [*R*-(*R**,*R**)]-[(η^5-$\mathrm{C_5H_5}$){1,2-$\mathrm{C_6H_4(PMePh)_2}$}Fe] fragment of the complex are also in good agreement with those found for related complexes (Hey, Willis

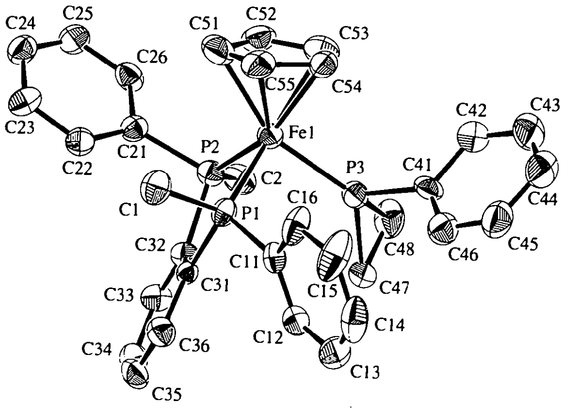


Fig. 1. An *ORTEP* plot (Johnson, 1965) of the cation of [*R*-(*R**,*R**)]-(1), with the non-H atoms shown as 30% probability ellipsoids and H atoms omitted for clarity.

& Wild, 1989; Crisp, Salem, Wild & Stephens, 1989; Salem, Shaw, Willis & Wild, 1993*a*,*b*; Bader *et al.*, 1995).

Experimental

Crystal data

$[Fe(C_5H_5)(C_8H_9P)(C_{20}H_{20}P_2)]PF_6$
$M_r = 724.36$
Orthorhombic
$P2_12_12_1$
$a = 12.575\,(2)$ Å
$b = 14.454\,(3)$ Å
$c = 18.365\,(4)$ Å
$V = 3338.0\,(10)$ Å^3
$Z = 4$
$D_x = 1.441$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 13–20°$
$\mu = 0.699$ mm^{-1}
$T = 293$ K
Fragment cleaved from block
0.34 × 0.21 × 0.14 mm
Orange

Data collection

Philips PW1100/20 diffractometer
ω scans
Absorption correction: analytical (De Meulenaer & Tompa, 1965)
$T_{min} = 0.89$, $T_{max} = 0.93$
3315 measured reflections
3315 independent reflections

1809 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 25°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 180 min
intensity decay: 4%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.032$
$S = 1.96$
1809 reflections
397 parameters
H-atom parameters not refined
Weighting scheme: see below

$(\Delta/\sigma)_{max} = 0.04$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe(1)	0.2864 (1)	0.4328 (1)	0.54446 (8)	0.0502 (5)
P(1)	0.3498 (2)	0.5722 (2)	0.5276 (1)	0.0502 (10)
P(2)	0.1379 (3)	0.5013 (2)	0.5731 (2)	0.0501 (10)
P(3)	0.3467 (2)	0.4211 (2)	0.6548 (1)	0.056 (1)
P(4)	0.1165 (3)	0.1233 (3)	0.6930 (2)	0.076 (1)
F(1)	0.2345 (5)	0.1559 (6)	0.6888 (4)	0.127 (3)
F(2)	0.1447 (10)	0.0552 (9)	0.7482 (9)	0.268 (7)
F(3)	0.1054 (9)	0.185 (1)	0.7563 (8)	0.253 (7)
F(4)	−0.0009 (6)	0.0898 (8)	0.6978 (4)	0.163 (4)
F(5)	0.0840 (9)	0.1989 (8)	0.6443 (9)	0.228 (7)
F(6)	0.1296 (8)	0.067 (1)	0.6286 (6)	0.238 (6)
C(1)	0.3559 (9)	0.6153 (7)	0.4333 (5)	0.074 (4)
C(2)	0.0533 (9)	0.4615 (7)	0.6444 (6)	0.069 (4)
C(11)	0.4845 (8)	0.5969 (7)	0.5597 (6)	0.054 (4)
C(12)	0.5085 (10)	0.6463 (8)	0.6211 (7)	0.066 (5)
C(13)	0.613 (1)	0.6620 (9)	0.6433 (9)	0.093 (6)
C(14)	0.694 (1)	0.624 (1)	0.6042 (9)	0.094 (6)
C(15)	0.672 (1)	0.572 (1)	0.5425 (7)	0.116 (6)
C(16)	0.5683 (10)	0.558 (1)	0.5223 (6)	0.079 (5)
C(21)	0.0446 (9)	0.5123 (8)	0.4970 (6)	0.052 (4)
C(22)	0.0548 (9)	0.5823 (8)	0.4457 (7)	0.061 (4)
C(23)	−0.0075 (9)	0.5824 (9)	0.3837 (6)	0.064 (4)
C(24)	−0.086 (1)	0.5149 (9)	0.3743 (7)	0.067 (5)
C(25)	−0.0990 (9)	0.4497 (9)	0.4263 (7)	0.072 (5)
C(26)	−0.0356 (9)	0.4472 (8)	0.4865 (6)	0.062 (4)
C(31)	0.2613 (8)	0.6553 (7)	0.5734 (5)	0.039 (3)
C(32)	0.1676 (9)	0.6200 (7)	0.5964 (6)	0.050 (4)
C(33)	0.0941 (9)	0.6789 (8)	0.6311 (7)	0.062 (5)
C(34)	0.118 (1)	0.7703 (9)	0.6433 (7)	0.069 (5)
C(35)	0.213 (1)	0.8040 (7)	0.6163 (7)	0.076 (5)
C(36)	0.2869 (10)	0.7488 (8)	0.5806 (6)	0.063 (4)
C(41)	0.4741 (10)	0.3667 (9)	0.6732 (6)	0.057 (4)
C(42)	0.482 (1)	0.270 (1)	0.6773 (7)	0.085 (6)
C(43)	0.578 (1)	0.229 (1)	0.6910 (8)	0.098 (6)
C(44)	0.672 (1)	0.274 (1)	0.6940 (8)	0.092 (6)
C(45)	0.665 (1)	0.370 (1)	0.6888 (7)	0.096 (6)
C(46)	0.570 (1)	0.4148 (9)	0.6795 (7)	0.079 (5)
C(47)	0.327 (1)	0.4944 (8)	0.7336 (6)	0.078 (5)
C(48)	0.278 (1)	0.3986 (9)	0.7392 (6)	0.087 (5)
C(51)	0.247 (1)	0.3870 (9)	0.4400 (7)	0.090 (6)
C(52)	0.203 (1)	0.3257 (10)	0.4925 (8)	0.081 (5)
C(53)	0.285 (1)	0.2914 (8)	0.5339 (7)	0.073 (5)
C(54)	0.381 (1)	0.3237 (9)	0.5062 (8)	0.075 (5)
C(55)	0.356 (1)	0.3842 (9)	0.4474 (7)	0.074 (5)

Table 2. *Selected geometric parameters (Å, °)*

Fe(1)—P(1)	2.189 (3)	P(1)—C(31)	1.84 (1)
Fe(1)—P(2)	2.178 (4)	P(2)—C(2)	1.78 (1)
Fe(1)—P(3)	2.170 (3)	P(2)—C(21)	1.83 (1)
Fe(1)—C(51)	2.09 (1)	P(2)—C(32)	1.81 (1)
Fe(1)—C(52)	2.10 (1)	P(3)—C(41)	1.82 (1)
Fe(1)—C(53)	2.05 (1)	P(3)—C(47)	1.81 (1)
Fe(1)—C(54)	2.10 (1)	P(3)—C(48)	1.81 (1)
Fe(1)—C(55)	2.11 (1)	C(31)—C(32)	1.35 (1)
P(1)—C(1)	1.84 (1)	C(47)—C(48)	1.52 (2)
P(1)—C(11)	1.83 (1)		
P(1)—Fe(1)—P(2)	85.9 (1)	C(2)—P(2)—C(21)	101.9 (5)
P(1)—Fe(1)—P(3)	94.4 (1)	C(2)—P(2)—C(32)	104.8 (5)
P(2)—Fe(1)—P(3)	96.3 (1)	C(21)—P(2)—C(32)	103.3 (5)
Fe(1)—P(1)—C(1)	117.4 (4)	Fe(1)—P(3)—C(41)	121.0 (4)
Fe(1)—P(1)—C(11)	118.1 (4)	Fe(1)—P(3)—C(47)	130.7 (4)
Fe(1)—P(1)—C(31)	108.4 (4)	Fe(1)—P(3)—C(48)	130.3 (5)
C(1)—P(1)—C(11)	101.5 (5)	C(41)—P(3)—C(47)	103.2 (5)
C(1)—P(1)—C(31)	103.5 (5)	C(41)—P(3)—C(48)	100.8 (5)
C(11)—P(1)—C(31)	106.5 (5)	C(47)—P(3)—C(48)	49.7 (5)
Fe(1)—P(2)—C(2)	122.8 (4)	P(3)—C(47)—C(48)	65.0 (6)
Fe(1)—P(2)—C(21)	113.9 (4)	P(3)—C(48)—C(47)	65.3 (7)
Fe(1)—P(2)—C(32)	108.2 (4)		

The ω-scan width was $(1.40 + 0.346\tan\theta)°$ and the scan rate 3° min^{-1}. Background counts were taken for 10 s at each side of every scan. The weighting scheme used was $w = 4F_o^2/\{[S^2(C + R^2B) + (0.005F_o^2)^2]/(\mathrm{Lp})^2\}$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan to background time, and B is the total background. Refinement of a model with coordinates transformed by $(-x, -y, -z)$ yielded a significantly higher R factor of 0.061, indicating that the absolute configuration of this crystal is as shown in Fig. 1.

Data collection: Philips PW1100/20 software. Cell refinement: *Xtal*3.2 *LATCON* (Hall, Flack & Stewart, 1992). Data reduction: *Xtal*3.2 *DIFDAT*, *ABSORB*, *ADDREF* and *SORTRF*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1995). Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chlorobis(η^5-cyclopentadienyl)methoxytitanium

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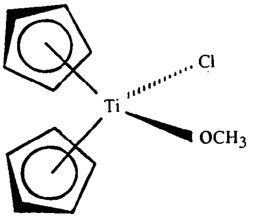
Abstract

The title compound, [TiCl(C_5H_5)$_2$(CH_3O)], is a 'bent metallocene' structural type typically found in Cp$_2$*MXY* complexes. The Ti—O—C bond angle of 141.4 (3)° is significantly greater than the corresponding angle in the ethoxy analog, resulting in a shortened O—Ti bond and indicating greater π character of the O—Ti bond of the title compound.

Comment

In the course of our work on the chemistry of compounds with bridging ethyleneoxy ligands bound to titanocene and zirconocene fragments (Gibson, Franco & Ding, 1995), we have sought to compare the properties of compounds bearing simple alkoxy ligands with those having related bridging ligands. The title compound, (I), has been prepared and characterized for this purpose.



(I)

If the vectors from Ti to the centroids of the two Cp rings are considered together with the bonds to O and Cl, then the geometry about the Ti atom can be described as distorted tetrahedral. The related compound with an ethoxy ligand bound to Ti has been structurally characterized at 148 K (Huffman, Moloy, Marsella & Caulton, 1980) and has closely similar geometry about the Ti atom. The Ti(1)—O(1)—C(1) bond angle is more obtuse in (I) [141.4 (3)°] than in the ethoxy analog [133.2 (2)°]. As would be expected from this larger bond angle, the Ti(1)—O(1) bond is slightly shorter at 1.839 (2) Å than in the ethoxy analog [1.855 (2) Å]. Also, the O(1)—C(1) bond is significantly shortened in (I) [1.367 (4) compared with 1.415 (4) Å] and the Ti(1)—Cl(1) bond in (I) is slightly longer than in the ethoxy analog [2.412 (1) compared with 2.405(1) Å]. These altered structural parameters suggest that the

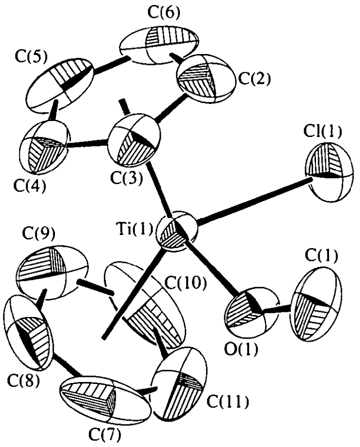


Fig. 1. View of the molecular structure of (I), showing the atom-numbering scheme with 50% probability displacement ellipsoids. H atoms are omitted for clarity.