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Structure of (*R*)-1-[(*S*)-1′,2-Bis(diphenylphosphino)ferrocenyl]ethyl Acetate

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Abstract

In the ferrocene moiety of [η^5-1-(1-acetoxyethyl)-2-diphenylphosphinocyclopentadienyl](η^5-diphenylphosphinocyclopentadienyl)iron, the planar and parallel cyclopentadienyl rings are slightly staggered with torsion angles about the centroids ranging from 22.8 to 24.9°. The average Fe—C distance in this moiety is 2.042 (4) Å and the average C—C bond distance is 1.423 (12) Å. The P—C—C angles are asymmetric and C—C distances in the phenyl rings range from 1.32 (2) to 1.42 (2) Å.

Comment

Although the acetate derivative of the (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]-amine (BPPFA) ligand was prepared some time ago (Hayashi *et al.*, 1980), the crystal structure of this ligand has not been determined. The acetate derivative has been shown to be a useful intermediate as the dimethylamino group in BPPFA can be replaced by other amino groups, OMe, OH and PPh_2 groups (Hayashi *et al.*, 1980).

As part of our work on ferrocenyl phosphines, we undertook the X-ray structure determination of the title compound so as to provide useful comparative data with other ferrocenyl phosphines. The compound was prepared from BPPFA in neat acetic anhydride held at 373 K for 1 h in a degassed sealed glass tube as reported by Hayashi *et al.* (1980). Dark-orange crystals precipitated when the tube was cooled overnight. Crystals were washed with MeOH at 273 K.

The structural study indicates that the planar cyclopentadienyl rings of the ferrocene moiety are almost parallel with a Cp_1(centroid)—Fe—Cp_2(centroid) angle of 179.2°. The rings are also slightly staggered with the torsion angles about the centroids of two rings ranging from 22.8 to 24.9°. The Fe—C distances of 2.026 (7)–2.054 (9) Å for ring 1 and 2.014 (10)–2.042 (10) Å for ring 2 are comparable with those found for 1,1′-bis(diphenylphosphino)ferrocene (Casellato *et al.*, 1988) and its derivatives (Einstein & Willis, 1980; Shawkataly *et al.*, 1992). The average of the C—C distances in the ferrocene moiety is 1.423 (12) Å. In the diphenylphosphino groups, the C—P—C angles are less than the ideal tetrahedral angle of 109.5°. The angle C(11)—P(1)—C(17) of 99.1 (4)° is very much less than 109.5° because of the steric effect of the acetate group. The resultant crowding of the phenyl and cyclopentadienyl rings causes the P—C—C angles to be asymmetric. For the phenyl rings, the C—C distances range from 1.32 (2) to 1.42 (2) Å with a mean of 1.38 (2) Å; the internal C—C—C angles range from 117.3 (12) to 122.1 (8)°. The methyl carbon C(36) is *cis* to C(4).

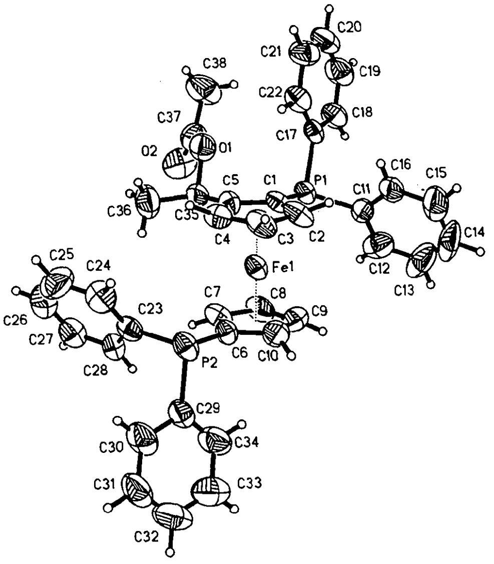

Fig. 1. A view of the molecule showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels.

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Experimental

Crystal data

$[Fe(C_{21}H_{20}O_2P)(C_{17}H_{14}P)]$
$M_r = 639.4$
Triclinic
$P1$
$a = 8.684\ (2)$ Å
$b = 10.100\ (2)$ Å
$c = 10.109\ (3)$ Å
$\alpha = 71.55\ (2)°$
$\beta = 85.42\ (2)°$
$\gamma = 73.97\ (2)°$
$V = 808.3\ (3)$ Å^3
$Z = 1$
$D_x = 1.314$ Mg m^{-3}
$D_m = 1.302$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 50 reflections
$\theta = 7.5$-$17.5°$
$\mu = 0.598$ mm^{-1}
$T = 298$ K
Needle
0.44 × 0.16 × 0.12 mm
Orange

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans (5.33-29.3° min^{-1} in ω)
Absorption correction: empirical
$T_{\min} = 0.894$, $T_{\max} = 0.926$
3978 measured reflections
3978 independent reflections
2493 observed reflections
$[F > 2.0\sigma(F)]$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = -13 \rightarrow 13$
2 standard reflections monitored every 200 reflections
intensity variation: insignificant

Refinement

Refinement on F
Final $R = 0.0483$
$wR = 0.0384$
$S = 0.87$
2493 reflections
420 parameters
H atoms riding, only U's refined
$w = 1.0/[\sigma^2(F) + 0.0003F^2]$
$(\Delta/\sigma)_{\max} = 0.424$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

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

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Fe(1)	0.0362	0.9607	0.1420	0.048 (1)
P(1)	0.1555 (3)	1.2302 (2)	0.1994	0.047 (1)
P(2)	−0.1197 (3)	0.6884 (2)	0.1326 (2)	0.056 (1)
O(1)	0.1433 (6)	1.0073 (5)	0.5288 (4)	0.067 (2)
O(2)	−0.0671 (8)	1.1452 (6)	0.6103 (6)	0.097 (3)
C(1)	0.1924 (9)	1.0396 (8)	0.2181 (8)	0.048 (4)
C(2)	0.2726 (10)	0.9628 (9)	0.1221 (9)	0.061 (4)
C(3)	0.2571 (9)	0.8201 (9)	0.1734 (9)	0.064 (4)
C(4)	0.1729 (10)	0.8032 (8)	0.3007 (9)	0.054 (4)
C(5)	0.1301 (9)	0.9397 (8)	0.3279 (8)	0.047 (3)
C(6)	−0.1326 (10)	0.8795 (8)	0.0891 (8)	0.048 (4)
C(7)	−0.2026 (10)	0.9824 (8)	0.1629 (9)	0.058 (4)
C(8)	−0.1726 (10)	1.1169 (8)	0.0861 (9)	0.065 (4)
C(9)	−0.0843 (12)	1.0982 (10)	−0.0323 (10)	0.076 (5)
C(10)	−0.0574 (11)	0.9547 (10)	−0.0313 (9)	0.068 (4)
C(11)	0.2161 (11)	1.3031 (8)	0.0187 (8)	0.053 (4)
C(12)	0.1051 (13)	1.4063 (9)	−0.0753 (9)	0.078 (5)
C(13)	0.1465 (21)	1.4638 (13)	−0.2127 (12)	0.120 (8)
C(14)	0.2945 (23)	1.4241 (16)	−0.2559 (13)	0.132 (11)
C(15)	0.4154 (16)	1.3182 (13)	−0.1636 (12)	0.103 (7)
C(16)	0.3724 (12)	1.2619 (10)	−0.0280 (10)	0.071 (5)
C(17)	0.3264 (9)	1.2382 (8)	0.2901 (8)	0.044 (3)
C(18)	0.3342 (10)	1.3730 (8)	0.2912 (8)	0.060 (4)
C(19)	0.4525 (12)	1.3870 (11)	0.3637 (10)	0.080 (5)
C(20)	0.5661 (12)	1.2681 (12)	0.4357 (10)	0.077 (6)
C(21)	0.5628 (12)	1.1335 (11).	0.4366 (9)	0.075 (5)
C(22)	0.4431 (10)	1.1161 (10)	0.3665 (9)	0.062 (4)
C(23)	−0.2050 (10)	0.6478 (8)	0.3067 (8)	0.051 (3)
C(24)	−0.1169 (11)	0.5372 (9)	0.4103 (10)	0.070 (4)
C(25)	−0.1790 (16)	0.5008 (11)	0.5472 (11)	0.096 (6)
C(26)	−0.3268 (13)	0.5735 (10)	0.5779 (11)	0.081 (5)
C(27)	−0.4162 (11)	0.6826 (9)	0.4712 (9)	0.069 (4)
C(28)	−0.3575 (10)	0.7192 (9)	0.3380 (9)	0.057 (4)
C(29)	−0.2871 (11)	0.6927 (11)	0.0287 (10)	0.063 (4)
C(30)	−0.3450 (11)	0.5727 (10)	0.0626 (10)	0.080 (5)
C(31)	−0.4657 (14)	0.5651 (13)	−0.0143 (12)	0.099 (6)
C(32)	−0.5260 (14)	0.6779 (16)	−0.1301 (13)	0.109 (8)
C(33)	−0.4682 (15)	0.7958 (15)	−0.1668 (13)	0.114 (7)
C(34)	−0.3480 (13)	0.8032 (12)	−0.0870 (12)	0.087 (6)
C(35)	0.0325 (8)	0.9771 (7)	0.4458 (6)	0.055 (3)
C(36)	−0.0286 (12)	0.8519 (9)	0.5454 (9)	0.085 (5)
C(37)	0.0746 (12)	1.1007 (9)	0.6026 (8)	0.070 (4)
C(38)	0.2037 (12)	1.1291 (12)	0.6714 (10)	0.109 (6)

Table 2. *Geometric parameters* (Å, °)

Fe(1)—C(1)	2.054 (9)	Fe(1)—C(2)	2.052 (9)
Fe(1)—C(3)	2.026 (7)	Fe(1)—C(4)	2.040 (7)
Fe(1)—C(5)	2.034 (8)	Fe(1)—C(6)	2.042 (10)
Fe(1)—C(7)	2.025 (9)	Fe(1)—C(8)	2.029 (7)
Fe(1)—C(9)	2.017 (8)	Fe(1)—C(10)	2.014 (10)
P(1)—C(1)	1.811 (9)	P(1)—C(11)	1.835 (8)
P(1)—C(17)	1.839 (10)	P(2)—C(6)	1.813 (8)
P(2)—C(23)	1.821 (8)	P(2)—C(29)	1.843 (11)
O(1)—C(35)	1.475 (10)	O(1)—C(37)	1.367 (11)
O(2)—C(37)	1.192 (12)	C(1)—C(2)	1.449 (12)
C(1)—C(5)	1.428 (10)	C(2)—C(3)	1.410 (12)
C(3)—C(4)	1.414 (12)	C(4)—C(5)	1.433 (12)
C(35)—C(5)	1.493 (10)	C(6)—C(7)	1.440 (12)
C(6)—C(10)	1.430 (11)	C(7)—C(8)	1.419 (11)
C(8)—C(9)	1.404 (13)	C(9)—C(10)	1.399 (11)
C(35)—C(36)	1.540 (11)	C(37)—C(38)	1.501 (17)
C(1)—P(1)—C(17)	103.8 (4)	Fe(1)—C(1)—C(2)	69.2 (5)
C(6)—P(2)—C(23)	102.6 (4)	Fe(1)—C(1)—C(5)	68.8 (5)
C(23)—P(2)—C(29)	100.6 (4)	C(2)—C(1)—C(5)	107.1 (7)
Fe(1)—C(1)—P(1)	122.2 (4)	Fe(1)—C(2)—C(3)	68.7 (5)
P(1)—C(1)—C(2)	128.2 (6)	Fe(1)—C(3)—C(2)	70.8 (4)
P(1)—C(1)—C(5)	124.4 (6)	C(2)—C(3)—C(4)	109.0 (8)
Fe(1)—C(2)—C(1)	69.4 (5)	Fe(1)—C(4)—C(5)	69.2 (4)
C(1)—C(2)—C(3)	107.9 (7)	Fe(1)—C(5)—C(1)	70.3 (5)
Fe(1)—C(3)—C(4)	70.2 (4)	C(1)—C(5)—C(4)	108.1 (7)
Fe(1)—C(4)—C(3)	69.1 (4)	C(1)—C(5)—C(35)	124.4 (7)
C(3)—C(4)—C(5)	107.9 (7)	Fe(1)—C(6)—P(2)	124.5 (4)
Fe(1)—C(5)—C(4)	69.6 (5)	P(2)—C(6)—C(7)	131.1 (6)
Fe(1)—C(5)—C(35)	124.0 (5)	P(2)—C(6)—C(10)	122.5 (7)
C(4)—C(5)—C(35)	127.4 (7)	Fe(1)—C(7)—C(6)	69.9 (5)
Fe(1)—C(6)—C(7)	68.6 (5)	C(6)—C(7)—C(8)	108.2 (7)
Fe(1)—C(6)—C(10)	68.3 (6)	Fe(1)—C(8)—C(9)	69.2 (5)
C(7)—C(6)—C(10)	106.4 (7)	Fe(1)—C(9)—C(8)	70.2 (5)
Fe(1)—C(7)—C(8)	69.7 (5)	C(8)—C(9)—C(10)	109.3 (8)
Fe(1)—C(8)—C(7)	69.4 (4)	Fe(1)—C(10)—C(9)	69.8 (6)
C(7)—C(8)—C(9)	107.7 (8)	P(1)—C(11)—C(12)	119.2 (7)
Fe(1)—C(9)—C(10)	69.5 (5)	P(1)—C(17)—C(18)	117.6 (5)
Fe(1)—C(10)—C(6)	70.4 (5)	P(2)—C(23)—C(24)	118.1 (6)
C(6)—C(10)—C(9)	108.4 (8)	P(2)—C(29)—C(34)	123.6 (10)
P(1)—C(11)—C(16)	123.1 (6)	O(1)—C(35)—C(36)	106.1 (6)
P(1)—C(17)—C(22)	124.3 (8)	O(1)—C(37)—O(2)	122.4 (10)
P(2)—C(23)—C(28)	123.7 (5)	O(2)—C(37)—C(38)	128.4 (9)
C(1)—P(1)—C(11)	102.0 (4)	P(2)—C(29)—C(30)	118.5 (7)
C(11)—P(1)—C(17)	99.1 (4)	O(1)—C(35)—C(5)	105.2 (6)
C(6)—P(2)—C(29)	101.3 (4)	C(5)—C(35)—C(36)	114.1 (6)
C(35)—O(1)—C(37)	115.9 (6)	O(1)—C(37)—C(38)	109.2 (8)

The structure was solved by direct methods and refined by full-matrix least squares. The preferred chirality was chosen on the basis of the Rogers (1981) and Hamilton (1965) tests. The given chirality has $\nu = 1.05\ (9)$ and the wR ratio of the two configurations is 1.006. The *SHELXTL/PC* (Sheldrick, 1990) program package was used for all calculations.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71212 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1031]

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Tetrakis(tetramethylammonium) Octamolybdate Dihydrate

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Abstract

The synthesis and crystal structure of tetrakis(tetramethylammonium) octamolybdate dihydrate, $[N(CH_3)_4]_4[Mo_8O_{26}].2H_2O$, is reported. The Mo_8O_{26} unit adopts the β configuration for that ion. Mo—O distances and angles are comparable with those found in previous studies of the same anion.

Comment

Acidifying a clear solution of $(TMA)_2(MoO_4)$ [TMA = tetramethylammonium cation], prepared from appropriate quantities of TMAOH and MoO_3, to a pH of about 7 gave a microcrystalline precipitate. On aging for several days at 373 K, crystals adequate for the structure determination were formed, of up to 1 mm in linear dimension.

The octamolybdate anion adopts the β-Mo_8O_{26} configuration (Fig. 1) in $[N(CH_3)_4]_4[Mo_8O_{26}].2H_2O$, as previously observed for the octamolybdate group in $(NH_4)_4[Mo_8O_{26}].4H_2O$ (Atovmyan & Krasochka, 1972), compared with the α-Mo_8O_{26} form observed in $[N(C_4H_9)_4]_4[Mo_8O_{26}]$ (Day, Fredrich, Klemperer & Shum, 1977). Mo—O distances and O—Mo—O angles agree with the previous study, and the center of the molecule is located at an inversion center; the approximate point symmetry is $2/m$ (C_{2v}). Since the α- and β-conformers of the Mo_8O_{26} unit are highly flexible and interconvertable (Masters, Gheller, Brownlee, O'Connor & Wedd, 1980), it is apparent that subtle packing forces are significant in determining which Mo_8O_{26} isomer crystallizes in combination with a particular organic cation.

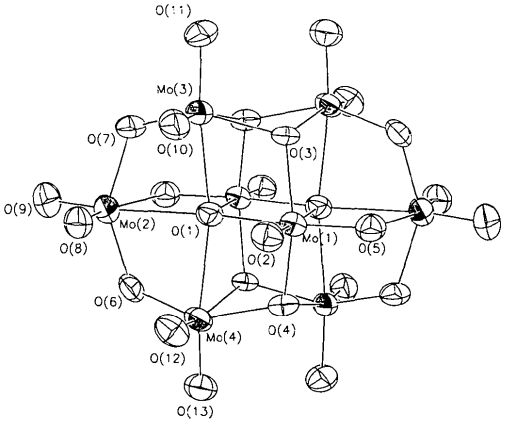

Fig. 1. View of the Mo_8O_{26} anion, showing the labeling of the asymmetric atoms. Thermal ellipsoids are shown at 50% probability levels.

Experimental

Crystal data

$[(CH_3)_4N]_4[Mo_8O_{26}].2H_2O$
$M_r = 1516.12$
Triclinic
$P\bar{1}$
$a = 10.539\ (2)$ Å
$b = 11.902\ (2)$ Å
$c = 9.714\ (2)$ Å
$\alpha = 96.301\ (6)^\circ$
$\beta = 108.962\ (5)^\circ$
$\gamma = 75.234\ (4)^\circ$
$V = 1114\ (2)$ Å^3
$Z = 1$

$D_x = 2.265$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–9°
$\mu = 2.22$ mm^{-1}
$T = 298$ K
Lump
0.50 × 0.40 × 0.40 mm
Colorless