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Structure of 1-[(*R*)-1',2-Bis(diphenylphosphino)ferrocenyl]-(*S*)-*N,N*-dimethylethylamine

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Abstract

In the ferrocene moiety, the cyclopentadienyl rings are planar and slightly staggered with a dihedral angle of 2.8°. The average Fe—C and C—C distances are 2.042 (4) and 1.417 (7) Å respectively. The P—C—C angles are asymmetric and the C—C distances in the phenyl rings range from 1.347 (9) to 1.413 (7) Å.

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Comment

Although the structures of several transition-metal complexes containing the 1-[(*R*)-1',2-bis(diphenylphosphino)ferrocenyl]-(*S*)-*N,N*-dimethylethylamine ligand have been determined (Hayashi, Kumada, Higuchi & Hirotsu, 1987; Hayashi *et al.*, 1989), the crystal structure of the ligand has not been determined. This may provide useful comparative data for understanding the activity of the asymmetric catalyst. The compound was prepared from optically resolved 1-ferrocenyl-*N,N*-dimethylethylamine (Marquarding, Klusacek, Gokel, Hoffmann & Ugi, 1970) according to the method of Hayashi *et al.*, (1980). Dark-orange crystals suitable for X-ray work were grown from a dichloromethane/ethanol mixture by slow solvent-diffusion techniques. The structural study indicates that the cyclopentadienyl rings in the ferrocene moiety are planar with a dihedral angle of 2.8°. The cyclopentadienyl rings are slightly staggered with torsion angles about the centroids of the two rings ranging from 17.2–19.0°. The Fe—C distances of 2.024 (5)–2.050 (4) Å for the C(1)–C(5) ring and 2.027 (5)–2.058 (4) Å for C(6)–C(10) ring are similar to those found for ferrocene (Seiler & Dunitz, 1982) and its derivatives (Krukonis, Silverman & Yannoni, 1972; Einstein & Willis, 1980). The average C—C distance in the ferrocene moiety is 1.417 (7) Å. In the diphenylphosphino groups, the C—P—C angles are smaller than the ideal tetrahedral angle of 109.5°. The resultant crowding of the phenyl and cyclopentadienyl rings causes the P—C—C angles to be asymmetric. The C—C distances within the phenyl rings range from 1.347 (9) to 1.413 (7) Å. The C(17)–C(22) and C(23)–C(28) phenyl rings are nearly coplanar whereas C(11)–C(16) and C(29)–C(34) rings are stacked at an angle of 141.9°. The N atom adopts a pyramidal configuration.

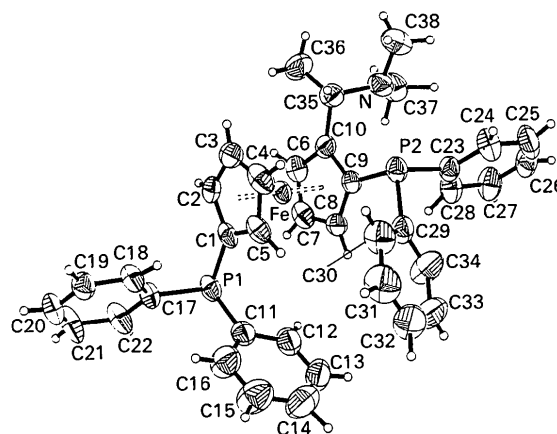
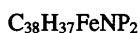


Fig. 1. A view of the molecule showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels.

Experimental

Crystal data



$M_r = 625.5$

Orthorhombic



$a = 8.729 (1) \text{ \AA}$

$b = 10.864 (2) \text{ \AA}$

$c = 34.350 (6) \text{ \AA}$

$V = 3257.5 (9) \text{ \AA}^3$

$Z = 4$

$D_x = 1.275 \text{ Mg m}^{-3}$

$D_m = 1.269 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 50 reflections

$\theta = 7.5\text{--}17.5^\circ$

$\mu = 0.588 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Needle

$1.0 \times 0.4 \times 0.3 \text{ mm}$

Dark orange

| | | | | |
|-------|-------------|-------------|------------|-----------|
| C(22) | 1.1089 (7) | -0.1697 (4) | 0.5218 (2) | 0.066 (2) |
| C(23) | 0.6414 (5) | 0.5595 (4) | 0.6804 (1) | 0.048 (1) |
| C(24) | 0.5507 (7) | 0.6128 (5) | 0.7086 (2) | 0.069 (2) |
| C(25) | 0.5634 (9) | 0.7380 (6) | 0.7173 (2) | 0.081 (2) |
| C(26) | 0.6615 (9) | 0.8097 (5) | 0.6973 (2) | 0.074 (2) |
| C(27) | 0.7532 (8) | 0.7590 (4) | 0.6701 (2) | 0.072 (2) |
| C(28) | 0.7432 (7) | 0.6336 (4) | 0.6614 (1) | 0.062 (2) |
| C(29) | 0.7645 (6) | 0.3250 (4) | 0.7002 (1) | 0.053 (1) |
| C(30) | 0.7424 (8) | 0.2059 (5) | 0.7131 (2) | 0.071 (2) |
| C(31) | 0.8495 (11) | 0.1477 (6) | 0.7357 (2) | 0.095 (3) |
| C(32) | 0.9796 (12) | 0.2063 (6) | 0.7467 (2) | 0.097 (3) |
| C(33) | 1.0062 (11) | 0.3226 (7) | 0.7338 (3) | 0.110 (3) |
| C(34) | 0.8973 (10) | 0.3808 (5) | 0.7109 (3) | 0.097 (3) |
| C(35) | 0.4275 (5) | 0.4035 (4) | 0.5887 (2) | 0.051 (1) |
| C(36) | 0.3546 (9) | 0.3955 (8) | 0.5486 (3) | 0.083 (3) |
| C(37) | 0.4444 (8) | 0.6309 (5) | 0.5899 (3) | 0.080 (2) |
| C(38) | 0.2482 (6) | 0.5292 (7) | 0.6260 (2) | 0.083 (2) |

Data collection

Siemens P4 diffractometer

2 θ / θ scansAbsorption correction:
empirical

$T_{\min} = 0.561, T_{\max} = 0.625$

4214 measured reflections

4213 independent reflections

3381 observed reflections

$[F > 3.0\sigma(F)]$

$\theta_{\max} = 55.0^\circ$

$h = 0 \rightarrow 11$

$k = 0 \rightarrow 14$

$l = 0 \rightarrow 44$

2 standard reflections

monitored every 100

reflections

intensity variation: none

Refinement

Refinement on F

Final $R = 0.038$

$wR = 0.0501$

$S = 0.89$

3381 reflections

520 parameters

All H-atom parameters re-
fined

$w = 1.0/[\sigma^2(F) + 0.0020F^2]$

$(\Delta/\sigma)_{\max} = 0.149$

$\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering fac-
tors from *SHELXTL/PC*
(Siemens Crystallographic
Research Systems, 1990)Table 1. Fractional atomic coordinates and equivalent isotropic displacement coefficients (\AA^2)

$U_{eq} = 1/3(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$

| | x | y | z | U_{eq} |
|-------|-------------|-------------|------------|-----------|
| Fe | 0.7132 (1) | 0.2174 (1) | 0.5907 (1) | 0.039 (1) |
| P(1) | 1.0194 (1) | 0.0322 (1) | 0.5647 (1) | 0.048 (1) |
| P(2) | 0.6112 (1) | 0.3943 (1) | 0.6705 (1) | 0.046 (1) |
| N | 0.4009 (4) | 0.5195 (3) | 0.6102 (1) | 0.058 (1) |
| C(1) | 0.8242 (5) | 0.0535 (3) | 0.5819 (1) | 0.045 (1) |
| C(2) | 0.6951 (7) | 0.0659 (4) | 0.5567 (2) | 0.057 (2) |
| C(3) | 0.5631 (6) | 0.0782 (4) | 0.5794 (2) | 0.062 (2) |
| C(4) | 0.6071 (6) | 0.0747 (4) | 0.6189 (2) | 0.061 (2) |
| C(5) | 0.7675 (6) | 0.0594 (4) | 0.6203 (2) | 0.050 (1) |
| C(6) | 0.6996 (7) | 0.3672 (4) | 0.5550 (1) | 0.051 (1) |
| C(7) | 0.8494 (6) | 0.3514 (4) | 0.5686 (2) | 0.053 (2) |
| C(8) | 0.8457 (5) | 0.3585 (4) | 0.6100 (2) | 0.048 (1) |
| C(9) | 0.6907 (5) | 0.3780 (3) | 0.6219 (1) | 0.042 (1) |
| C(10) | 0.5989 (5) | 0.3827 (3) | 0.5876 (1) | 0.044 (1) |
| C(11) | 1.1199 (5) | 0.0231 (4) | 0.6115 (2) | 0.053 (1) |
| C(12) | 1.1658 (7) | 0.1324 (6) | 0.6287 (2) | 0.069 (2) |
| C(13) | 1.2361 (7) | 0.1339 (7) | 0.6651 (2) | 0.085 (3) |
| C(14) | 1.2617 (8) | 0.0272 (8) | 0.6841 (2) | 0.095 (3) |
| C(15) | 1.2228 (10) | -0.0829 (7) | 0.6673 (2) | 0.096 (3) |
| C(16) | 1.1535 (8) | -0.0850 (6) | 0.6313 (2) | 0.079 (2) |
| C(17) | 1.0089 (5) | -0.1306 (3) | 0.5498 (1) | 0.045 (1) |
| C(18) | 0.9060 (5) | -0.2137 (4) | 0.5656 (1) | 0.051 (1) |
| C(19) | 0.9056 (6) | -0.3346 (4) | 0.5530 (2) | 0.052 (1) |
| C(20) | 1.0032 (7) | -0.3737 (4) | 0.5244 (2) | 0.061 (2) |
| C(21) | 1.1037 (8) | -0.2927 (5) | 0.5085 (2) | 0.079 (2) |

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

| | | | |
|------------------|-----------|-------------------|------------|
| P(1)—C(1) | 1.819 (4) | N—C(35) | 1.479 (6) |
| P(1)—C(11) | 1.833 (5) | N—C(37) | 1.447 (8) |
| P(1)—C(17) | 1.844 (4) | N—C(38) | 1.444 (7) |
| P(2)—C(9) | 1.816 (5) | C(10)—C(35) | 1.514 (6) |
| P(2)—C(23) | 1.846 (4) | C(35)—C(36) | 1.521 (10) |
| P(2)—C(29) | 1.842 (5) | | |
| C(1)—P(1)—C(11) | 99.8 (2) | P(2)—C(9)—C(8) | 129.8 (4) |
| C(1)—P(1)—C(17) | 99.6 (2) | P(2)—C(9)—C(10) | 122.8 (3) |
| C(11)—P(1)—C(17) | 102.5 (2) | P(2)—C(23)—C(24) | 117.1 (4) |
| C(9)—P(2)—C(23) | 102.1 (2) | P(2)—C(23)—C(28) | 125.2 (3) |
| C(9)—P(2)—C(29) | 101.0 (2) | P(2)—C(29)—C(30) | 117.3 (4) |
| C(23)—P(2)—C(29) | 101.1 (2) | P(2)—C(29)—C(34) | 126.0 (4) |
| P(1)—C(1)—C(2) | 123.6 (4) | C(35)—N—C(37) | 115.5 (5) |
| P(1)—C(1)—C(5) | 129.7 (4) | C(35)—N—C(38) | 113.2 (4) |
| P(1)—C(11)—C(12) | 117.7 (4) | C(37)—N—C(38) | 111.3 (5) |
| P(1)—C(11)—C(16) | 125.2 (4) | N—C(35)—C(10) | 107.1 (4) |
| P(1)—C(17)—C(18) | 123.3 (3) | N—C(35)—C(36) | 115.8 (5) |
| P(1)—C(17)—C(22) | 117.5 (3) | C(10)—C(35)—C(36) | 112.5 (5) |

The data were collected using a variable scan speed of 5.3–29.3° min⁻¹ in ω . 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 value of η for the given chirality is 1.00(5) and the wR ratio for the two configurations is 1.002. *SHELXTL/PC* was used for all calculations.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55363 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1012]

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Structure of Tetrakis(dimethylphenylphosphine)rhodium(I) Chloride

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Abstract

The monomeric cation $[\text{Rh}(\text{PMe}_2\text{Ph})_4]^+$ exhibits a four-coordinate distorted square-planar coordination geometry about the Rh atom. The chloride counter ion is not coordinated to the rhodium metal [Rh...Cl distance 3.984(3) Å].

Comment

The coordination number and geometry of the phosphine complexes of rhodium(I) are of interest because of the catalytic activity of these complexes (Nomura, Saito & Shimoda, 1989). The monomeric complexes most commonly have coordination numbers of four, but a few five-coordinate monomeric complexes have been reported (Burk & Harlow, 1990). It is possible that a four-coordinate cationic rhodium(I) complex may become five coordinate in the presence of a coordinating anion. Previous workers have characterized the cation of $[\text{Rh}(\text{PMe}_2\text{Ph})_4]\text{BF}_4 \cdot \text{C}_4\text{H}_2\text{O}$ as four coordinate but the BF_4 anion is generally non-coordinating (Lundquist, Streib & Caulton, 1989). This work characterizes $[\text{Rh}(\text{PMe}_2\text{Ph})_4]\text{Cl}$ in which the chloride counter ion could act as a coordinating ligand. The structure reported here is four coordinate, even in the presence of the coordinating anion. The presence of a coordinating anion does not increase the coordination number of the metal in the solid state for this particular complex. The structure of the $[\text{Rh}(\text{PMe}_2\text{Ph})_4]^+$ cation is similar to those previously reported for the cations $[\text{Rh}(\text{PMe}_2\text{Ph})_4]^+$ and $[\text{Rh}(\text{PMe}_3)_4]^+$ (Blum, Calabrese, Frolow & Milstein, 1990).

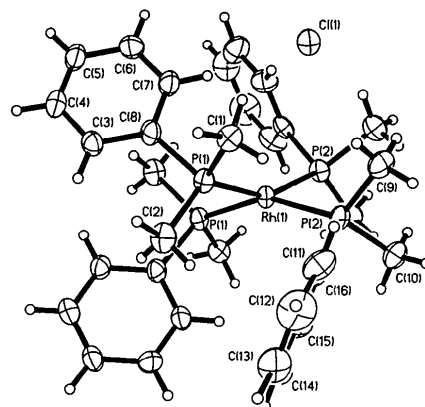


Fig. 1. Thermal ellipsoid plot (50% probability) of $[\text{Rh}(\text{PMe}_2\text{Ph})_4]\text{Cl}$. H atoms are drawn as spheres of arbitrary radius.

Experimental

Crystal data

$[\text{Rh}(\text{C}_8\text{H}_{11}\text{P})_4]^+ \cdot \text{Cl}^-$

$M_r = 691.0$

Orthorhombic

$C222_1$

$a = 14.754(3) \text{ \AA}$

$b = 14.805(5) \text{ \AA}$

$c = 15.277(4) \text{ \AA}$

$V = 3337(2) \text{ \AA}^3$

$Z = 4$

$D_x = 1.375 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 16.99\text{--}28.58^\circ$

$\mu = 0.792 \text{ mm}^{-1}$

$T = 197 \text{ K}$

Plate

$0.40 \times 0.18 \times 0.02 \text{ mm}$

Orange

Data collection

Siemens $R3m/V$ diffractometer

ω scans

Absorption correction:

Semi-empirical

$T_{\min} = 0.9159$, $T_{\max} =$

0.9645

1670 measured reflections

1662 independent reflections

1662 observed reflections

$R_{\text{int}} = 0.018$

$\theta_{\text{max}} = 25.00^\circ$

$h = -17 \rightarrow 0$

$k = -18 \rightarrow 0$

$l = -19 \rightarrow 0$

3 standard reflections

frequency: 97 min

intensity variation: 1%

Refinement

Refinement on F

Final $R = 0.0501$

$wR = 0.0512$

$S = 1.0197$

1662 reflections

174 parameters

Calculated weights $w =$

$1/[\sigma^2(F) + 0.00100F^2]^2$

$(\Delta/\sigma)_{\text{max}} = 0.0104$

$\Delta\rho_{\text{max}} = 0.6100 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.0120 \text{ e \AA}^{-3}$

Extinction correction:

Lorentzian isotropic (Larson, 1967)

Extinction coefficient:

0.00034 (6)

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Siemens $P3VAX$ version 3.4. Data reduction: *REFRED* (Reibenspies, 1992). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.