

[1,1'-Bis(diphenylphosphino)ferrocene- κ^2P,P'](1,5-cyclooctadiene)rhodium(I) trifluoromethanesulfonate dichloromethane disolvate

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Key indicators

Single-crystal X-ray study

$T = 180\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.012\text{ \AA}$

R factor = 0.082

w R factor = 0.234

Data-to-parameter ratio = 20.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{C}_{34}\text{H}_{28}\text{P}_2\text{Fe})]\text{CF}_3\text{SO}_3 \cdot 2\text{CH}_2\text{Cl}_2$ or $[\text{RhFe}(\text{C}_8\text{H}_{12})(\text{C}_{17}\text{H}_{14}\text{P})_2]\text{CF}_3\text{SO}_3 \cdot 2\text{CH}_2\text{Cl}_2$, was synthesized by reacting 1,1'-bis(diphenylphosphino)ferrocene (dppf) with $[\text{Rh}(1,5\text{-cyclooctadiene})(\text{THF})_2]^+$ in tetrahydrofuran (THF), and shows dppf acting as a P,P' -bidentate chelating ligand. The compound crystallizes in the space group $P2_1/n$ and features one crystallographically unique Rh^+ metal centre, which appears in a distorted square-planar geometry.

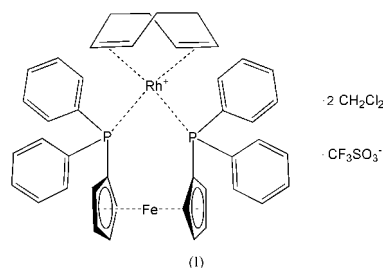
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Comment

Ferrocene was first synthesized in 1951 (Cotton & Wilkinson, 1966) and, since then, literally thousands of systems include this 'sandwich' compound as a moiety in their structure. The electronic properties of ferrocene derivatives are severely influenced by the different functional groups attached to the cyclopentadienyl (Cp) rings (Oberhoff *et al.*, 1996). In particular, 1,1'-bis(diphenylphosphino)ferrocene (dppf) still remains one of the most interesting and commonly used ferrocene derivatives due to its unique chemical reactivity and interesting potential applications in catalysis and industry. To the best of our knowledge, the title compound, (I), is one of the simplest Rh -dppf adducts. It was synthesized in the course of our research for novel Rh^+ catalysts (Jones *et al.*, 2003), using a synthetic method previously described (Longato *et al.*, 1991).



The structure contains the complex $[\text{Rh}(1,5\text{-cyclooctadiene})(\text{dppf})]^+$ cation (Fig. 1), showing the Rh^+ metal centre present in a slightly distorted square-planar geometry (Fig. 1 and Table 1). Dppf appears as a P,P' -bidentate ligand, forming a chelating ring with Rh^+ and imposing an $\text{Fe} \cdots \text{Rh}$ separation of $4.4388(10)\text{ \AA}$. The ferrocene moiety shows the typical eclipsed conformation for the cyclopentadienyl rings (Cp), although these are slightly non-parallel (interplanar angle *ca* 1.7°). The $\text{Rh}-\text{P}$, $\text{Rh}-\pi$ and $\text{Fe}-\text{Cp}$ bond distances are consistent with those found in similar complexes (see Table 1) (Jones *et al.*, 2003; Beller *et al.*, 1998; Dinoto *et al.*, 1995).

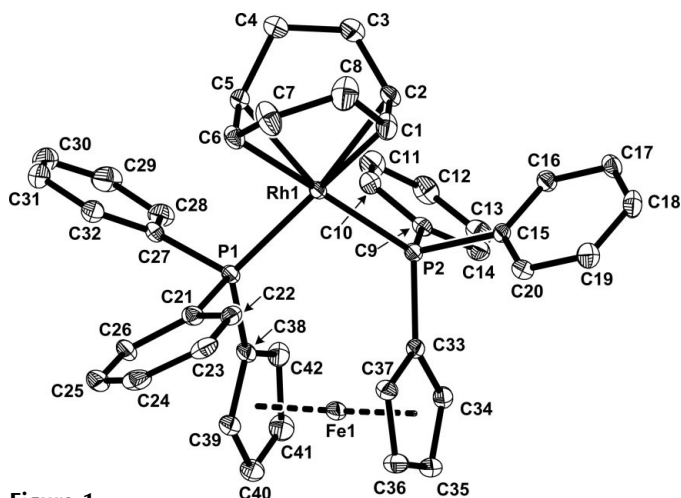


Figure 1
A view of the complex cation present in (I), showing the labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

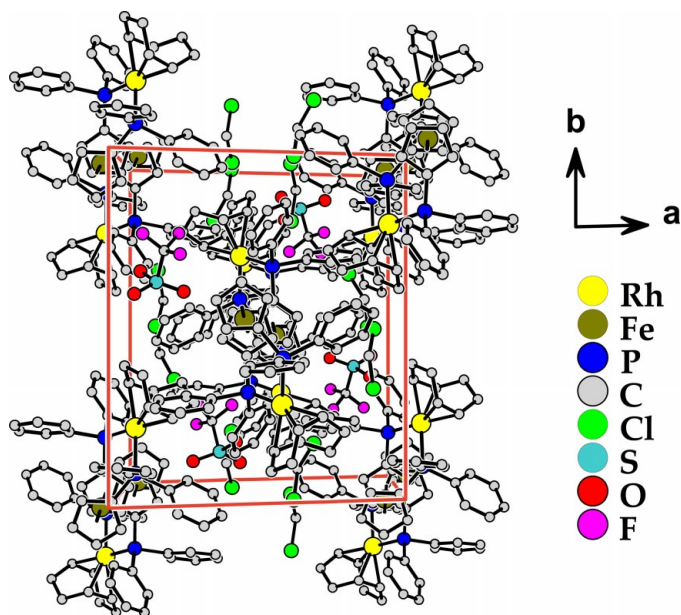


Figure 2
Perspective view of (I) along the *c* direction.

Experimental

All chemicals were purchased from Aldrich and used without further purification. Solvents were dried and degassed using appropriate methods. Standard Schlenk line techniques were also employed. $[\text{RhCl}(\text{1,5-cyclooctadiene})_2]$ (100 mg) was dissolved in THF (10 ml), followed by the addition of AgCF_3SO_3 (104 mg). The resulting solution was stirred at ambient temperature for 1 h, after which it was filtered in order to remove AgCl. The filtrate was added to a solution of 1,1'-bis(diphenylphosphino)ferrocene (dppf, 225 mg) in THF and stirred for another hour. The addition of *ca* 20 ml of hexane led to the precipitation of the title compound as an orange powder, which was washed with diethyl ether ($3 \times ca$ 20 ml) and then dried *in vacuo*. Crystals suitable for X-ray diffraction analysis were obtained using recrystallization methods from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution. Elemental composition, calculated (using single-crystal data): C 56.46, H 4.38, P 6.78%; found: C 56.16, H 4.43, P 7.01%. $M^+ = 764 \text{ g mol}^{-1}$. ^1H NMR

(CDCl_3): 2.16 (*br, m*, 4H, CH_2 cod), 2.35 (*br, m*, 4H, CH_2 cod), 4.2–4.4 (*m*, 12H, Cp CH cod), 7.5–7.9 (*m*, 20H, Ph). ^{13}C NMR: 30.5 (CH_2), 74.5 (*d*, $J_{\text{C-Rh}} = 90 \text{ Hz}$, CH), 99.3, 129.1, 131.7, 134.1 (Cp, Ph). ^{31}P NMR: 22.7 (*d*, $J_{\text{P-Rh}} = 150 \text{ Hz}$).

Crystal data

$[\text{RhFe}(\text{C}_8\text{H}_{12})(\text{C}_{17}\text{H}_{14}\text{P})_2]\text{CF}_3\text{SO}_3 \cdot 2\text{CH}_2\text{Cl}_2$
 $M_r = 1084.36$
 Monoclinic, $P2_1/n$
 $a = 15.1298$ (2) Å
 $b = 16.5875$ (3) Å
 $c = 19.1186$ (4) Å
 $\beta = 112.723$ (1)°
 $V = 4425.69$ (14) Å³
 $Z = 4$

$D_x = 1.627 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 51598 reflections
 $\theta = 1.0\text{--}27.5^\circ$
 $\mu = 1.12 \text{ mm}^{-1}$
 $T = 180$ (2) K
 Block, yellow
 $0.16 \times 0.07 \times 0.05 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 Thin-slice ω and φ scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\text{min}} = 0.896$, $T_{\text{max}} = 0.958$
 32010 measured reflections
 10110 independent reflections

8021 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -19 \rightarrow 19$
 $k = -21 \rightarrow 21$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.082$
 $wR(F^2) = 0.234$
 $S = 1.05$
 10110 reflections
 496 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1147P)^2 + 36.1684P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 2.99 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.23 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Rh1—C1	2.221 (7)	Fe1—C42	2.032 (7)
Rh1—C2	2.234 (7)	Fe1—C39	2.039 (7)
Rh1—C6	2.240 (6)	Fe1—C37	2.041 (6)
Rh1—C5	2.248 (7)	Fe1—C34	2.043 (7)
Rh1—P2	2.3255 (16)	Fe1—C41	2.069 (7)
Rh1—P1	2.3488 (16)	Fe1—C40	2.073 (7)
Fe1—C33	2.009 (6)	Fe1—C36	2.074 (7)
Fe1—C38	2.012 (6)	Fe1—C35	2.075 (7)
C1—Rh1—C2	35.8 (3)	C6—Rh1—P2	168.8 (2)
C1—Rh1—C6	79.9 (3)	C5—Rh1—P2	154.2 (2)
C2—Rh1—C6	92.7 (3)	C1—Rh1—P1	156.7 (2)
C1—Rh1—C5	86.8 (3)	C2—Rh1—P1	165.9 (2)
C2—Rh1—C5	78.3 (3)	C6—Rh1—P1	87.11 (18)
C6—Rh1—C5	35.4 (3)	C5—Rh1—P1	93.76 (18)
C1—Rh1—P2	93.44 (19)	P2—Rh1—P1	95.95 (6)
C2—Rh1—P2	86.89 (19)		

H atoms bound to C atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The trifluoromethanesulfonate anion is poorly resolved; atoms in the moiety were refined with common isotropic displacement parameters, and bond-length restraints were also applied in order to ensure a reasonable geometry for the trifluoromethanesulfonate. The highest peak and deepest hole were located 0.63 and 0.54 Å, respectively, from atom S1.

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXTL (Bruker, 2001); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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