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**Crystal Structure
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Azido[1,1′-bis(diphenylphosphino)ferrocene](pentamethylcyclopentadienyl)rhodium(III) hexafluorophosphate

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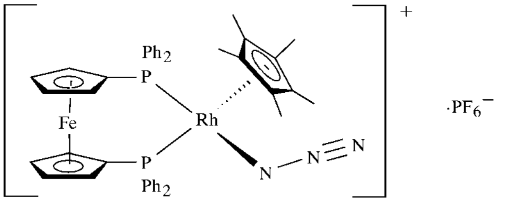
In the title compound, azido-2κ*N*-bis[μ-(1η^5:2κ*P*)-diphenylphosphinocyclopentadienyl][2(η^5)-pentamethylcyclopentadienyl]iron(III)rhodium(III) hexafluorophosphate, $[\{Rh(C_{10}H_{15})(N_3)\}\{Fe(\mu\text{-}C_{17}H_{14}P)_2\}]PF_6$ or $[FeRh(C_{10}H_{15})(\mu\text{-}C_{17}H_{14}P)_2(N_3)]PF_6$, the coordination sphere of Rh^{III} can be described as pseudo-tetrahedral, composed of two P atoms from a 1,1′-bis(diphenylphosphino)ferrocene (dppf) ligand, an azido N atom and the centroid of the ring of a C_5Me_5 (Cp*) ligand. The two cyclopentadienyl rings in the dppf moiety adopt an eclipsed conformation. The Rh···Fe distance is 4.340 (2) Å.

Comment

Various redox-active ligands are employed to control the reactivities of transition-metal complexes (Gan & Hor, 1995). The dppf ligand [1,1′-bis(diphenylphosphino)ferrocene, $Fe(C_5H_4PPh_2)_2$] and its derivatives are well known redox-active ligands, and their complexes usually exhibit a ferrocene-based oxidation process, together with additional redox processes at other metal centres. Recently, an interesting Rh–dppf chloro complex, $[Cp^*RhCl(dppf)]PF_6$, was reported (Cp* is C_5Me_5), which was prepared by treating a chloro-bridged Rh^{III} dimer, $[Cp^*RhCl_2]_2$, with dppf and $NaPF_6$ (Ma & Yamamoto, 1999). In order to compare structural features and to examine the redox properties of the Rh–dppf azide complex with respect to its chloro analogue, we have prepared the title compound, (I), and present its structure here.



(I)

The coordination sphere of the Rh metal in (I) can be described as pseudo-tetrahedral. The two Cp (cyclopentadienyl) rings of the dppf ligand are not perfectly parallel, but are twisted from each other with a dihedral angle of 3.4 (1)°. The P1—C11···C16—P2 pseudo-torsion angle is 3.0 (4)°, indicating that the two Cp rings adopt an eclipsed conformation. For comparison, the ideal torsion angle for a *gauche* (or staggered) conformation is 36°. Both Fe—*Cg* (*Cg* is the centroid of a Cp ring) distances are 1.63 Å, and the *Cg*1—Fe—*Cg*2 angle (*Cg*1 is the centroid of the C11–C15 ring and *Cg*2 is the centroid of the C16–C20 ring) is 177.5°. The *Cg**···Rh1—P1, *Cg**···Rh1—P2 and *Cg**···Rh1—N1 angles (*Cg** is the centroid of the C1–C5 ring) are 125.5, 127.01 and 126.8°, respectively. The P1···Fe···P2 bite angle is 60.68 (5)°, and the P1···P2 distance is 3.526 (3) Å. These bonding parameters within a ferrocene moiety are consistent with those found in the chloro analogue $[Cp^*RhCl(dppf)]PF_6$ (Ma & Yamamoto, 1999).

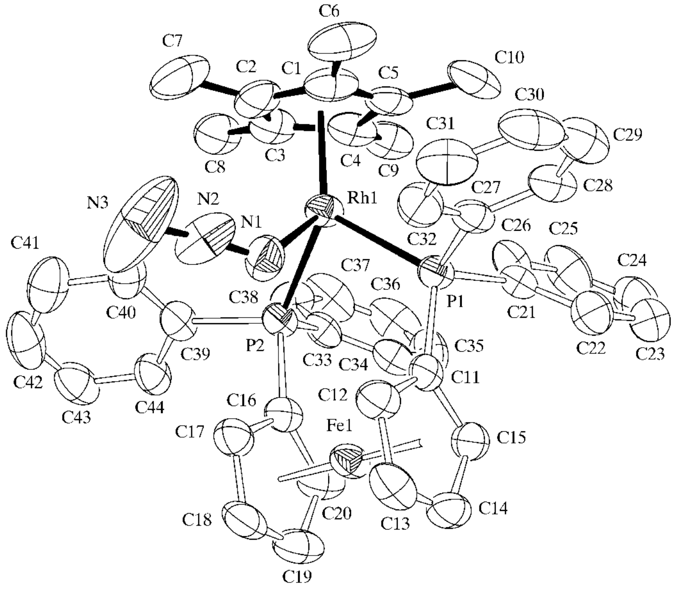


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The Rh—N1—N2 bond angle of 127.6 (7)° in (I) agrees well with the values found in six-coordinate Rh^{III}–azide complexes (Seok *et al.*, 2002). Atom N3 in the azide ligand has a large displacement ellipsoid, probably due to its terminal position. The Rh—N bond length of 2.111 (7) Å indicates an Rh—N single bond (Davis *et al.*, 1969; Lee & Lee, 1999). The Rh···Fe distance is 4.340 (2) Å, which clearly rules out a direct bonding interaction between the two metal atoms.

Experimental

A solution of $[Cp^*RhCl(dppf)]PF_6$ (100 mg, 0.12 mmol) and $AgNO_3$ (62 mg, 0.36 mmol) in a mixture of dichloromethane and acetone (1:1, 30 ml) was stirred for 3 h at room temperature, and the solvent was removed under vacuum. The resulting solid was extracted with

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dichloromethane and neat N_3SiMe_3 (16 µl, 0.12 mmol) was added. The resulting solution was then stirred for 18 h and the solvent was removed. The remaining solid was washed with diethyl ether (20 ml × 2) to give the title compound, (I), which was recrystallized from dichloromethane–hexane (1:1) to give red crystals (0.074 g, 62.6%; m.p. 471–473 K). Spectroscopic analysis, IR (KBr, ν, cm^{-1}): 2029 (N_3), 843 (PF_6); ^1H NMR ($CDCl_3$, p.p.m.): 7.74–7.33 (20H, *m*, Ph), 4.91, 4.39, 4.29, 4.12 (8H, C_5H_4), 1.15 (15H, *t*, J_{PH} = 4.0 Hz, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$, p.p.m.): 135.7–128.8 (Ph), 104.7 (*d*, J_{RhC} = 6.4 Hz, Cp* C_5), 77.5–76.6 (C_5H_4), 8.59 (Cp* Me_5); $^{31}P\{^1H\}$ NMR ($CDCl_3$, p.p.m.): 38.79 (*d*, J_{RhP} = 146.5 Hz, dppf), −143.8 (*sep*, J_{PF} = 708.2 Hz); analysis calculated for $C_{44}H_{43}F_6Fe$- N_3P_3Rh: C 53.95, H 4.43, N 4.29%; found: C 54.23, H 4.39, N 4.24%.

Crystal data

$[FeRh(C_{10}H_{15})(C_{17}H_{14}P)_2(N_3)]PF_6$
$M_r = 979.48$
Monoclinic, $P2_1/n$
$a = 14.759\ (3)$ Å
$b = 17.829\ (4)$ Å
$c = 15.736\ (4)$ Å
$\beta = 92.669\ (12)°$
$V = 4136.3\ (16)$ Å^3
$Z = 4$
$D_x = 1.573$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 reflections
$\theta = 5.1–13.1°$
$\mu = 0.93$ mm^{-1}
$T = 295\ (2)$ K
Block, red
0.26 × 0.24 × 0.18 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.698$, $T_{max} = 0.914$
7547 measured reflections
7252 independent reflections
3968 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 25.0°$
$h = -17 \rightarrow 0$
$k = 0 \rightarrow 21$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.065$
$wR(F^2) = 0.159$
$S = 1.01$
7252 reflections
523 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2 + 2.6079P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh1—N1	2.111 (7)	N1—N2	1.114 (10)
Rh1—P2	2.366 (2)	N2—N3	1.155 (12)
Rh1—P1	2.373 (2)		
N1—Rh1—P2	85.5 (2)	N2—N1—Rh1	127.6 (7)
N1—Rh1—P1	82.3 (2)	N1—N2—N3	174.3 (13)
P2—Rh1—P1	96.19 (7)		

All H atoms were generated in ideal positions and refined in a riding model, with C—H distances in the range 0.93–0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Difference maps show that the methyl H atoms were not well resolved and for the final refinement they were positioned using the HFIX 33 instruction of *SHELXTL* (Sheldrick, 1997).

Data collection: *XSCANS* (Siemens, 1995); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1171). Services for accessing these data are described at the back of the journal.

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