

An arene–ruthenium(II) complex containing novel hybrid phosphino-fluoro ligands

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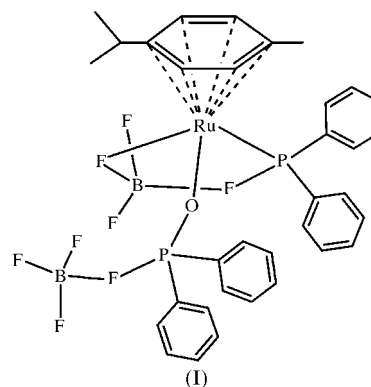
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In the title compound, $(\eta^6\text{-}p\text{-cymene})[(\text{diphenylphosphino-fluorido})\text{trifluoroborato-}\kappa^2\text{P},\text{F}][(\text{diphenylphosphino}(\text{fluorido})\text{trifluoroborato-}\kappa\text{O})\text{ruthenium(II)}], [\text{Ru}(\text{C}_{12}\text{H}_{10}\text{BF}_4\text{OP})(\text{C}_{12}\text{H}_{10}\text{BF}_4\text{P})(\text{C}_{10}\text{H}_{14})]$, the hybrid Ph_2PFBF_3 ligand is bidentate ($\kappa^2\text{P},\text{F}$) and thus forms a five-membered chelate ring. The Ph_2PFBF_3 ligand is unusually ligated to the metal through the P atom of the PPh_2 moiety and through one of the F atoms of the BF_4 moiety. The phosphine-oxidized $\text{Ph}_2\text{P}(\text{O})\text{FBF}_3$ ligand is bonded to the Ru atom *via* the O atom. The Ru centre has a pseudo-octahedral coordination environment, in which the phenyl ring occupies three of the corners of the distorted octahedron. The Ru–O, Ru–F and Ru–P bond lengths are 2.107 (3), 2.135 (4) and 2.3145 (15) Å, respectively.

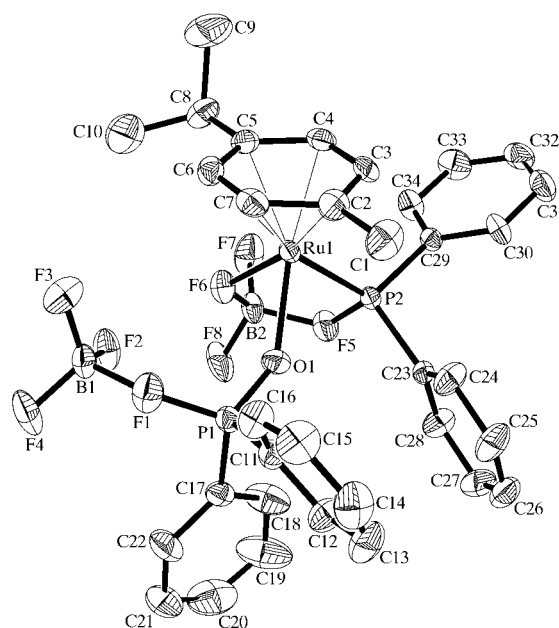
Comment

The chemistry of half-sandwich ($\eta^6\text{-arene}$)ruthenium(II) complexes is currently of much interest because of the numerous applications of new catalytic systems for a variety of organic transformation reactions (Noyori, 1994). Ruthenium-based catalytic systems are effective in the hydrogenation of ketones for the synthesis of chiral alcohols (Bernard *et al.*, 2000). Studies by Noyori and co-workers have shown that the transfer hydrogenation of prochiral ketones can be achieved in high enantiomeric excess by tailoring chiral ruthenium catalysts; accordingly, investigations of chiral ruthenium catalysts are now common (Yamakawa *et al.*, 2000). As part of our research on ruthenium complexes with S- and Se-donor ligands, we are interested in preparing some new bulk ligands by the hybridization of different atoms (Zhang *et al.*, 2002). The most intriguing properties of alkylphosphine ligands are related to the strong σ -donor P atom and electron-donating alkyl groups, which can stabilize the 16e ruthenium species to convert to their 18e congeners by oxidative addition at the metal centre (Halpern, 1970). Tetrafluoroborate as a ligand in reactive complexes can be easily replaced by π - and σ -donors, suggesting that tetrafluoroborate is a very good leaving group (Appel & Beck, 1985). Thus, we attempted the reaction of

Ph_2PCl and $\text{Ag}(\text{BF}_4)$ in order to isolate the hybrid phosphino-fluoro Ph_2PFBF_3 ligand with one P–F bond (see reaction Scheme in *Experimental*). In order to reveal the coordination modes of this ligand in ruthenium complexes, we prepared the title complex, (I), and carried out a diffraction analysis. In this paper, we report our initial findings on the structure of (I). To our knowledge, this is the first structural example of a transition metal complex containing the hybrid Ph_2PFBF_3 ligand.



In the neutral complex (I), the Ru atom exhibits a distorted octahedral coordination sphere, with the phenyl ring of the *p*-cymene ligand formally occupying three octahedral sites. The structure of (I) is depicted in Fig. 1. The O atom of $\text{Ph}_2\text{P}(\text{O})\text{FBF}_3$ and the bidentate Ph_2PFBF_3 ligand, which is bonded to the metal centre *via* the P and an F atom, complete the coordination sphere, which may infer that the Ru atom exhibits a chiral centre. The hybrid Ph_2PFBF_3 ligand is unusually ligated to the metal through the P atom of the PPh_2 moiety and through one of the F atoms of the BF_4 moiety. This novel coordination mode is the first example of a ruthenium complex system. Ph_2PFBF_3 acts as a bidentate ligand to form a


Figure 1

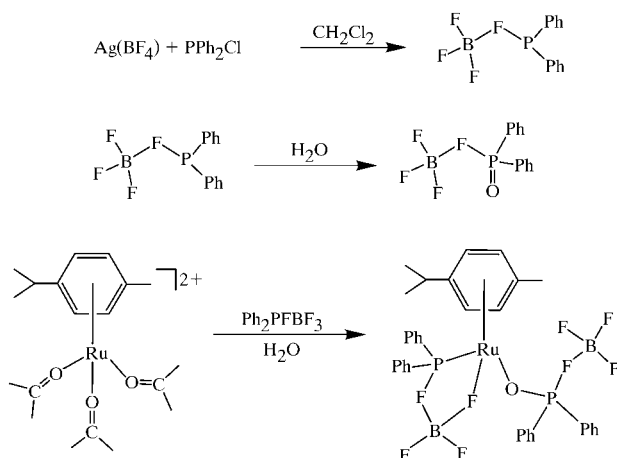
A perspective view of (I). H atoms have been omitted for clarity and displacement ellipsoids are drawn at the 50% probability level.

five-membered chelate ring with a bite angle of 78.48 (12)°, which is more acute than that found for the bidentate Me₂PCHCHPMe₂ phosphine ligand in Ru^{II} complexes (Field *et al.*, 1994). The Ru—C(ring) distances are in the range 2.158 (5)–2.245 (7) Å and agree well with those found in other (*p*-cymene)ruthenium(II) complexes, for example, [(*p*-cymene)RuCl(Me₂PCH₂CH₂SMe)](BPh₄) [2.198 (5)–2.267 (6) Å; Suzuki *et al.*, 1996] and [(*p*-cymene)RuCl₂(PH₂Cy)] [2.175 (4)–2.238 (5) Å; Van der Maelen Uría *et al.*, 1994]. Note that the longest Ru—C bond (Ru1—C6; see Table 1) is *trans* with respect to the P atom, as a result of the strong *trans* influence of the PPh₂ group. The Ru—O bond length in (I) indicates considerable single-bond character. The Ru—F bond length in (I) is comparable to those in *cis*-[Ru(dmpe)₂F(F·HF)] [2.101 (3) and 2.168 (3) Å; Kirkham *et al.*, 2001]. The Ru—P bond distance is normal and also agrees well with those in related complexes (Suzuki *et al.*, 1996; Van der Maelen Uría *et al.*, 1994).

The P2—F5 bond length of the coordinated chelate ligand is slightly longer than the P1—F1 bond length of the terminal coordination ligand (Table 1). There are three types of B—F bond in (I), *viz.* B—μ-F(P) bonds [B2—F5 = 1.485 (8) Å and B1—F1 = 1.472 (8) Å], the B—μ-F(Ru) bond [B2—F6 = 1.452 (8) Å] and terminal B—F bonds [1.344 (9)–1.399 (8) Å]. On the other hand, the B2—F5—P2 angle is smaller than both the B1—F1—P1 angle (Table 1) and that in the reported complex [Mo(η⁵-C₉H₇)(CO)₂{P-η³-(^tBu)CPC-(^tBu)PFBF₃}] [131.1 (6)°; Hitchcock *et al.*, 1994]. Thus, it is reasonable to say that the coordination of the Ru atom by the Ph₂PFBF₃ chelate ligand results in the elongation of the P—F and B—μ-F(P) bonds and the reduction of the B—F—P angle (Barthazy *et al.*, 2000). Angles involving P atoms reflect a tetrahedral geometry, and it is also noteworthy that the Ru—P—C and O—P—F angles are larger than the F—P—C angles.

Experimental

Treatment of Ph₂PCl in dry CH₂Cl₂ with an equivalent amount of Ag(BF₄) resulted in a light yellow solution with a white precipitate



(see Scheme above). The solution was filtered to remove the AgCl precipitate and the solvent was pumped off to give a yellow oily

product (Ph₂PFBF₃). Spectroscopic analysis, ¹H NMR (CDCl₃, p.p.m.): δ 7.12–7.75 (*m*, Ph); ³¹P{¹H} NMR (CDCl₃, p.p.m.): δ -76.5; ¹⁹F NMR (CDCl₃, p.p.m.): δ -187.2 (*d*, *J* = 118 Hz, PFB), -319.3 (BF₃); MS (EI): *m/z* 273 (*M*⁺ + 1); IR (Nujol, cm⁻¹): ν (B—F) 1154 (*s*), 901 (*s*), 856 (*s*) and 712 (*m*). Ph₂PFBF₃ was dissolved in CH₂Cl₂, affording Ph₂P(O)FBF₃. Spectroscopic analysis, ¹H NMR (CDCl₃, p.p.m.): δ 7.09–7.77 (*m*, Ph); ³¹P{¹H} NMR (CDCl₃, p.p.m.): δ 84.1; ¹⁹F NMR (CDCl₃, p.p.m.): δ -164.6 (*d*, *J* = 96 Hz, PFB), -302.7 (BF₃); MS (EI): *m/z* 288 (*M*⁺); IR (Nujol, cm⁻¹): ν(B—F) 1148 (*s*), 892 (*s*), 843 (*s*) and 716 (*m*); ν(P=O) 1016 (*vs*).

For the synthesis of (I), Ph₂PFBF₃ (272 mg, 1.0 mmol) was dissolved in CH₂Cl₂ (5 ml) and the solution was added to a flask containing a solution of [(*p*-cymene)Ru(acetone)₃](BF₄) (248 mg, 0.5 mmol) in CH₂Cl₂ (5 ml). The resulting solution was stirred for 2 h and the solvent removed *in vacuo*. Hexane (20 ml) was added to the flask to give an orange precipitate. Recrystallization from CH₂Cl₂/hexane afforded orange prismatic crystals.

Crystal data

[Ru(C ₁₂ H ₁₀ BF ₄ OP)- (C ₁₂ H ₁₀ BF ₄ P)(C ₁₀ H ₁₄)]	<i>D</i> _x = 1.550 Mg m ⁻³
<i>M</i> _r = 795.24	Mo <i>K</i> α radiation
Monoclinic, <i>Cc</i>	Cell parameters from 3433 reflections
<i>a</i> = 17.7179 (13) Å	<i>θ</i> = 2.2–25.6°
<i>b</i> = 11.2784 (8) Å	<i>μ</i> = 0.63 mm ⁻¹
<i>c</i> = 18.4455 (13) Å	<i>T</i> = 294 (2) K
<i>β</i> = 112.410 (2)°	Prism, orange
<i>V</i> = 3407.6 (4) Å ³	0.22 × 0.18 × 0.15 mm
<i>Z</i> = 4	

Data collection

Bruker SMART APEX CCD diffractometer	6382 independent reflections
<i>ω</i> scans	5757 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	<i>R</i> _{int} = 0.028
<i>T</i> _{min} = 0.294, <i>T</i> _{max} = 0.401	<i>θ</i> _{max} = 26.0°
10 808 measured reflections	<i>h</i> = -21 → 21
	<i>k</i> = -11 → 13
	<i>l</i> = -22 → 22

Table 1

Selected geometric parameters (Å, °).

Ru1—P2	2.3145 (15)	Ru1—C5	2.186 (5)
Ru1—F6	2.135 (4)	Ru1—C6	2.245 (6)
Ru1—O1	2.107 (3)	Ru1—C7	2.220 (5)
Ru1—C2	2.189 (6)	P1—F1	1.554 (4)
Ru1—C3	2.159 (5)	P2—F5	1.581 (4)
Ru1—C4	2.159 (5)	P1—O1	1.478 (4)
P2—Ru1—F6	78.48 (12)	O1—Ru1—C6	113.6 (2)
P2—Ru1—O1	84.93 (11)	O1—Ru1—C7	93.68 (18)
P2—Ru1—C2	117.3 (2)	F1—P1—O1	115.5 (2)
P2—Ru1—C3	93.74 (16)	F1—P1—C11	103.9 (2)
P2—Ru1—C4	96.71 (16)	F1—P1—C17	109.4 (3)
P2—Ru1—C5	123.63 (15)	O1—P1—C11	110.1 (3)
P2—Ru1—C6	160.86 (18)	O1—P1—C17	108.4 (3)
P2—Ru1—C7	154.51 (18)	C11—P1—C17	109.3 (3)
O1—Ru1—C2	97.8 (2)	Ru1—P2—F5	106.39 (16)
F6—Ru1—O1	81.78 (15)	Ru1—P2—C23	115.38 (17)
F6—Ru1—C2	164.1 (2)	Ru1—P2—C29	118.74 (17)
F6—Ru1—C3	148.8 (2)	F5—P2—C23	105.6 (2)
F6—Ru1—C4	112.55 (18)	F5—P2—C29	104.2 (2)
F6—Ru1—C5	90.82 (19)	C23—P2—C29	105.3 (2)
F6—Ru1—C6	98.8 (2)	Ru1—O1—P1	147.6 (3)
F6—Ru1—C7	126.6 (2)	P1—F1—B1	134.7 (4)
O1—Ru1—C3	128.1 (2)	P2—F5—B2	120.2 (4)
O1—Ru1—C4	165.64 (19)	Ru1—F6—B2	121.5 (3)
O1—Ru1—C5	148.56 (19)		

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.08$	$\Delta\rho_{\max} = 1.07 \text{ e } \text{\AA}^{-3}$
6382 reflections	$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$
439 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.03 (3)

H atoms were treated as riding using the normal *SHELXTL* (Sheldrick, 1997b) parameters.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1160). Services for accessing these data are described at the back of the journal.

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