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Key indicators

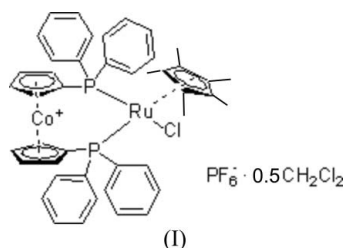
Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.049
 wR factor = 0.144
Data-to-parameter ratio = 18.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**[1,1'-Bis(diphenylphosphino)cobaltocenium- κ^2P,P']chloro(η^5 -pentamethylcyclopentadienyl)ruthenium(II) hexafluorophosphate dichloromethane hemisolvate**

In the title structure, $[\text{CoRu}(\text{C}_{10}\text{H}_{20})\text{Cl}(\text{C}_{17}\text{H}_{14}\text{P})_2]\text{PF}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$, the Ru atom is coordinated by a pentamethylcyclopentadienyl ring, one Cl atom and two P atoms of the chelating 1,1'-bis(diphenylphosphino)cobaltocenium ligand, giving a three-legged piano-stool geometry. The solvent molecule lies on a twofold rotation axis. In the crystal structure, weak $\text{C}-\text{H}\cdots\text{F}$ and $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds link molecules into a two-dimensional framework.

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Comment

Ferrocene derivatives having electron-donating heteroatoms at the 1,1'-positions are good starting materials for preparing hetero-bimetallic complexes. In addition, cobaltocene derivatives are also effective ligands. Following the procedure of Oshima & Suzuki (1984), who investigated the phosphine displacement in 1,1'-bis(diphenylphosphino)ferrocene (dppf) with $[\text{Cp}^*\text{RuCl}_2]_n$ (Cp^* is pentamethylcyclopentadienyl), we have studied a similar reaction with the ligand 1,1'-bis(diphenylphosphino)cobaltocenium (dppc) and the structure of the resulting compound, (I), is presented here.



The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The dichloromethane C atom lies on a twofold rotation axis. The Ru—Cl bond length in (I) is not significantly different from that of 2.434 (2) Å in $\text{Cp}^*\text{Ru}(\text{dppm})\text{Cl}$ [dppm = bis(diphenylphosphino)methane] and 2.4532 (5) Å in $\text{Cp}^*\text{Ru}(\text{dppe})\text{Cl}$ [dppe = bis(diphenylphosphino)methane] (Bruce, 2003). On the other hand, the Ru—P bond lengths in (I) are longer than those in the above neutral complexes [2.282 (2) and 2.294 (2) Å in $\text{Cp}^*\text{Ru}(\text{dppm})\text{Cl}$; 2.2882 (5) and 2.2812 (5) Å in $\text{Cp}^*\text{Ru}(\text{dppe})\text{Cl}$]. The Ru—C(Cp^*) bond lengths range from 2.213 (4) Å to 2.261 (4) Å, not significantly different from those in $\text{Cp}^*\text{Ru}(\text{dppm})\text{Cl}$ and $\text{Cp}^*\text{Ru}(\text{dppe})\text{Cl}$. The Ru—Cg1, Co—Cg2 and Co—Cg3 bond lengths (where Cg1 is the centroid of the Cp^* ring atoms, and Cg2 and Cg3 are the centroids of atoms C23–C27 and C28–C32, respectively) are 1.8802 (18), 1.6330 (18) and 1.6346 (18) Å, respectively, and are not significantly different from those found in $\text{Cp}^*\text{Ru}(\text{dppf})\text{H}$ (Hembre *et al.*, 1996). The P—Ru—P angle in

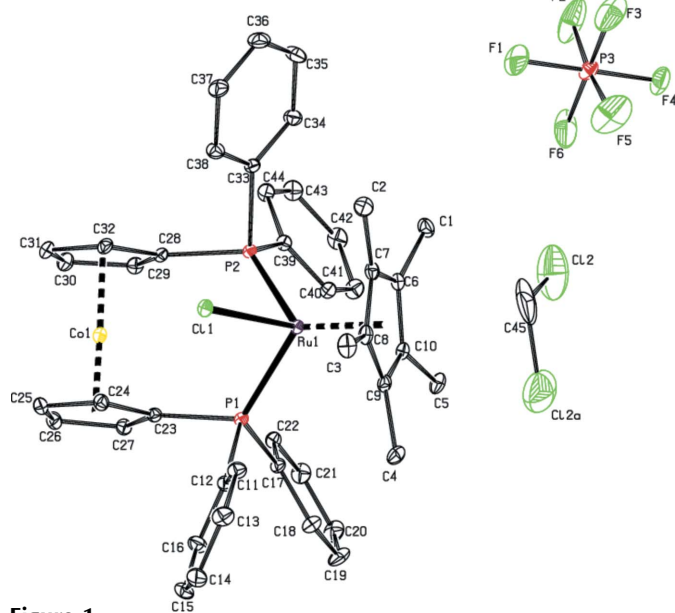


Figure 1

The molecular structure of (I), shown with 30% probability displacement ellipsoids. H atoms have been omitted. Cl2a is related to Cl2 by C_{2v} symmetry.

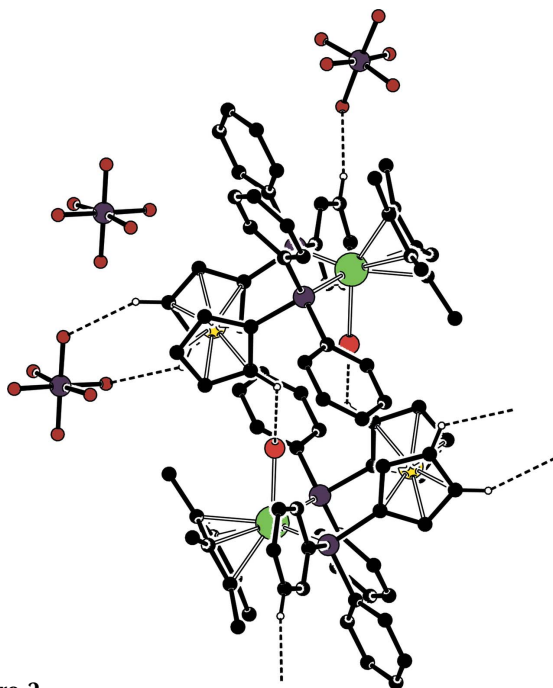


Figure 2

Part of the crystal structure of (I), showing the C—H...F/Cl hydrogen bonds as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

(I) is larger than those found in the dp_{pp}m and dp_{pe} complexes [71.53 (6)° in Cp*Ru(dp_{pp}m)Cl and 82.15 (2)° in Cp*Ru(dp_{pe})Cl], possibly due to the steric demand of the chelating dp_{pc} ligand in (I). The P—Ru—Cl angles are similar to those in the dp_{pp}m and dp_{pe} complexes. The relative conformation of the cyclopentadienyl (Cp) rings of the cobaltocene group is best described as synperiplanar eclipsed, as reflected in the P1...Cg1...Cg2...P2 pseudo-torsion angle of 0.18 (5)°. The

dihedral angle between the planes of the two Cp rings is 2.7 (1)°.

In the crystal structure, weak C—H...F and C—H...Cl hydrogen bonds link molecules into a two-dimensional framework (Table 2 and Fig. 2).

Experimental

The title compound was prepared according to the literature procedure of Oshima & Suzuki (1984). Slow diffusion of hexane into a dichloromethane solution of (I) gave single crystals suitable for X-ray analysis.

Crystal data

[CoRu(C₁₀H₂₀)Cl(C₁₇H₁₄P)₂]PF₆·
0.5CH₂Cl₂
M_r = 1016.61
Monoclinic, C_{2/c}
a = 22.0859 (16) Å
b = 19.8170 (16) Å
c = 20.7479 (16) Å
β = 106.629 (2)°
V = 8701.1 (12) Å³
Z = 8

D_x = 1.552 Mg m⁻³
Mo Kα radiation
Cell parameters from 9389
reflections
θ = 2.3–27.8°
μ = 1.02 mm⁻¹
T = 292 (2) K
Block, brown
0.40 × 0.30 × 0.30 mm

Data collection

Bruker SMART-CCD area-detector
diffractometer
φ and *ω* scans
Absorption correction: none
28478 measured reflections
9465 independent reflections

7551 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.068
*θ*_{max} = 27.0°
h = -28 → 28
k = -23 → 25
l = -24 → 26

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.049
wR (*F*²) = 0.144
S = 1.03
9465 reflections
524 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0877*P*)²]
where *P* = (*F_o*² + 2*F_c*²)/3
(Δ/*σ*)_{max} = 0.002
Δ*ρ*_{max} = 1.21 e Å⁻³
Δ*ρ*_{min} = -0.82 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1—C6	1.508 (5)	C23—P1	1.844 (4)
C2—C7	1.497 (6)	C28—P2	1.852 (4)
C3—C8	1.505 (5)	C33—P2	1.853 (4)
C4—C9	1.494 (6)	C39—P2	1.836 (3)
C5—C10	1.506 (5)	Cl1—Ru1	2.4451 (9)
C11—P1	1.850 (4)	P1—Ru1	2.3222 (9)
C17—P1	1.833 (4)	P2—Ru1	2.3061 (9)
P1—C23—Co1	129.52 (18)	C39—P2—Ru1	118.23 (12)
P2—C28—Co1	128.77 (18)	C28—P2—Ru1	121.80 (12)
C23—Co1—C28	107.09 (14)	C33—P2—Ru1	112.86 (12)
C17—P1—Ru1	118.36 (12)	P2—Ru1—P1	96.69 (3)
C23—P1—Ru1	122.09 (12)	P2—Ru1—Cl1	88.10 (3)
C11—P1—Ru1	114.66 (13)	P1—Ru1—Cl1	88.29 (3)
Ru1—C6—C7—C2	124.7 (4)	C35—C36—C37—C38	1.3 (8)
Ru1—C7—C8—C9	-62.1 (2)	C30—C29—Co1—C24	160.1 (4)
P1—C23—C24—Co1	-124.1 (3)	C23—C24—Co1—C29	51.8 (5)
Co1—C24—C25—C26	-59.2 (3)	P2—C28—Co1—C29	119.7 (3)
C23—C24—C25—Co1	59.2 (3)	C6—C10—Ru1—C7	36.7 (2)
Co1—C28—C29—C30	-59.9 (3)	C6—C10—Ru1—P1	-162.6 (2)
P2—C28—C29—Co1	-123.2 (3)	C7—C8—Ru1—P2	15.9 (3)
Co1—C29—C30—C31	-58.7 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C31—H31 \cdots F4 ⁱ	0.98	2.52	3.234 (5)	130
C35—H35 \cdots F4 ⁱⁱ	0.93	2.48	3.398 (6)	170
C30—H30 \cdots F3 ⁱ	0.98	2.50	3.347 (7)	144
C24—H24 \cdots Cl1 ⁱⁱⁱ	0.98	2.79	3.433 (4)	124

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x, -y+1, z-\frac{1}{2}$; (iii) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+2$.

All H atoms were placed in calculated positions and constrained to ride on their parent atoms, with methyl C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, and cyclopentadienyl and phenyl C—H = 0.98 and 0.93 Å, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest electron density peak is 1.10 Å from atom F6.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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