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A new optically pure half-sandwich Cp–Ru diphosphine complex with a chiral metal centre, (*S*)-Ru(η^5-C_5H_5)(EPHOS)Cl {EPHOS is (+)-(1*R*,2*S*)-2-[(diphenylphosphino)methylamino]-1-phenylpropyl diphenylphosphinite}

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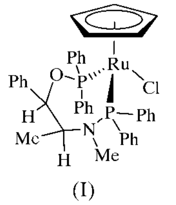
The crystal structure of the title compound, chloro(η^5-cyclopentadienyl){(1*R*,2*S*)-2-[(diphenylphosphino)methylamino]-1-phenylpropyl diphenylphosphinite-κ^2P,P'}ruthenium(II), [Ru(C_5H_5)Cl($C_{34}H_{33}NOP_2$)], is reported. The pseudo-octahedral complex is chiral and the configuration at the Ru atom is *S*. The seven-membered metallacycle adopts a boat-like conformation.

Comment

Organometallic complexes containing a chiral metal centre have attracted considerable attention due to their potential application as reagents in asymmetric synthesis (Brunner, 1999). For this purpose, half-sandwich Cp–Ru complexes (Cp is cyclopentadienyl) bearing a chelating diphosphine without C_{2v} symmetry are attractive targets, since these species have been shown to be configurationally stable at the chiral metal centre (Davies *et al.*, 1990). We present here the molecular structure of the title complex, (I), a new optically pure half-sandwich Ru complex, which was obtained by reaction of the diphosphine (+)-(2*S*,3*R*)-2-[(diphenylphosphino)methylamino]-3-phenylpropyl diphenylphosphinite with Cp-Ru(PPh_3)$_2$Cl.



(I)

Compound (I) was synthesized as a single diastereomer and crystallized from a pentane–CH_2Cl_2 solvent mixture in the chiral space group $P2_12_12_1$. Our X-ray data allowed determination of the absolute configuration at the Ru centre in (I). The molecular structure of (I) is shown in Fig. 1 and selected dimensions are given in Table 1.

The Ru atom adopts a pseudo-octahedral coordination geometry, which can also be described as a distorted tetrahedral structure if one simplifies the Ru(η^5-C_5H_5) moiety to an Ru–*Cg* (*Cg* is the Cp centroid) moiety. The P1—Ru—P2, P1—Ru—Cl and P2—Ru—Cl bond angles [mean 93.76 (3)°] are smaller than the ideal tetrahedral angle (109.47°), which is compensated for by the opening of the Cp—Ru—*L* (*L* is P1, P2 or Cl) angles [mean 122.44 (15)°]. In accordance with the stereochemical convention adopted for organometallics (Brunner, 1980), the ligand priority is C_5H_5 > Cl > P(O) > P(N) and the absolute configuration of the metal centre is *S*. The seven-membered Ru–ligand chelate ring adopts a boat-like conformation, with the O atom close to the Ru/P1/P2 plane, as shown by the small O—P1—Ru—P2 torsion angle (−5.0°). The N atom is clearly out of the Ru/P1/P2 plane (P2—Ru—P1—N 42.6°).

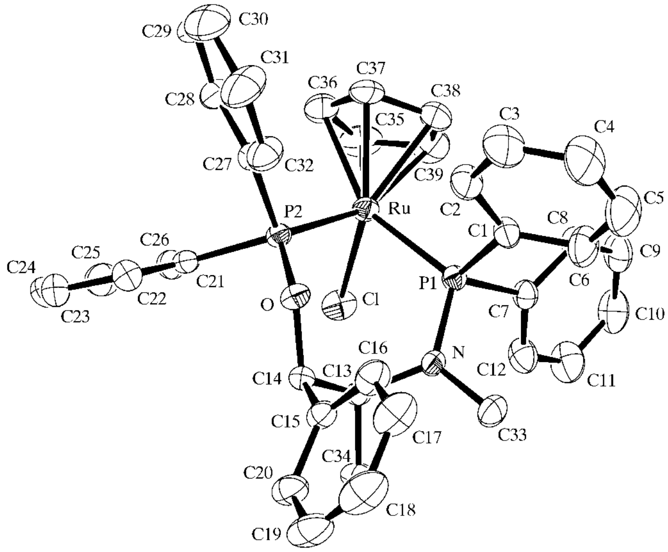


Figure 1
A view of the molecular structure of complex (I). Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.

The Ru—P(N) and Ru—P(O) bond distances [2.2906 (8) and 2.2675 (8) Å, respectively] are slightly longer than those in the related complex (*S*)-Ru(η^5-C_5H_5)[(*S*)-dpompyr-*PP*′]Cl [2.269 (2) and 2.242 Å, respectively; dpompyr is *N*-diphenylphosphino-2-(diphenylphosphinoxymethyl)pyrrolidone (Cesarotti *et al.*, 1987)]. The Ru—P(N) distance is longer than the Ru—P(O) distance, as is generally observed in transition metal complexes containing aminophosphine–phosphinite ligands (Cesarotti *et al.*, 1987; Baldovino *et al.*, 1992).

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Experimental

Compound (I) was synthesized by the reaction of (+)-EPHOS (2.670 g, 5 mmol) with CpRu(PPh_3)$_2$Cl (1.815 g, 2.5 mmol) in refluxing toluene (20 ml) over a period of 18 h. Purification of the crude product by flash chromatography (CH_2Cl_2) afforded pure (I) (1.164 g, 63%) as an orange solid. Recrystallization from a dichloromethane–hexane (1:1) mixture afforded orange crystals suitable for X-ray analysis.

Crystal data

[Ru(C_5H_5)Cl($C_{34}H_{33}NOP_2$)]
M_r = 735.16
Orthorhombic, $P2_12_12_1$
a = 13.2734 (1) Å
b = 14.3376 (1) Å
c = 18.6640 (2) Å
V = 3551.92 (5) Å^3
Z = 4
D_x = 1.375 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 14 894 reflections
θ = 1.8–30.0°
μ = 0.64 mm^{-1}
T = 296 (2) K
Parallelepiped, orange
0.30 × 0.28 × 0.14 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{\min}$ = 0.832, $T_{\max}$ = 0.916
25 398 measured reflections

9351 independent reflections
6619 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.044
$\theta_{\max}$ = 30°
$h = -18 \rightarrow 13$
$k = -18 \rightarrow 19$
$l = -22 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.078
S = 1.01
9351 reflections
409 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.015
$\Delta\rho_{\max}$ = 0.37 e Å^{-3}
$\Delta\rho_{\min}$ = −0.59 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00095 (12)
Absolute structure: Flack (1983), with 3652 Friedel pairs
Flack parameter = −0.03 (2)

H atoms were treated as riding, with C—H distances in the range 0.93–0.98 Å.

Table 1
Selected geometric parameters (Å, °).

Ru—P2	2.2675 (8)	P1—N	1.684 (2)
Ru—P1	2.2906 (8)	P2—O	1.631 (2)
Ru—Cl	2.4382 (9)		
C38—Ru—P2	126.79 (14)	C38—Ru—Cl	135.41 (15)
C38—Ru—P1	91.46 (11)	P2—Ru—Cl	97.53 (3)
P2—Ru—P1	93.01 (3)	P1—Ru—Cl	90.73 (3)

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); 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: GD1228). Services for accessing these data are described at the back of the journal.

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