

A ruthenium(II) complex with *p*-cymene and (*S*)-2-(anilinomethyl)pyrrolidine

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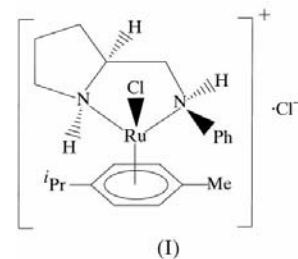
The title compound, [(*S*)-2-(anilinomethyl)pyrrolidine-*N,N'*]-chloro(η^6 -*para*-cymene)ruthenium(II) chloride, [RuCl(C₁₀H₁₄)(C₁₁H₁₆N₂)]Cl, has been synthesized by the reaction of [RuCl₂(*p*-cymene)]₂ (*p*-cymene is *para*-isopropyltoluene) with (*S*)-2-(anilinomethyl)pyrrolidine in triethylamine/2-propanol. The Ru atom is in a pseudo-tetrahedral environment coordinated by a chloride ligand, the aromatic hydrocarbon is linked in a η^6 manner and the amine is linked *via* its two N atoms. The chloride anion is involved in hydrogen bonding with the diamine moieties through N—H...Cl interactions, with N...Cl distances of 3.273 (4) and 3.352 (4) Å.

Comment

The recent discovery of highly reactive chiral metal complexes has led to rapid advances in catalytic asymmetric transfer hydrogenation (Touchard *et al.*, 1997; Noyori & Hashiguchi, 1997; Inoue *et al.*, 1997; Suzuki *et al.*, 1996). Chiral diamine-based ruthenium(II) complexes are particularly efficient catalysts for the enantioselective reduction of prochiral ketones under mild conditions using 2-propanol as the hydrogen source (Hashiguchi *et al.*, 1995; Fujii *et al.*, 1996; Püntener *et al.*, 1996; Uematsu *et al.*, 1996; Haack *et al.*, 1997).

In previous research, we have shown that the diamine (*S*)-2-anilinopyrrolidine can be used as the basic component in the synthesis of diaminophosphine chiral ligands for the catalytic asymmetric reduction of olefins (Aitali *et al.*, 1995). More recently, we have shown that the diamine–Ru^{II} complex catalyses the asymmetric transfer hydrogenation of aromatic ketones with high activity and enantioselectivity (Aitali *et al.*, 2000). The absolute configuration of the resulting alcohol depends on that of the ligand coordinated to the metal centre. The present work follows related research by our group on organometallic compounds of terpene hydrocarbons (Abouhamza *et al.*, 1999) and we report here the crystal structure of

the complex synthesized by refluxing [RuCl₂(*p*-cymene)]₂ and (*S*)-2-(anilinomethyl)pyrrolidine in 2-propanol/triethylamine, (I).



The title compound consists of [RuCl(*p*-cymene){(*S*)-2-aminomethylpyrrolidine}]⁺ cations, the charge being balanced by interstitial chloride anions. The environment around the Ru^{II} atom is made up of a chloro ligand, the amine linked in a bidentate manner through its two N atoms, defining a five-membered chelate ring, and the hydrocarbon linked through its π -cloud in a typical organometallic η^6 bond (see Fig. 1). The geometry around the metal atom may be regarded as a tetrahedron with considerable trigonal distortion, considering the linkage to the hydrocarbon as a single bond. Defining *X* as the centroid of the aromatic ring, the Ru—*X* distance is 1.671 (5) Å and the angles Cl1—Ru—*X*, N1A—Ru—*X* and N7A—Ru—*X* are, respectively, 125.2 (1), 128.9 (2) and 130.1 (2)°.

Three other examples have been found in the bibliography of Ru^{II}– η^6 -*p*-cymene complexes (García *et al.*, 1994; Suzuki *et al.*, 1996; Trabesinger *et al.*, 1997), the overall geometric features being analogous to the compound described here and the distance from the metal atom to the aromatic ring appearing to be modulated by the steric repulsion of the other ligands present. Quite surprisingly, there are very few references in the literature to analogous compounds with other

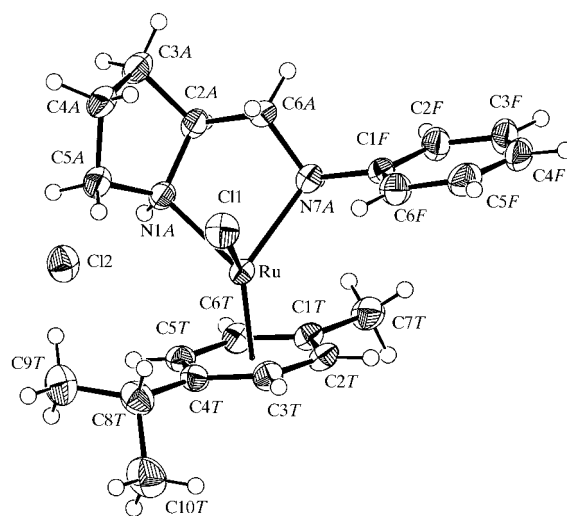


Figure 1

View of the title compound, with the non-H atoms represented by 50% probability ellipsoids and the H atoms represented by open spheres of arbitrary radii.

aromatic hydrocarbons (Werner *et al.*, 1986). Three new chiral centres appear upon complex formation: N1A, N7A and the metal atom itself. The absolute configuration of C2A necessitates the absolute configuration of the other atoms. This configuration is found to be *S* for the four chiral centres.

The non-coordinated chloride anion is linked *via* N—H...Cl hydrogen bonds to the N atoms of two different cations. The N...Cl distances are 3.273 (4) Å for N1A—H1A...Cl2 and 3.352 (4) Å for N7A—H7A...Cl2ⁱ [symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$]. These interactions link the cation/anion moieties to one another, forming rows along the [100] direction.

Experimental

A mixture of [RuCl₂(*p*-cymene)]₂ (264 mg, 0.43 mmol), synthesized according to literature procedures (Bennett & Smith, 1974), (*S*)-2-(anilinomethyl)pyrrolidine (152 mg, 0.86 mmol) and triethylamine (0.24 ml, 1.72 mmol) in 2-propanol was heated at 353 K for 1 h. The orange-red solution obtained was then concentrated to dryness and the resulting solid was treated with absolute ethanol. After filtration from the resulting solution, crystals of the title compound were obtained (yield 90%). The entire procedure was driven under an atmosphere of nitrogen using standard Schlenk-type glassware.

Crystal data

[RuCl(C ₁₀ H ₁₄)(C ₁₁ H ₁₆ N ₂)]Cl	Mo K α radiation
$M_r = 482.44$	Cell parameters from 45 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 12.5\text{--}18.2^\circ$
$a = 8.2107$ (3) Å	$\mu = 1.031$ mm ⁻¹
$b = 9.3093$ (4) Å	$T = 295$ (1) K
$c = 26.8707$ (9) Å	Brick-shaped, yellow
$V = 2053.89$ (13) Å ³	$0.63 \times 0.39 \times 0.24$ mm
$Z = 4$	
$D_x = 1.560$ Mg m ⁻³	

Data collection

Stoe Stadi-4 diffractometer	$R_{\text{int}} = 0.019$
ω scans	$\theta_{\text{max}} = 32.5^\circ$
Absorption correction: ψ scan	$h = -12 \rightarrow 12$
(<i>X-RED</i> ; Stoe & Cie, 1996)	$k = 0 \rightarrow 14$
$T_{\text{min}} = 0.466, T_{\text{max}} = 0.781$	$l = 0 \rightarrow 40$
8338 measured reflections	3 standard reflections
7328 independent reflections	frequency: 60 min
6503 reflections with $I > 2\sigma(I)$	intensity decay: 5.7%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0700P)^2 + 3.0000P]$
$R(F) = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.142$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.105$	$\Delta\rho_{\text{max}} = 1.14$ e Å ⁻³
7328 reflections	$\Delta\rho_{\text{min}} = -1.63$ e Å ⁻³
238 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.05 (5)

Table 1

Selected geometric parameters (Å, °).

Ru—Cl1	2.4254 (12)	Ru—C3T	2.174 (5)
Ru—N1A	2.146 (4)	Ru—C4T	2.214 (4)
Ru—N7A	2.190 (4)	Ru—C5T	2.179 (4)
Ru—ClT	2.199 (5)	Ru—C6T	2.180 (5)
Ru—C2T	2.196 (5)		
N1A—Ru—N7A	79.26 (15)	N7A—Ru—Cl1	90.75 (11)
N1A—Ru—Cl1	87.70 (11)		

The H atoms were treated as riding using *SHELXL97* defaults with displacement parameters fixed at $1.2U_{\text{eq}}$ of their parent atoms.

Data collection: *STADI4* (Stoe & Cie, 1996); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1008). Services for accessing these data are described at the back of the journal.

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