

[(1*R*,2*R*)-2-Amino-1,2-diphenyl-*N*-(*p*-tolylsulfonyl)ethylamido]chloro-(η^6 -ethoxybenzene)ruthenium(II) methanol solvate

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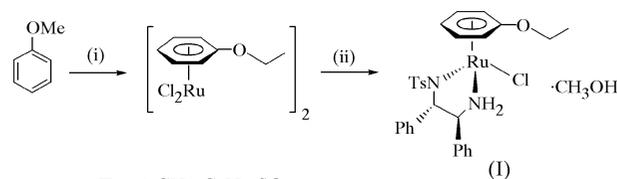
The title compound, [Ru(C₂₁H₂₁N₂O₂S)Cl(C₈H₁₀O)]·CH₄O or [Ru(TsDPEN)Cl(η^6 -C₆H₅OCH₂CH₃)]·CH₄O [where TsDPEN is (1*R*,2*R*)-1,2-diphenyl-*N*-(*p*-toluenesulfonyl)ethylenediamine], contains an *S*-chiral Ru centre in a distorted octahedral environment, with similar bond lengths and angles to analogous complexes. The very short (N—)H···Cl distance of 2.61 Å is ascribed to an intramolecular hydrogen bond.

Comment

Arene–ruthenium(II) derivatives are of interest both as reagents in organic chemistry (Pigge & Coniglio, 2001) and as catalysts for a wide range of reactions, including arene hydrogenation (Boxwell *et al.*, 2002), alkene metathesis (Zaja *et al.*, 2003) and Diels–Alder reactions (Davenport *et al.*, 2004). Arene–ruthenium complexes containing chiral diamine ligands are of particular interest, since Noyori and co-workers (Noyori & Hashiguchi, 1997) have demonstrated that they are active enantioselective hydrogen-transfer catalysts. We have recently developed a simple method of synthesizing functionalized arene–ruthenium complexes, *e.g.* [RuCl₂(η^6 -C₆H₅OCH₂CH₂OH)]₂ (Soleimannejad & White, 2005), and we wish to exploit this using the functionality to link the arene to polymer supports in order to prepare easily recyclable ‘Noyori-type’ catalysts (Soleimannejad *et al.*, 2003). During this study, the title compound, (I), was synthesized, crystallizing with a methanol solvent molecule.

The Ru atom in (I) has a pseudo-octahedral geometry, being coordinated to a chloride ligand, an η^6 -arene occupying three facial coordination sites, and a five-membered chelate ligand with neutral amine and anionic sulfonamide moieties. The configuration of this chiral ruthenium centre is *S* (Stanley & Baird, 1975). The Ru–Cl bond length of 2.4526 (16) Å is slightly longer than those observed in the analogous complexes found in a search of the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002), [RuCl(TsDPEN)-

(η^6 -1,4-MeC₆H₄CHMe₂)] [2.435 (4) Å; CSD refcode TAX-FON10; Haack *et al.*, 1997] and [RuCl(TsDPEN)(η^6 -C₆H₅OCH₂CH₂OH)] [2.430 (4) Å; refcode OKAMIW; Soleimannejad *et al.*, 2003], but in agreement with that reported for [RuCl{(1*S*,2*S*)-*N*-(SO₂CF₃)NCH(C₆H₅)CH(C₆H₅)NH₂}(η^6 -C₆H₆)] [2.463 (3) Å; refcode ZALWIS; Hashiguchi *et al.*, 1995]. The η^6 -arene ring in (I) is planar [average r.m.s. deviation from the plane Δ = 0.014 (4) Å], as are the other three arene rings [Δ 0.006 (4) Å for the C9–C14 ring, 0.008 (3) Å for the C15–C20 ring and 0.008 (3) Å for the C23–C28 ring]. The distance of the Ru atom from the centre of the η^6 -arene ring is 1.670 Å, whereas the mean Ru–C distance is 2.194 (7) Å, similar to the other arene–ruthenium compounds noted above.

Ts = 4-CH₃-C₆H₄-SO₂-(i) RuCl₂/C₂H₅OH (351 K)(ii) H₂NCH(Ph)CH(Ph)NHTs/Et₃N/^{*i*}PrOH (353 K)

The –OCH₂CH₃ side chain is on the same side as the chloride ligand, rather than the tosyl group, to minimize unfavourable steric interactions. A similar orientation of the alkoxy side chain was reported for [RuCl(NH₂CH₂CH₂-NTs)(η^6 -C₆H₅OCH₂CH₂OH)] (Soleimannejad *et al.*, 2003), whereas in OKAMIW, the alkoxy side chain is directed away from the chloride ligand on the opposite site of the molecule. The Ru–N2 and Ru–N1 bond lengths are 2.134 (5) and 2.111 (5) Å, respectively, and both bond distances are comparable with those in TAFON10, OKAMIW, ZALWIS and [RuCl{C₅H₄N-2-C(Me)=N(CHMePh)}(η^6 -1,3,5-C₆H₃Me₃)]⁺ (Davies *et al.*, 1997).

The five-membered chelate ring of the (*R,R*)-TsDPEN ligand is highly skewed and has two diastereotopic N-bound H

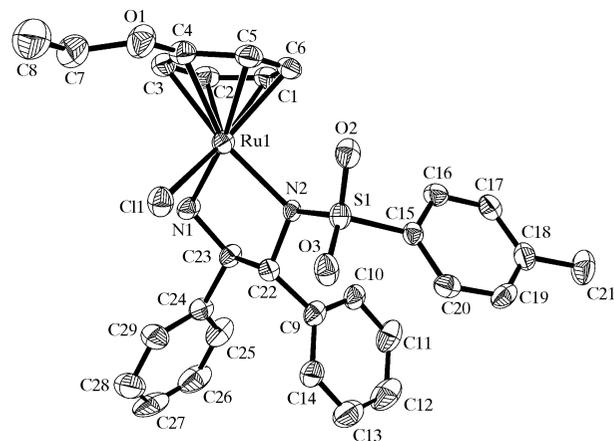


Figure 1

A view of the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and the methanol solvent molecule have been omitted for clarity.

atoms, labelled H1B and H1C. The H1B...Cl distance of 2.61 Å is much shorter than the sum of the van der Waals radii (2.95 Å; Bondi, 1964), suggesting the existence of a hydrogen-bond attraction. Similar hydrogen bonding has been proposed in related 'Noyori-type catalysts' (Haack *et al.*, 1997). Noyori has reported that complexes of this type eliminate HCl to form hydrogen-transfer catalysts of the type [Ru(η^6 -arene){TsN-CH(Ph)CH(Ph)NH}], and presumably such an interaction between Cl⁻ and NH facilitates this elimination.

One methanol solvent molecule per molecule of the complex is also present in the crystal lattice of (I). Hydrogen bonding between the methanol and the complex is responsible for the formation of a one-dimensional chain of molecules in the [100] direction. Evidence for these interactions can be seen in Table 2, with the last entries, though weak, included for completeness (the methanol O atom is O1S).

Experimental

The title compound was synthesized in 72% yield by the reaction of [RuCl₂(η^6 -C₆H₅OC₂H₅)₂] (Soleimannejad & White, 2005; 0.20 g, 0.34 mmol) and (*R,R*)-1,2-diphenyl-*N*-(*p*-toluenesulfonyl)ethylenediamine [(*R,R*)-TsDPEN]H; 0.25 g, 0.68 mmol] in the presence of triethylamine (0.20 ml, 1.36 mmol) in 2-propanol (7 ml) at 353 K for 1 h. The orange solution was concentrated to 2 ml and the resulting solid was filtered off, washed with water and dried under vacuum. Yellow crystals of (I) were grown from methanol. Analysis found: C 54.3, H 5.1, Cl 5.9, N 4.1, S 4.8%; C₂₉H₃₁ClN₂O₃RuS·MeOH requires: C 54.9, H 5.4, Cl 5.4, N 4.3, S 4.9%. MS, *m/z* (FAB⁺): 624 ([M⁺], 6%), 589 ([M⁺] - Cl, 100%).

Crystal data

[Ru(C ₂₁ H ₂₁ N ₂ O ₂ S)Cl(C ₈ H ₁₀ O)]·CH ₄ O	<i>D_x</i> = 1.462 Mg m ⁻³
<i>M_r</i> = 656.18	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁	Cell parameters from 3067 reflections
<i>a</i> = 7.8880 (15) Å	<i>θ</i> = 5.2–51.8°
<i>b</i> = 14.591 (3) Å	<i>μ</i> = 0.72 mm ⁻¹
<i>c</i> = 12.955 (2) Å	<i>T</i> = 150 (2) K
<i>β</i> = 91.799 (3)°	Block, yellow
<i>V</i> = 1490.3 (5) Å ³	0.21 × 0.08 × 0.08 mm
<i>Z</i> = 2	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	5928 independent reflections
<i>ω</i> scans	4729 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 1997)	<i>R_{int}</i> = 0.049
<i>T_{min}</i> = 0.863, <i>T_{max}</i> = 0.944	<i>θ_{max}</i> = 27.5°
9704 measured reflections	<i>h</i> = -10 → 10
	<i>k</i> = -18 → 14
	<i>l</i> = -16 → 14

Table 1

Selected interatomic distances (Å).

Ru1–N1	2.110 (4)	Ru1–C4	2.243 (5)
Ru1–N2	2.131 (3)	Ru1–Cl1	2.4532 (13)
Ru1–C2	2.162 (5)	S1–O2	1.433 (3)
Ru1–C6	2.172 (5)	S1–O3	1.446 (3)
Ru1–Cl1	2.179 (5)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1S–H1S...Cl1 ⁱ	0.84	2.32	3.146 (4)	168
N1–H1B...Cl1	0.92	2.61	2.971 (4)	104
N1–H1C...O1S	0.92	2.11	2.892 (6)	143
C2–H2A...O1S	1.00	2.46	3.252 (7)	136
C6–H6A...O2	1.00	2.38	2.916 (6)	112
C20–H20A...O3	0.95	2.47	2.859 (6)	105

Symmetry code: (i) $-x, y + \frac{1}{2}, -z + 1$.

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.083$	(Δ/σ) _{max} < 0.001
<i>S</i> = 0.96	$\Delta\rho_{max} = 1.14 \text{ e } \text{Å}^{-3}$
5928 reflections	$\Delta\rho_{min} = -0.32 \text{ e } \text{Å}^{-3}$
352 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	with 2454 Friedel pairs
	Flack parameter: -0.01 (3)

H atoms were positioned geometrically and refined using a riding model (including torsional freedom for methyl groups), with C–H distances in the range 0.95–0.98 Å and N–H distances of 0.92 Å, and with *U*_{iso}(H) = 1.2 (1.5 for methyl groups) times *U*_{eq} of the parent atom.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1080). Services for accessing these data are described at the back of the journal.

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