

$(\eta^6$ -Hexamethylbenzene)(mesidine)-
ditriflatoruthenium(II)

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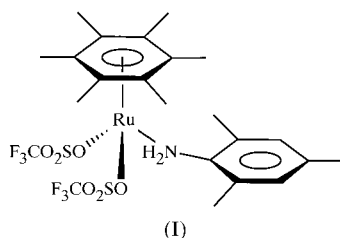
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The crystal structure of the title complex, (η^6 -hexamethylbenzene)bis(trifluoromethanesulfonato-*O*)(2,4,6-trimethylaniline-*N*)ruthenium(II), $[\text{Ru}(\text{CF}_3\text{O}_2\text{S})_2(\text{C}_{12}\text{H}_{18})(\text{C}_9\text{H}_{13}\text{N})]$, is described. The complex has the classic three-legged piano-stool structure with a planar arene 1.667 Å from the metal, two monodentate *O*-bound trifluoromethanesulfonate ligands [$\text{Ru}-\text{O}$ 2.169 (2) and 2.174 (2) Å] and one *N*-bound mesidine ligand [$\text{Ru}-\text{N}$ 2.198 (2) Å]. The $\text{Ru}-\text{N}$ distance is relatively long and the average $\text{Ru}-\text{O}$ distance is relatively short when compared with previously characterized Ru^{II} complexes.

Comment

Crystals of the title compound, (I), were obtained during an investigation of ruthenium–arene complexes as potential precursors to C–N bond-forming catalysts. The lability of the trifluoromethanesulfonate ligand has meant that complexes containing this moiety can be useful precursors to unsaturated species which can affect organic transformations.



Complex (I) was prepared by reaction of $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)]_2$ with an excess of silver trifluoromethanesulfonate in CH_2Cl_2 , followed by addition of a stoichiometric amount of mesidine (2,4,6-trimethylaniline). The Ru^{II} atom in this complex is best described as having an octahedral coordination environment (Fig. 1), with the arene occupying three coordination sites. Two further coordination sites are occupied by oxygen-bound trifluoromethanesulfonate ligands, with $\text{Ru}-\text{O}$ distances of 2.169 (2) and 2.174 (2) Å, while the sixth site is occupied by the *N*-bonded mesidine ligand, with an $\text{Ru}-\text{N}$ distance of 2.198 (2) Å. The rotational orientation of the arene is such that the tripodal ligands are staggered with respect to the arene C atoms, *i.e.*, when viewed along the arene

centroid–Ru bond axis, the ligands eclipse the arene C–C bonds rather than the C atoms.

The ring centroid of the arene is situated 1.667 Å from the Ru atom. While there are substantial differences in the C–C [1.417 (4)–1.443 (4) Å] and C–Ru [2.175 (2)–2.213 (2) Å] distances for the arene ring, there is no evidence of the alternating C–C bonds observed in some ruthenium–arene complexes (Begley *et al.*, 1991). The arene ring is essentially planar, with the mean deviation from the plane being 0.041 Å, in contrast with the bent arene observed in such complexes as $[\text{Ru}(\eta^6\text{-paracycme})\text{Cl}_2(\text{PMePh}_2)]$, (II) (Bennett *et al.*, 1972). This suggests that the *trans* influence of the *N*-donor ligand is smaller than that of the phosphine ligand, which is thought to induce the loss of planarity in (II).

Several complexes of Ru^{II} containing coordinated trifluoromethanesulfonate have previously been characterized crystallographically (Sutter *et al.*, 1996; Abbenhuis *et al.*, 1998; Fong *et al.*, 1998; Gemel *et al.*, 1997; Burns & Hubbard, 1994; Blosser *et al.*, 1992; Svetlanova-Larsen *et al.*, 1996; Kraakman *et al.*, 1992; de Klerk-Engels *et al.*, 1994; Mauthner *et al.*, 1997). The $\text{Ru}-\text{O}$ distances in these complexes range from 2.125 to 2.299 Å. The average $\text{Ru}-\text{O}$ distance of 2.172 Å found for (I) is at the lower end of this range, suggesting a relatively strong Ru –trifluoromethanesulfonate bond. This is consistent with the experimentally observed low lability of trifluoromethanesulfonate ligands. The metrical parameters of the trifluoromethanesulfonate ligand itself in (I) do not differ significantly from those observed for other complexes.

Many ruthenium–arene complexes containing aromatic amine donor ligands have been characterized crystallographically (Mitra *et al.*, 1997; Burrell & Steedman, 1997; Begley *et al.*, 1991; Manoli *et al.*, 1974). The $\text{Ru}-\text{N}$ distances in these complexes are in the range 2.135–2.213 Å. The $\text{Ru}-\text{N}$ distance for (I) is 2.198 (2) Å, which is at the higher end of this range. This could be a consequence of the relatively large steric bulk of the hexamethylbenzene and mesidine ligands. This is also reflected in the $\text{Ru}-\text{N}-\text{C}_{\text{arom}}$ angle observed for

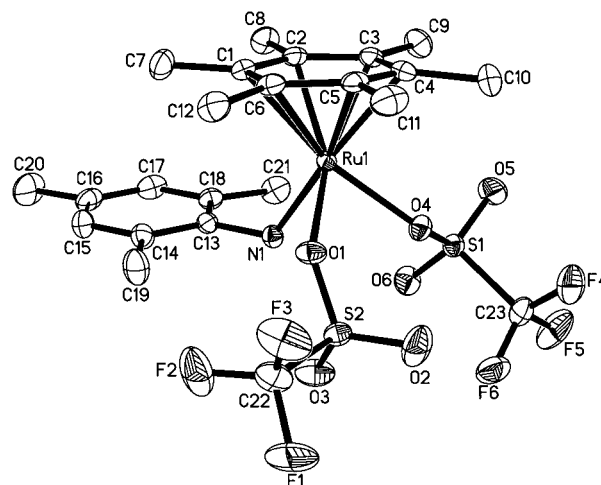


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

the amine ligand, which is greater in the case of (I) [124.9 (2)^o] than the range 117.4–121.5^o observed in previously reported complexes (Manoli *et al.*, 1974; Begley *et al.*, 1991; Burrell & Steedman, 1997). Tilting of the arene away from the Ru atom is consistent with the observation that the bulkier 2,6-diisopropylaniline could not be induced to form a complex analogous to (I).

Experimental

[RuCl₂(η⁶-C₆Me₆)₂] (Bennett *et al.*, 1982; 153 mg, 0.2365 mmol) and AgCF₃SO₄ (243 mg, 0.9642 mmol) were stirred under nitrogen in CH₂Cl₂ (5 ml) overnight. The resulting orange suspension was centrifuged to give a yellow solution and grey precipitate; the precipitate was presumably AgCl and excess AgCF₃SO₄. The yellow solution was carefully decanted and mesidine was added (300 μl, 3.44 mmol). After 5 min, the solution was reduced in volume under vacuum and layered carefully with Et₂O. After 2 h, a dark-yellow microcrystalline powder, (I), was collected by vacuum filtration (yield 261 mg, 82%). Crystallization from CH₂Cl₂/Et₂O by vapour diffusion gave single crystals suitable for X-ray crystallography. Spectroscopic analysis: ¹H NMR (CD₂Cl₂, 300 MHz, δ, p.p.m.): 7.03 (s, 2H, C₆H₂Me₃), 4.65 (br, s, 2H, NH₂), 2.39 [s, 6H, CH₃(mesidine)], 2.35 [s, 3H, CH₃(mesidine)], 1.96 [s, 18H, C₆, C₆(CH₃)₆]; ¹³C{¹H} NMR (CD₂Cl₂, 125.7 MHz, δ, p.p.m.): 136.14, 135.9, 130.44, 130.06 [4 s, C_{arom}(mesidine)], 90.41 (s, 6C, Ru–C), 20.85 [s, C, *para*-CH₃(mesidine)], 18.98 [s, 2C, *ortho*-CH₃(mesidine)], 15.83 [s, 6C, C₆(CH₃)₆].

Crystal data

[Ru(CF ₃ O ₃ S) ₂ (C ₁₂ H ₁₈)(C ₉ H ₁₃ N)]	<i>D</i> _x = 1.703 Mg m ⁻³
<i>M</i> _r = 696.68	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Cell parameters from 35 reflections
<i>a</i> = 13.9497 (13) Å	<i>θ</i> = 5.36–14.49 ^o
<i>b</i> = 14.7055 (15) Å	<i>μ</i> = 0.811 mm ⁻¹
<i>c</i> = 14.049 (2) Å	<i>T</i> = 163 K
<i>β</i> = 109.430 (8) ^o	Cuboid, red–orange
<i>V</i> = 2717.8 (6) Å ³	0.27 × 0.27 × 0.17 mm
<i>Z</i> = 4	

Data collection

Siemens <i>P</i> 4 diffractometer	<i>R</i> _{int} = 0.020
2θ/ω scans	<i>θ</i> _{max} = 27.5 ^o
Absorption correction: numerical (SHELXTL; Sheldrick, 1997)	<i>h</i> = 0 → 18
<i>T</i> _{min} = 0.811, <i>T</i> _{max} = 0.874	<i>k</i> = 0 → 19
6422 measured reflections	<i>l</i> = -18 → 17
6237 independent reflections	3 standard reflections every 97 reflections
5082 reflections with <i>I</i> > 2σ(<i>I</i>)	intensity decay: <1.0%

Table 1

Selected geometric parameters (Å, °).

*C*_g is the centroid of the C1–C6 benzene ring.

Ru1–O1	2.1692 (17)	S1–O4	1.4696 (18)
Ru1–O4	2.1739 (17)	S2–O1	1.4731 (18)
Ru1–N1	2.198 (2)	N1–C13	1.444 (3)
Ru1– <i>C</i> _g	1.667		
O1–Ru1–O4	81.68 (7)	O4–Ru1–N1	81.15 (7)
O1–Ru1–N1	83.41 (8)	C13–N1–Ru1	124.89 (16)

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 2.7894P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	(Δ/σ) _{max} = 0.011
<i>S</i> = 1.038	Δρ _{max} = 0.44 e Å ⁻³
6237 reflections	Δρ _{min} = -0.35 e Å ⁻³
477 parameters	Extinction correction: SHELXTL
All H-atom parameters refined	Extinction coefficient: 0.00175 (13)

The C–H and N–H bond-length ranges are 0.79 (4)–1.04 (4) and 0.84 (3)–0.94 (4) Å, respectively.

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: CARESS (Broach, 1978); program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; 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: DA1103). Services for accessing these data are described at the back of the journal.

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