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Molecular Structure of Pentahaptocyclopentadienebis(tetrahydrothiophene)triphenylphosphineruthenium(II) triflate

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Running Title: Molecular Structure of [CpRu(PPh₃)(tht)₂]Otf

The synthesis of [CpRu(PPh₃)(tht)₂]Otf (tht = tetrahydrothiophene; Otf = triflate), **I**, was previously reported by Nave and coworkers (Nave et al. 1999). Compound **I** is a useful starting material, because it reacts with excess thietane (thie) (Nave et al. 2001) or pentamethylene sulfide (pms) (Nave et al. 1999) to give the di-thie or di-pms complexes, respectively. Herein, we report on the molecular structure of **I**.

Single crystals of **I** were obtained by the slow diffusion of hexane into a CH₂Cl₂ solution of **I**. The crystallographic data are given in Table 1. A yellow crystal (0.10 x 0.14 x 0.28 mm) was mounted on a glass fiber with silicone rubber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo K α radiation. Cell constants were obtained from a least-squares refinement using the setting angles of 24 reflections in the range 17.0 < 2 θ < 22.0°. The intensities of three standard reflections measured after every 60 min. of X-ray exposure time showed a drift of 1.3 %. A total of 6171 reflections (5843 unique reflections, R_{int} = 0.02) were collected using the θ -2 θ scan technique to a maximum 2 θ value of 50°. The data were corrected for Lorentz and polarization effects and a psi-scans absorption correction was applied. Neutral atom scattering factors were taken from Cromer and Waber (1974). Anomalous dispersion effects were included in F_{calc}, the values of $\Delta f'$ and $\Delta f''$ were those of Cromer (Cromer 1974).

The structure was solved by direct methods and refined by full matrix least-squares. The final cycle of the full matrix least-squares refinement was based on 3154 observe reflections (I > 3.00 σ (I)) and 386 parameters and converged with R = 0.045, R_w = 0.060. The β -carbons on one of the tht ligands was disordered. These atoms (C29, C30) were refined isotropically with a 50% occupancy factor. The thermal ellipsoid of C28 suggests it may also be slightly disordered, but the disorder was not enough to

Table 1. Crystal, data collection and refinement parameters for [CpRu(PPh₃)(tht)₂]Otf.

Formula	RuS ₃ P F ₃ O ₃ C ₃₂ H ₃₆
Formula weight	753.85
Temperature (K)	293
Unit cell dimensions	
a (Å)	10.675(2)
b (Å)	11.089(2)
c (Å)	14.858(3)
α (°)	70.898(18)
β (°)	88.050(17)
γ (°)	88.869(17)
V (Å ³)	1660.9(6)
D _{calc} (g/cm ³)	1.51
Space group	triclinic P ₁ -
Z	2
F(000)	770.3
λ (Å)	0.7107
μ (mm ⁻¹)	0.74
2 θ range (°)	4 to 50
Absorption correction	analytical
Total reflections	6171
Unique reflections	5843
R for merge	0.020
Data for refinement	3154
Parameters	386
R(F), Rw(F)	0.045, 0.060
GOF	0.90
Largest diff. peak and hole	0.42(9), -0.42(9)

support splitting of that atom into two components. All hydrogen atoms were constrained to idealized positions (C-H = 0.95 Å, U = U_c + 0.01). Selected bond distances and angles are given in Table 2.

The structure of **I** is seen in Figure 1. The Ru atom is coordinated to a π -bound cyclopentadienyl ligand,

the phosphorus atom of the triphenylphosphine and two S-bound tht ligands. Selected bond distances and angles are given in Table 2.

Fig. 1. Ortep of **I** showing atom labeling scheme. Hydrogens have been omitted for clarity.

Table 2. Selected bond distances (Å) and angles (°) for **I**.

Ru-S1	2.370(2)	S1-Ru-S2	82.45(8)
Ru-S2	2.379(2)	S1-Ru-P	91.65(8)
Ru-P	2.318(2)	S2-Ru-P	91.30(7)
S1-C28	1.818(11)	Ru-S1-C28	114.0(4)
S1-C31	1.838(10)	Ru-S1-C31	110.8(3)
S2-C6	1.838(8)	C28-S1-C31	92.1(5)
S2-C9	1.834(9)	Ru-S2-C6	111.8(3)
C6-C7	1.509(13)	Ru-S2-C9	114.5(3)
C7-C8	1.504(14)	C6-S2-C9	93.7(4)
C8-C9	1.517(12)	S2-C6-C7	105.1(6)
C28-C291	1.39(3)	C6-C7-C8	106.7(7)
C28-C292	1.52(3)	C7-C8-C9	106.5(7)
C291-C301	1.41(3)	S2-C9-C8	105.6(6)
C292-C302	1.57(3)	S1-C28-C291	111.4(11)
C301-C31	1.59(3)	S1-C28-C292	105.3(11)
C302-C31	1.43(2)	C28-C291-C301	110.4(19)
		C28-C292-C302	107.5(16)
		C291-C301-C31	112.5(18)
		C292-C302-C31	101.4(15)
		S1-C31-C301	103.9(10)
		S1-C31-C302	108.2(9)

The Ru-S bond distances of 2.370(2) and 2.379(2) Å are slightly shorter than the Ru-S bond distance of 2.395(2) Å in the mono-tht complex [CpRu(PPh₃)₂(tht)]BF₄ (Jiang et al. 1996). The slighter shorter distances in **I** may be due to the loss of one of the bulky PPh₃ ligands upon coordination of the second tht. A significant decrease in the Ru-P distance is seen

in **I** as compared to the Ru-P distances in the mono-tht compound (2.318(2) Å compared to 2.366(2) and 2.367(2) Å).

Supplemental Materials

Supplemental materials (atomic coordinates, bond distances and angles) are available from the authors upon request.

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