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Synthesis and molecular structure of $[\text{CpRu}(\text{PPh}_3)(\text{pms})_2]\text{OTf} \cdot 3/4 \text{C}_2\text{H}_4\text{Cl}_2$

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The cyclooligomerization of thietane in the presence of metal carbonyl clusters to yield cyclothioethers has been demonstrated by Adams and coworkers (Adams and Falloon, 1995). The reaction of the cyclothioethers, 1,3-dithiane and 1,4-dithiane, on a single metal species was investigated by Sabo-Etienne, Chaudret, and coworkers, using the Cp^*Ru^+ moiety (Rondon, et al., 1994). In this paper, we report the synthesis and molecular structure of the $[\text{CpRu}(\text{PPh}_3)(\text{pms})_2]\text{OTf} \cdot 3/4 \text{C}_2\text{H}_4\text{Cl}_2$, continuing our studies of the coordination of sulfur donor ligands to $\text{CpRu}(\text{PPh}_3)_2^+$.

Syntheses were carried out under a dry nitrogen atmosphere using Schlenk techniques. All other reagents were used as purchased without further purification.

For the synthesis of $[\text{CpRu}(\text{PPh}_3)(\text{pms})_2]\text{OTf} \cdot 3/4 \text{C}_2\text{H}_4\text{Cl}_2$, I, a 0.0506 g (0.0744 mmol) sample of $(\text{CpRu}(\text{PPh}_3)(\text{tht})_2)\text{OTf}$ was dissolved in 3 mL of 1,2-dichloroethane. A large excess (1 mL) of pentamethylene sulfide was added and the solution stirred under nitrogen for 5 days. The mixture was evaporated under a stream of nitrogen and the solid, yellow residue was recrystallized from 1,2-dichloroethane. The product was washed with hexane and dried. Yield = 0.0364 g, 57.1%.

$[\text{CpRu}(\text{PPh}_3)(\text{tht})_2]\text{OTf}$ was prepared from $[\text{CpRu}(\text{PPh}_3)_2(\text{tht})]\text{OTf}$ (Jiang, et al., 1996) by dissolving approx. 1.0 g (1.1 mmol) of $[\text{CpRu}(\text{PPh}_3)_2(\text{tht})]\text{OTf}$ in 20 mL of tetrahydrothiophene, THT. The mixture was refluxed for 2.5 hr. Upon cooling, $[\text{CpRu}(\text{PPh}_3)(\text{tht})_2]\text{OTf}$ precipitated from solution. The yellow product was filtered, washed with 50:50 hexane: CH_2Cl_2 solution and dried. Yield = 0.5678 g, 46.1%.

The X-Ray structure analysis of $[\text{CpRu}(\text{PPh}_3)(\text{pms})_2]\text{OTf} \cdot 3/4 \text{C}_2\text{H}_4\text{Cl}_2$, I, is described below. A crystal of I (isolated from the reaction flask) was mounted in a glass capillary. The crystallographic data are given in Table 1. Data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer using $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) graphite-monochromated radiation. A total of 6884 unique reflections was collected using the e-2e scan technique to a maximum 2θ value of 50° . Absorption corrections were made using psi scans data from three reflections. The instrument factor p in the weighting expression $W^{-1} = [0^2(I) + pI^2] / 4F^2$ was 0.05.

The structure was solved by the Patterson method and refined by full matrix least-squares. All programs used for the solution and refinement were those of the NRC386 (PC version of NRCVAX) package (Gabe, et al., 1989). All non-H atoms were refined with anisotropic displacement parameters except the C atoms of the solvate molecule. H atoms were constrained to idealized positions ($\text{C-H} = 0.95 \text{ \AA}$) with isotropic thermal parameters U equal to 0.01 plus the U of the attached C atom. The solvate molecule was modeled at 0.75 occupancy. The maximum shift for the last cycle of full-matrix least-squares was 0.00 sigma.

Final atomic coordinates and equivalent thermal parameters for the non-hydrogen atoms are given in Table 2. Selected bond distances and angles are given in Table 3.

Dissolution of $\text{CpRu}(\text{PPh}_3)(\text{tht})_2^+$ in PMS/1,2-dichloroethane with stirring yields the compound $[\text{CpRu}(\text{PPh}_3)(\text{pms})_2]\text{OTf} \cdot 3/4 \text{C}_2\text{H}_4\text{Cl}_2$, I. The structure of I is seen in Fig. 1. The Ru-S distances of 2.363(2) and 2.362(2) Å in I are comparable to the Ru-S distances of 2.365(3) Å in $(\text{CpRu}(\text{PPh}_3)_2(\text{pms}))\text{OTf}$. These distances are slightly longer than the Ru-S distance of 2.3459(20) Å in the thietane complex, $(\text{CpRu}(\text{PPh}_3)_2(\text{SC}_3\text{H}_6))\text{S}_2\text{O}_3\text{CF}_3$ (Park et al., 1994). In the Os-octaethylporphyrin complexes,

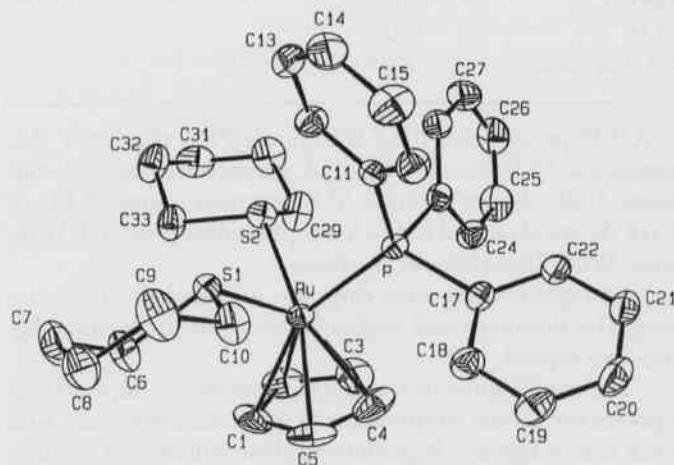


Fig. 1 ORTEP plot of the cation of I (30% probability ellipsoids) showing atom labeling scheme. Hydrogen atoms are omitted for clarity.

Table 1. Crystal and Refinement Data for [CpRu(PPh₃)₂](pms)₂]OTf·3/4 C₂H₄Cl₂.

formula	RuPS ₃ F ₃ O ₃ C _{35.5} H ₄₃ Cl _{1.5}
fw	856.12
size, mm	0.10, 0.22, 0.48
a, Å	11.033(4)
b, Å	11.4395(18)
c, Å	16.582(2)
α, deg	75.858(13)
β, deg	81.48(2)
γ, deg	75.960(18)
V, Å ³	1960.1(8)
2θ for cell	16-19
d _{calc} , gcm ⁻³	1.45
space group	P ₁ ⁻
Z	2
F000	877.7
abs coef, mm ⁻¹	0.73
2θ max, deg	50
h, k, l ranges	0, 13 -13, 13 -19, 19
std refl	-4, 0, -3 -3, 2, -2 -2, -3, 3
stds drift, %	1.1
absorp range	0.87 - 1.00
refl meas	7278
unique refls	6884
R for merge	0.022
I>3σ(I) data	3758
parameters	432
R(F ²)	0.052
Rw(F ²)	0.072
GOF	1.10
diff map, eÅ ⁻³	-0.36(107), 0.76(10)

Os(OEP)(pms)₂ and [Os(OEP)(pms)₂]PF₆, the Os-S distances are 2.352(2) and 2.382(2)Å, respectively (Scheidt and Nasri, 1995). Slightly longer M-S distances (range: 2.401 to 2.418 Å) are observed in the tris-μ-pms compound, Cl₃W (μ-pms)₃WCl₃ (Boorman et al., 1998).

As expected, the pms rings are in the chair configuration. The distances and angles (Table 3) in these sulfur ligands are typical.

The significance of complex I may prove important as a precursor for the preparation of other Ru complexes with weak donor ligands. If pentamethylene sulfide can displace tht from the CpRu(PPh₃)₂(tht)₂⁺ moiety, similar substitutions using (CpRu(PPh₃)₂(pms)₂]OTf should be possible.

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 Table 2. Atomic Parameters (x, y, z) and Beq for [CpRu(PPh₃)₂](pms)₂]OTf·3/4 C₂H₄Cl₂. E.S.D.'s refer to the last digit printed.

	x	y	z	Biso/Beq
Ru	0.05056 (6)	0.29895 (6)	0.22157 (4)	2.93 (3)
P	0.01141 (19)	0.18333 (17)	0.13496 (13)	2.85 (9)
S1	-0.02942 (19)	0.17440 (18)	0.34380 (13)	3.26 (9)
S2	0.24444 (19)	0.15705 (19)	0.24074 (14)	3.53 (10)
S3	0.5117 (3)	0.5185 (3)	0.2728 (2)	5.70 (15)
F1	0.5368 (11)	0.7403 (9)	0.2686 (7)	12.6 (7)
F2	0.3920 (11)	0.7360 (9)	0.2050 (7)	13.6 (7)
F3	0.3739 (12)	0.6966 (9)	0.3349 (7)	15.5 (8)
O1	0.4090 (10)	0.4698 (11)	0.2698 (8)	12.2 (8)
O2	0.5710 (11)	0.4738 (10)	0.3458 (7)	11.5 (7)
O3	0.5947 (12)	0.5257 (10)	0.2012 (8)	13.8 (8)
C1	0.0190 (13)	0.4714 (8)	0.2684 (7)	6.0 (6)
C2	0.1260 (10)	0.4639 (8)	0.2153 (9)	5.7 (6)
C3	0.0965 (14)	0.4651 (9)	0.1364 (8)	6.5 (7)
C4	-0.0262 (14)	0.4701 (9)	0.1395 (10)	6.7 (7)
C5	-0.0816 (10)	0.4753 (8)	0.2198 (10)	6.1 (7)
C6	-0.0488 (10)	0.2512 (10)	0.4297 (6)	5.5 (6)
C7	-0.1124 (12)	0.1815 (11)	0.5092 (6)	6.6 (7)
C8	-0.2446 (10)	0.1776 (10)	0.4962 (6)	5.8 (6)
C9	-0.2506 (11)	0.1140 (12)	0.4266 (7)	6.6 (7)
C10	-0.1948 (8)	0.1790 (9)	0.3432 (6)	4.7 (5)
C11	-0.0221 (7)	0.0289 (6)	0.1805 (5)	2.8 (3)
C12	0.0591 (8)	-0.0561 (8)	0.2346 (6)	4.0 (4)
C13	0.0330 (10)	-0.1719 (8)	0.2715 (6)	4.9 (5)
C14	-0.0729 (11)	-0.2011 (8)	0.2558 (7)	5.4 (6)
C15	-0.1525 (10)	-0.1181 (9)	0.2033 (7)	5.4 (5)
C16	-0.1276 (9)	-0.0053 (8)	0.1657 (6)	4.3 (4)
C17	-0.1179 (8)	0.2537 (7)	0.0682 (5)	3.3 (4)
C18	-0.2283 (8)	0.3209 (8)	0.1011 (6)	4.4 (4)
C19	-0.3311 (9)	0.3682 (9)	0.0540 (7)	5.2 (5)
C20	-0.3234 (10)	0.3473 (9)	-0.0249 (7)	5.0 (5)
C21	-0.2128 (9)	0.2820 (8)	-0.0584 (5)	4.1 (4)
C22	-0.1105 (8)	0.2346 (7)	-0.0118 (5)	3.7 (4)
C23	0.1442 (8)	0.1548 (7)	0.0577 (5)	3.3 (4)
C24	0.1787 (9)	0.2552 (8)	0.0017 (5)	4.4 (4)
C25	0.2883 (10)	0.2421 (10)	-0.0542 (6)	5.4 (5)
C26	0.3605 (9)	0.1267 (11)	-0.0553 (6)	5.5 (6)
C27	0.3269 (9)	0.0254 (9)	-0.0009 (7)	5.2 (5)
C28	0.2194 (8)	0.0396 (8)	0.0543 (5)	3.9 (4)
C29	0.3722 (9)	0.2100 (11)	0.1719 (6)	5.7 (6)
C30	0.4966 (9)	0.1212 (11)	0.1917 (7)	5.7 (6)
C31	0.5293 (9)	0.1135 (10)	0.2790 (8)	6.0 (6)
C32	0.4305 (9)	0.0713 (11)	0.3456 (6)	5.8 (6)
C33	0.3019 (8)	0.1565 (10)	0.3370 (6)	5.0 (5)
C34	0.4441 (14)	0.6778 (14)	0.2716 (8)	7.7 (8)
C11	0.1566 (4)	0.4619 (5)	0.4866 (4)	10.2 (3)
C12	0.3285 (6)	0.1894 (4)	0.5525 (3)	9.6 (3)
C35	0.3057 (17)	0.4317 (17)	0.5133 (11)	8.0 (4)
C36	0.3786 (20)	0.3174 (20)	0.5174 (13)	9.5 (5)

Beq is the Mean of the Principal Axes of the Thermal Ellipsoid

Table 3. Selected Bond Distances and Angles for [CpRu(PPh₃)₂](pms)₂OTf·3/4 C₂H₄Cl₂.

Distances (Å)		Angles (°)	
Ru-P	2.321 (2)	P-Ru-S1	93.27 (7)
Ru-S1	2.363 (2)	P-Ru-S2	87.47 (8)
Ru-S2	2.362 (2)	S1-Ru-S2	86.26 (8)
Ru-C1	2.224 (9)	Ru-S1-C6	109.1 (4)
Ru-C2	2.215 (9)	Ru-S1-C10	112.2 (3)
Ru-C3	2.193 (9)	C6-S1-C10	95.9 (5)
Ru-C4	2.154 (10)	Ru-S2-C29	112.5 (4)
Ru-C5	2.180 (9)	Ru-S2-C33	111.0 (3)
S1-C6	1.811 (9)	C29-S2-C33	96.7 (5)
S1-C10	1.813 (9)	S1-C6-C7	111.9 (7)
S2-C29	1.805 (10)	C6-C7-C8	110.9 (9)
S2-C33	1.802 (9)	C7-C8-C9	113.9 (8)
C6-C7	1.533 (15)	C8-C9-C10	111.2 (9)
C7-C8	1.517 (18)	S1-C10-C9	112.1 (7)
C8-C9	1.524 (16)	S2-C29-C30	110.6 (7)
C9-C10	1.521 (14)	C29-C30-C31	112.6 (9)
C29-C30	1.522 (15)	C30-C31-C32	112.0 (8)
C30-C31	1.519 (16)	C31-C32-C33	113.1 (9)
C31-C32	1.509 (15)	S2-C33-C32	110.3 (7)
C32-C33	1.518 (13)		

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Supplementary Material Available

Hydrogen atomic coordinates and isotropic thermal parameters (Table 4S), anisotropic displacement parameters (Table 5S), bond distances and angles (Table 6S), least-square planes (Table 7S), observed and calculated structure factors (Table 8S, 35 pages) are available from the authors upon request.

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