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# Synthesis and Molecular Structure of [CpRu(PPh$_3$)(pms)$_2$]OTf1.3/4 C$_{2>}$H$_4$C1$_2$

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# Synthesis and molecular structure of [CpRu($PPh_3$) $(pms)_2$]1OTf1• 3/4 $C_2H_4Cl_2$

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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 [CpRu ($PPh_3$) $(pms)_2$] OTf1• 3/4 $C_2H_4Cl_2$, continuing our studies of the coordination of sulfur donor ligands to $CpRu(PPh_3)_2^+$.

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 [CpRu($PPh_3$) $(pms)_2$]OTf1• 3/4 $C_2H_4Cl_2$, I, a 0.0506 g (0.0744 mmol) sample of (CpRu($PPh_3$) $(tht)_2$]OTfl 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%.

[CpRu($PPh_3$) $(tht)_2$]OTf1 was prepared from [CpRu($PPh_3)_2$(tht)] OTFl (Jiang, et al., 1996) by dissolving approx. 1.0 g (1.1 mmol) of [CpRu($PPh_3)_2$(tht)]OTfl in 20 mL of tetrahydrothiophene, THT. The mixture was refluxed for 2.5 hr. Upon cooling, [CpRu($PPh_3$)$(tht)_2$]OTfl 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 [CpRu($PPh_3$)$(pms)_2$]OTf1• 3/4 $C_2H_4Cl_2$, 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 MoKα (λ=0.71073 Å) graphite-monochromated radiation. A total of 6884 unique reflections was collected using the e-2e scan technique to a maximum 2e 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 (C-H = 0.95 Å) 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 $CpRu(PPh_3)(tht)_2^+$ in PMS/1,2-dichloroethane with stirring yields the compound [CpRu($PPh_3$) $(pms)_2$]OTf1• 3/4 $C_2H_4Cl_2$, 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 (CpRu($PPh_3)_2$(pms)]OTf1. These distances are slightly longer than the Ru-S distance of 2.3459(20)Å in the thietane complex, (CpRu($PPh_3)_2$ $(SC_3H_6)$]$S0_3CF_3$ (Park et al., 1994). In the Os-octaethylporphyrin complexes,

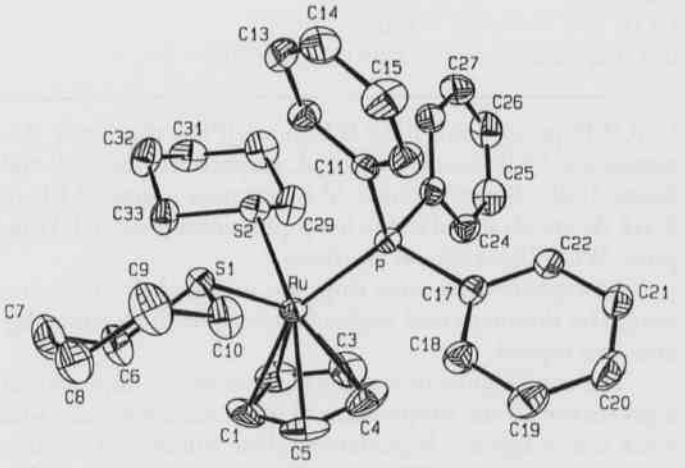


Fig. 1 ORTEP plot of the cation of I (30% probability ellipsoids) showing atom labeling scheme. Hydrogen atoms are omitted for clarity.

Table 1. Crystal and Refinement Data for [CpRu($PPh_3$) ($pms)_2$]OTf1•3/4 $C_2H_4Cl2$.

| | |
|---|---|
| formula | $RuPS_3F_3O_3C_{35.5}H_{43}Cl_{1.5}$ |
| 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 | 1960.1(8) |
| 2θ for cell | 16-19 |
| $d_{cal}$, $gcm^{-3}$ | 1.45 |
| space group | $P_1^-$ |
| Z | 2 |
| F000 | 877.7 |
| abs coef, $mm^{-1}$ | 0.73 |
| $^2\theta$ 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 $[Os(OEP)(pms)_2]PF_6$, 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, $Cl_3W$ (u-$pms)_3WCl_3$ (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($PPh_3$) $(tht)_2^+$ moiety, similar substitutions using (CpRu($PPh_3$) $(pms)_2$]OTf1 should be possible.

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Table 2. Atomic Parameters (x, y, z) and Beq for [CpRu($PPh_3$) $(pms)_2$]OTfl•3/4 $C_2H_4Cl_2$. 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($PPh_3$)($pms)_2$]OTF1• 3/4 $C_2H_4Cl_2$.

| 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.

### Literature Cited

**Adams, R. D.** and **S. B. Falloon.** 1995. The chemistry of thietane ligands in polynuclear metal carbonyl complexes. Chem. Rev. 95:2587-2598.

**Boorman, P. M., N. L. Langdon, V. J. Mozol, M. Parvez** and **G. P. A. Yap.** 1998. Syntheses, crystal structures, spectroscopic characterization, and electrochemical studies of the ditungsten(III) complexes $Cl_3W(\mu\text{-}L)_3WCl_3$ and $[Cl_3W(\mu\text{-}L)_2(\mu\text{-}Cl)WCl_3]^-$ (L=1,4-dithiane, 1,4-thioxane, pms = pentamethylene sulfide). C-S bond cleavage of the bridging thioether(s) in $Cl_3W(\mu\text{-}L)_3WCl_3$. Inorg. Chem. 37:6023-6029

**Gabe, E. J., Y. LePage, J. P. Charland, F. L. Lee,** and **P. S. White.** 1989. NRCVAX-an interactive program system for structure analysis. J. Appl. Cryst. 22:384-387.

**Jiang, Y., M. Draganjac,** and **A. W. Cordes.** 1996. Molecular structure of $[CpRu(PPh_3)_2(tht)]BF_4$, tht = tetrahydrothiophene. J. Cryst. Chem. 26:657-660.

**Park, H., M. Draganjac, S. R. Scott, A. W. Cordes,** and **G. Eggleton.** 1994. The reaction of $CpRu(PPh_3)_2^+$ with trimethylenesulfide. Synthesis and molecular and crystal structure of $[CpRu(PPh_3)_2(SC_3H_6)]CF_3SO_3$. Inorg. Chim. Acta 221:157-160.

**Rondon, D., J. Delbeau, X.-D. He, S. Sabo-Etienne,** and **B. Chaudret.** 1994. Activation of carbon-sulfur and carbonchlorine bonds by the electrophilic ruthenium fragment '$Ru(\eta\text{-}C_5Me_5)^+$'. J. Chem. Soc., Dalton Trans. 1895-1901.

**Scheidt, W. R.** and **H. Nasri.** 1995. Synthesis and molecular structures of the redox pair (octaethylporphinato) bis (pentamethylene sulfide) osmium(II) and (octaethylporphinato)bis(pentamethylene sulfide)osmium(III) hexafluorophosphate. Inorg. Chem. 34:2190-2193.