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L. A. Thornton  
Arkansas State University

Mark Draganjac  
Arkansas State University

Andres Meza  
University of Arkansas, Fayetteville

A. W. Cordes  
University of Arkansas, Fayetteville

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Synthesis of a Ruthenium-tetra(tht)dichloride Compound and the Molecular Structure of the Partially Oxidized Compound RuCl$_2$(tht)$_{2.2}$(tht-O)$_{1.8}$

L. A. Thornton, Jr., M. Draganjac,*, Andres Meza and A. W. Cordes

1Arkansas State University, Department of Chemistry and Physics, State University, AR 72467
2University of Arkansas, Department of Chemistry and Biochemistry, Fayetteville, AR 72701

*Corresponding Author

Attempts to prepare CpRu(thietane)$_3^+$ from CpRu(PPh$_3$)$_2^+$, in order to model potential ligand interactions in the metal carbonyl-catalyzed cyclooligomerization of thietane (Adams and Falloon, 1995), were unsuccessful. The di-thietane complex, [CpRu(PPh$_3$)(thietane)$_2$]OTf, can be prepared by direct ligand substitution from the di-tht complex, [CpRu(PPh$_3$)(tht)$_2$]OTf, tht = tetrahydrothiophene. The shortening of the Ru-P bond distance in the di-thietane complex as compared to the mono-thietane complex, [CpRu(PPh$_3$)$_2$(thietane)]OTf, may explain why a third thietane ligand can not be attached (Nave et al., 2001).

One method for the synthesis of tri- and tetra-thietane complexes may employ RuCl$_2$(dmso)$_4$ (Evans et al., 1973) as a starting material. Due to less ring strain, initial reactions were carried out with THT as a ligand. Herein, we report the synthesis of RuCl$_2$(tht)$_4$ and the crystal structure of the partially oxidized reaction product, RuCl$_2$(tht)$_{2.2}$(tht-O)$_{1.8}$.

Under N$_2$, 0.700 g (1.44 mmol) RuCl$_2$(dmso)$_4$ was dissolved in 5 mL THT. The reaction was refluxed overnight. Upon cooling, the precipitate was filtered, washed with acetone, and dried. Yield = 0.279 g, 36.8%. $^1$H NMR (δ, ppm, CDCl$_3$): 3.0, 2.1.

Fig. 1. Ortep (30% probabilities) of RuCl$_2$(tht)$_{2.2}$(tht-O)$_{1.8}$ showing S and O labeling scheme.
Synthesis of a Ruthenium-tetra(tht) Dichloride Compound and the Molecular Structure of the Partially Oxidized Compound RuCl₂(tht)₂₂(tht-O)₁₈

The NMR spectrum of RuCl₂(tht)₄ shows two peaks of equal intensity at positions different than the peaks observed for the RuCl₂(dmso)₄ protons (3.5, 2.8 ppm) [Evans et al., 1973]. Also, the IR spectrum of the RuCl₂(tht)₄ compound shows the disappearance of the S=O stretches (1055 cm⁻¹) seen in the RuCl₂(dmso)₄ compound. This evidence suggests the formulation of RuCl₂(tht)₄.

Attempts to obtain single crystals of RuCl₂(tht)₄ failed. However, single crystals were obtained from the filtrate upon evaporation in air. Crystal data are given in Table 1. Examination of the structure (Fig. 1) shows each of the tht ligands has been partially oxidized to the tht-oxide. The occupancy factors for the O atoms are 0.41, 0.65, 0.47, and 0.27 for O1-O4, respectively, giving an average of 0.45 for the oxidized tht ligands. At present, the source of the oxidation is not known. The IR data for the crystals isolated from the filtrate does show the expected S=O stretches (1064 cm⁻¹).

The Ru-S distances are 2.296(2), 2.286(2), 2.350(2), and 2.371(2) Å for S1-S4, respectively. The shorter Ru-S distances are cis to the Cl ligands. This effect is also observed in the two different crystallographic forms for cis-RuCl₂(tht-O)₄ [Yapp et al., 1990]. Selected bond distances and angles are given in Table 2 for RuCl₂(tht)₂₂(tht-O)₁₈.

Though RuCl₂(tht)₄ formed easily, it does not appear to be a good starting material for the synthesis of thietane complexes due to its ease of oxidation. RuCl₂(tht)₄ may allow for an improved synthesis of the RuCl₂(tht-O)₄ complex. Further studies on the ease of oxidation and crystallization of RuCl₂(tht)₄ are underway.

### Literature Cited


