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Synthesis and Characterization of a Ruthenium-Thioxane Complex

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Sabo-Etienne, Chaudret, and coworkers (see Rondon et al., 1994) have investigated the reaction of Cp^*Ru^+ with a variety of sulfur ligands. The addition of 1,4-dithiane at room temperature yields the chelated species, $[\text{Cp}^*\text{Ru}(1,4\text{-dithiane})\text{OTf}]$, whereas a similar reaction at 80°C yields the tris-1,4-dithiane complex. When 1,3-dithiane is reacted with Cp^*Ru^+ , carbon-sulfur bond cleavage is noted, and two different products are formed. Furthermore, Sabo-Etienne gave no explanation why carbon-sulfur bond cleavage occurs in the reaction with 1,3-dithiane whereas chelation occurs in the reaction with 1,4-dithiane. The reaction of pentamethylene sulfide (pms) was also mentioned, but the results were inconclusive (Rondon et al., 1994).

The reaction of pms with $\text{CpRu}(\text{PPh}_3)_2^+$ yields the sulfur-bound complex with the pms ligand in the chair configuration. The reaction of 1,4-dithiane with $\text{CpRu}(\text{PPh}_3)_2^+$ results in the loss of a triphenylphosphine and gives a chelated species similar to the 1,4-dithiane complexes seen by Sabo-Etienne (Rondon et al., 1994). The reaction of 1,3-dithiane with $\text{CpRu}(\text{PPh}_3)_2^+$ gives a single sulfur-bound ligand with two triphenylphosphines still attached to the ruthenium atom (Green et al., 2001). The purpose of the following experiment is to explore the coordination chemistry of the mixed heteroatom ring 1,4-thioxane with $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$, i.e., to determine whether the product coordinates the 1,4-thioxane ligand through the sulfur, the oxygen or if chelation occurs (analogous to the 1,4-dithiane complexes).

Reactions were carried out under a dry nitrogen atmosphere using Schlenk techniques. $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ was prepared as described in the literature (Bruce and Windsor, 1977). All other reagents were used as purchased without further purification. The ^1H NMR spectrum was obtained on a JEOL GSX 270 MHz NMR spectrometer. Powder patterns were obtained on a Rigaku D/MAX-B X-ray powder diffractometer. The visible spectrum was obtained on a HP8952A diode array spectrophotometer. Elemental analysis was performed at Galbraith Laboratories, Knoxville, TN, USA.

Synthesis of $[\text{CpRu}(\text{PPh}_3)_2(1,4\text{-thioxane})]\text{BF}_4$, 1. Under N_2 , 0.100 g (0.138 mmol) $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ was dissolved in 20 mL of CH_2Cl_2 , and 0.027 g (0.138 mmol) AgBF_4 was added to the stirring solution. The mixture was reacted for fifteen minutes, then filtered through celite into a flask that

contained 20 mL of CH_2Cl_2 and 0.1 mL (1.069 mmol) of 1,4-thioxane. The solution was concentrated to approximately 10 mL under a N_2 stream and then layered with hexanes. Yellow microcrystals were isolated by filtration and washed with hexanes. Yield = 0.068 g, 50.04%. Elemental analysis, calc. for $[\text{CpRu}(\text{PPh}_3)_2(\text{thioxane})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$: 56.45% C, 4.64% H, 3.28% S; found: 55.44% C, 5.24% H, 3.65% S. ^1H NMR (δ , ppm, in CDCl_3): 7.24 (m, 30H), 4.80 (s, 5H), 3.72 (s, 4H), 2.58 (s, 4H). Visible spectrum (nm, in CHCl_3): 360 ($\epsilon = 2384 \text{ M}^{-1}\text{cm}^{-1}$).

The elemental analysis of the yellow crystals supports single atom 1,4-thioxane coordination. Upon examination of the NMR spectrum (Fig. 1), the peaks between 6.96 and 7.37 ppm represent the hydrogens of the triphenylphosphine ligands. The peak at 4.80 ppm corresponds to the cyclopentadienyl hydrogens. The peaks at 3.72 and 2.58 ppm represent the hydrogens next to the oxygen and sulfur, respectively. As with previous sulfur-containing compounds of $\text{CpRu}(\text{PPh}_3)_2^+$, coordination does not cause a large shift in ligand protons (Park et al., 1994; Green et al., 2001). This lack of a large shift also indicates that no C-S bond cleavage has occurred as was reported for 1,3-dithiane. The NMR spectrum of the yellow crystals suggests 1,4-thioxane coordination, but single crystals are needed to determine the mode of coordination, using X-ray diffraction techniques.

Due to the inability to obtain single crystals of **1**, powder patterns of a series of triflate (CF_3SO_3^-) salts were undertaken. Powder patterns were taken on the following five compounds: $[\text{CpRu}(\text{PPh}_3)_2(1,3\text{-dithiane})]\text{CF}_3\text{SO}_3$, $[\text{CpRu}(\text{PPh}_3)(1,4\text{-dithiane})]\text{CF}_3\text{SO}_3$, $[\text{CpRu}(\text{PPh}_3)_2(1,3,5\text{-trithiane})]\text{CF}_3\text{SO}_3$, $[\text{CpRu}(\text{PPh}_3)_2(\text{pms})]\text{CF}_3\text{SO}_3$, and the triflate salt of $[\text{CpRu}(\text{PPh}_3)_2(\text{thioxane})]^+$, for comparison. The powder pattern for the yellow crystals is not x-ray isomorphous to those compounds previously characterized. The results are inconclusive at this point.

Problems in crystal growth may be due to the reaction of the dechlorinating agent (AgBF_4 or AgCF_3SO_3) and the 1,4-thioxane. Two polymeric forms have been isolated from the reaction of AgO_3SCF_3 with 1,4-thioxane (Buchholz et al., 1996). The polymers contain either terminal or bridging thioxane ligands. Multiple attempts to recrystallize $[\text{CpRu}(\text{PPh}_3)_2(\text{thioxane})]\text{BF}_4$ gave very thin plates. A marginal unit cell was obtained and the cell volume was consistent with the proposed formulation.

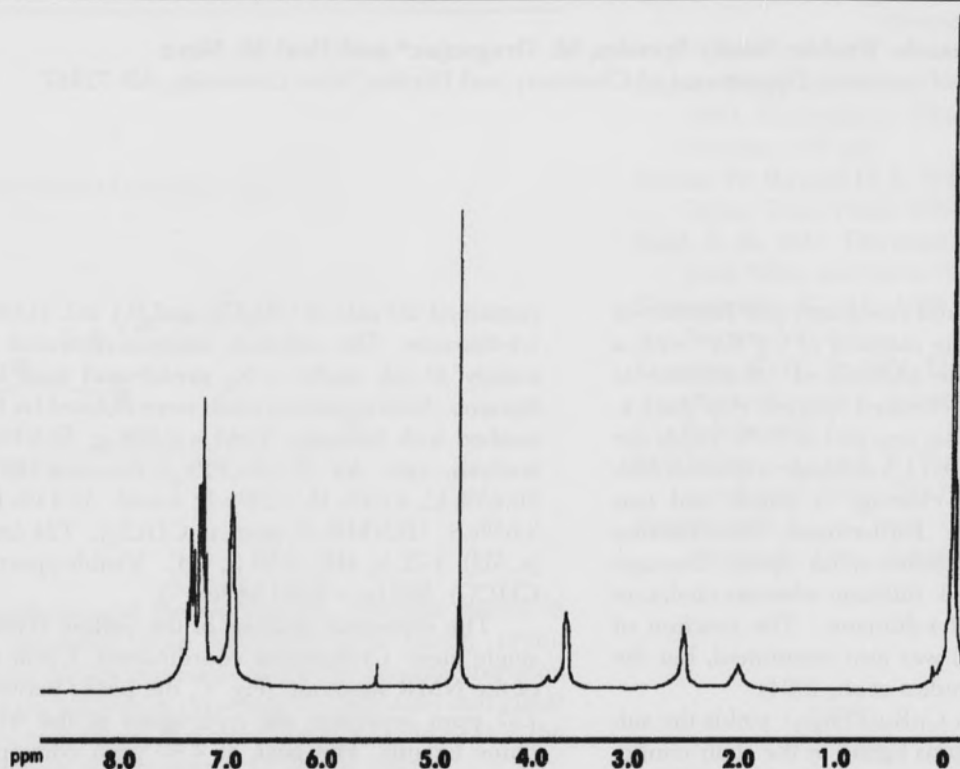


Fig. 1. NMR spectrum of $[\text{CpRu}(\text{PPh}_3)_2(\text{thioxane})]\text{BF}_4$.

Sulfur coordination of the 1,4-thioxane ligand to a metal center has been shown for platinum (Burgarcic, et al., 1993), palladium (Moulet et al., 1997), and tungsten (Boorman et al., 1998). Reaction of $\text{K}_2[\text{PtCl}_4]$ with 1,4-thioxane at room temperature yields the *cis*- $[\text{PtCl}_2(1,4\text{-thioxane})_2]$ complex, but reaction of PtCl_2 with 1,4-thioxane at 70°C gives the *trans*- $[\text{PtCl}_2(1,4\text{-thioxane})_2]$ complex (Burgarcic et al., 1993). The tetrakis(1,4-thioxane)palladium(II) complex has been synthesized by the reaction of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ with 1,4-thioxane at room temperature (Moulet et al., 1997).

The ditungsten(III) tris-bridged cyclic thioether complex with the formula $\text{Cl}_3\text{W}(\mu\text{-}1,4\text{-thioxane})_3\text{WCl}_3$ and $[\text{Cl}_3\text{W}(\mu\text{-}1,4\text{-thioxane})_2(\mu\text{-Cl})\text{WCl}_3]^-$ have been prepared. The coordination of thietane, pms, and 1,4-dithiane were also studied. Thietane and pms were investigated in an attempt to prepare a precursor which, when ring-opened, would create pendant arms of varying lengths. Attempts to see the effect of incorporation of a heteroatom into the thioether ring upon ring-opening were investigated by reaction of 1,4-thioxane and 1,4-dithiane (Boorman et al., 1998).

The reaction of 1,4-thioxane with $\text{CpRu}(\text{PPh}_3)_2^+$ precedes rapidly. The NMR spectrum confirms the product is $[\text{CpRu}(\text{PPh}_3)_2(1,4\text{-thioxane})\text{O}_3\text{SCF}_3]$. Sulfur coordination is suspected due to the affinity of Ru(II) for sulfur, and the fact

that in all of the previous examples of 1,4-thioxane coordination, only the sulfur-bound ligand is observed. Also, the charge transfer band at 360 nm is consistent with sulfur coordination of the thioxane ligand. Further studies will look at the potential line broadening of the NMR spectrum due to coupling to the $^{99}, ^{101}\text{Ru}$ ($I = 5/2$) nuclei and the synthesis of the 1,4-dioxane compound for comparison.

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