

Progress Report for
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**Studies of Carbon-Sulfur Bond Cleavage by Homogeneous
Transition Metal Complexes**

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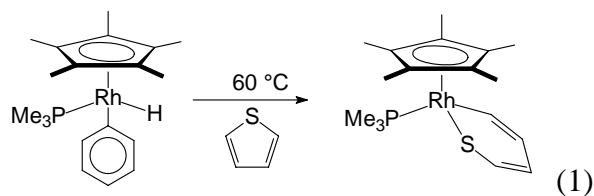
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Introduction

Cleavage of the C-S bond is thought to be an important step in the removal of sulfur from thiophene in the hydrodesulfurization (HDS) process.¹ Thiophene and its benzo derivatives represent abundant sulfur-containing impurities in coal and petroleum feedstocks, and are among the most difficult to desulfurize.^{2,3} Homogeneous transition metal complexes are ideal for probing the mechanism for this process by allowing analysis of specific steps in the proposed HDS cycle.^{4,5,6}

A. Structures of Parent Thiophene, Benzothiophene, and Dibenzothiophene Complexes

We have completed a series of X-ray structures of the parent C-S insertion complexes $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{C,S-thiophene})$, $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{C,S-benzothiophene})$, and $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{C,S-dibenzothiophene})$, and are writing a paper in collaboration with Prof. Suzanne Harris (U. Wyoming) (eq 1). Her graduate student, Michael Palmer, has performed a series molecular mechanics and extended Hückel calculations on these complexes. We have written up the structural portion of this paper, and Dr. Harris is now completing the write up of the theoretical study. The manuscript should be submitted by the end of 1996.



The dibenzothiophene complex shows a puckering of the 6-membered metallathiacycle of $\sim 35^\circ$ (see Figure 1), as seen in all 9 of the other structurally characterized complexes in which $[\text{Cp}^*\text{Rh}(\text{PMe}_3)]$ has inserted into a thiophene or dibenzothiophene C-S bond. The calculations suggest that the origin of the puckering is steric, not electronic, and furthermore predict that the structure of the parent thiophene complex the 6-membered ring should be planar. As shown in Figure 1, the structure of the thiophene complex indeed is planar as predicted! The benzothiophene complex crystallizes with two molecules in the asymmetric unit. In one, the 6-membered ring is planar, whereas in the other, the ring is bent at 44° !

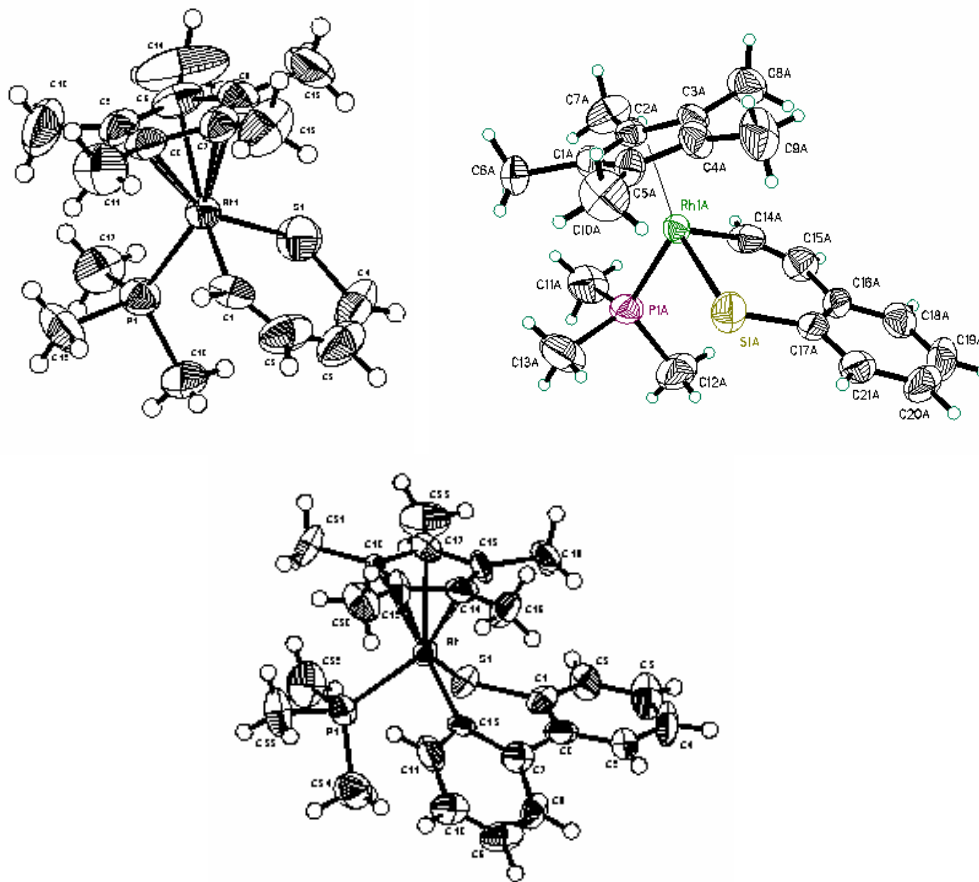


Figure 1. Structures of $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{C,S-thiophene})$, $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{C,S-benzothiophene})$, and $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{C,S-dibenzothiophene})$.

B. New Binuclear Complexes for C-S bond Cleavage

We have examined a number of new complexes for cleavage of C-S bonds. The goal has been to probe binuclear metal polyhydrides with the notion that the hydride ligands would already be present on the metal center to effect reduction of the thiophene. Furthermore, the presence of two adjacent metal centers will better serve to model a real Co/MoS_2 heterogeneous catalyst. The active centers in these systems are proposed to be small MoS_2 rafts with sulfur vacancies around the edge of the crystal (Figure 2).⁷ We have been investigating a di-iridium system that mimics these sites, with bridging hydrides, thiolates, and sulfides.

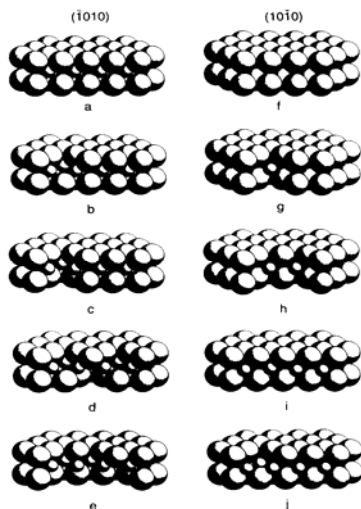
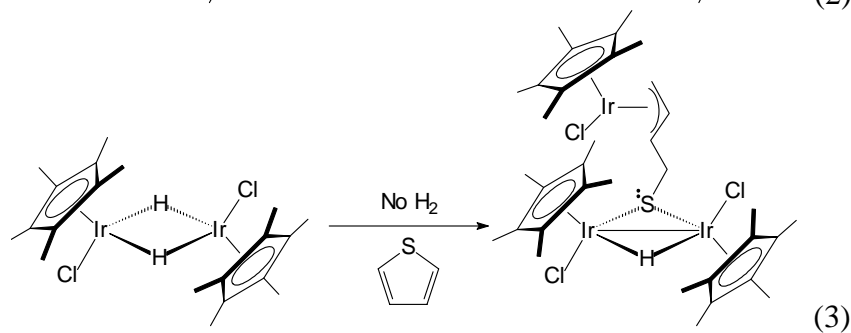
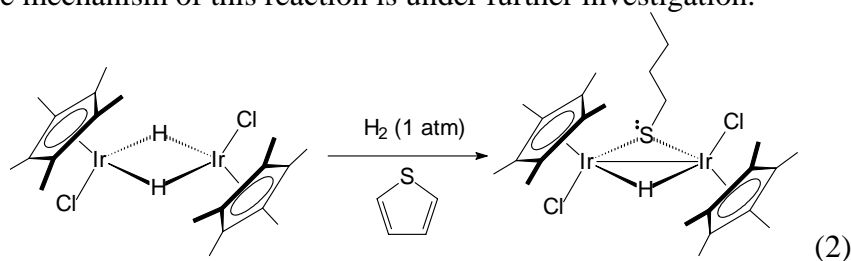


Figure 2. Illustration of some of the different types of coordinatively unsaturated sites which are possible at the $\bar{1}010$ (a-e) and $10\bar{1}0$ (f-j) edges of MoS_2 .

One of the iridium complexes we have been investigating is $[\text{Cp}^*\text{IrHCl}]_2$. This complex reacts with thiophene in the presence of hydrogen to give a ring-opened butanethiolate product as shown in eq 2. An X-ray structure shows the sulfur to be pyramidal, thereby rendering the adjacent methylene hydrogens inequivalent (Figure 3). No intermediates are seen in the reaction, although in the absence of added H_2 a different trinuclear product is isolated (eq 3) and characterized by X-ray diffraction (Figure 3). This species, however, is *not* an intermediate on the way to the butanethiolate complex, as it does not react with hydrogen under the reaction conditions. The mechanism of this reaction is under further investigation.



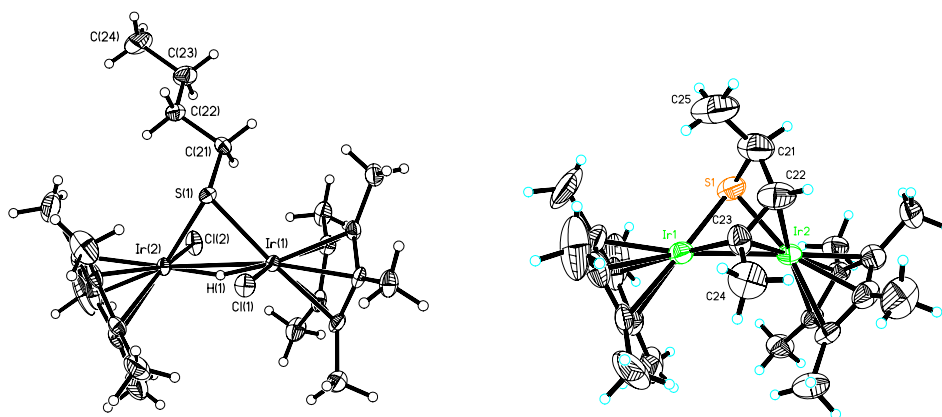
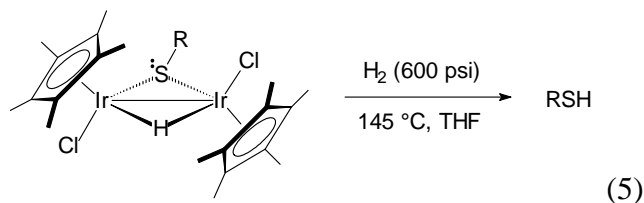
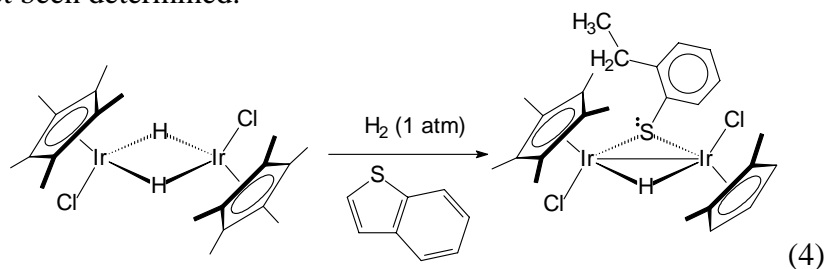


Figure 3. X-ray structures of $[\text{Cp}^*\text{Ir}]_2(\mu\text{-H})(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ and $[\text{Cp}^*\text{Ir}]_2(\mu\text{-H})[\mu\text{-}\eta^3\text{-SCH}_2\text{CHCHCH}_2(\text{Cp}^*\text{IrCl})]$.

Benzothiophene also reacts with the $[\text{Cp}^*\text{IrHCl}]_2$ dimer to give a C-S cleavage product. In the presence of hydrogen, the vinyl group is completely reduced to an ethyl group (eq 4, Figure 4). Again, an X-ray structure shows the lone pair on sulfur to be stereochemically active, and the methylene hydrogens on the ethyl group appear as an AB quartet of doublets.

Both the thiophene and the benzothiophene insertion complexes react with hydrogen under higher temperatures and pressures to generate the corresponding thiols (eq 5). The fate of the metal has not yet been determined.



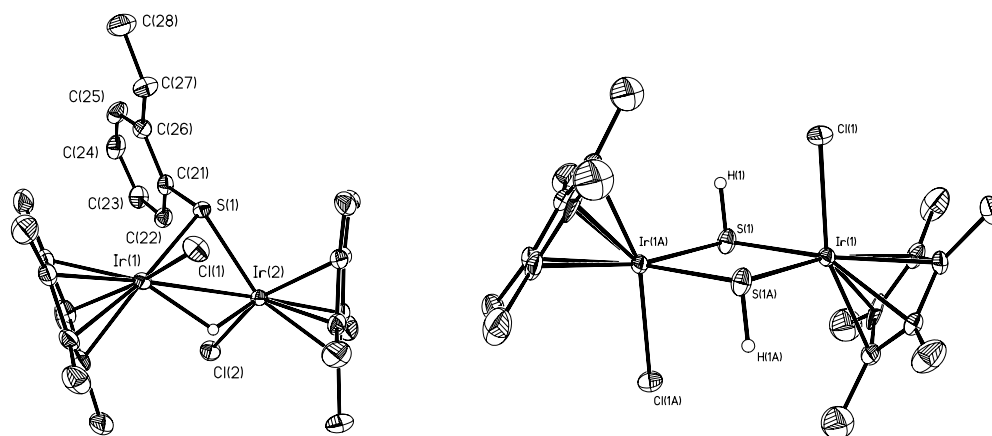
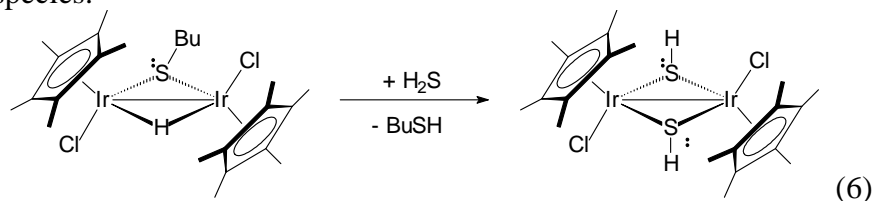


Figure 4. X-ray structure of $[\text{Cp}^*\text{Ir}]_2(\mu\text{-H})(\mu\text{-SC}_6\text{H}_3\text{CH}_2\text{CH}_3)$

More recently, we have investigated the reaction of the butanethiolate complex with H_2S . This compound reacts to give free butanethiol along with a new organometallic complex (eq 6). The complex was characterized by X-ray diffraction (Figure 4) and NMR spectroscopy. Curiously, two isomers are seen by ^1H NMR spectroscopy at low temperature. These correspond to the cis and trans isomers with respect to the S-H groups. Inversion at sulfur is slow on the NMR time scale, giving rise to the observation of two types of Cp^* ring in the cis isomer and one type of Cp^* ring in the trans isomer. Upon warming, inversion at sulfur interconverts the four possible species.



References and Notes

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Statement of Funds Estimated to be Unobligated.

We anticipate that none of the funds allocated for the current project year will remain unobligated at the end of the current year.