

Progress Report for  
NSF Grant CHE-9421727

for the period  
January 15, 1995-January 14, 1996

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

William D. Jones, P.I.

Department of Chemistry  
University of Rochester  
Rochester, NY 14627  
716-275-5493

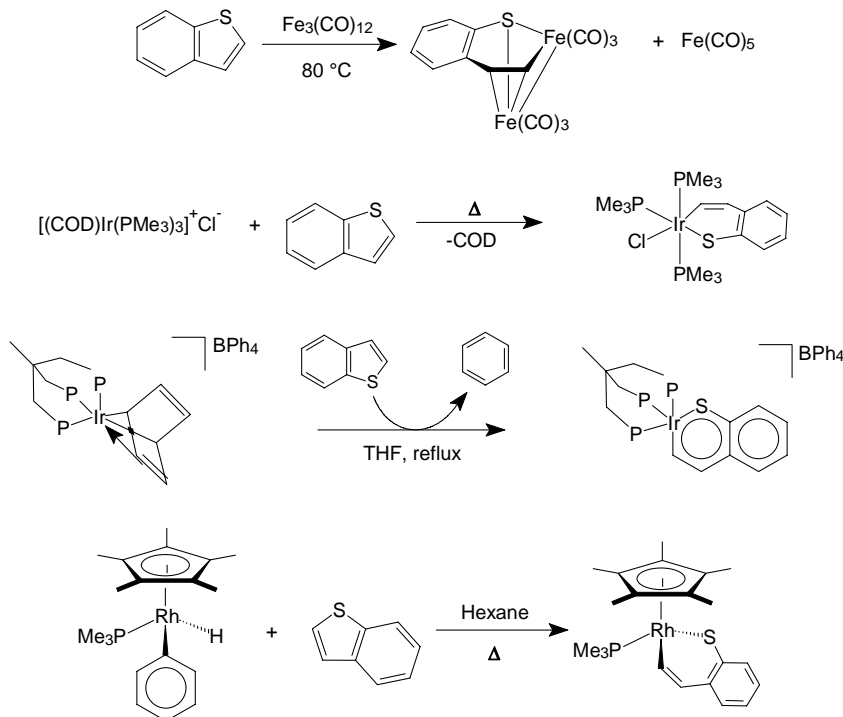
## Introduction

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.<sup>1</sup> Thiophene and its benzo derivatives represent abundant sulfur-containing impurities in coal and petroleum feedstocks, and are among the most difficult to desulfurize.<sup>2,3</sup> Homogeneous transition metal complexes are ideal for probing the mechanism for this process by allowing analysis of specific steps in the proposed HDS cycle.<sup>4,5,6</sup>

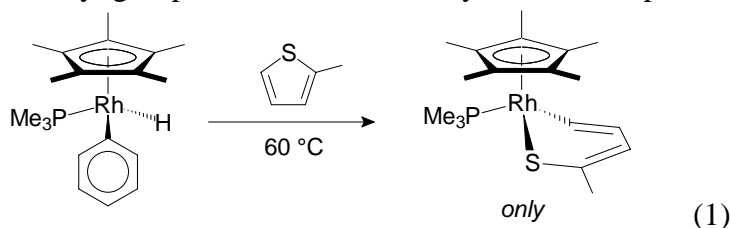
## B. Selectivity in Benzothiophene Insertion Reactions

Earlier studies of low oxidation state metal complexes that are capable of insertion into the C-S bonds of benzothiophene have all demonstrated that insertion occurs into the C-S bond away from the bulky aromatic ring. These examples include not only our work with  $[\text{Cp}^*\text{Rh}(\text{PMe}_3)]$ , but also examples by King with  $[\text{Fe}(\text{CO})_3]$ ,<sup>7</sup> Merola with  $[\text{Ir}(\text{PMe}_3)_3]^+$ ,<sup>8</sup> and Bianchini with  $[(\text{triphos})\text{Ir}]^+$ <sup>9</sup> (Scheme I). Maitlis has also observed the reversible insertion of an electron rich  $\text{Pt}^0$  fragment into the vinyl-S bond in benzothiophene.<sup>10</sup>

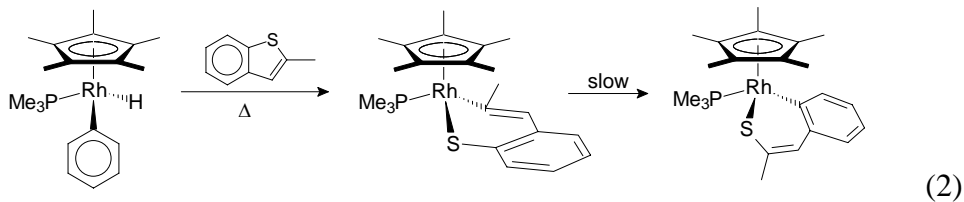
### Scheme I.



Based upon earlier work in C-H activation in our laboratory, we anticipated that insertion into the aryl-S bond should be thermodynamically preferred over insertion into the vinyl-S bond, since a stronger metal-carbon bond would be formed in the former case. A similar line of reasoning explains why benzene C-H bond activation is preferred over ethylene C-H bond activation.<sup>11</sup> We had also observed in earlier studies that C-S bond cleavage in 2-methylthiophene by [Cp\*Rh(PMe<sub>3</sub>)] occurs exclusively away from the methyl group (eq 1). Consequently, we examined the reactivity of 2-methylbenzothiophene with the same rhodium fragment, expecting the methyl group to destabilize the vinyl-S insertion product.



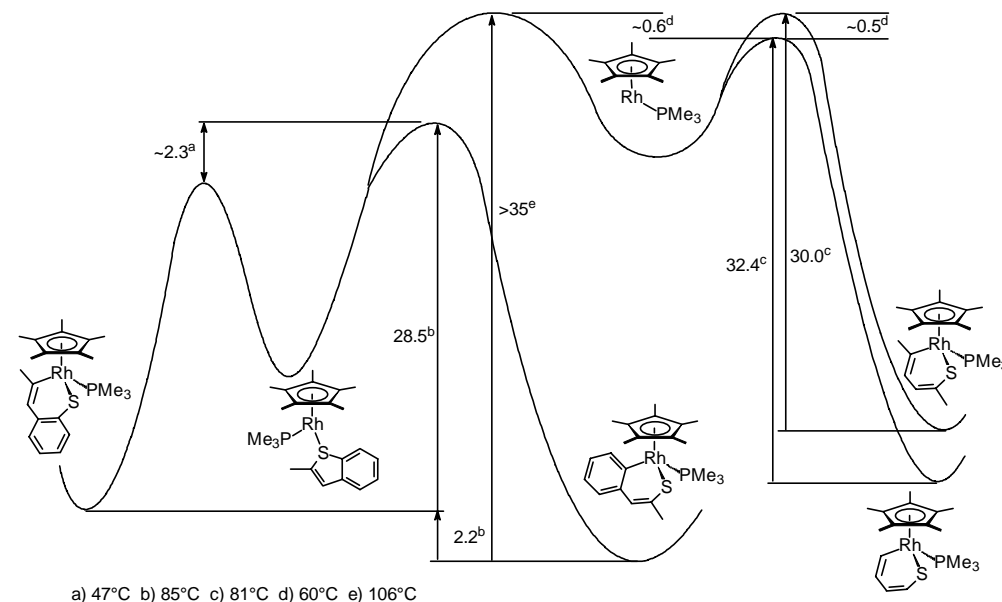
The results of the study are summarized in equation 2.<sup>12</sup> Reaction of Cp\*Rh(PMe<sub>3</sub>)PhH with 2-methylbenzothiophene at 60 °C results in the initial formation of the ‘usual’ C-S insertion product resulting from vinyl-S bond cleavage. Upon further heating, however, this product is observed to be converted into the product in which the metal has inserted into the aryl-S C-S bond. This rearrangement can be conducted in the presence of 30 equiv of thiophene and no formation of the thiophene C-S insertion product is formed, demonstrating that the conversion of the kinetic product to the thermodynamic product occurs without dissociation of the 2-methylbenzothiophene from the metal center.



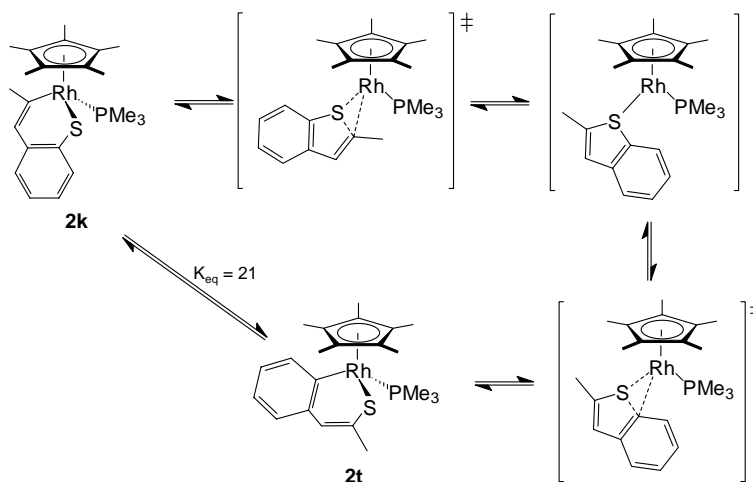
Scheme II shows a free energy profile for formation of the kinetic and thermodynamic products as well as relative values for thiophene and 2,5-dimethylthiophene activation at ~ 80 °C. The kinetic selectivity for formation of the kinetic product over the thermodynamic product is estimated at ~2.3 kcal/mol, based upon the nearly exclusive formation of the former at early

reaction times. The structures involved in the interconversion are viewed in terms of the intermediates and transition states shown in Scheme III. The final equilibrium concentrations of 21:1 for thermodynamic:kinetic product were measured near the limit of sensitivity of NMR and thus give only an approximate  $\Delta G^\circ$  value of 2.2 kcal/mol.

### Scheme II



### Scheme III.



Attempts to measure the activation barrier for loss of 2-methylbenzothiophene from the thermodynamic isomer were unsuccessful, but the conditions under which no reaction was

observed (106 °C, 66 h) allow calculation of a minimum activation barrier, had thiophene loss only just begun. The minimum barrier of 35 kcal/mol reflects the increased strength of the Rh-aryl bond as compared with the Rh-C (vinyl) bonds in  $(C_5Me_5)Rh(PMe_3)(S-CH=CH-CH=CH)$  ( $\Delta G^\ddagger = 32.4$  kcal/mol) and  $(C_5Me_5)Rh(PMe_3)(S-CMe=CH-CH=CMe)$  ( $\Delta G^\ddagger = 30.0$  kcal/mol).

## B. Structures of Parent Thiophene, Benzothiophene, and Dibenzothiophene Complexes

We have just completed a series of X-ray structures of the parent C-S insertion complexes  $Cp^*Rh(PMe_3)(C,S\text{-thiophene})$ ,  $Cp^*Rh(PMe_3)(C,S\text{-benzothiophene})$ , and  $Cp^*Rh(PMe_3)(C,S\text{-dibenzothiophene})$ . 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  $[Cp^*Rh(PMe_3)]$  has inserted into a thiophene or dibenzothiophene C-S bond. Suzanne Harris (U. Wyoming) has been doing theoretical studies on these molecules, and suggested that the origin of the puckering is steric, not electronic, and that if we could obtain a 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  $44^\circ$ !

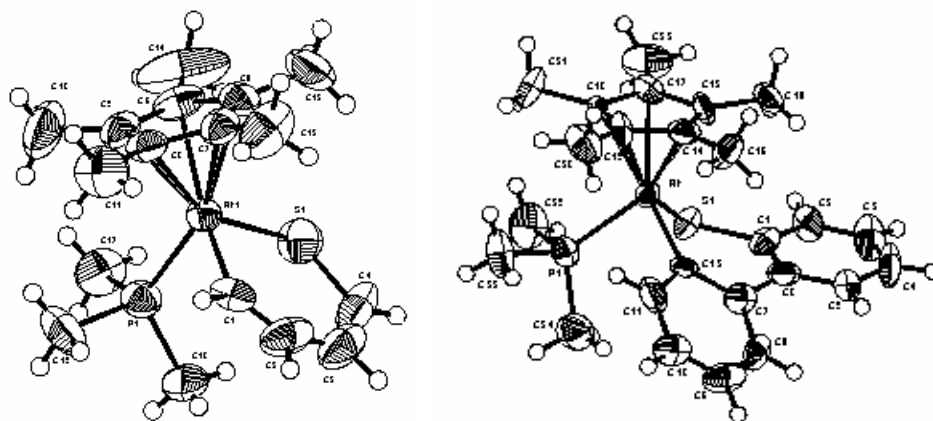
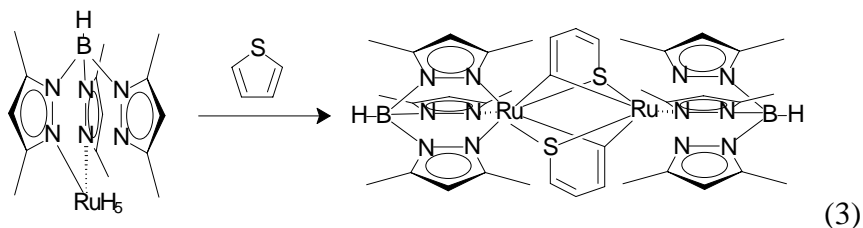


Figure 1. Structures of  $Cp^*Rh(PMe_3)(C,S\text{-thiophene})$  and  $Cp^*Rh(PMe_3)(C,S\text{-dibenzothiophene})$ .

### C. New 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 metal polyhydrides with the notion that the hydride ligands would already be present on the metal center to effect reduction of the thiophene. Complexes that have been examined to date include *fac* and *mer*-Ir(PPh<sub>3</sub>)<sub>3</sub>H<sub>3</sub>, MoH<sub>4</sub>(PMe<sub>3</sub>)<sub>4</sub>, MoH<sub>4</sub>(dppe)<sub>2</sub>, and [HB(Me<sub>2</sub>Pyr)<sub>3</sub>]RuH<sub>5</sub>. Of these complexes, the trispyrazolylborate complex has been found to undergo a clean reaction with thiophene, giving a new product that has not been fully characterized. Equation 3 shows our tentative assignment for the product.



### 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.