

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

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Part II - Summary of Completed Project

This project used homogenous organometallic complexes to explore the mechanistic pathways for the hydrodesulfurization of thiophene and related sulfur containing derivatives. The studies involved physical organometallic experiments designed to probe the nature of the carbon-sulfur bond breaking step. The structures of the intermediates involved were elucidated and the kinetic and thermodynamic parameters that control the reactivity and selectivity were determined. New complexes were found that not only break C-S bonds, but also do further chemistry resulting in the total elimination of sulfur from the organic portion of the molecule. Substituted dibenzothiophenes were examined in some detail, as these compounds prove the most difficult to desulfurize with commercial HDS catalysts. Several binuclear metal systems were examined for HDS activity. These studies have an impact on problems ranging from air pollution (acid rain) due to oil combustion to catalyst poisoning in industrial processes and in catalytic converters.

Part III - Technical Information

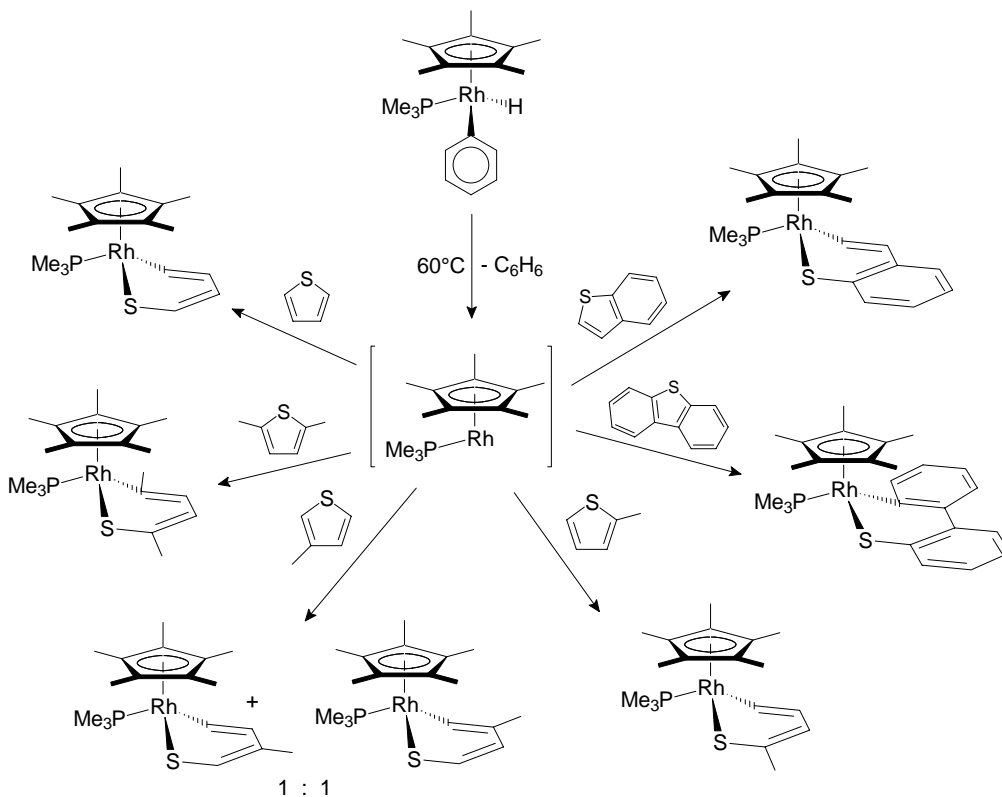
A. Publications resulting from this award:

1. "Bond Cleavage Reactions in Heterocycles by a Rhodium Complex," William D. Jones, Lingzhen Dong, Andrew W. Myers, *Organometallics* **1995**, *14*, 855-861.
2. "Regiochemical Selectivity in the Carbon-Sulfur Bond Cleavage of 2-Methylbenzothiophene: Synthesis, Characterization and Mechanistic Study of Reversible Insertion into a C-S Bond," Andrew W. Myers, William D. Jones, and Shawn M. McClements, *J. Am. Chem. Soc.* **1995** *117*, 11704-11709.
3. "Steric and Electronic Effects of the Insertion into the C-S Bond of Substituted Dibenzothiophenes by a Rhodium Phosphine Complex: A Homogeneous Model for the Hydrodesulfurization Process," Andrew W. Myers and William D. Jones, *Organometallics* **1996**, *15*, 2905-2917.
4. "Hydrodesulfurization of Thiophene and Benzothiophene to Butane and Ethyl Benzene by a Homogeneous Iridium Complex," David A. Vivic and William D. Jones, *Organometallics* **1997**, *16*, 1912-1917.
5. "Carbon-Selenium bond Cleavage by a Rhodium Complex, David A. Vivic, Andrew W. Myers, and William D. Jones," *Organometallics* **1997**, *16*, 2751-2753.
6. "Homogeneous Models of Thiophene HDS Reactions. Selectivity in Thiophene C-S Cleavage and Thiophene Reactions with Dinuclear Metal Complexes," William D. Jones, David A. Vivic, R. Martin Chin, James H. Roache, and Andy W. Myers, *Polyhedron*, **1997**, *16*, 3115-3128.
7. "The Structure of Metallathiabenzenes: Planar vs. Nonplanar Geometries. An Experimental and Theoretical Investigation," Christine Blonski, Andrew W. Myers, Michael Palmer, Suzanne Harris, and William D. Jones, *Organometallics* **1997**, *16*, 3819-3827.
8. "Room Temperature Desulfurization of Dibenzothiophene Mediated by $[(i\text{-Pr}_2\text{PCH}_2)_2\text{NiH}]_2$," David A. Vivic and William D. Jones, *J. Am. Chem. Soc.* **1997**, *119*, 10855-10856.

B. Technical Report.

The reactive fragment $[(C_5Me_5)Rh(PMe_3)]$ produced by heating solutions of $(C_5Me_5)Rh(PMe_3)(Ph)H$ has been found to insert into a wide variety of thiophene C-S bonds (Scheme I).¹ One of the first products to be structurally characterized was the adduct formed with 2,5-dimethylthiophene. This C-S insertion product shows a bent 6-membered ring in which the sulfur and butadiene portion of the ring form a plane that is oriented at an angle of 26° to the rhodium-sulfur- C_α plane. The distances around the ring are consistent with a localized bonding structure. At least a dozen other thiophene/benzothiophene/dibenzo-thiophene derivatives have been structurally characterized and all show a similar puckering of the metallathiacycle ring. In contrast, the structure of the parent thiophene insertion product displays a planar metallathiabenzene ring (Figure 1), although once again bond length alternation is seen in the diene portion of the ring. The parent benzothiophene also shows a nearly planar metallathiabenzene structure. A collaborative study in conjunction with Prof. Suzanne Harris at the University of Wyoming revealed that the origin of the puckering in these systems is not due to electronic effects, but rather to simple steric interactions of the group on the α -carbon of the metallacycle with the pentamethylcyclopentadienyl ring.²

Scheme I:



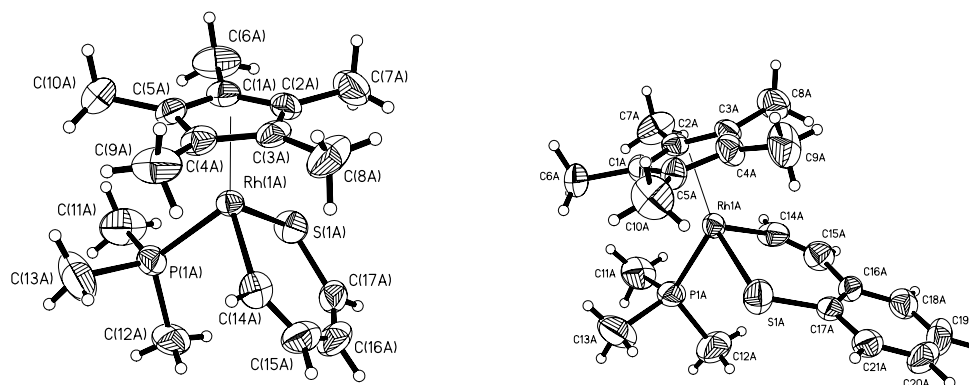


Figure 1. X-ray structures of the parent complexes $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S\text{-thiophene})$ and $(C_5Me_5)Rh(PMe_3)(\eta^2-C,S\text{-benzothiophene})$.

The mechanism of insertion of $[(C_5Me_5)Rh(PMe_3)]$ into the C-S bond of thiophene has been investigated using a variety of labeling techniques. While attempts to directly observe an intermediate in the reaction at low temperature failed, use of deuterium labels provided evidence for the intermediacy of an S-bound intermediate as the immediate precursor to carbon-sulfur bond cleavage in thiophene.¹ Evidence was also provided for η^2 -thiophene complexes, but only as fleeting intermediates in C-H activation reactions at the α and β positions of the thiophene rings. Our conclusions are summarized in the free energy diagram shown in Figure 2. Note that the figure shows the preferred kinetic selectivity for C-S bond cleavage over C-H bond activation, and that the C-S insertion product is more stable than the C-H insertion product. Support for this reaction sequence comes from *ab initio* calculations done by Sargent, which indicate the presence of a low energy pathway from the S-thiophene complex to the C-S insertion complex.³

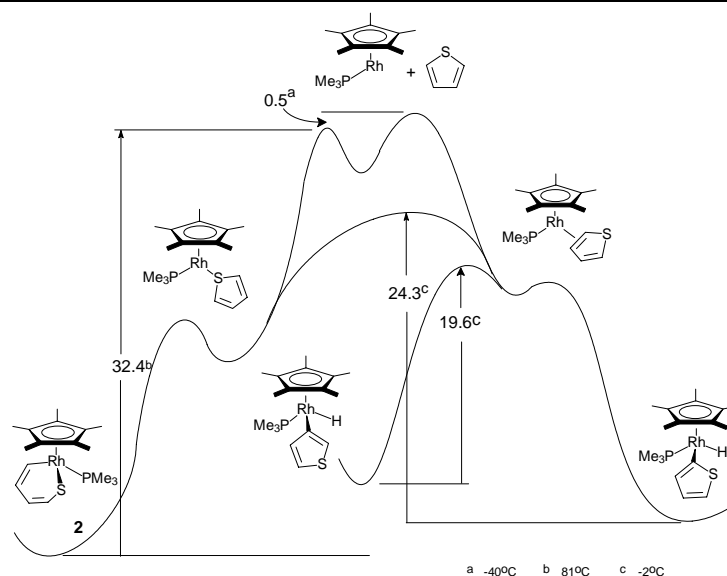
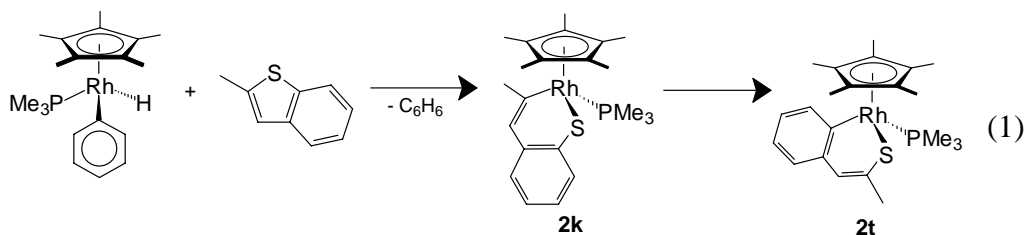


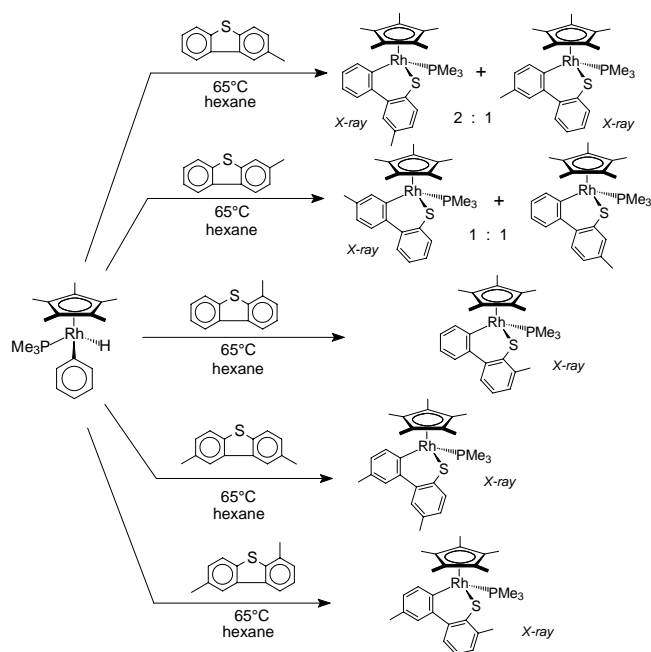
Figure 2. Free energy diagram for the interaction of $(C_5Me_5)Rh(PMe_3)$ with thiophene.

As mentioned above, benzothiophene was also found to undergo cleavage upon reaction with $(C_5Me_5)Rh(PMe_3)PhH$ to give a planar metallacycle product. Reaction of $(C_5Me_5)Rh(PMe_3)PhH$ with 2-methylbenzothiophene results in a similar product with cleavage of the sulfur-vinyl bond. In this case, however, continued heating of the sample leads to the rearrangement to a more stable product in which the metal has inserted into the sulfur-aryl bond (Eq 1). Apparently, the methyl group destabilizes the kinetic product sufficiently to allow it to rearrange to the thermodynamically preferred product. The origin of this preference can be attributed to the greater bond strength of a rhodium-aryl bond compared to a rhodium-vinyl bond. X-ray examination of both of these adducts show puckered, localized bonding structures. The rearrangement of the kinetic product to the thermodynamic product is intramolecular, as addition of 10 equivalents of thiophene during the rearrangement does not result in the formation of any of the thiophene C-S insertion product. The selectivities and interconversion can be accounted for in terms of the choices available to the S-bound complex, that is formed reversibly. At equilibrium, there is a 21:1 ratio of thermodynamic to kinetic product.⁴



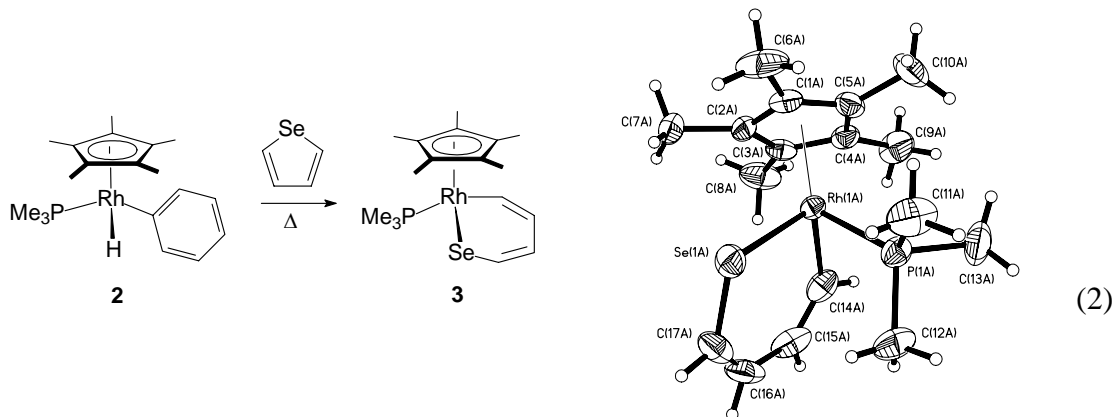
We have also examined the reaction of $(C_5Me_5)Rh(PMe_3)PhH$ with a wide variety of substituted dibenzothiophenes. In an effort to determine the effects of methyl substitution, reactions of 2-methyldibenzothiophene, 3-methyldibenzothiophene, and 4-methyldibenzothiophene with $(C_5Me_5)Rh(PMe_3)PhH$ were examined. While the former two substrates showed little preference for cleavage of one C-S bond vs the other, the latter substrate showed exclusive cleavage of the C-S bond away from the adjacent methyl substituent. A similar observation was made with disubstituted 2,6-dimethyldibenzothiophene (Scheme II). Heteroatom substituents on dibenzothiophene were found to have only modest effects on the insertion selectivity. Benzonaphthothiophenes were also found to undergo cleavage, with steric effects determining the direction of insertion. Most of the above dibenzothiophene products were characterized by X-ray crystallography, since this proved to be the only reliable method for determining the direction of insertion. In all cases except thiophene and benzothiophene, significant puckering of the 6-membered ring was observed. For the dibenzothiophenes, a twisting along the biphenyl linkage was also seen. This major study appeared recently in a full paper, the only one to treat substituent effects on dibenzothiophene activation and demonstrate the importance of steric effects on C-S bond cleavage.⁵

Scheme II.



Only one dibenzothiophene complex did not undergo C-S cleavage upon reaction with $(C_5Me_5)Rh(PMe_3)PhH$. 4,6-dimethyldibenzothiophene reacts to give an S-bound complex that is labile, reacting with PMe_3 to give $(C_5Me_5)Rh(PMe_3)_2$ plus free 4,6-dimethyldibenzo-thiophene ($\Delta G^\ddagger = 24.5$ kcal/mol, 25 °C). A similar S-bound complex is formed with 4,6-diethyldibenzothiophene.

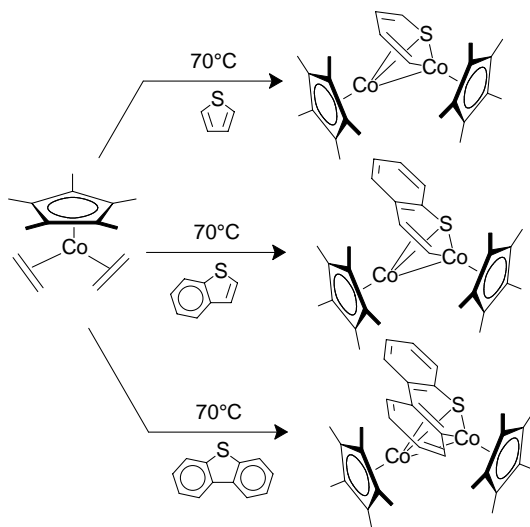
We have also examined reaction of selenophene with $Cp^*Rh(PMe_3)PhH$. Reaction occurs similarly to that of thiophene to give the C-Se insertion product (Eq 2).⁶ X-ray examination of the structure of the product shows a planar geometry, as with thiophene.



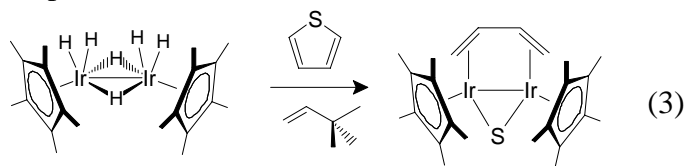
The above reactivity patterns of substituted dibenzothiophenes are remarkably similar to those observed with the commercial Mo/Co industrial catalysts.⁷ The similarity ends here, however, in that the $(C_5Me_5)Rh(PMe_3)$ fragment can only cleave one C-S bond and then becomes unreactive towards further cleavages or reaction with hydrogen.

The lack of further reactivity of the rhodium C-S insertion products can be attributed to the fact that the products are non-labile, coordinatively saturated Rh(III) complexes. In an attempt to produce a product with enhanced reactivity, the reactions of $(C_5Me_5)Co(C_2H_4)_2$ with thiophene,⁸ benzothiophene,⁹ and dibenzothiophene¹⁰ were examined. In all three cases, a similar product was observed upon heating the cobalt complex (70 °C) in the presence of the substrate. The product can be described as a C-S cleavage adduct similar to those found with $(C_5Me_5)Rh(PMe_3)$, except that the coordination site occupied by PMe_3 is replaced by a bridging $(C_5Me_5)Co$ fragment (Scheme III). Similar structures were observed in the reaction of benzothiophene with $Fe_3(CO)_{12}$ ¹¹ and of $(C_5Me_5)Rh(\eta^4-C_4Me_4S)$.¹²

Scheme III.



Since the rhodium complex was only capable of breaking one C-S bond, and the cobalt complex showed a tendency to form a dinuclear complex, a binuclear iridium complex was next examined for reactivity with thiophene. The complex $[(C_5Me_5)IrH_3]_2$ was found to react with thiophene in the presence of a hydrogen acceptor to give a product in which both C-S bonds had been cleaved to give a butadiene ligand, and the sulfur remained as a μ -sulfido ligand (Eq 3).¹³ Two intermediates are seen in the course this reaction, each of which grows in and then goes away. The reaction is proposed to proceed by way of intermediates whose structures are similar to those in the cobalt complexes identified above.

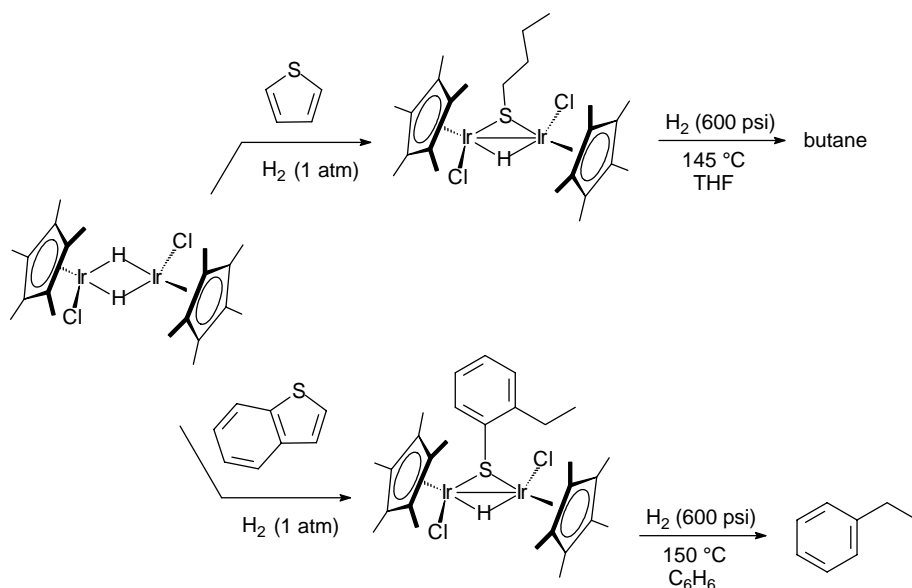


The dinuclear iridium and cobalt models for thiophene C-S cleavage would require two adjacent metal centers, a situation that could readily be accommodated at the edge of a MoS_2 crystallite in the commercial catalyst, either on the $\bar{1}010$ or $10\bar{1}0$ edge.⁷ One can imagine a thiophene molecule undergoing C-S cleavage at one of these exposed metal centers and forming a μ -sulfido bridge as in the dinuclear cobalt complexes. Further reaction as seen with the diiridium system would then lead to desulfurization and the generation of the organic product

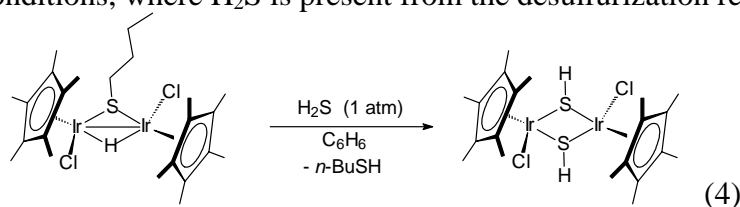
plus a sulfur filled coordination site. Regeneration of the vacant site would occur under the reducing conditions of high temperature and high hydrogen pressure. Our proposed future studies will have to be able to also cleave C-S bonds of the hindered alkylated dibenzothiophenes, and it is hoped that studies such as these will lead to the next generation of catalysts.

We have also examined the chemistry of the related dinuclear iridium system in which two of the hydride ligands have been replaced by chlorides. Reaction of the dimer $[\text{Cp}^*\text{IrHCl}]_2$ in benzene solution with either thiophene or benzothiophene at 90°C in the presence of H_2 gives the hydrogenolysis products $[\text{Cp}^*\text{IrCl}]_2(\mu\text{-H})(\mu\text{-SC}_4\text{H}_9)$ and $[\text{Cp}^*\text{IrCl}]_2(\mu\text{-H})[\mu\text{-S}(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_3]$, respectively, in high yields (Scheme IV). Upon further thermolysis under H_2 , the completely desulfurized products, butane and ethylbenzene, are produced. Both of the μ -thiolato complexes were structurally characterized. In the absence of H_2 , reaction of $[\text{Cp}^*\text{IrHCl}]_2$ with thiophene gives an additional trinuclear product $[\text{Cp}^*\text{IrCl}]_3(\text{H})(\text{SC}_4\text{H}_6)$, which was also structurally characterized.¹⁴

Scheme IV:



The bis-iridium- μ -thiolato complex also reacts with H_2S to give a μ -sulfhydryl product, which displays dynamic SH behavior of the two SH groups (Eq 4). (We were ‘scooped’ on the publication of the structure and dynamics of this compound.¹⁵) Products of this type are likely to form under HDS conditions, where H_2S is present from the desulfurization reactions.



Both iridium based hydrodesulfurization reactions proceed via organometallic intermediates/products containing bridging thiolate moieties, providing further evidence that cleavage of both carbon-sulfur bonds in various thiophenes may require the participation of more

than one metal center with the capability to form a bridging thiolate intermediate. This conclusion is in agreement with the Topsøe model for the heterogeneous reactive site in MoS₂ catalysts.⁷

Despite the fact that binuclear systems appear to be important for HDS to occur, we have evidence that the [Cp*IrHCl]₂ system proceeds via monomeric species. Reaction of a mixture of the C₅Me₅ and C₅Me₄Et dimeric starting materials leads to products in which the cyclopentadienyl groups are scrambled between the products. A control experiment demonstrated that the scrambling did not occur prior to reaction with thiophene. It is possible, however, that thiophene induces reversible cleavage of the dimers but that the dimer is still required for desulfurization of the second C-S bond.

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