

Progress Report for
NSF Grant CHE-9816365

for the period
February 1, 2000-January 31, 2001
(year 2 of 3)

**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

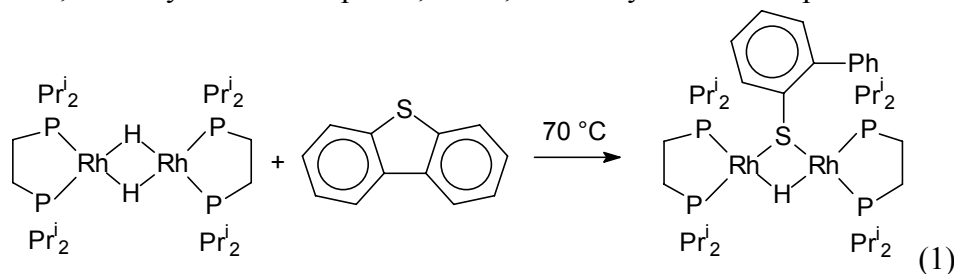
A. Introduction

Cleavage of the C-S bond is 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} In the coming years, environmental regulations will require that the present levels of sulfur in fuels (300ppm) be dropped to approximately 30ppm, and industry does not have in place the technology to achieve this level. Consequently, alternative catalysts for HDS are now being considered.

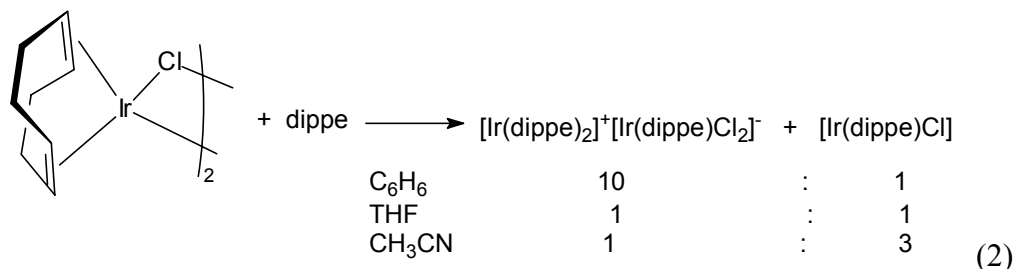
Homogeneous transition metal complexes are ideal for probing the mechanism for this process by allowing analysis of specific steps in the proposed HDS cycle.^{4,5,6} In addition, such complexes can show reactivity patterns that differ from commercial HDS catalysts. Many obstacles will have to be overcome to make these systems usable in any real process, including supporting the homogeneous species on a heterogeneous support. In this report, we summarize our studies of homogeneous C-S bond cleavage that have appeared since the termination of our prior grant in December of 1997, focussing on the second year and one-half. (The project was renewed in February of 1999.) These investigations show promising results for a new generation of environmentally interesting catalysts.

B. New Complexes for C-S bond Cleavage.

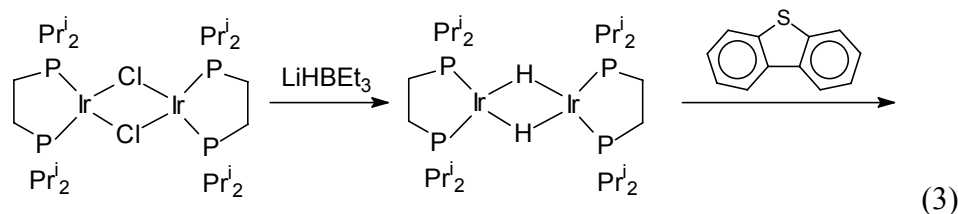
We have been successful in synthesizing several new complexes for investigation in C-S bond cleavage. Specifically, the rhodium hydride dimer [(dippe)RhH]₂ reported by Fryzuk⁷ has been prepared and its reaction with dibenzothiophene examined. A new product is obtained, which has been tentatively identified as the C-S cleavage product shown in equation 1. Further reactions are under investigation using this dinuclear hydride for the cleavage of thiophene, benzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene.



The related dinuclear iridium complex is unknown, and we have found a route to the complex. The synthesis is complicated by the fact that the reaction leads to undesirable coproducts, as shown in equation 2. Fortunately, this synthetic difficulty was overcome by changing solvent, which has a remarkable effect on the product distribution.



With [Ir(dippe)Cl]₂ in hand, we will now look at the borohydride reduction to the hydride and then look at reactions with the thiophenes (equation 3).



We have also investigated the use of palladium complexes for C-S bond cleavage. Reduction of Pd(dippe)Cl₂ with borohydride in the presence of thiophene leads to the formation of the C-S insertion adduct, which has been structurally characterized (equation 4, figure 1). To our knowledge, this is the first example of a palladium complex that cleaves C-S bonds. The thiametallacycle ring is planar, as is seen with the nickel⁸ and Cp*Rh(PMe₃)⁹ analogs.

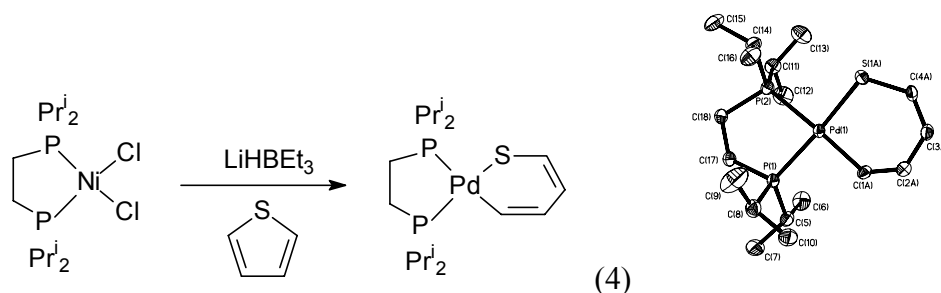


Figure 1.
ORTEP of (dippe)Pd(thiophene)

A similar reaction generating the palladium hydride dimer leads to the activation of dibenzothiophene. Upon standing for several days at room temperature, the desulfurization product is observed (equation 5). An X-ray structure of the DBT insertion adduct was determined (Figure 2). Further studies of this reaction are required.

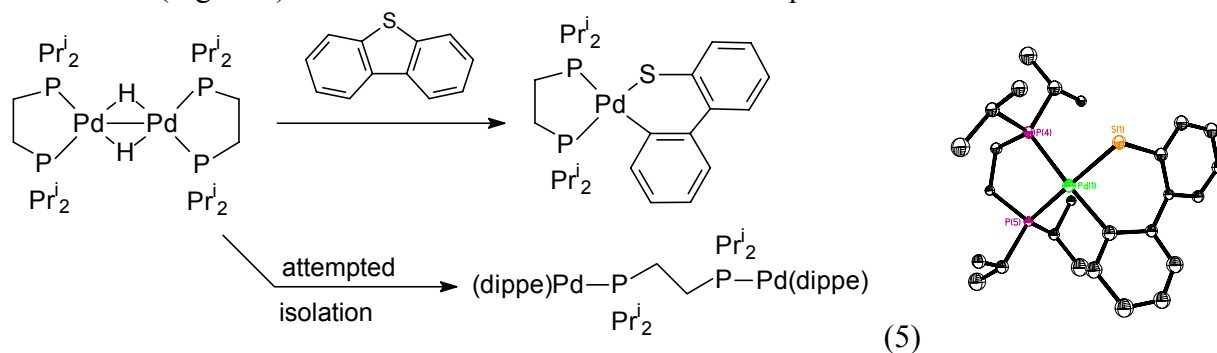
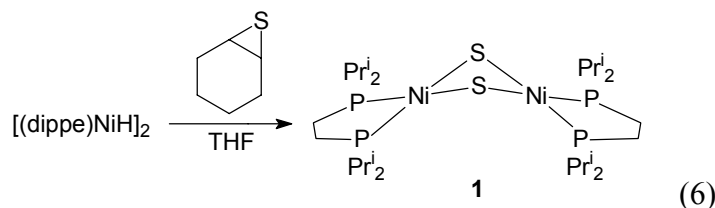


Figure 2. ORTEP of (dippe)Pd(DBT)

C. Reactivity of μ -Sulfido Complexes.

We have also examined the chemical reactivity of several μ -sulfido complexes. Our goal is to learn about the basic chemistry of these species so that they might be recycled to the dihydrides that are active in HDS chemistry. We have looked extensively at the chemistry of the nickel dimer, [Ni(dippe)(μ -S)]₂, which can be conveniently prepared by the reaction shown in

equation 6. This compound has a folded structure,¹⁰ a feature not commonly seen in this class of compounds.



The compound can be alkylated with a variety of alkyl halides giving rise to bridging thiolato cations (equation 7).¹¹ Single crystal X-ray structures have been determined for R = Me, Et, and *i*-Pr (Figure 3).

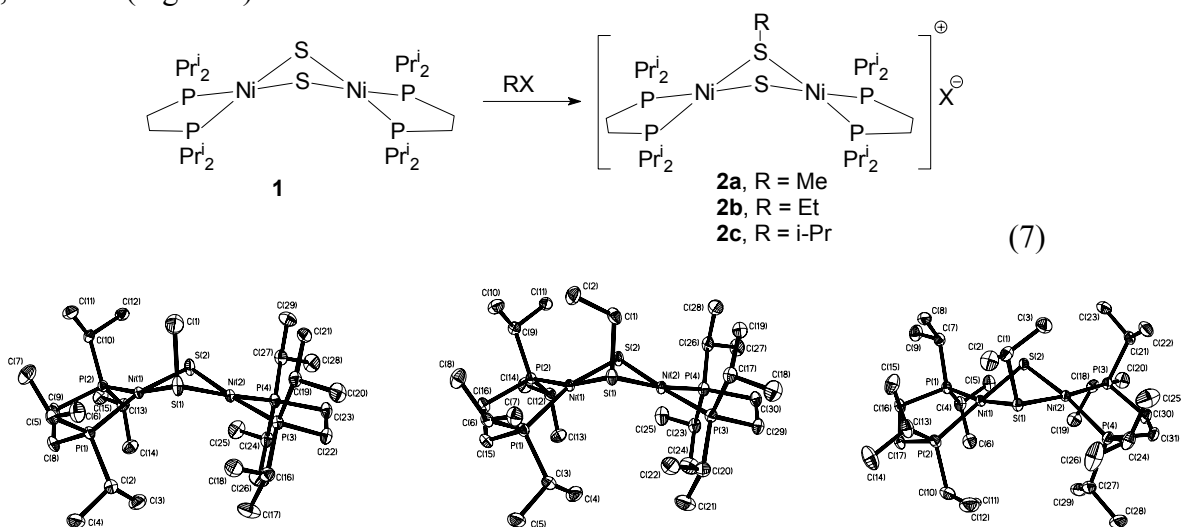
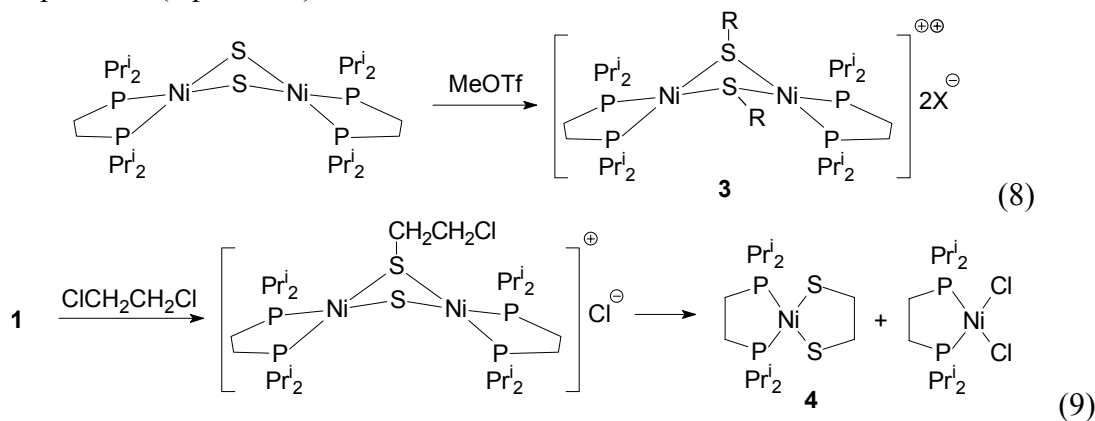
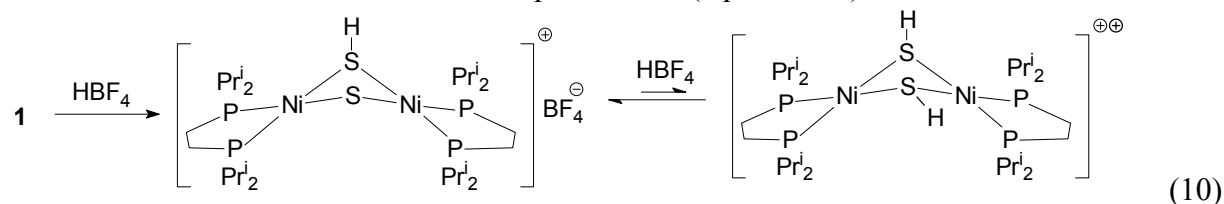


Figure 3. ORTEPs of $[(\text{dippe})_2\text{Ni}_2(\mu\text{-S})(\mu\text{-SR})]^+$ (R = Me, Et, *i*-Pr).

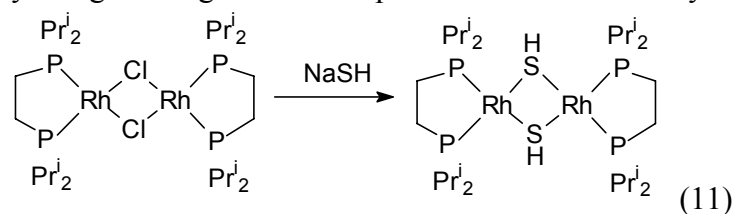
A second alkylation does *not* occur with alkyl halides, but stronger alkylating reagents such as methyl triflate give rise to dialkylated dicationic species (equation 8). Use of dihalo reagents permits dialkylation using alkyl chlorides due to the intramolecular nature of the second alkylation. While the monoalkylated intermediate can be observed, the dialkylated product is unstable towards cleavage of the thiolate bridges by the chloride ion that is generated, giving rise to two separate products (equation 9).



Protonation of the bis- μ -sulfido complex was also examined. Monoprotonation could be effected with HBF_4 . Diprotonation appears to be unfavorable, although NMR studies provide evidence for a small amount of a second protonation (equation 10).



We have also prepared a bridging dithiolate of rhodium (equation 11). Reactions of this complex are currently being investigated for comparison with the nickel system.



D. Statement of Funds Estimated to be Unobligated.

None of the funds allocated for the current project year will remain unobligated at the end of the current year.

E. Publications appearing during the first two years of this grant:

1. "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.
2. "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.
3. "Deep Hydrodesulfurization in Homogeneous Solution: Access to a Transition-Metal Insertion Complex of 4,6-Dimethyldibenzothiophene," Vivic, D. A.; Jones, W. D. *Organometallics*, **1998**, *17*, 3411-3413.
4. "Synthesis and Reactions of Cp-Linked Phosphine Complexes of Rhodium," Laurent Lefort, Todd W. Crane, Michael D. Farwell, David M. Baruch, John A. Kaeuper, Rene J. Lachicotte, and William D. Jones, *Organometallics* **1998**, *17*, 3889-3899.
5. "Activation of Sulfur and Nitrogen-Containing Heterocycles by a Dinuclear Iridium Complex," David A. Vivic and William D. Jones, *Organometallics*, **1999**, *18*, 134-138.
6. "Cleavage of the Carbon-Sulfur Bonds in Thiophenes by a Polynuclear Ruthenium Complex, William D. Jones,* R. Martin Chin, and Christine L. Hoaglin," *Organometallics*, **1999**, *18*, 1786-1790.

7. "Evidence for the Existence of a Late-Metal Terminal Sulfido Complex," David A. Vivic and William D. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 4070-4071.
8. "Modeling the Hydrodesulfurization Reaction at Nickel. Unusual Reactivity of Dibenzothiophene Relative to Thiophene and Benzothiophene," David A. Vivic and William D. Jones, *J. Am. Chem. Soc.*, **1999**, *121*, 7606-7617.
9. "Selective Carbonylation Routes to Thiocarbamates. An Alternative to Phosgene," William D. Jones, Kelly A. Reynolds, Caroline K. Sperry, Rene J. Lachicotte, Steven A. Godleski, Ronald Valente, *Organometallics* **2000**, *19*, 1661-1669.
10. "Nickel Mediated Selective Carbonylation Routes to Thiocarbamates," Josemon Jacob, Kelly A. Reynolds, William D. Jones, Stephen A. Godleski, and Ronald R. Valente, *Organometallics* **2001**, *20*, 1028-1031.
11. "Cobalt Catalyzed Selective Conversion of Diallylanilines and Arylimines to Quinolines," Josemon Jacob, William D. Jones, Stephen A. Godleski, and Ronald R. Valente, *J. Mol. Catal.* **2001**, submitted.
12. "Structure of $[\text{Ni}(\text{dippe})(\mu\text{-S})_2]$ and its Reaction Products. The Nucleophilicity of the Ni_2S_2 Fragment," Stephen S. Oster, Rene J. Lachicotte, and William D. Jones, *Inorg. Chim. Acta*, submitted.

F. References and Notes

- (1) "Hydrodesulfurization," Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245-313.
- (2) "Current state of the problem of the study of organosulfur compounds from petroleums," Lyapina, N. K. *Russ. Chem. Rev. (Engl. Transl.)* **1982**, *51*, 189. Aksenov, V. A.; Kamyranov, V. F. in *Organic Sulfur Chemistry*; Freidina, R. Kh.; Skorova, A, E. Eds.; Pergamon: New York, 1981; p. 201. Thompson, C. J. *ibid.* p.9.
- (3) "Deep desulfurization of light oil. Part 2: hydrodesulfurization of dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene," Kabe, T.; Ishihara, A.; Zhang, Q. *Appl. Catal. A* **1993**, *97*, L1-L9. "Deep hydrodesulfurization of alkyl-substituted dibenzothiophenes in light oil," Ishihara, A.; Tajima, H.; Kabe, T. *Chem. Lett.* **1992**, 669-670. "Deep Hydrodesulfurization of Light Gas Oil. 1. Kinetics and Mechanisms of Dibenzothiophene Hydrodesulfurization," Kabe, T.; Ishihara, A.; Tajima, H. *Ind. Eng. Chem. Res.* **1992**, *31* (6), 1577-1580.
- (4) "Studies of the Mechanism of Thiophene Hydrodesulfurization: Conversion of 2,3- and 2,5-Dihydrothiophene Model Organometallic Compounds," Sauer, N. N.; Markel, E. J.; Schrader, G. L.; Angelici, R. J. *J. Catal.* **1989**, *117*, 295-297.
- (5) "Heterogeneous Catalysis of the Hydrodesulfurization of Thiophenes in Petroleum: An Organometallic Perspective of the Mechanism," Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387-394.
- (6) "Activation of C-S Bond Homolysis by Coordination to a Mo/Co/S-Containing Cluster," Druker, S. H.; Curtis, M. D. *J. Am. Chem. Soc.* **1995**, *117*, 6366-6367.

-
- (7) "Fryzuk, Michael D.; Jones, T.; Einstein, F. W. B. Reactivity of electron-rich binuclear rhodium hydrides. Synthesis of bridging alkenyl hydrides and x-ray crystal structure of $[[(\text{Me}_2\text{CH})_2\text{PCH}_2\text{CH}_2\text{P}(\text{CHMe}_2)_2]\text{Rh}]_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH:CH}_2)$," *Organometallics* **1984**, *3*, 185-91.
- (8) "Modeling the Hydrodesulfurization Reaction at Nickel. Unusual Reactivity of Dibenzothiophene Relative to Thiophene and Benzothiophene," David A. Vivic and William D. Jones, *J. Am. Chem. Soc.*, **1999**, *121*, 7606-7617.
- (9) "Structure of Metallathiacycles: Planar vs. Nonplanar Geometries. A Theoretical and Experimental Investigation," Christine Blonski, Andrew W. Myers, Michael Palmer, Suzanne Harris, and William D. Jones, *Organometallics* **1997**, *16*, 3819-3827.
- (10) "Evidence for the Existence of a Late-Metal Terminal Sulfido Complex," David A. Vivic and William D. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 4070-4071.
- (11) "Structure of $[\text{Ni}(\text{dippe})(\mu\text{-S})]_2$ and its Reaction Products. The Nucleophilicity of the Ni_2S_2 Fragment," Stephen S. Oster, Rene J. Lachicotte, and William D. Jones, *Inorg. Chim. Acta*, submitted.