Organometallic modeling of the hydrodesulfurization (HDS) process: rhenium carbonyl-promoted C-S bond cleavage and hydrogenation of thiophenes and benzothiophenes

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Organometallic modeling of the hydrodesulfurization (HDS) process: Rhenium carbonyl-promoted C-S bond cleavage and hydrogenation of thiophenes and benzothiophenes

by

Michael Anthony Reynolds

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Inorganic Chemistry

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For the Major Program

Signature was redacted for privacy.

For the Graduate College
This dissertation is dedicated to the memory of my grandparents

Anthony & Amelia Shedbar; and Michael & Mary Reynolds.
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GENERAL INTRODUCTION

Catalytic hydrodesulfurization (HDS) is the commercial process for removing sulfur from organosulfur compounds that are present in petroleum fuels. This process is important industrially since sulfur poisons precious metal-based reforming catalysts which increases the cost of fuel reforming. HDS is also important environmentally due to the possible formation of toxic sulfur oxides (SO_x, x = 2 or 3) that can be produced during the combustion of fossil fuels which contain organosulfur compounds. The organosulfur compounds that are present in crude petroleum include thiols, thioethers, disulfides and thiophenes. However, it is the thiophenic molecules which are the most difficult to desulfurize during HDS due to aromatic stabilization of the thiophene rings.

Organometallic modeling of the HDS process at single or multiple metal centers is one approach to better understanding the mechanisms that govern commercial HDS. Therefore, we have currently been investigating the use of Re_2(CO)_10 as a potential model system for catalytic HDS with respect to S-binding, ring-opening, and hydrogenation of thiophenes and benzothiophenes. We have also been investigating the use of UV-light as a method for activating thiophenic molecules towards C-S and C-H bond cleavage.

Dissertation organization

This dissertation consists of 4 main chapters: the first is an overview of current literature on metal clusters as HDS catalysts; subsequent chapters (2-4) are papers, submitted for publication, that discuss the role of Re_2(CO)_10 in promoting binding, C-H and C-S bond cleavage and partial hydrogenation of thiophenes and benzothiophenes. In each chapter, the literature citations, figures and tables correspond only to the chapters in which they appear.
1. ORGANOMETALLIC CLUSTERS USED AS MODELS FOR THE CATALYTIC HYDRODESULFURIZATION (HDS) OF THIOPHENES AND BENZOTHIOPHENES

Heterogeneous Catalytic Hydrodesulfurization (HDS) is the commercial process for removing sulfur from organosulfur compounds that are present in petroleum-based feedstocks. This process is important for two primary reasons: First, sulfur poisons precious metal-based reforming catalysts thereby making catalytic reforming more difficult and; Second, during the combustion of petroleum fuels poisonous sulfur oxides (SO$_x$, x = 2, 3) could be produced which are known precursors to acid rain formation and a threat to the environment.

The sulfur content of crude petroleum varies from 0.2 to 4% (by weight) which is higher than the limits allowed under current U.S. federal regulations. The types of organosulfur compounds present in petroleum distillates include thiols (RSH), thioethers (RSR'), disulfides (RSSR'), thiophenes and benzothiophenes. It is the thiophenic molecules (Scheme 1), however, which are the most difficult to desulfurize using current commercial hydrotreating processes. This is due, in part, to the aromatic stabilization of the thiophenic ring systems. Commercial HDS is achieved by treating petroleum-based feedstocks with H$_2$ at high temperatures (300-400 °C) and pressures (>200 atm) (also known as hydrotreating) and in the presence of sulfided metal-based catalysts to produce hydrocarbons and H$_2$S (eq. 1). The catalysts typically used are MoS$_2$ or WS$_2$ that are promoted by Co or Ni and supported on alumina.

$$\text{C}_a\text{H}_b\text{S} + c\text{H}_2 \xrightarrow{\text{Cat.}} \text{H}_2\text{S} + \text{C}_a\text{H}_d$$  \text{Eq. 1}
In order to develop better catalytic systems for the commercial HDS process, it is important to understand how organosulfur compounds, such as thiophenes, are desulfurized at the sulfided-metal catalyst surfaces. One approach to studying the HDS process is to use organometallic models that could provide insight into possible HDS reaction mechanisms, intermediates and products that are relevant to the commercial process. Thus, organometallic modeling has become an area of increasing interest in recent years and the subject of several reviews.\textsuperscript{1,2,7}

A key step in commercial HDS is the binding of organosulfur compounds, such as thiophenes, to catalyst metal centers. The known binding modes of thiophenes and benzothiophenes include $\eta^1(S)$, $\eta^2$, $\eta^4$, $\eta^5$ and $\eta^6$ (Scheme 2) and many transition metal complexes containing thiophene ligands bound in several different ways have been
reported.\textsuperscript{1,2,7} The subsequent steps in the commercial HDS process (such as C-S and C-H bond cleavage) which lead to desulfurization of sulfur containing compounds are as yet still unclear and have been the subject of several studies.

Organometallic model complexes containing C-S or C-H cleaved thiophene and benzothiophene ligands have been reported for single metal and some bimetallic transition metal complexes.\textsuperscript{1,2,7} However, few reactions have been reported between thiophenic molecules and organometallic cluster complexes. This is surprising since the few examples of reactions between metal-metal bonded clusters and thiophenes have demonstrated, in general, a higher activity of the clusters towards C-S and C-H bond cleavage and desulfurization of the thiophene substrates compared to their single metal and bimetallic counterparts.
The following review will identify the few organometallic cluster complexes that have been shown to react with thiophenes and benzothiophenes to give complexes which contain coordinated, C-S or C-H bond cleaved, hydrogenated and/or desulfurized thiophene ligands. The term “cluster” will be limited to metal-metal bonded clusters that contain 3 or more metal centers and common organometallic ligands such as carbonyls, hydrides, sulfido-groups and phosphines in terminal or bridging positions. The three main types of clusters that will be discussed include metal carbonyls (including Fe, Ru, Os and Co); organometallic-sulfido cluster complexes; and organometallic clusters, which contain hydride ligands. The relevance of these systems to heterogeneous HDS will be discussed in brief following the completion of each section.

**$\text{M}_3(\text{CO})_{12}$ Clusters ($\text{M} = \text{Fe, Ru or Os}$) and $\text{Co}_4(\text{CO})_{12}$**

Among the most common organometallic metal-metal bonded clusters known are the homoleptic metal carbonyl clusters of Fe, Ru, Os and Co. The Group 8 transition metals form clusters of type $\text{M}_2(\text{CO})_9$ (for $\text{M} = \text{Fe or Os}$) or $\text{M}_3(\text{CO})_{12}$ (where $\text{M} = \text{Fe, Ru or Os}$) with carbon monoxide. The $\text{M}_3(\text{CO})_{12}$ clusters have been observed to react both thermally and photochemically with thiophenes by undergoing metal-metal bond cleavage or loss of CO. Examples of C-S and C-H bond cleavage of thiophenes in the presence of these clusters have been reported and will be discussed in detail later.

The Group 9 metal carbonyl clusters include $\text{M}_2(\text{CO})_8$ (where $\text{M} = \text{Co or Rh}$) and $\text{M}_4(\text{CO})_{12}$ ($\text{M} = \text{Co, Rh, Ir}$). However, only the Co clusters, $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ have been demonstrated to react with thiophenes and benzothiophenes to produce interesting HDS model complexes. This is surprising since Rh and Ir single metal complexes are known to react with thiophenes to produce ring-opened complexes.
Fe₃(CO)₁₂

Stone and coworkers⁸⁻¹⁰ were the first to demonstrate the reactivity of organometallic clusters with thiophenic molecules, such as thiophene (T) and benzothiophene (BT), under thermal conditions to produce ring-opened or desulfurized thiophene-containing transition metal complexes. In these early studies it was found that when Fe₃(CO)₁₂ (I) was heated in neat thiophene, an orange product was afforded in low yield that was proposed to be the desulfurized ferrole, (C₄H₄)Fe₂(CO)₆ (2) based on spectroscopic data (Scheme 3).⁸

![Scheme 3](image)

A black precipitate was also present and identified as FeS, based on its reactivity with HCl to produce H₂S. Detlaff and Weiss¹¹ repeated the reaction of thiophene with 1 and fully characterized the ferrole product 2, proposed by Stone⁸, using both spectroscopic and X-ray structural methods. In the molecular structure of 2, the C₄H₄ functionality is shown to form a metallacyclopentadiene with one Fe(CO)₃ moiety while acting as an η⁴-π ligand to the other Fe(CO)₃ group as Stone had previously postulated. Furthermore, one of the six carbonyl ligands was determined to be semi-bridging based on the X-ray study of 2.

The analogous reaction of BT with Fe₃(CO)₁₂ produced the first thiaferrole complex, Fe₂(CO)₆(μ-BT) (3)¹⁰, in which the C_vinyl-S bond of the BT ligand is cleaved and bridges the Fe₂(CO)₆ backbone (Scheme 4). No evidence of desulfurized organic products or ferrole
complexes were observed during this reaction. The reaction of Fe₃(CO)₁₂ with 2-methylthiophene (2-MeT) in refluxing heptane produced both the corresponding thiaferrole, Fe₂(CO)₆(μ-2-MeT) (4) in 0.7% yield, and also the desulfurized ferrole product Fe₂(CO)₆(2-MeC₄H₃) (5), analogous to 2, in 4.2% yield with detectable amounts of FeS.¹² The structure of 4, which was established by X-ray crystallography, showed no evidence for a bridging carbonyl ligand such as that found in 2. This reaction is significant because it is the first report of both C-S cleavage and desulfurization of thiophenes at metal centers of organometallic complexes.

Rauchfuss¹³ more recently demonstrated that the thiaferroles could be prepared from 1 and either 2,5-dimethylthiophene (2,5-Me₂T) or 2-MeT which indicates that the thiophene methyl groups do not protect the S from attack by 1 and therefore do not inhibit the formation of the thiaferroles. Thiaferroles, such as 4, are readily converted into the corresponding ferrole products by thermolysis in benzene solution thereby indicating that the thiaferrole complexes can undergo desulfurization to form ferroles. In this same study¹³, complex 3 was demonstrated to react with H₂ (700 psi, 160 °C) to give the further ring-opened and desulfurized organic products ethylbenzene and 2-mercaptoethylbenzene in good yields. Reductive elimination of BT from 3 was observed at high pressures of CO (700 psi,
160 °C) with subsequent formation of Fe(CO)₅; and also by heating 3 in vacuo to give Fe metal.

In summary, the first examples of ring-opened and desulfurized thiophenes by a metal-metal bonded cluster were demonstrated using Fe₃(CO)₁₂ (1). Cluster 1 was shown to react with thiophenes and benzothiophenes to afford thiaferroles and ferroles as HDS model complexes. In some cases, reactions of these metal insertion products with H₂ produced hydrocarbons that were similar to those products observed under commercial HDS conditions. Furthermore, the success of cluster 1 in reacting with thiophenic molecules to give interesting HDS model complexes has paved the way for those interested in studying the reactivity of thiophenes with metal-metal bonded clusters.

**Ru₃(CO)₁₂**

Recently, Ru₃(CO)₁₂ (6) has been reported to react with thiophenes and benzo thiophenes to afford both ring-opened and desulfurized thiophene-containing complexes, some of which are similar to those observed in the analogous reactions of Fe₃(CO)₁₂. For instance, when Ru₃(CO)₁₂ and 2-MeT are heated in refluxing THF, three Ru-based thiophene complexes are produced in low to moderate yields (Scheme 5). The first complex, Ru₃(CO)₁₀(μ-2-Me-C₄H₄S)(μ-H) (7a,b), exists in both the _exo-(7a)_ and _endo-(7b)_ isomeric forms (17% yield) as defined by the position of the S atom with respect to the Ru(CO)₄ moiety. These isomers were not separated, but were characterized as a mixture using spectroscopic methods (IR and NMR). Complex 7 consists of a planar Ru₃(CO)₁₀ unit in which the C-H cleaved 2-Me-5-thienyl species bridges the two Ru(CO)₃ centers in an η²- and an η¹-fashion with the hydride bridging the two Ru(CO)₃ fragments.
Scheme 5

\[
\text{Ru}_3(\text{CO})_{12} + \text{C}_5\text{H}_4\text{S} \\
\xrightarrow{\Delta \text{ THF}}
\]

\[7a, (\text{exo})\]

\[7b, (\text{endo})\]

\[8\]

\[9\]
Variable temperature NMR studies of a mixture of both isomers of 7 showed evidence for the interconversion of the two isomers with the exo-isomer (7a) proposed as the dominant form at lower temperatures (<-27 °C). The complex Ru₂(CO)₆(MeC₄H₃) (8) is structurally analogous to the ferrole complexes previously reported, such as Fe₂(CO)₆(C₄H₄)⁸ and Fe₂(CO)₆(MeC₄H₃)¹³, which were prepared in a similar manner from Fe₃(CO)₁₂. Since complex 8 is spectroscopically similar to the previously mentioned ferroles, the structure was not obtained.

A rather remarkable tetraruthenium-sulfido complex was also isolated from the reaction mixture and structurally identified as Ru₄(μ₃-S)(2-MeC₄H₃)(CO)₁₁ (9). The molecular structure of 9 reveals that the sulfur has been extruded from the thiophene ring and replaced by a Ru(CO)₂ moiety to form a metallacyclopentadiene species. The extruded sulfur caps the Ru(CO)₂ unit and two of the Ru(CO)₃ moieties of the Ru₃-plane. A third Ru(CO)₃ unit is bonded to the Ru(CO)₂ unit and is also η⁴-bound to the butadienyl group. Complex 9 is significant in that it demonstrates a transition metal-thiophene complex in which all components of a desulfurized thiophene are present within the same cluster unit.

Notably, unsubstituted thiophene reacts with 6 under similar conditions to afford the complexes Ru₂(CO)₆(C₄H₄) (20% yield) and Ru₄(μ₃-S)(C₄H₄)(CO)₁₁ (10) (7% yield)¹⁴ which are analogous to 8 and 9 respectively based on spectroscopic evidence. No evidence for the thiophene analog of 7 was observed which is surprising since the unsubstituted thiophene is less sterically hindered than the 2-MeT derivative.

Benzothiophene also reacts with 6 in refluxing THF to produce the three cluster complexes Ru₃(CO)₆(μ-C₈H₆) (11), Ru₂(CO)₆(μ-C₈H₆S) (12) and Ru₂(CO)₆(C₈H₆) (13)
\[
\text{Ru}_3(\text{CO})_{12} + \text{benzothiophene} \\
\xrightarrow{\text{Scheme 6}} \\
\begin{array}{c}
\text{11} \\
\text{12} \\
\text{13}
\end{array}
\]
(Scheme 6)\textsuperscript{15} all of which contain ring-opened or desulfurized BT ligands. Complexes 11, 12 and 13 were separated by TLC in yields of 28, 17 and 10\% respectively and were characterized both spectroscopically (NMR and IR) and by their X-ray structures. These three complexes are proposed to have formed via a transient intermediate of type A (Scheme 6). The structure of 11 contains a desulfurized BT ligand in which the S atom has been replaced by a Ru(CO)\textsubscript{3} group with the resulting (C\textsubscript{8}H\textsubscript{6})Ru(CO)\textsubscript{3} moiety acting as a \pi-ligand towards the Ru\textsubscript{2}(CO)\textsubscript{5} backbone. The formation of Ru\textsubscript{3}(CO)\textsubscript{6}(\mu-C\textsubscript{8}H\textsubscript{6}) (11) can be explained by the unobserved intermediate A undergoing desulfurization followed by ring closure. Complex 11 reacts further in CDCl\textsubscript{3} after 24 h at room temperature and under CO (1 atm) to afford the final desulfurized complex Ru\textsubscript{2}(CO)\textsubscript{6}(C\textsubscript{8}H\textsubscript{6}) (13) with proposed loss of Ru(CO)\textsubscript{3}. The complex Ru\textsubscript{2}(CO)\textsubscript{6}(\mu-C\textsubscript{8}H\textsubscript{6}S) (12), which is a structural analog of the thiaferrole 3, is also produced during the reaction of Ru\textsubscript{3}(CO)\textsubscript{12} with BT and occurs through the intermediate A, which eliminates RuS\textsubscript{2} to afford 13. Complex 13 is similar to the ferrole complex 2, in which one Ru(CO)\textsubscript{3} unit forms a metallacycle with the desulfurized hydrocarbon and the other Ru binds \pi\textsuperscript{2} to the vinyl group. Strangely, 13 does not satisfy the 18-electron rule based on the proposed structure and no explanation has been offered by the authors.

The reactions of Ru\textsubscript{3}(CO)\textsubscript{12} with thiophenic molecules under thermal conditions have been demonstrated to produce ring-cleaved, C-H bond cleaved and desulfurized thiophene containing products which are in some cases different from those observed in the analogous reactions of thiophenes and benzothiophenes with Fe\textsubscript{3}(CO)\textsubscript{12}. The complexes 7-13 are therefore useful structural models for studying intermediates that could be formed during the commercial HDS process. The difference in reactivity of Ru\textsubscript{3}(CO)\textsubscript{12} compared to Fe\textsubscript{3}(CO)\textsubscript{12} warrants further investigations into the reactivity of homoleptic and mixed metal with
thiophenic molecules. Such studies could lead to the preparation of new HDS models for thiophene activation which have not been observed in either Ru or Fe clusters alone.

**Os₃(CO)₁₀(CH₃CN)₂ and related clusters.**

The osmium carbonyl cluster [Os₃(CO)₁₀(CH₃CN)₂] (14) reacts with thiophenes and benzothiophenes to give a series of novel Os-thiophene complexes in which the thiophene has undergone bond cleavage. For example, 14 was first found to react with the 2-formyl derivatives of the heterocycles, C₄H₃X(CHO) (X = NH, S or O), including 2-formylthiophene (X = S), to produce the triosmium hydride clusters Os₃(CO)₁₀(μ-H)(μ₂-(CO)C₄H₃E) (15) and [Os₃(CO)₁₀(μ-H)(μ₂-C₄H₂E(CHO))] (16) (E = S only) (Scheme 7). In complex 15, the aldehyde C-H bond of the 2-formylthiophene has undergone oxidative addition of the C-H bond to the triosmium unit of 14 resulting in a bridging hydride. The formyl functionality in 15 acts as a bidentate ligand coordinating through both the carbon and oxygen of the formyl-CO group to the two Os(CO)₃ units.

\[
[\text{Os₃(CO)₁₀(CH₃CN)₂}] + \text{C₄H₃X(CHO)} \rightarrow \text{Os₃(CO)₁₀(μ-H)(μ₂-(CO)C₄H₃E)} (15) \text{ and } \text{[Os₃(CO)₁₀(μ-H)(μ₂-C₄H₂E(CHO))]} (16) (E = S only) \ (\text{Scheme 7})
\]
The thiophene ligand in 16 behaves as a chelating ligand to a Os(CO)₃ moiety with C-H activation occurring at the 3-position of the thiophene to form an Os-C bond and a bridging hydride. Surprisingly, complex 16 was only observed for 2-formylthiophene and not when E = NH or O.

Complex 14 also reacts with unsubstituted thiophene (or furan) to produce a C-H, rather than a C-S (or C-O) cleaved complex, identified as the *exo* and *endo*-isomers of [Os₃(CO)₁₀(μ-C₄H₄S)(μ-H)] (17a,b) (Scheme 8).

Variable temperature (VT)-NMR studies indicated that interconversion of the *exo* and *endo* isomers is fast for the thienyl complex and slow for the furanyl complex. These isomers are isostructural with those reported for the previously described Ru analog (7a,b)¹⁴ which was prepared from Ru₃(CO)₁₂ and 2-MeT. It is unclear which isomer (17a or 17b) is the thermodynamic product in the thiophene system although the *exo*-isomer is the major
product in the furan complexes. No evidence of C-S cleavage in the thienyl or furanyl complexes was observed in this system. However, in contrast to the reactions with thiophenes and furans, complex 14 does cleave C-E (E = Se or Te) bonds in some non-sulfur containing heterocyclic compounds (Scheme 8). Selenophene (C4H4Se) and tellurophene (C4H4Te), for example, react with 14 and undergo preferential cleavage of C-E (E = Se or Te) bonds to give complexes of the type [Os3(CO)10(μ-C4H4E)] (18) (E = Se, 20% or Te, 35%) in which the resulting cleaved heteroatom bridges two Os(CO)3 groups while the resulting terminal vinyl carbon also bridges the two Os groups acting as both an η1- and an η2-vinyllic ligand.

The versatility of complex 14 has also been extended to C-S and C-H bond cleavage in BT and dibenzo thiophene (DBT) compounds. Arce, et al. found that 14 reacts with BT in refluxing cyclohexane to give the two hydride clusters [Os3(CO)10(μ-H)(μ-C8H5S)] (19) and [Os3(CO)9(μ-H)2(μ3-C8H4S)] (20) in low yields (20% and 12% respectively), and the ring-cleaved complex [Os3(CO)10(μ-C8H6S)] (21) in 12% yield (Scheme 9). Complex 19 is composed of a Os3(CO)10 unit in which the BT moiety has undergone oxidative addition of the C-H bond in the 2-position at the Os(CO)3 centers and behaves as a bridging ligand through the vinyl group in an η1- and η2-fashion to give a structure similar to that of related thiophene clusters (17a,b). In chloroform solution, 19 will slowly undergo C_vinyl-S bond cleavage to afford 21 quantitatively at room temperature after 60 days by going through a bridging S-bound BT intermediate (Scheme 9). When heated in refluxing cyclohexane complex 19 affords the decarbonylated dihydride product 20 with loss of CO. In 20, the μ3-bridging BT ligand is coordinated to the Os3(CO)9 cluster unit μ3-η1,η1,η2-coordinated and
\[
\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2 + \text{cyclohexane} \rightarrow \text{19}
\]

\[
\text{CHCl}_3 \quad 60 \text{ d} \quad \rightarrow \text{21}
\]

\[
\text{Scheme 9}
\]
can be described as a bridging "thiophyne" which is analogous to a benzyne ligand.

Dibenzothiophene reacts with **14** in refluxing cyclohexane to produce, \([\text{Os}_3(\text{CO})_9(\mu-\text{H})_2(\mu-\text{C}_{12}\text{H}_8\text{S})](22)\) in 23% yield after separation by TLC on silica gel (Scheme 10). Complex 22 is bound to the Os₃ unit as a 'benzyne' type ligand as described for 20 in which two C-H bonds of the DBT ring have been oxidatively added to the Os₃ cluster unit resulting in two bridging hydride ligands. It is possible that complex 22 is formed via an intermediate species such as that shown in Scheme 8 by oxidative addition of a second C-H bond to another Os center of the proposed intermediate.

\[
\begin{align*}
\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2 + & \quad \text{Dibenzothiophene} \\
\rightarrow & \quad \Delta, \text{cyclohexane} \\
\begin{array}{c}
\text{Os}_3(\text{CO})_3 \quad \text{Os}_3(\text{CO})_3 \\
(\text{OC})_4 \quad (\text{OC})_4 \\
\text{Os}_3(\text{CO})_3 \quad \text{Os}_3(\text{CO})_3 \\
\end{array} \\
\rightarrow & \quad \text{C-H oxad}
\end{align*}
\]

Scheme 10
The \( \eta^1, \eta^2 \)-DBT-Os intermediate species in scheme 10 was not observed during the reaction. The thiophyne ligands in 20 and 22 represent the first examples of this type of binding for sulfur heterocycles, such as BT and DBT. No evidence of S-binding or desulfurization of BT or DBT ligands was observed in this system.

In yet another interesting HDS model study, complex 14 was found to react with 2-methylthiothiophene (2-MeS-T) at 20 °C to form the hydride complex \([\text{Os}_3(\text{CO})_{10}(\mu-H)(\mu-2-\text{MeSC}_4\text{H}_2\text{S})]\) (23) in 68% isolated yield. The molecular structure of 23 was established and showed that the C-H bond in the 3-position of the thiophene has oxidatively added to a Os(CO)\(_3\) unit of the Os\(_3\) cluster core with formation of a bridging hydride ligand (Scheme 11). The \( \eta^1(S) \) binding of –SMe group in 23 is to a Os(CO)\(_3\) unit allows the thienyl group to act as a bidentate ligand. No evidence was found for coordination of the thiophene-ring sulfur to any Os center in 23.

![Scheme 11](image-url)
In refluxing octane, complex 23 loses CO from the Os(CO)$_4$ group with subsequent η$^2$-binding of a C=C bond to the resulting Os(CO)$_3$, to afford the isomers 24 and 25 (36% mixture). The X-ray structures of single crystals of both isomers were determined. In the molecular structure of 24, the thienyl ligand is μ$_3$-bridging the Os$_3$ unit and exhibits binding modes that include η$^1$- through the 3-carbon, η$^2$-through the C2-C3 vinyl carbons and η$^1$(S) through the –SMe group. In the structure of 25, the MeS-group has migrated from the 2-position to the 3-position of the thienyl functionality with the resulting thienyl ligand bridging the Os$_3$ core in a μ$_3$-fashion similar to that in 24 (Scheme 11). No evidence of thiophene sulfur binding to an Os center was observed in either complex 24 or 25.

Interestingly, the ratio of the isomers 24 to 25 in the reaction mixture is dependent on room sunlight. For instance, when an octane solution of [Os$_3$(CO)$_{10}$(μ-H)(μ-2-MeSC$_4$H$_2$S)] (23) is refluxed in the dark, only 24 is produced (1 h). Complex 24 can then be isolated and further converted into 25 at room temperature in CD$_2$Cl$_2$ with stirring (2 h) in sunlight. The authors propose a mechanism to account for the formation of 24 and 25 (Scheme 12). In the first step, the thiophene ligand in 24 “switches” its binding at the Os(2) and Os(3) metal centers to produce 24'. In the next step, the C-S bond between the thienyl group and the –SMe functionality in 24' could cleave to afford an intermediate X in which the –SMe group has migrated and bridges the Os(1) and Os(2) centers. The MeS-group could then transfer from the Os centers to the 3-carbon of the thienyl ligand to form isomer 25, or if the hydride ligand in intermediate X migrates to the thiophyne functionality (to give X') before the MeS group does, then complex 27 would be formed (Scheme 12).
Scheme 12
Indeed, complex 25 will isomerize in hexanes solution when exposed to sunlight for extended time periods (7d) to produce complex \([\text{Os}_3(\text{CO})_9(\mu-\text{SMe})(\mu_3-\text{C}_4\text{H}_3\text{S})]\) (27) (Scheme 12 and 13). The thienyl group in 27 caps the \(\text{Os}_3(\text{CO})_9\) unit by coordinating \(\eta^1(\text{S})\), \(\eta^2\)-through the C2-C3 double bond and \(\eta^1\)-at the 2-position to the Os metal centers. Complex 27 was characterized spectroscopically (\(^1\text{H NMR}\)), and is possibly a result of the pathway shown in Scheme 12. However, it was observed that when a CD\(_2\)Cl\(_2\) solution of 23 was placed in direct sunlight for 3 d, the new complex 26 and also the previously described 27, were both observed and isolated in 19% and 71% yield, respectively. The new triosmium species, \([\text{Os}_3(\text{CO})_{10}(\mu-\text{SMe})(\mu_2-\text{C}_4\text{H}_3\text{S})]\) (26), consists of a bridging \(-\text{SMe}\) ligand and a thienyl functionality that bridges the \(\text{Os}_3\) core both \(\eta^1\) through the 2-carbon and \(\eta^1(\text{S})\) through the thiophene as in 27. Complex 26 will undergo either thermal or photochemical loss of a CO ligand to produce 27 in which there is \(\eta^2\)-binding of the thienyl group at the vacant Os metal center (Scheme 13).
In conclusion to this section, it has been demonstrated that both thermal and photochemical reactions of Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$ (14) with thiophenic molecules leads to complexes that contain thiophene ligands that are modified by C-H or C-S bond cleavage or by complete desulfurization. Surprisingly, no intermediate complexes were observed that contain only coordinated thiophenes. The Os complex systems described in the preceding section have exhibited a variety of reactivity with thiophenes and benzothiophenes resulting in new and novel HDS model systems. To our knowledge, no examples of Os-thiophene complexes have been observed resulting from Os$_3$(CO)$_{12}$.

**Co$_4$(CO)$_{12}$**

As a promoter, cobalt is an important component of the Co-Mo/Al$_2$O$_3$ catalyst system used in the commercial HDS of petroleum feeds.\(^1\) Despite its importance in this process, very few reactions have been reported for thiophenes and benzothiophenes with cobalt cluster complexes. Recently, Chen and Angelici\(^{20}\) found that Co$_4$(CO)$_{12}$ will react with DBT in refluxing hexanes to produce the π-bound complex (η$^6$-DBT)Co$_4$(CO)$_9$ (28) in moderate yield (44%) (Scheme 14).

\[ \text{Co}_4(\text{CO})_{12} \text{ or } \text{Co}_2(\text{CO})_8 + \]

\[ \quad \text{[Diagram]} \quad \text{28} \]

**Scheme 14**
The molecular structure of 28 contains a Co₄(CO)₉ tetrahedral fragment in which the benzo ring of the DBT ligand is π-bound to one of the Co centers. Furthermore 28 reacts in refluxing n-butyl ether with Cr(CO)₆ to give the previously reported (η⁶-DBT)Cr(CO)₃ (29) and the new complex (η⁶-DBT)[Cr(CO)₃]₂ (30) in which both Cr(CO)₃ units are on opposite sides of the DBT ring (Scheme 15).

Surprisingly, (η⁶-DBT)Co₄(CO)₉ also reacts with (CO)₃Cr(CH₃CN)₃ to give an η⁶-benzene complex, (η⁶-benzene)Co₄(CO)₉ (31) in 41% yield. It is unclear as to how the desulfurization and fragmentation of the DBT ligand occurs as no organic products were identified. Benzothiophene also reacts with Co₄(CO)₁₂ to give 31 in 41% isolated yield with no evidence of an η⁶-bound BT intermediate complex such as that found for DBT.

\[
28 + (CO)_3Cr(CH_3CN)_3 \rightarrow 29 + 30
\]

Scheme 15

Organometallic sulfide clusters

Curtis and coworkers prepared a series of mixed metal sulfido clusters that are similar in composition to commercial HDS catalysts. For example, the complex Cp₃Co₂Mo₂(CO)₄S₃ (32), when supported on alumina and then sulfided produces a sulfided cluster species that has been proposed to contain the same active sites as those found in commercial HDS catalysts. In the homogeneous phase, complex 32 reacts with thiophene at
150 °C to produce the cubane cluster $\text{Cp'}^2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ (33) quantitatively along with a carbon-based black residue following desulfurization of the thiophene (Scheme 16).\textsuperscript{24} In the presence of $\text{H}_2$ (150 °C, 200 psi), complex 32 reacts with thiophene to form complex 33. A GC/MS analysis of the head gases showed the presence of methane, ethane, propane, ethylene, butane, propene and butenes. The black residue obtained in the absence of $\text{H}_2$ was not evident in this reaction. Notably, when 32 is heated in toluene alone (150 °C), complex 33 is not formed thereby ruling out decomposition of 32 to form complex 33.

Complexes 32 and 33 are both inert towards $\text{H}_2$ (150 °C, 500 psi) if thiophene in not present, thereby supporting the possibility that hydrogenation and hydrogenolysis of the thiophene takes place through an intermediate thiophene-sulfide-cluster complex which could exhibit any of the binding modes in Scheme 2. No bound thiophene-cluster intermediates were observed or isolated, during the desulfurization reactions. In an effort to create thiophene-containing complexes \textit{in situ}, 32 was reacted with alkynes such as PhCCH and RCCR ($R = \text{H, Pr or Ph}$);\textsuperscript{25,26} however, only sulfided-clusters of the type $\text{Cp'}^2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_3(\mu_3-\text{RCCR})$ (34) and the alkyne coupled complex $\text{Cp'}^2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_3$...
(\(\mu_3\)-RCCR\(_2\)) (35) containing molybdacyclopentadiene moieties were formed (Scheme 17). Sulfur was not incorporated into the metallacyclopentadienes to give thiophenes in these reactions. The bow-tie complex 34 was reacted further with excess alkynes to yield complexes of type 35 in high yields. An attempt to prepare a thiophene adduct by addition of propylene sulfide to 35 did not give a product in which sulfur was incorporated into the molybdacyclopentadiene.

Complex 32 reacts with organic thiols (RSH) by extracting a sulfur atom to produce the cubane cluster 33 quantitatively, and the corresponding hydrocarbon RH (R = t-butyl or Ph). Sulfur abstraction was also reported from isothiocyanates (RNCS) by cluster 32 to produce a variety of clusters that are similar to both 32 and 33 in which CO ligands have
been replaced by isocyanide (RCN) groups (Scheme 18). These complexes were
categorized spectroscopically\textsuperscript{24,26} however, they were not characterized using X-ray
diffraction studies.

![Scheme 18](image)

In order to develop a homogeneous catalytic process, employing 32 and 33 as the
catalysts, it had to be shown that 33 could be converted back to 32 in the presence of H\textsubscript{2}.
While complex 33 did react with H\textsubscript{2} or CO/H\textsubscript{2} (50 psi, CO and 400 psi H\textsubscript{2}, 200 °C), it also
produced other sulfided clusters of which did not include 32. Only at pressures exceeding
1000 psi of CO and 150 °C did 33 convert to 32, but the conversion was low. Desulfurization
of thiophene by cluster 32 in the presence of both CO and H\textsubscript{2} at high pressures did not occur.
Since thiophene adsorption at a vacant metal site on cluster 32 is a likely prerequisite to
desulfurization, the presence of excess CO probably inhibits the thiophene binding thereby making desulfurization unlikely under these conditions.\textsuperscript{26}

In an effort to support the possibility of a thiophene adduct of 32 as an intermediate in the thiophene desulfurization reaction presented in Scheme 16, complex 32 was reacted with isolobal analogs of H\textsubscript{2}S, such as PH\textsubscript{2}R to form P-bound clusters.\textsuperscript{26,27} Cluster 32 readily reacts with alkyl phosphines at 80 °C (1 h) to afford Cp\textsubscript{2}Mo\textsubscript{2}Co\textsubscript{2}S\textsubscript{3}(CO)\textsubscript{3}(\eta\textsuperscript{1}(P)-PH\textsubscript{2}R) (36) in 65% yield (Scheme 19) with loss of CO. The reaction of 36 with excess PH\textsubscript{2}R in refluxing benzene produced the phosphinidene cluster 37 and the CO-substituted phosphinidene adduct 38.

\[
32 + \text{PH}_2\text{Ph} \xrightarrow{80 \, ^\circ \text{C}, \, 1 \, \text{h}} \text{36}
\]

\[
\text{36} \xrightarrow{80 \, ^\circ \text{C}} \text{PH}_2\text{Ph} \rightarrow \text{37} + \text{38}
\]

\textbf{Scheme 19}
These complexes are structurally similar to 33, except a bridging PR group in 37 has replaced a sulfide ligand in 33. Complex 38 is readily converted into 37 by reaction with CO at room temperature. These results suggest that similar intermediates in the reactions of thiophenes (Scheme 16) with H₂S may also occur, but on a faster time scale such that intermediates containing these moieties cannot be observed.

In more recent studies by the Curtis group,²⁸,²⁹ evidence has been found for the coordination of thiols and thiolates to 32. Based on a series of 'H NMR studies, cluster 32 was proposed to have reacted with tetraethylammonium p-toluenethiolate at 213 K to give the red complex 32a in which the thiolate (RS) binds to a Co metal center and facilitates opening of the cluster (Scheme 20). Upon increasing the temperature to 249 K, the solution
changed from red to green, CO was evolved, and a new complex, \( \text{Cp}_2\text{Mo}_2\text{Co}_2\text{S}_3(\text{CO})_4(\text{SAr})^{-1} \) (39), was detected. Upon warming in CD$_3$CN solvent, 39 was converted into the radical anion 33b. The only other detectable product in the reaction was \( d_1 \)-toluene as a result of homolytic C-S bond cleavage and radical abstraction of a deuterium (D) from the solvent by the \( p \)-tolyl radical. The structure of 33b was confirmed by X-ray analysis which showed a notable increase in the Co-Co distance from 2.56 Å (reported for parent 33) to 2.75 Å (in 33b) which is consistent with an electron occupation of the Co-Co \( \sigma^* \) orbital.

In conclusion to this section, Mo/Co/S clusters have been shown to model HDS reactions by desulfurizing thiophenes. No coordinated thiophene complexes were observed, but their existence has been supported by the success in reacting PH$_2$R with clusters to give phosphine adducts (37 and 38); and in the reaction of 32 with thiols and thiolates to give 32a, 33b and 39. Although the clusters 32 and 33 are not catalytic in the desulfurization of thiophenes, much can be learned about the desulfurization process through the use of this model system primarily due the presence of representative catalytic metals (Co and Mo) within the infrastructure of these clusters.

**Organometallic Hydride Clusters**

Only one metal-hydride cluster has been used in HDS modeling studies. One example involves the reaction of \((\text{Cp}^*\text{Ru})_3(\mu-\text{H})_3(\mu_3-\text{H})_2\) (40) with BT and DBT in toluene solution to give both C-S cleaved and desulfurized thiophenic cluster complexes (Scheme 21).\(^{30}\) When complex 40 reacts with BT in toluene (50 °C), hydrogen is evolved (16 h) and the C-S cleaved BT complex \( \text{Cp}^*\text{Ru}_3\text{H}_3(\mu-\text{BT}) \) (41) is formed as an intermediate which was characterized by \(^{1}\text{H} \) NMR spectroscopy. Intermediate 41 slowly converts into the desulfurized BT complex 42 following pseudo-first order kinetics. The molecular structure
of 42, obtained by X-ray diffraction studies, shows that the triangular Cp*Ru trimer backbone is capped on one face by a \( \mu_3 \)-sulfido group and on the opposite face by a C-CH\(_2\)Ph moiety. The \( \mu_3 \)-C-CH\(_2\)Ph functionality is formed presumably from hydrogen transfer to the BT 3-carbon. Complex 42 reacts further with H\(_2\) (7.2 atm) in THF to give the capped sulfido cluster \([\text{Cp}^*\text{RuH}]_3(\mu_3-S)\) (43) quantitatively with elimination of ethyl benzene.

![Scheme 21](image)

Dibenzothiophene reacts with cluster 41 in toluene (110 °C, 8 d) to also produce the sulfido cluster \([\text{Cp}^*\text{RuH}]_3(\mu_3-S)\) 43 (67%) and biphenyl (64%). No intermediate species were observed in this conversion of DBT to biphenyl, but a DBT ring-opened cluster similar to 41 could be involved.
Conclusions

Organometallic clusters, which contain various ligands such as CO, μ-H, μ-S or phosphines and multiple metal centers have been shown to react with thiophenes in ways that suggest possible steps in the mechanisms that lead to the hydrodesulfurization of thiophenes at three or more metal centers. Examples of thiophene coordination, C-S and C-H bond cleavage and desulfurization of thiophenes and benzothiophenes have been discussed throughout this review. Unlike the typical reactions of thiophenes with mononuclear metal centers of complexes which often give products containing intact thiophenes coordinated to the metal center, reactions with cluster complexes rarely give simple coordinated thiophene complexes. Instead, clusters typically undergo reactions that lead to products which contain bond cleaved or fragmented thiophene ligands. Furthermore, much can be learned from ongoing studies of cluster reactions with organosulfur substrates with potential for the design of new homogeneous catalysts. Exploring mixed metal clusters containing hydridies and simple ligands (such as CO or phosphines) could lead to new useful models for thiophene activation at metal centers.

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2. ORGANOMETALLIC MODELS OF CATALYTIC HYDRODESULFURIZATION: Re₂(CO)₁₀-PROMOTED CLEAVAGE OF C-S BONDS IN BENZOTHIOPHENE

A paper published in the Journal of the Chemical Society; Chemical Communications

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Abstract

Ultraviolet photolysis of hexanes solutions containing Re₂(CO)₁₀ and benzothiophene (BT) give the C-S cleavage product Re₂(CO)₇[η²(C₂,C₃)-μ₂(C₂,S)-BT] (1) which reacts with PMe₃ at room temperature to yield two phosphine-substituted products, 2 and 3, in which the fragmented BT ligand is partially displaced from the metals; molecular structures of 1, 2, and 3 are models for possible intermediates in the HDS of BT on catalyst surfaces.

Introduction

Heterogeneous catalytic hydrodesulfurization (HDS), the commercial process used for the removal of sulfur from organosulfur compounds present in petroleum-based feedstocks, is important in industry and for the environment. Typically, the sulfur in crude petroleum is present in the form of organic thiols, sulfides, disulfides, and thiophenes. It is the thiophenic molecules, however, such as benzothiophene (BT) that are the most difficult to desulfurize under current hydrotreating conditions. In order to improve the efficiency of current HDS catalytic systems, much needs to be learned about intermediates that are present on transition-metal sulfide-based catalysts during the HDS of benzothiophene.

Results and Discussion

The present paper reports preliminary results of reactivity studies of Re₂(CO)₁₀ with BT under mild conditions to produce the C-S cleavage product (1) containing a Re-Re backbone.
Upon addition of PMe₃ to 1, two unexpected, phosphine substitution products are formed (2 and 3) in which both the C-S and Re-Re bonds have been cleaved (Scheme 1).

Complex 1 was prepared by UV photolysis (Hanovia 450 W, medium pressure Hg lamp) of a stirred hexanes solution containing Re₂(CO)₁₀ and 2 eqv. of BT in a quartz reaction vessel under nitrogen for 24-36 h at 10 °C. The progress of the reaction was monitored by IR spectroscopy of samples taken during the reaction. The IR bands corresponding to Re₂(CO)₁₀ (vCO hexanes: 2071 (w), 2015 (s), 1977 (m) cm⁻¹) were gradually replaced by those of 1 (vCO hexanes: 2099 (m), 2043 (s), 2027(s), 1981 (s), 1977 (s), 1957 (m), 1947(s) cm⁻¹). Solvent removal, followed by extraction with CH₂Cl₂ and column chromatography on silica gel packed in hexanes, produced orange 1 in 30-45% yield.¹,²
The molecular structure of 1 was confirmed by single crystal X-ray structure analysis (Figure 1). It contains a bridging BT ligand in which the vinylic C-S bond of the BT has been cleaved, and 3 CO ligands have been displaced from the Re$_2$(CO)$_{10}$. The sulfur bridges both Re atoms asymmetrically with distances of 2.506(2) Å for Re(1)-S and 2.431(3) Å for Re(2)-S. The vinyl carbon also bridges the two Re atoms asymmetrically acting as a $\eta^1$-ligand to Re(1) and $\eta^2$ to Re(2) with distances of 2.142(10) Å for Re(1)-C(8) and 2.208(10) Å for Re(2)-C(8). The Re-Re distance (2.8945(7) Å) is shorter than that in Re$_2$(CO)$_{10}$ (3.0413(11) Å). Other previously reported dinuclear complexes, prepared by quite different methods, that contain a similar bridging BT ligand are Fe$_2$(CO)$_5$(PPh$_3$)(C$_8$H$_6$S)$^6$ and [Cp$^*$Co]$_2$(μ-C$_8$H$_6$S)$^7$.

The addition of PMe$_3$ (1-5 equiv) (1 M in toluene) to a toluene solution of 1 at room temperature causes an immediate color change from orange to pale yellow with no evolution of CO. Solvent removal, extraction with CH$_2$Cl$_2$, and fractional crystallization of the crude residue produced yellow crystals of 2 and white 3. Both complexes have been characterized spectroscopically$^8$ and by X-ray structure analysis of their single crystals.

The X-ray structure of 2 (Figure 2)$^6$ shows that the C(1)-C(2) double bond is no longer $\eta^2$-coordinated and the Re-Re bond has been cleaved. Both Re atoms are pseudo-octahedral and each contains a PMe$_3$ ligand. The S bridges both Re atoms almost symmetrically with distances of 2.5027(9) Å for Re(1)-S and 2.5320(9) Å for Re(2)-S.

A single crystal X-ray analysis of 3 (Figure 3)$^8$ shows that there are no single atom bridges between the two Re centers nor is there a metal-metal bond. The Re centers are pseudo-octahedral with respect to the C-Re-C angles between Re and adjacent CO ligands. The
Re(1)-C(1) distance is 2.205(3) Å which is longer than that in either 1 or 2. The Re(2)-S distance is 2.5086(9) Å which is similar to those in both 1 and 2.

In the reaction (Scheme 1) of 1 with PMe3, the relative amounts of 2 and 3 formed are the same whether 1 or 5 equivalents of PMe3 are used. This means that the tri-phosphine product 3 is not formed from the di-phosphine product 2 even in the presence of excess PMe3. Therefore 2 and 3 must form by independent pathways. The structures of 2 and 3 are also fundamentally different from each other because the terminal vinyl carbon is bound to the Re(CO)3 unit in 2 whereas in 3 it is coordinated to the Re(CO)4 group. The formation of these products may be understood in terms of a mechanism that involves two forms of 1 resulting (Scheme 2) either from a “flip-flop” of the vinyl group from one Re to the other, as

![Scheme 2](image)

proposed for related bridging thiophene complexes (Fe2(CO)6(C8H6S)6, [(C5Me5)Co]2(μ-C4H4S)8, and [(dippe)Ni]2(μ-C8H6S)9), or the migration of a CO group from one Re to the other.

The reaction of isomer 1’ with two equiv. of PMe3 would lead to product 2 in which the olefin is displaced and the Re-Re bond is cleaved, leaving the terminal vinyl carbon coordinated to the Re(CO)3 unit. On the other hand, the reaction of isomer 1 with three
equiv. of PMe₃ would lead to product 3 with the vinyl carbon bonded to the Re(CO)₄ moiety while undergoing Re-olefin, Re-S and Re-Re bond cleavages. An attempt to detect the two isomers of 1 by low temperature (-50 °C, CD₂Cl₂ solvent) ¹H NMR spectroscopy showed only the same isomer that is present in the room temperature spectrum. However, variable temperature ¹³C NMR spectra of 1 (-50 °C to +20 °C) showed that the CO ligands are fluxional. Thus, while the two isomers are not detected by the NMR studies, a low concentration of the highly reactive 1' would reasonably account for the formation of 2.

Conclusions and Acknowledgements

The reactions in Scheme 1 are of special interest because they indicate the variety of ways that a bridging, C,S-cleaved BT ligand can bind to two metal centers. Were C-S cleavage to occur on a HDS catalyst, all three forms of BT represented in compounds 1-3 would be potential modes of BT adsorption on the catalyst surface.

The authors thank the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, under contract W-7405-Eng-82 with Iowa State University for financial support.

Experimental Data

† Iowa State University Molecular Structure Laboratory.

¥ Satisfactory elemental analyses were obtained for 1-3.

⊗ Selected spectroscopic data for 1: ¹H NMR (CD₂Cl₂, 300 MHz) δ 8.63 (d, 1 H, J=11.4 Hz), 7.11 (m, 2 H), 7.05 (dt, 1 H, J₁=7.5 Hz, J₂=1.5 Hz), 7.00 (d, 1 H, J=11.4 Hz), 6.93 (dt, 1 H, J₁=7.2 Hz, J₂=1.5 Hz). IR (hexanes) νCD₂Cl₂: 2099 (m), 2043 (s), 2027 (s), 1981 (s), 1977 (s), 1957 (m), 1947 (s) cm⁻¹. For 2: ¹H NMR (CD₂Cl₂, 300 MHz): 8.06 (dd, 1 H, J₁=14.1 Hz, ...
J_2=2.4\ \text{Hz}),\ 7.44\ (dd,\ 1\ \text{H},\ J_1=14.1\ \text{Hz},\ J_2=3.6\ \text{Hz}),\ 7.26\ (d,\ 1\ \text{H},\ J=7.8\ \text{Hz}),\ 7.00\ (m,\ 2\ \text{H}),\ 6.87\ (m,\ 1\ \text{H}),\ 1.87\ (d,\ 9\ \text{H},\ \text{PMe}_3,\ J=9.3\ \text{Hz}),\ 1.19\ (d,\ 9\ \text{H},\ \text{PMe}_3,\ J=8.4\ \text{Hz}).\ \text{IR (CH}_2\text{Cl}_2)\ \nu_{\text{CO}}:\ 2100\ (w),\ 2003\ (s),\ 1953\ (m,\ \text{br}),\ 1896\ (m,\ \text{br}),\ 1873\ (m,\ \text{br})\ \text{cm}^{-1}.\ \text{For 3: 'H NMR (CD}_2\text{Cl}_2,\ 300\ \text{MHz}:\ 7.89\ (dd,\ 1\ \text{H},\ J_1=13.5\ \text{Hz},\ J_2=3.9\ \text{Hz}),\ 7.43\ (dd,\ 1\ \text{H},\ J_1=7.8\ \text{Hz},\ J_2=1.2\ \text{Hz}),\ 7.21\ (d,\ 1\ \text{H},\ J=7.2\ \text{Hz}),\ 6.99\ (dt,\ 1\ \text{H},\ J_1=7.5\ \text{Hz},\ J_2=1.5\ \text{Hz}),\ 6.92\ (m,\ 2\ \text{H}),\ 1.62\ (m,\ 27\ \text{H},\ 3\text{PMe}_3).\ \text{IR (CH}_2\text{Cl}_2)\ \nu_{\text{CO}}:\ 2079\ (w),\ 2018\ (s),\ 1978\ (s,\ \text{sh}),\ 1972\ (s),\ 1933\ (s),\ 1893\ (s)\ \text{cm}^{-1}.

§ Crystal data for C_{15}H_{6}O_{7}Re_2S: M = 702.66, triclinic, P\bar{\text{T}}, a = 9.167(1), b = 12.544(1), c = 16.019(2) \text{Å}, V = 1668.3(2) \text{Å}^3, Z = 4, T = 293(2) K, \mu = 14.659 \text{mm}^{-1}, 5258 reflections collected, 4337 unique (R_{int} = 0.0312), R1 = 0.0311, wR2 = 0.0796 [I>2\sigma(I)]. Single crystals of 1 were grown from CH_2Cl_2 and hexanes at -15 °C. There are two independent molecules of complex 1 in the asymmetric unit; however since the bond lengths and angles are similar between the two molecules, only structural data for one of them is given above.

ζ Crystal data for C_{21}H_{24}O_{7}P_{2}Re_2S: M = 854.80, monoclinic, P2_1/n, a = 8.1110(4), b = 27.1151(13), c = 12.3490(6) \text{Å}, V = 2655.7(2) \text{Å}^3, Z = 4, T = 173(2) K, \mu = 9.344 \text{mm}^{-1}, 23953 reflections collected, 6297 unique (R_{int} = 0.0394), R1 = 0.0231, wR2 = 0.0331 [I>2\sigma(I)]. Single crystals of 2 were grown from CH_2Cl_2 and hexanes at -15 °C and separated by hand from a mixture of 2 and 3.

ϕ Crystal data for C_{24}H_{33}O_{7}P_{3}Re_2S: M = 930.87, orthorhombic, Pbca, a = 9.6900(4), b = 25.4267(12), c = 25.8065(13) \text{Å}, V = 6358.3(5) \text{Å}^3, Z = 8, T = 173(2) K, \mu = 7.862 \text{mm}^{-1}, 57303 reflections collected, 7716 unique (R_{int} = 0.0583), R1 = 0.0242, wR2 = 0.0327
[I>2σ(l)]. Single crystals were grown from CH₂Cl₂ and hexanes at -15 °C and separated by hand from a mixture of 2 and 3.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI). The absorption corrections were applied by using program DIFABS (Walker, N. and Stuart, D. in Acta Cryst., 1983, A39, 158) for 1 and SADABS (Blessing, R. H., Acta Cryst., 1995, A51, 33-38) for 2 and 3.

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Figure 1. Molecular structure of 1 in the solid state. Selected bond lengths (Å) and angles (°): Re(1)-Re(2) 2.8945, Re(1)-S 2.506(2), Re(2)-S 2.431(3), Re(1)-C(8) 2.142(10), Re(2)-C(8) 2.208(10), Re(2)-C(9) 2.413(11), C(8)-C(9) 1.370(14), S-C(15) 1.805(11), Re(2)-S-Re(1) 71.77(7), Re(1)-C(8)-Re(2) 83.4(3), C(8)-Re(2)-S 82.8(3); C(8)-Re(1)-S 82.3(3), C(8)-C(9)-C(10) 126.6(10).
Figure 2. Molecular structure of complex 2 in the solid state. Selected bond distances (Å) and angles (°): Re(1)---Re(2) 4.2874(3), Re(1)-S 2.5027(9), Re(2)-S 2.5320(9), C(8)-S 1.796(3), Re(1)-C(1) 2.169(3), C(1)-C(2) 1.343(5), Re(1)-S-Re(2) 116.76(3), C(1)-Re(1)-S 86.51(10), Re(1)-S-C(8) 109.94(12), Re(2)-S-C(8) 105.40(12), P(1)-Re(1)-S 87.24(3), P(2)-Re(2)-S 88.04(3).
Figure 3. Molecular structure of 3 in the solid state. Selected bond distances (Å) and angles (°): Re(1)-C(1) 2.205(3), Re(2)-S 2.5086(9), C(1)-C(2) 1.327(4), S-C(8) 1.769(3), C(2)-C(3) 1.479(4), Re(1)-C(1)-C(2) 134.8(3), C(8)-S-Re(2) 113.18(12), P(2)-Re(2)-S 84.54(3), C(1)-C(2)-C(3) 129.8(3), C(1)-Re(1)-P(1) 82.44(8).
3. HOMOGENEOUS MODELS FOR CATALYTIC HYDRODESULFURIZATION: Re₂(CO)₁₀ MEDIATED C-H AND C-S BOND CLEAVAGE IN DIBENZOTHIOPHENE AND 2,5-DIMETHYLTHIOPHENE

A paper to be submitted to the Journal *Organometallics*

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Abstract

Ultraviolet photolysis of Re₂(CO)₁₀ and excess dibenzothiophene (DBT) in the non-coordinating solvent hexanes produces the S-bound eq-Re₂(CO)₉(η¹(S)-DBT) (1) and the novel C-H cleaved DBT complex Re₂(CO)₈(μ-C₁₂H₁₇S)(μ-H) (2). Under similar conditions, Re₂(CO)₁₀ reacts with excess 2,5-dimethylthiophene (2,5-Me₂T) to give the interesting C-S cleaved 2,5-Me₂T complex Re₂(CO)₇(μ-2,5-Me₂T) (3) as the only product. The photolysis reactions of Re₂(CO)₁₀ with DBT and 2,5-Me₂T were inhibited by CO (1 atm) and also by the radical scavenger TEMPO, which suggests that both CO dissociation and homolytic Re-Re bond cleavage are involved. The η¹(S)-bound thiophene complexes 1 and Re₂(CO)₉(η¹(S)-2,5-Me₂T) (5) were prepared from Re₂(CO)₉(THF) (4). The DBT ligand in 1 is labile and rapidly (< 2 min) reacts with CO (1 atm) to form Re₂(CO)₁₀ in 1,2-DCE. Based on its X-ray structure, complex 1 has one of the smallest tilt angles (θ = 113°) observed for a metal-thiophene complex, which may be understood in terms of π-back bonding arguments. Complexes 1-3 were characterized by spectroscopic (IR, NMR) methods and by their structures that were determined by X-ray crystallography. Mechanisms for the formation of 1-3 are presented and discussed.
Introduction

Hydrodesulfurization (HDS), the catalytic hydrotreating process used for removing sulfur from organosulfur compounds present in petroleum feedstocks, is important for two primary reasons. First, current US Federal regulations require refineries to reduce gasoline sulfur levels by as much as 300 ppm (by the year 2004) in order to decrease the amount of sulfur oxides \( (\text{SO}_x, x = 2, 3) \) produced during the combustion of petroleum fuels. These sulfur oxides are known precursors to acid rain and present a significant threat to the environment. Second, sulfur poisons precious metal reforming catalysts, which consequently increases the cost of petroleum reforming. The sulfur in crude petroleum, whose amount ranges from 0.2-4%\(^{2,4}\), is present in the form of thiols (RSH), thioethers (RSR), disulfides (RSSR) and thiophenes (T*) such as thiophene (T), benzo thiophene (BT) and dibenzothiophene (DBT) (Scheme 1).

**Scheme 1**

![Chemical structures](image-url)
It is the thiophenic compounds, however, that are the most difficult to desulfurize under current commercial hydrotreating conditions due to aromatic stabilization of the thiophene and benzothiophene rings.5

The common commercial HDS catalysts are typically MoS2 or WS2 promoted by Co or Ni on an alumina support, but several other metal sulfides, MSx (M = Ru, Re, Os, Rh, and Ir) have demonstrated higher catalytic activity for the desulfurization of thiophenes and benzothiophenes under various hydrotreating conditions.6,7 The most active catalysts are those of the second-(such as Ru and Rh) and third-(such as Re, Os and Ir) row elements, but their high costs prevent them from being used commercially.2

Organometallic modeling of possible thiophene binding modes and ring-opened intermediates formed at transition metal centers is one approach to better understanding how desulfurization might occur in the commercial HDS catalytic process. Examples of organometallic complexes that contain thiophenes and benzothiophenes bound to transition metal centers through many different binding modes (i.e.; η1(S), η2, η4, η5 and η6)8-10 are known. Several organometallic complexes of ring-opened thiophenes and benzothiophenes at single metal centers have also been reported;11-13 however, there are few reports of such complexes with two or more metals. Some recent examples of bimetallic complexes in which a C-S bond of the thiophene ligand is cleaved are Mn2(CO)7(μ-T*)14-17, [(dippe)Ni]2(μ-T*)18, Fe2(CO)6(μ-T*)19,20 (T* = T or BT), and Re2(CO)7(μ-BT)21. Sweigart et al.14-17 described the synthesis of the C-S cleaved thiophene complexes Mn2(CO)7(μ-T*) by reduction of [(η5-T)Mn(CO)3]+ and [(η6-BT)Mn(CO)3]+. Jones and Vicic18 recently reported that the bimetallic Ni complex, [(dippe)Ni(H)]2, reacts with T or BT under mild
conditions (22 °C) in hexanes solvent, with loss of H₂, to produce the metal inserted thiophene-based metallacycles (dippe)Ni(η²-C,S-T) and (dippe)Ni(η²-C,S-BT). Both complexes react further in solution to give the bimetallic species [(dippe)Ni]₂(μ-T) and [(dippe)Ni]₂(μ-BT) respectively, which contain bridging, ring opened thiophenes.

Building on previous studies¹⁹, Rauchfuss²⁰ reported both C-S cleavage and desulfurization of thiophenes and benzothiophene during thermolysis with Fe₃(CO)₁₂ to obtain the thiaferroles Fe₂(CO)₆(μ-T*)¹⁹,²⁰ (T* = T and BT) and, in the case of thiophene, ferroles such as Fe₂(CO)₆(C₄H₄) resulting from metal insertion and desulfurization of the parent thiophene ligand.

Recently, we reported the preparation of the C-S cleaved BT complex Re₂(CO)₇(μ-BT)²¹, prepared by UV irradiation of Re₂(CO)₁₀ and benzothiophene (BT) in hexanes solvent (Scheme 2). In this novel bimetallic Re complex, the BT ligand is opened at the Cᵥinyl-S position and bridges the two Re centers of a Re₂(CO)₇ moiety through both the S atom and the vinyl group which behaves as an η¹- and η²-ligand to the two Re centers. Our recent success in preparing this C-S cleaved benzothiophene (BT) complex, Re₂(CO)₇(μ-BT), according to Scheme 2 prompted us to investigate the reactivity of DBT and thiophenes, such as 2,5-Me₂T under similar conditions. Here we report our results of UV-light-promoted
reactions of dibenzothiophene (DBT) and 2,5-dimethylthiophene (2,5,-Me₂T) with Re₂(CO)₁₀ to afford dinuclear Re complexes with S-bound, C-H cleaved, and C-S cleaved thiophene ligands.

Experimental Section

**General Considerations.** All reactions were performed under a nitrogen or argon atmosphere in reagent grade solvents, using standard Schlenk techniques. Hexanes, THF, ethyl ether and methylene chloride were dried and purified using the Grubbs solvent purification process purchased from Solv-Tek, Inc. Benzene was dried over CaH₂ and then distilled prior to use. Deutero-methylene chloride (Cambridge) was stored over 4 Å molecular sieves. Rhenium carbonyl was purchased from Strem Chemicals Inc. Dibenzothiophene and 2,5-dimethylthiophene were purchased from Aldrich Chemical Co. and used without further purification. TEMPO (2,2,6,6,-tetramethyl-1-piperidinyloxy free radical) was purchased from Aldrich Chemical Co. Trimethylamine oxide hydrate (Aldrich) was dried by azeotropic distillation of the water from benzene. Silica gel (J.T. Baker, 40-140 mesh) was dried under vacuum for 14 h and stored under argon prior to use. Neutral alumina (Aldrich, Brockmann I) was dried under vacuum for 14 h and treated with 10% (by weight) water under argon with vigorous shaking.

The ¹H NMR spectra for all complexes were recorded on either a Varian VXr-300 MHz or an in-house 400 MHz NMR spectrometer using the deuterated solvent as both internal lock and internal reference. Solution infrared spectra were recorded on a Nicolet-560 spectrophotometer using NaCl cells with 0.1 mm spacers. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. All photochemical reactions were carried out in a 40 mL capacity quartz, Schlenk photolysis tube fitted with a cold-finger
which was immersed into the reaction solution. Irradiation was performed using a Hanovia 450 W Hg medium pressure lamp as the light source (inserted into either a quartz or Pyrex, water-cooled jacket). The reaction temperature was controlled using an Isotemp 1013P refrigerated circulating bath (Fisher Scientific) with circulation hoses connected to the cold-finger.

Preparation of eq-Re₂(CO)₉(η¹(S)-DBT) (1) and Re₂(CO)₉(μ⁻C₁₂H₁₄S)(μ⁻H) (2). A hexanes solution (30 mL) of Re₂(CO)₁₀ (150 mg, 0.230 mmol) and DBT (82.6 mg, 0.448 mmol) was prepared under an Ar atmosphere in a quartz photolysis tube, equipped with a magnetic stir-bar. A cold-finger (15 °C) was immersed into the reaction solution and an oil bubbler was connected to the tube. The solution was irradiated under nitrogen for 18-24 h with stirring, during which time a light yellow solution containing a brown precipitate was produced. A yellow precipitate was also present above the solution on the sides of the tube. The solution was filtered into a Schlenk flask, and the solvent was removed under vacuum to produce a crude lemon-yellow solid residue containing complexes 1 and 2, unreacted Re₂(CO)₁₀ and DBT, and the Re cluster HRe₅(CO)₁₄⁻ (9<10% based on Re₂(CO)₁₀). The yellow residue on the photolysis tube wall was washed with hexanes (2 x 5 mL), dried in vacuo and dissolved in CH₂Cl₂. This solution was then filtered and the filtrate was combined with the lemon-yellow solid residue from the previous filtration. More CH₂Cl₂ was added to the now yellow-brown solution until all solids were dissolved (3-6 mL). The resulting solution was layered with hexanes and cooled (-20 °C) overnight. After 1 d, yellow crystals of complex 2 formed and complex 1 also precipitated from solution as a yellow powder. The crystals and yellow solid were filtered and dried in vacuo. Complexes 1 (9.2-28 mg, 5-15%) and 2 (18-36 mg, 10-20%) were separated by hand-picking crystals of 2 from the mixture.
Attempts to purify the crude mixture of products by chromatography on silica gel or alumina were unsuccessful due to decomposition. However, HRe₃(CO)₁₄ was recovered during chromatography of the crude mixture on silica gel. The crude powder of complex 1 was characterized by IR and ¹H NMR spectroscopy of the mixture of 1 and 2 and compared to an authentic sample that was prepared as described below from Re₂(CO)₉(THF) and DBT. For 2: ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.06 (m, 1 H), 7.87 (d, 1 H, J=7.2 Hz), 7.80 (d, 1 H, J=7.2 Hz), 7.69 (m, 1 H), 7.56 (m, 2 H), 7.21 (t, 1 H, J=7.2 Hz), -14.8 (s, 1 H). IR (hexanes): ν₃CO 2114 (w) 2087 (w), 2023 (vs), 2013 (s), 1995 (m), 1985 (s), 1958 (m). Anal. Calcd for C₂₀H₈O₈Re₂S: C, 30.77, H, 1.03; Found: C, 30.74, H, 1.03.

**Preparation of Re₂(CO)₇(C,S-Me₂T) (3).** A hexanes solution (30 mL) of Re₂(CO)₁₀ (204 mg, 0.313 mmol) and 2,5-Me₂T (0.20 mL, 1.76 mmol) was prepared in a quartz reaction tube equipped with a magnetic stir bar. The solution was irradiated with stirring for 15-20 h, at 15 °C under a constant flow of nitrogen. During this time, the solution turned yellow-orange and a brown precipitate formed. The solution was then transferred to a column of silica gel (1 x 8 cm) packed in hexanes. A yellow band eluted using a combination of CH₂Cl₂ and hexanes (1:5) and was collected. The volatiles were removed in vacuo leaving a yellow-orange oily residue which was then dissolved in CH₂Cl₂ (1 mL) and layered with hexanes (5 mL) followed by storage at -20 °C until yellow crystals of 3 formed (1 d). The solution was then filtered, and the yellow crystals of 3 (20-30 mg, 10-15% yield based on Re₂(CO)₁₀) were dried under vacuum. ¹H NMR (CD₂Cl₂) 400 MHz: δ 6.49 (d, 1 H, J = 6.0 Hz), 5.05 (d, 1 H, J = 5.6 Hz), 2.71 (s, 3 H, Me), 2.31 (s, 3 H, Me). IR (hexanes): ν₃CO 2093 (w), 2039 (s), 1993
Preparation of Re$_2$(CO)$_9$(thf) (4). Complex 4 was prepared using the following preparation (Method A) and a previously described procedure (Method B)$^{24}$. Method A: In a typical experiment, a THF solution (30 mL) of Re$_2$(CO)$_{10}$ (200 mg, 0.307 mmol) was prepared in a quartz photolysis tube equipped with a magnetic stir bar. A cold-finger was then inserted into the solution (10 °C) and an oil bubbler was connected to the tube. The solution was then irradiated with stirring under N$_2$ until the v$_{CO}$ bands for 4 reached a maximum (1-1.5 h). The solution of 4, which contains some residual Re$_2$(CO)$_{10}$, was then ready for use in further experiments (see below). Complex 4 was isolated as an impure orange-yellow oil by removing the solvent under vacuum. The oil also contained unreacted Re$_2$(CO)$_{10}$ (based on IR spectroscopy) and other unidentified impurities (based on $^1$H NMR spectroscopy).

Attempts to purify 4 on silica gel or alumina using THF as the solvent produced an orange band that did not elute in THF, CH$_2$Cl$_2$ or benzene solvents. $^1$H NMR (CD$_2$Cl$_2$) 300 MHz: $\delta$ 3.86 (m, 4 H), 1.89 (m, 4 H). IR (THF): 2101 (w), 2038 (m), 1987 (vs), 1980 (sh), 1952 (m), 1912 (m) cm$^{-1}$.

Preparation of Re$_2$(CO)$_9$(η$^1$(S)-T*) complexes, 1 and 5, from 4. Complex 1 (from Method A). A solution of Re$_2$(CO)$_9$(thf) (4) was prepared as described above (using Method A) from a THF (30 mL) solution of Re$_2$(CO)$_{10}$ (206 mg, 0.316 mmol). The solution of complex 4 was allowed to warm to room temperature followed by the addition of DBT (114 mg, 0.619 mmol) under argon with stirring. The orange-yellow solution lightened in color after 1-2 h, and stirring was continued for an additional 18 h. The solvent was then removed in vacuo, and the remaining yellow residue was extracted with CH$_2$Cl$_2$ (1 mL) and layered
with hexanes (5 mL) followed by cooling to -20 °C until crystals of 1 were produced (1-2 d).
The crystals were then filtered, washed with hexanes (2 x 10 mL) and dried producing pure 1
(70 mg, 27% based on Re2(CO)10). 1H NMR (CD2Cl2, 400 MHz): δ 8.17 (m, 2 H), 7.84 (m, 2 H), 7.61 (m, 4 H). IR (CH2Cl2): νCO 2102 (w), 2042 (m), 1988 (vs), 1963 (m), 1933 (m).
Anal. Calcd. For C21H8O9Re2S: C, 31.19, H, 1.00; Found C, 31.09, H 0.83.

Complex 1 (from Method B).24 A THF solution (20 mL) of Re2(CO)10 (306 mg, 0.469 mmol) was prepared in a 100 mL Schlenk flask equipped with a magnetic stir bar. Anhydrous Me3NO (35.6 mg, 0.475 mmol) was then added and the yellow solution was stirred for an additional 50 min. At this time, an IR spectrum of the solution showed νCO bands corresponding to complex 4. The volatiles (THF and NMe3) were then removed under vacuum followed by the addition of more THF (20 mL) and DBT (94.7 mg, 0.514 mmol) with stirring for an additional 15 h. The solvent was then removed in vacuo and the yellow residue was dissolved in CH2Cl2 (1-2 mL) and layered with hexanes (5-8 mL). Yellow crystals of 1 (128 mg, 34% based on Re2(CO)10) were grown after 1 d (-20 °C) and isolated after filtration, washing with hexanes (1 x 5 mL), and drying in vacuo.

Re2(CO)9(η1(S)-2,5-Me2T) (5). Complex 5 was prepared in a similar manner as 1 (Method A) from a solution of Re2(CO)9(thf) (0.222 mmol based on Re2(CO)10). The freshly prepared Re2(CO)9(thf) solution and 2,5-Me2T (0.150 mL, 1.32 mmol) were stirred at room temperature for 23 h during which time the solution lightened in color. The solvent and residual 2,5-Me2T were removed in vacuo leaving a yellow-brown oil. Attempts to purify the crude product by column chromatography on silica gel or neutral alumina were unsuccessful.
due to complete decomposition of 5. $^1H$ NMR (CD$_2$Cl$_2$) 300 MHz: δ 6.71 (s, 2 H), 2.42 (s, 6 H, Me’s). IR (hexanes): 2101 (w), 2047 (m), 1991 (s), 1987 (s), 1961 (m), 1928 (m) cm$^{-1}$.

**Crystallographic Structural Determinations of 1-3.** The single crystal X-ray diffraction experiments were performed on a Bruker CCD-1000 diffractometer for 1 and 3 and on a CAD4 diffractometer for 2. The systematic absences in the diffraction data were consistent for space groups $P1$ and $P\bar{1}$ for 1 and 3, and for space groups $Cc$ and $C2/c$ for 2. In all cases the latter centrosymmetric space groups were chosen based on the chemically reasonable and computationally stable results of refinement$^{24}$. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. The empirical absorption corrections for 1 and 3 were applied by using program SADABS$^{25}$ and by using program DIFABS$^{26}$ for 2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. In the case of 1, there was a severely disordered solvent molecule also present in the asymmetric unit. Attempts to identify and refine this molecule gave models that suggested the molecule was mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON$^{27}$ was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecules. PLATON calculated the upper limit of volume that can be occupied by the solvent to be 110.6 Å$^3$, or 9.4% of the unit cell volume. The program calculated 40 electrons in the unit cell for the diffuse species. This approximately corresponds to one dichloromethane molecule in the unit cell (42 electrons). All data in Table 1 reflect the presence of one half molecule of dichloromethane per molecule of complex in the lattice of 1. In the case of 2, the hydride ligand was restrained to be equidistant from the Re atoms.
Results and Discussion

Reaction of Re$_2$(CO)$_{10}$ with DBT. Irradiation of a stirred hexanes solution (10 °C) containing Re$_2$(CO)$_{10}$ and a 2-fold excess of DBT produced the bi- and tri-metallic Re complexes eq-Re$_2$(CO)$_9$(η$^1$(S)-DBT) (1), Re$_2$(CO)$_8$(μ-C$_{12}$H$_7$S)(μ-H) (2) and HRe$_3$(CO)$_{14}$ after 18-24 h (Scheme 3).

Hexanes was chosen as the reaction solvent because it is non-coordinating, inert during UV photolysis, and easy to remove under reduced pressure. No reaction occurred between Re$_2$(CO)$_{10}$ and DBT under similar conditions in either benzene or ethyl ether. The photolysis reaction of DBT (2-4 fold excess) and Re$_2$(CO)$_{10}$ in CH$_2$Cl$_2$ produced only (CO)$_5$ReCl$_2$ ($<10\%$) and Re$_2$(CO)$_8$(μ-Cl)$_2$ ($>90\%$) within 1 h, and no evidence for complexes 1 or 2 was observed. Although THF reacts with Re$_2$(CO)$_{10}$ during photolysis to give
Re$_2$(CO)$_9$(THF), no Re-DBT containing complexes were observed when Re$_2$(CO)$_{10}$ and DBT were irradiated in THF.

Complexes 1 and 2 were not completely separated since column chromatography of the mixture of 1 and 2 on either silica gel or neutral alumina resulted in decomposition of the complexes. However, crystals of complex 2 were formed together with a pale yellow powder (1) when the reaction mixture was crystallized. Yellow crystals of 2 were hand-picked from the mixture of 1 and 2.

Complex 1 is an air-stable solid that is soluble in CH$_2$Cl$_2$, CHCl$_3$ and aromatic solvents such as benzene, but sparingly soluble in hydrocarbons such as hexanes. The DBT ligand in 1 is labile and is completely replaced by CO to give Re$_2$(CO)$_{10}$ in 1,2-DCE solvent in less than 2 min. The X-ray structure of 1, discussed in more detail later, confirms S-binding of the DBT ligand in the equatorial position. Coordination of donor ligands to the equatorial position of Re$_2$(CO)$_9$ is common, and $eq$-Re$_2$(CO)$_9$(L) complexes are known for $L = CH$_3$CN$^{30}$, phosphines$^{31}$ and pyridine$^{32}$. When the donor ligand (L) is bulky, such as for $L = PPh$_3$^{31}$ then axial substitution dominates. No evidence of a disubstituted DBT-Re complex of the type Re$_2$(CO)$_8$(L)$_2$ was observed although disubstituted complexes are known for $L =$ phosphines$^{31}$ and pyridine$^{32}$.

The $^1$H NMR spectrum of 1 indicates S-binding of DBT because the ring proton signals are shifted only 0.05-0.12 ppm downfield in comparison to those of free DBT. This small shift is common for $\eta^1$(S)-bound DBT complexes such as CpRe(CO)$_2$(S)-DBT$^{33}$, [CpFe(CO)$_2$(S)-DBT]$^+$,$^{34}$ Cp*Ir(Cl)$_2$(S)-DBT$^{35}$, CpMn(CO)$_2$(S)-DBT$^{36}$, (CO)$_5$W(S)-DBT$^{36}$ and (CpSiMe$_2$Cp)Mo(S)-DBT$^{37}$. 
Complex 2 is a moderately air-stable yellow solid that is soluble in benzene, chloroform, CH₂Cl₂ and moderately soluble in hexanes. Crystals of 2, hand-picked from the mixture of 1 and 2, were characterized by elemental analysis, spectroscopic methods (¹H NMR and IR) and by X-ray diffraction studies. The IR spectrum for 2 is complicated and consists of 7 unique bands in the νCO region arising from the eight inequivalent CO ligands.

The ¹H NMR spectrum for 2 shows 6 signals in the aromatic region with chemical shifts in the range δ 8.06-7.21 ppm for the ring protons of the C-H cleaved DBT ligand. This spectrum differs from that of the DBT in complex 1 (δ 8.20-7.55 ppm) and free DBT (8.21-7.47 ppm), both of which have only 3 signals (multiplets) for the DBT ring protons in the aromatic region. A resonance signal for the hydride ligand was also observed in the spectrum of 2 with a chemical shift of -14.8 ppm, in a region which is characteristic of a bridging hydride residing between two Re metal centers as reported for other Re-H-Re complexes.³⁸,³⁹ Interestingly, Re₂(CO)₁₀ did not react with 4,6-dimethyldibenzothiophene (4,6-Me₂DBT) under photolysis conditions; only Re₂(CO)₁₀ and free 4,6-Me₂DBT were recovered.

Complex 2 is a rare, structural example of selective C-H cleavage in DBT at a transition metal center. Jones, et al.⁴⁰ reported complexes of Cp*Rh(PMe₃) which resulted from C-H bond cleavage of substituted dibenzothiophenes. These complexes were characterized spectroscopically (³¹P and ¹H NMR) and subsequently converted into complexes with C-S cleaved DBT ligands. More recently⁴¹, Os₃(CO)₁₀(CH₃CN)₂ was reported to react with DBT to give the triosmium, benzyne cluster, Os₃(CO)₅(μ-C₆H₆S)(μ-H)₂ in which the C-H bonds of DBT were cleaved in the 2- and 3-positions. This complex was proposed to form by initial DBT C-H bond cleavage to give the triosmium intermediate,
Os₃(CO)₁₀(μ-C₁₂H₇S)(μ-H). Although it was not detected, the formation of such an intermediate is supported by the isolation and characterization of complex 2.

**Reactions of Re₂(CO)₁₀ with Thiophenes.** UV photolysis of a hexanes solution (10 °C) containing Re₂(CO)₁₀ and a 3-5 fold excess of 2,5-Me₂T in a quartz photolysis tube produced the ring-cleaved thiophene complex Re₂(CO)₇(μ-2,5-Me₂T) (3) in 15-20% yield after 24 h (Scheme 4).

![Scheme 4](image)

Complex 3, which is soluble in most organic solvents such as benzene, CH₂Cl₂ and hexanes, is stable for months in air but will decompose in solution unless kept under an inert atmosphere. Separation of 3 from unreacted starting materials and other impurities was achieved by chromatography on silica gel packed in hexanes using CH₂Cl₂/hexanes (1:5) as the eluent.

Complex 3 has been characterized by IR and ¹H NMR spectroscopies, elemental analysis and also by an X-ray diffraction study. Its IR spectrum (in hexanes) shows 6 νₐ₅ bands at 2093 (w), 2039 (s), 1993 (s), 1990 (s), 1963 (m) and 1950 (vs) cm⁻¹. This spectrum
is similar to that of its Mn analog, Mn₂(CO)₇(μ-2,5-Me₂T)¹⁴ (in hexanes: 2079 (m), 2033 (vs), 1995 (s), 1991 (vs), 1969 (m) and 1958 (vs)) which was prepared using a very different synthetic method.

The ¹H NMR spectrum (in CD₂Cl₂) of complex 3 consists of two doublets at δ 6.49 and 5.05 ppm which correspond to the two inequivalent protons, H3 and H4, of the cleaved 2,5-Me₂T ligand. The chemical shifts of the H3 and H4 protons for 3 are similar to those observed in the Mn analog, Mn₂(CO)₉(μ-2,5-Me₂T)¹⁴, which has proton signals at δ 7.05 and 5.62 ppm (in d₆-acetone). The two inequivalent methyl groups in 3 were observed at δ 2.71 and 2.31 ppm in the ¹H NMR spectrum and are shifted 0.3 ppm downfield and 0.1 ppm upfield from those in free 2,5-Me₂T, which is also similar to those of the Mn analog. The free ligand exhibits a signal for the equivalent methyl groups at δ 2.41 ppm (in CD₂Cl₂). Complex 3 does not react with electrophiles such as triflic acid or methyl triflate (MeOSO₂CF₃). This is not surprising since the Mn analog also did not react with the same electrophiles due to the sulfur being non-nucleophilic.¹⁴a

The Mn analog of 3, Mn₂(CO)₇(μ-2,5-Me₂T), and several similar complexes with thiophene (T), 2-methylthiophene (2-MeT) and 3-methylthiophene (3-MeT) were reported previously as mentioned and are both structurally and spectroscopically similar to 3¹⁴b. However, in our hands, photolysis reactions of T, 2-MeT and 3-MeT with Re₂(CO)₁₀ in hexanes solvent and under similar conditions to those used in the preparation of 3 did not produce any isolable complexes. This lack of reactivity may be attributed to the fact that thiophene, 2-MeT and 3-MeT are weaker S-donor ligands⁴² than 2,5-Me₂T and may not form
the S-bounded precursor Re₂(CO)$_9$(η¹(S)-T*) (T* = T, 2-MeT or 3-MeT) to the C-S cleaved product analogous to 3.

**Preparation and Characterization of Re₂(CO)$_9$(THF) (4).** Complex 4 was prepared using two separate methods (A and B). The first, Method A, involves irradiation of a dry THF solution containing Re₂(CO)$_{10}$ at 10 °C with UV light (1-1.5 h), which produced a yellow-orange solution characterized as predominately 4 (>50). The second, Method B, was previously reported$^{24}$ and involves the removal of a CO ligand from Re₂(CO)$_{10}$ using anhydrous Me$_3$NO. Both methods yielded solutions with ν$_{CO}$ bands at 2101 (w), 2038 (m), 1987 (vs), 1980 (sh), 1952 (m) and 1912 (m) cm$^{-1}$, which correspond well to those previously reported for 4$^{24}$. Solvent removal under reduced pressure from solutions of 4 generated by either Method A or B gave an oily yellow-orange residue that was dried under vacuum and dissolved in CD$_2$Cl$_2$. The $^1$H NMR spectrum of this solution revealed two multiplets (δ 3.86, 1.89 ppm) that integrated in a 1:1 ratio and were assigned as the THF adduct complex 4. Addition of a 5-10 fold excess of THF to the NMR sample, followed by collection of another $^1$H NMR spectrum, revealed a second set of two multiplet signals (δ 3.69 and 1.86 ppm) for free THF adjacent to those observed for the proposed complex, 4. This indicates that the signals at δ 3.86 and 1.89 are due to the complexed THF and not free or rapidly exchanging THF. Further evidence for the existence of species 4 is given by its reactivity with thiophenes to produce the S-bound complexes of type Re₂(CO)$_9$(η¹(s)-T*) (1 and 5, see below). The $^1$H NMR spectrum (in CD$_2$Cl$_2$) of crude 4, prepared using Method B, also exhibits signals for 4 as well as other signals which could be attributed to the previously reported Re₂(CO)$_9$(NMe$_3$)$^{24}$ (δ 2.89 ppm) and unreacted Me$_3$NO (δ 3.04 ppm).
Synthesis and Characterization of Re₂(CO)₉(η¹(S)-T*) Complexes (1 and 5). The S-bound thiophene complexes Re₂(CO)₉(η¹(S)-T*) (T* = DBT (1) and 2,5-Me₂T (5)) were prepared in low to moderate yields (20-50%) by addition of DBT (2 eq.) or 2,5-Me₂T (3-5 eq.) to a THF solution of 4 (prepared using Method A or B) with stirring for 15-20 h. Unreacted Re₂(CO)₁₀, Re₂(CO)₉(NMe₃) (Method B only), and other unidentified species were observed in the reaction mixtures when the crude products were analyzed spectroscopically (¹H NMR and IR). No reaction was observed under similar conditions when a 3-5 fold excess of T, 2-MeT or 4,6-Me₂DBT was added to 4 in THF solution. These results suggest that these thiophenes are poor donor ligands and cannot compete with other σ-donors such as NMe₃ or THF that are also present in these reactions. It was surprising that 4,6-Me₂DBT did not coordinate to the Re₂(CO)₉ unit as DBT does in 1; this could be due to steric or electronic effects caused by the methyl groups in the 4,6-Me₂DBT ligand.

Complex 1, prepared by both methods A and B, was characterized by elemental analyses, ¹H NMR and IR spectroscopies and also by its molecular structure which was determined by X-ray diffraction studies (Figure 2.). The yields of 1 were similar (27-34%) using both Methods A and B, which implies that DBT is a better σ-donor ligand under these reaction conditions than THF and NMe₃.

Complex 5 was prepared using method A, from a stirred THF solution of 4 and a 3-5 fold excess of 2,5-Me₂T. After removal of the volatiles in vacuo, a brownish-yellow oil of impure 5 was afforded. Attempted purification of 5 by either column chromatography (silica gel and alumina) or recrystallization was unsuccessful, but 5 was stable long enough to characterize by NMR and IR spectroscopies. The ¹H NMR spectrum of 5 in CD₂Cl₂ shows a singlet (δ 6.71) for the equivalent H₃ and H₄ protons on the thiophene ring of the 2,5-Me₂T
ligand; this signal is shifted 0.19 ppm downfield compared to that in the free ligand (6.52 ppm in CD$_2$Cl$_2$). The methyl signal for the two chemically equivalent Me groups in $\mathbf{5}$ is also a singlet ($\delta$ 2.42 ppm), which is shifted only 0.02 ppm from that in the free ligand (2.40 ppm). Chemical shifts in the range of ± 0.02-0.20 ppm are common for $\eta^1(S)$-bound 2,5-Me$_2$T ligands such as CpRe(CO)$_2(\eta^1(S)-2,5$-$\text{Me}_2$T)$_3$ and (CO)$_5M(\eta^1(S)-2,5$-$\text{Me}_2$T) ($M = \text{Cr}$ or $\text{W}$)$_{36}$. Notably, the S-bound thiophene ligand in $\mathbf{5}$ is labile and partially dissociates in solution (CD$_2$Cl$_2$, 20 °C) at room temperature based on $^1$H NMR studies. This is not surprising since the DBT ligand in $\mathbf{1}$, which is expected to be a better donor$^{42}$, was shown to be displaced by CO in less than 2 min.

**Mechanism for the Reactions in Scheme 3 and 4.** It has been established that Re$_2$(CO)$_{10}$ is activated by UV light to, [1] lose a CO group to generate Re$_2$(CO)$_9$ species (eq. 1), or [2] to undergo metal-metal bond homolysis to produce the 17-electron •Re(CO)$_5$ radical species$^{43}$ (eq. 3). Such processes have been proposed for the formation of Re$_2$(CO)$_9$(L) and Re$_2$(CO)$_8$(L)$_2$ complexes (L = phosphines and pyridine)$^{44-45}$ during UV photolysis of M$_2$(CO)$_{10}$ ($M = \text{Mn}$ or Re) and L donor ligands (eq. 1-5). Complex $\mathbf{1}$ is also a Re$_2$(CO)$_9$(L) type complex (L = DBT) and could be formed by either pathway [1] (eq. 1 and 2) or pathway [2] (eq. 3-5) during UV photolysis of Re$_2$(CO)$_{10}$ and DBT.

In an effort to understand how the photolysis reaction of Re$_2$(CO)$_{10}$ and DBT (Scheme 3) occurs, a series of experiments were undertaken. When the UV-light promoted reactions of Re$_2$(CO)$_{10}$ with a 3-fold excess of DBT in hexanes was carried out under a CO atmosphere instead of N$_2$, complexes 1 and 2 were inhibited and only unreacted Re$_2$(CO)$_{10}$ remained. However, during UV photolysis of Re$_2$(CO)$_{10}$ with a 3-fold excess of DBT under
N₂ was performed in the presence of the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) (1 equiv. based on Re₂(CO)₁₀) produced a modest yield of complex 2 after 8 h as detected by IR spectroscopy with no indication of the formation of 1. Furthermore, when the ratio of Re₂(CO)₁₀ to TEMPO was changed to 1:2, which is stoichiometric with respect to the formation of Re(CO)₅ radicals, neither complex 1 nor 2 was observed after 10 h (10-15 °C). It is known⁴⁶ that TEMPO reacts with photochemically generated M(CO)₅ (M = Mn or Re) radicals to form neutral M-N-O cyclic complexes of type (TEMPO)M(CO)₅. In a related reaction, when Re₂(CO)₁₀ and DBT (3 equiv.) were irradiated with UV light in CH₂Cl₂ solution, complexes 1 and 2 were not formed and both Re₂(CO)₈(μ-Cl)₂²⁹a and Re(CO)₅Cl²⁹b were produced as the only products after 1 h.

The observation that TEMPO and CH₂Cl₂ prevent the formation of 1 and 2 suggests that Re(CO)₅ radicals are involved in the formation of both products. If decarbonylation of Re₂(CO)₁₀ were a major pathway (eq. 1 and 2), then complex 1 should have been observed during the photolysis reactions of Re₂(CO)₁₀, DBT and TEMPO which is not the case.

Therefore, we propose that complex 1 forms by UV light-induced homolytic Re-Re bond cleavage of Re₂(CO)₁₀ to give Re(CO)₅ radicals (eq.3-5). Some of these Re(CO)₅ radicals
could undergo thermal substitution of CO with \( \eta^1(S) \)-binding of DBT to give Re(CO)₄(\( \eta^1(S) \)-DBT) radical species (eq. 4) which could then cross-couple with Re(CO)₅ radical fragments to produce 1 (eq. 5).

Since complex 1 is formed during the UV photolysis reaction of Re₂(CO)₁₀ and DBT, it is possible that 1 is also an intermediate in the formation of Re₂(CO)₉(μ-C₁₂H₁₇S)(μ-H) (2). A possible mechanism (Scheme 5) for the conversion of 1 and 2 could involve loss of a CO ligand from the Re(CO)₅ unit in 1, followed by oxidative addition of a C-H bond in the 4- or 6-position of the S-bound DBT to the unsaturated Re(CO)₄ unit resulting in the formation of the Re-C bond and a bridging hydride in 2. However, Re₂(CO)₉(\( \eta^1(S) \)-DBT) (1) is insufficiently soluble in hexanes, and only decomposition occurred during photolysis of 1. No reaction was observed under similar conditions for solutions of 1 in benzene, diethyl ether or THF solvents.
Thermolysis of 1 in refluxing toluene produced only free DBT and unidentified Re decomposition products that did not contain DBT.

The cluster HRe$_3$(CO)$_{14}$ was mentioned earlier as a minor product formed during the preparation of 1 and 2 by UV photolysis of Re$_2$(CO)$_{10}$ and excess DBT. The HRe$_3$(CO)$_{14}$ cluster likely forms from Re-Re bond cleavage of Re$_2$(CO)$_{10}$ and cross-coupling of HRe(CO)$_5$ and HRe(CO)$_4$ radical fragments during photolysis although the exact mechanism is uncertain. HRe$_3$(CO)$_{14}$, which could also be a precursor to 2, does react with excess DBT in hexanes solvent to produce 2 during UV photolysis (8-10 h, 10 °C). However, complex 2 was not isolated from this reaction, and was only observed spectroscopically (IR) in the reaction solution which suggests that HRe$_3$(CO)$_{14}$ is either not a dominant intermediate in the formation of 2, or a minor product resulting from the decomposition of 1 or 2.

The mechanism for the formation of complexes 1 and 2 is still uncertain although the presence of Re$_2$(CO)$_9$(η$^1$(S)-DBT) (1) with Re$_2$(CO)$_9$(μ-C$_{12}$H$_7$S)(μ-H) (2) during the photolysis of Re$_2$(CO)$_{10}$ and DBT, suggests that 1 might be a precursor in the formation of 2. However, the mechanism proposed does account for the products (1 and 2) observed during the photolytic reaction.

The formation of complex Re$_2$(CO)$_7$(μ-2,5-Me$_2$T) (3) could be formed from the S-bound complex Re$_2$(CO)$_9$(η$^1$(S)-2,5-Me$_2$T) (5) during UV photolysis, even though 5 itself was not observed during the reaction (Scheme 6). If complex 5 were produced during the photolysis of Re$_2$(CO)$_{10}$ and 2,5-Me$_2$T, it is possible that it could convert into 3 via photochemically induced loss of CO from the Re(CO)$_5$ unit, followed by η$^2$-binding of a
Scheme 6
C=C double bond of the 2,5-Me$_2$T ligand to give an intermediate of type (CO)$_4$Re($\mu$-$\eta^1(S),\eta^2$-2,5-Me$_2$T)Re(CO)$_4$ (A). Intermediate A could then undergo oxidative addition of a C-S bond to give a complex of type Re$_2$(CO)$_8$(\mu-2,5-Me$_2$T) (B) followed by loss of an additional CO ligand and subsequent $\eta^2$-binding of the second vinyl group to form 3. Although intermediates A and B were not observed during the photolysis of Re$_2$(CO)$_{10}$ and 2,5-Me$_2$T or during photolysis of 5, thiophene complexes that are structurally similar to B are known for Ni, Co and Fe; Fe$_2$(CO)$_6$(\mu-2-MeT)$^{106}$, [Cp*Co]$_2$(\mu-T)$^{17}$, and [(dippe)Ni]$_2$(\mu-T)$^{18}$. Because of the very different route for the synthesis of the Mn analog of 3, Mn$_2$(CO)$_7$(\mu-2,5-Me$_2$T), it is not surprising that the proposed mechanism for the formation of 3 differs significantly from that proposed by Sweigart for the formation of Mn$_2$(CO)$_7$(\mu-2,5-Me$_2$T). This complex was prepared by the chemical reduction of [(\eta$^5$-2,5-Me$_2$T)Mn(CO)$_3$]$^+$ with cobaltocene. The proposed mechanism$^{14,15}$ involves electron transfer to [(\eta$^5$-2,5-Me$_2$T)Mn(CO)$_3$]$^+$ to generate a (\eta$^4$-2,5-Me$_2$T)Mn(CO)$_3$$^-$ species which then attacks the thiophene of a second molecule of [(\eta$^5$-2,5-Me$_2$T)Mn(CO)$_3$]$^+$ with subsequent formation of a bimetallic species which then converts into Mn$_2$(CO)$_7$(\mu-2,5-Me$_2$T).

**Comparison of the Structures of Re$_2$(CO)$_9$(\eta$^1$(S)-DBT) (1) and Re$_2$(CO)$_8$(\mu-C$_{12}$H$_7$S)(\mu-H) (2).** The structure of 1 (Figure 1) shows an S-bound DBT ligand coordinated in an equatorial position to the Re$_2$(CO)$_9$ unit. The structure of complex 2 (Figure 2) shows the C-H cleaved DBT ligand bridging two Re(CO)$_4$ fragments both through the sulfur and also through the C4 carbon of the DBT benzo-ring in an $\eta^1$-fashion. The hydride ligand which bridges the two Re centers, was not located, but was observed in the $^1$H NMR.
spectrum of 2. In both 1 and 2, each Re metal center has nearly octahedral geometry with C-Re-C angles between adjacent carbonyl ligands at the central Re atoms of nearly 90°.

The Re(2)-S distance for 1 is 2.5375(8) Å with the sulfur essentially coplanar with the DBT ring plane deviating by only 0.04 Å on the same side as the Re(2) center. For complex 2 the Re(1)-S bond distance (2.475(2) Å) is shorter than that in 1, and the sulfur is bent 0.11 Å out of the DBT plane in the direction away from the metal center. The Re-S distances for both 1 and 2 are similar to those reported for other cyclic-organosulfur complexes of Re such as Re₂(CO)₉(SCH₂CMe₂CH₂) (2.485(4) Å)⁴⁸, Re₂2(CO)₉[(SCH₂CH₂CH₂)₃]¹⁹ (2.498(3) Å) and Re₂(CO)₆(μ-SPh)(μ-H)³⁸ (2.471(3) and 2.468(3) Å). However, the Re-S distances are much longer compared to the more electron-rich Re complexes Cp*Re(CO)₂(η¹(S)-T)³³ (2.360(3) Å) and Cp*Re(CO)₂(η¹(S)-3-MeBT)⁵⁰ (3-MeBT = 3-methylbenzothiophene) (2.356(4) Å) which contain the electron-donating π-donor ligand Cp* (Cp* = C₅Mes).

The geometry about the sulfur of the S-bound DBT ligands for both 1 and 2 is pseudo-sp³ as determined by the tilt angle (θ). The tilt angle θ is defined as the angle between the Re-S bond and the vector from the sulfur to the midpoint of the C15 and C16 ring carbon atoms of the DBT ligand in 1. The tilt angle for 1 (θ = 113.6°) is smaller than the analogous angle for 2 (θ = 124.8°). This difference may be due to the bridging nature of the DBT ligand in complex 2 as compared to 1. Both angles are similar to those reported for other η¹(S)-bound DBT complexes including (CO)₅W(η¹(S)-DBT)³⁶ (118.8°), [CpFe(CO)₂(η¹(S)-DBT)⁺]³⁴ (119.4°), (CO)₅Cr(η¹(S)-DBT)³⁶ (121.8°), and Cp*Ir(Cl)₂(η¹(S)-DBT)³⁵ (128.0°) that contain relatively electron-deficient metal centers. Interestingly, the tilt angle in 1 (113.6°) is much smaller than that found in other S-bound thiophene complexes of
Re, including \( \text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(S)-\text{T}) \) \( (140.4^\circ) \)\(^{33} \) and \( \text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(S)-3\text{-MeBT}) \) \( (131.0^\circ) \) in which the Re center is more electron-rich than 1. The larger tilt angles suggest greater \( \pi \)-backbonding from the Re to the thiophene ligand in the \( \text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(S)-\text{T}^*) \) complexes \( (\text{T}^* = \text{T} \text{ and } 3\text{-MeBT}) \) compared to complex 1. This result is in agreement with Harris’ proposal\(^{51} \) which suggests that the more electron-rich the metal center, the more \( \pi \)-backbonding from the metal to the thiophene ligand, and hence, the larger the tilt angle. This argument is further substantiated by the significantly shorter Re-S distances observed in the structures of \( \text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(S)-\text{T}) \) \( (2.360(3) \text{ Å}) \) and \( \text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(S)-3\text{-MeBT}) \) \( (2.356(4) \text{ Å}) \) than in 1. We previously noted the smaller tilt angles (°) and longer metal-sulfur distances (Å) in \( \text{[CpFe(\text{CO})_2(\eta^1(S)-\text{DBT})]^+} \)\(^{34} \) as compared with those parameters for the more electron-rich \( \text{CpMn(\text{CO})_2(\eta^1(S)-\text{DBT})} \)\(^{36} \) complex.

The average C-S distance for 1 is 1.782 Å, which compares well with that for 2 (1.766 Å). These distances are both larger than the average C-S distance observed in free DBT\(^{52} \) (1.740 Å). The C-S-C angle in the DBT ligand for both 1 (90.98(16)°) and 2 (92.7(4)°) is similar to that for free DBT (91.5(4)°).\(^{52} \)

The Re-Re bond distance in 1 is 3.0389(2) Å which is similar to that observed in \( \text{Re}_2(\text{CO})_{10} \) (3.0413(11) Å).\(^{53} \) However, the Re-Re distance for 2 (3.345 Å) is much larger due to the bridging hydride ligand in 2.

**Crystal Structure of \( \text{Re}_2(\text{CO})_7(\mu-2,5\text{-Me}_2\text{T}) \) (3).** In the structure of 3 (Figure 3) a Re(\text{CO})_4 fragment is inserted into a C-S bond of the 2,5-Me_2T ring and bent out of the thiophene plane; the resulting ring-opened thiophene is also \( \eta^5 \)-coordinated to the Re(\text{CO})_3 unit. The structure of 3 is very similar to that reported by Sweigart\(^{14} \) and coworkers for the 2-MeT...
derivative, Mn₂(CO)₇(μ-2-MeT). Both Re atoms have pseudo-octahedral geometry with the angles between adjacent CO ligands at the metal center of nearly 90°. The distance between Re atoms is approximately 3.749 Å which is out of bonding range compared to the reported Re-Re distance for both Re₂(CO)₁₀ (3.0413(11) Å)⁵³ and complex 1 (3.0389(2) Å). The Re(1)-S distance of 2.5048(13) Å and the Re(2)-S distance of 2.4722(14) Å are nearly the same (difference of 0.03 Å). In Mn₂(CO)₇(μ-2-MeT) this difference between Mn-S distances is also reported as 0.03 Å.

**Conclusion**

In summary, we report that Re₂(CO)₁₀ reacts with excess DBT in the presence of UV light and hexanes solvent to give the S-bound DBT complex Re₂(CO)₉(η¹(S)-DBT) (1) and the C-H cleaved DBT complex Re₂(CO)₈(μC₁₂H₇S)(μ-H) (2) (Scheme 3). These products were not expected since under similar conditions the reaction of Re₂(CO)₁₀ with benzothiophene (BT) did not produce S-bound or C-H cleaved BT complexes, but rather the C_vinyli-S bond was cleaved to give Re₂(CO)₇(μ-BT) as the only product (Scheme 2).²¹ However, irradiation of Re₂(CO)₁₀ and excess 2,5-Me₂T with UV light produces complex 3 in which the C-S bond of the 2,5-Me₂T ligand is cleaved. Thiophene, 4,6-Me₂DBT, 2-MeT and 3-MeT did not react with Re₂(CO)₁₀ during UV photolysis possibly due to electronic or steric effects. The pathway for the formation of 2 is proposed to occur through the isolable intermediates 1. The S-bound complexes Re₂(CO)₉(η¹(S)-T*) were prepared for T* = DBT (1) and 2,5-Me₂T (5) by substituting the THF ligand in the reactive species Re₂(CO)₉(THF) (4). Although mechanistic pathways for the photolytic reactions between Re₂(CO)₁₀ and thiophenes are not clear, the formation of the C-H cleaved DBT product 2 and the C-S
cleaved 2,5-Me₂T product 3 represent new types of reactivity not previously reported for
dinuclear metal complexes. Finally, we conclude that π-backbonding from Re to the DBT
ligand in 1 is much less important than in the more electron rich Re complexes
\( \text{Cp}^*\text{Re(CO)}_2(\eta^1(S)\text{-T}) \) and \( \text{Cp}^*\text{Re(CO)}_2(\eta^1(S)\text{-3-MeBT}) \). This conclusion is based on the
smaller tilt angle (θ) and longer Re-S distance in 1 (113.6°; 2.5375(8) Å) than in
\( \text{Cp}^*\text{Re(CO)}_2(\eta^1(S)\text{-T}) \) (140.4°; 2.360(3) Å) and \( \text{Cp}^*\text{Re(CO)}_2(\eta^1(S)\text{-3-MeBT}) \) (131.0°; 2.356(4) Å).

Acknowledgement. This work was supported by the U.S. Department of Energy, Office of
Science, Office of Basic Energy Sciences, Chemical Sciences Division, under contract W-7405-Eng-82 with Iowa State University.

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† Iowa State University Molecular Structure Laboratory

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5046.

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Table 1. Crystallographic Data for 1-3.

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<tr>
<td>R(wF²), %</td>
<td>4.24</td>
<td>7.77</td>
<td>5.99</td>
</tr>
</tbody>
</table>

\(^{a}\) Quantity minimized = \(R(wF^2) = \frac{\sum w(F_o^2 - F_c^2)²}{\sum (wF_o^2)²}^{1/2}; R = \frac{\Delta}{\Sigma(F_o). \Delta = |(F_o - F_c)|}\)
Figure 1. Molecular Structure of Re$_2$(CO)$_9$(η$^1$(S)-DBT) (1). Selected bond distances (Å) and angles (°): Re(1)-Re(2), 3.0389(2); Re(2)-S, 2.5375(8); S-C(10), 1.781(3); S-C(21), 1.782(3); Re(1)-C(1), 1.933(4); Re(2)-C(9), 1.926(3); C(9)-Re(2)-S 174.69(10); Re(2)-S-C(10), 107.08(11); Re(2)-S-C(21), 106.60(11); C(10)-S-C(21), 90.98(16); Re(2)-S-Midpt, 113.6.
Figure 2. Molecular structure of Re₂(CO)₈(μ-C₁₂H₇S)(μ-H) (2). Selected bond distances (Å) and angles (°): Re(1)-S, 2.475(2); Re(2)-C(19), 2.230(9); Re(1)--Re(2), 3.345; S-C(9), 1.765(8); S-C(20), 1.768(7); Re(1)-C(2), 1.996(10); Re(1)-C(3), 1.961(10); Re(1)-C(4), 2.002(10); Re(2)-C(5), 1.981(11); Re(2)-C(6), 1.962(10); Re(2)-C(7), 1.897(11); Re(2)-C(8), 2.009(12); C(1)-Re(1)-S, 173.5(3); C(3)-Re(1)-S, 94.5(3); C(6)-Re(2)-C(19), 172.6(4); C(7)-Re(2)-C(19), 87.8(4); Re(1)-S-C(9), 116.0(3); C(9)-S-C(20), 92.7(4); Re(1)-S-C(20), 107.4(3); Re(1)-S-Midpt, 124.8.
Figure 3. Molecular structure of Re₂(CO)₇(2,5-Me₂T) (3). Selected bond distances (Å) and angles (°): Re(1)-S, 2.5048(13); Re(2)-S, 2.4722(14); Re(1)-C(12), 2.554(5); Re(2)-C(12), 2.206(6); S-C(9), 1.773(5); C(9)-C(10), 1.382(8); C(10)-C(11), 1.473(7); C(11)-C(12), 1.370(8); Re(1)-S-Re(2), 97.74(5); Re(1)-C(12)-Re(2), 103.7(2); S-Re(2)-C(12), 80.73(14); C(9)-S-Re(1) 62.77(18); C(9)-S-Re(2), 108.40(18).
4. ORGANOMETALLIC MODELING OF THE HYDRODESULFURIZATION (HDS) PROCESS: \( \text{Re}_2(\text{CO})_{10} \)-PROMOTED S-BINDING, C-S BOND CLEAVAGE AND HYDROGENATION OF BENZOTHIOPHENES

A paper to be submitted to the *Journal of the American Chemical Society*

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**Abstract:** Ultraviolet photolysis of \( \text{Re}_2(\text{CO})_{10} \) and excess benzothiophenes (BT*) in hexanes solution (10-15 °C) produced the ring-opened BT* complexes \( \text{Re}_2(\text{CO})_7(\mu-\text{BT}^*) \) (1a-d) (BT* = benzothiophene (BT) 1a, 2-methylbenzothiophene (2-MeBT) 1b, 3-methylbenzothiophene (3-MeBT) 1c, and 3,5-dimethylbenzothiophene (3,5-Me₂BT) 1d). The \( \eta^1(S) \)-bound BT* complexes \( \text{Re}_2(\text{CO})_5(\eta^1(S)-\text{BT}^*) \) (2a-d) were prepared by two different synthetic routes and were readily converted into 1a-d in good yields (40-60%) during UV photolysis in hexanes solution (10-15 °C). These results suggest that the \( \eta^1(S) \)-bound complexes 2a-d could be precursors in the formation of 1a-d. When \( \text{Re}_2(\text{CO})_{10} \) and 3,5-Me₂BT were irradiated with UV light under an atmosphere of \( \text{H}_2 \) (10 °C, 24 h) in decane solution, complex 1d and the partially hydrogenated BT* complex \( \text{Re}_2(\text{CO})_7(\mu-3,5-\text{Me}_2\text{BT-H}(\mu-\text{H}) \) (3d) in which the terminal vinyl carbon of the BT* ligand is protonated, were produced. Furthermore, UV irradiation of complexes 1c and 1d under a \( \text{H}_2 \) atmosphere (10°C) in decane solution also afforded the partially hydrogenated BT* complexes \( \text{Re}_2(\text{CO})_7(\mu-3-\text{MeBT-H}(\mu-\text{H}) \) (3c) and 3d. Complexes 1a-d were not reactive towards electrophiles such as methyl iodide, methyl trifluoromethanesulfonate (MeOTf) and triflic acid, but they did react with nucleophiles such
as phosphines to form further ring-opened BT-Re complexes of the type Re$_2$(CO)$_7$(PMe$_3$)$_3$(μ-BT) (4) and Re$_2$(CO)$_7$(PR$_3$)$_2$(μ-BT) (R = Me (5), iso-Pr (6), and Cy (7)). Complexes 1-7 were characterized by spectroscopic methods (IR and $^1$H NMR) and X-ray crystallography. Mechanisms for the formation of 1, and 4-7 are presented and discussed.

Introduction

Hydrodesulfurization (HDS) is the commercially important, transition metal catalyzed hydrotreating process used for removing sulfur from organosulfur contaminants present in petroleum feedstocks.$^{1,2}$ This large-scale catalytic process is typically performed by treating crude petroleum with H$_2$ at high pressures (<200 atm) and temperatures (300-400 °C) in the presence of sulfided metal-based catalysts such as Ni- and Co-promoted MoS$_2$ and WS$_2$ supported on alumina.$^2$ Several different types of organosulfur compounds are present in petroleum distillates including thiols, thioethers, disulfides and thiophenes (T*). It is the alkyl substituted benzothiophenes (BT*)$^3$ and dibenzothiophenes (DBT*), however that are among the most difficult to desulfurize during the HDS process due to their greater molecular size and aromatic character.$^{1,2}$ Two fundamentally important steps in the HDS of petroleum distillates include adsorption and C-S bond cleavage of organosulfur compounds at heterogeneous catalyst metal centers. In order to improve current HDS catalysts, a better understanding of thiophene and benzothiophene adsorption, C-S bond cleavage, and hydrogenation at catalyst metal centers is important.

One approach to studying the HDS of thiophenes and benzothiophenes at transition metal centers is to use organometallic complexes as models for the HDS catalysts. Binding thiophenic molecules to centers of organometallic complexes has been studied by many groups and has been the subject of several reviews.$^{4,5}$ There are also many examples of single
metal complexes in which the metal inserts into a C-S bond of a thiophene or benzothiophene compound.\textsuperscript{6-9} However, few examples of C-S bond cleavage of thiophenes in complexes that contain multiple metal centers have been reported.\textsuperscript{10-13} The complexes Mn\textsubscript{2}(CO)\textsubscript{7}(\mu-T\textsuperscript{*})\textsuperscript{14-17}, [Cp*Co]\textsubscript{2}(\mu-T\textsuperscript{*})\textsuperscript{18}, [(dippe)Ni]\textsubscript{2}(\mu-T\textsuperscript{*})\textsuperscript{19} and Fe\textsubscript{2}(CO)\textsubscript{6}(\mu-T\textsuperscript{*})\textsuperscript{20} (T\textsuperscript{*} = T and BT) represent some of the bimetallic complexes that contain bridging, ring-opened thiophenes. Recently, we reported the Re\textsubscript{2}(CO)\textsubscript{10}-promoted C-H cleavage of DBT to produce Re\textsubscript{2}(CO)\textsubscript{8}(\mu-\text{C}_1\text{H}_2\text{H}_7\text{S})(\mu-\text{H}) and C\text{\textit{vinyl}}-S cleavage in 2,5-Me\textsubscript{2}T to afford Re\textsubscript{2}(CO)\textsubscript{7}(\mu-2,5-Me\textsubscript{2}T) during UV photolysis.\textsuperscript{21} We have also communicated our results for the preparation of Re\textsubscript{2}(CO)\textsubscript{7}(\mu-BT) and its reactions with PMes.\textsuperscript{22}

Herein we report further studies in the Re\textsubscript{2}(CO)\textsubscript{10}-promoted cleavage of the C\text{\textit{vinyl}}-S bonds in alkyl-substituted benzothiophenes (BT\textsuperscript{*}) during UV photolysis to afford the BT\textsuperscript{*} complexes of type Re\textsubscript{2}(CO)\textsubscript{7}(\mu-BT\textsuperscript{*}). These complexes react with phosphines and H\textsubscript{2} to produce new dinuclear ring-opened and partially hydrogenated BT\textsuperscript{*}-Re complexes.

Results and Discussion

Synthesis of Re\textsubscript{2}(CO)\textsubscript{7}(\mu-BT\textsuperscript{*}) complexes (1a-d). Irradiation of a hexanes solution containing Re\textsubscript{2}(CO)\textsubscript{10} and a 2-3 fold excess of BT\textsuperscript{*} (BT\textsuperscript{*} = BT, 2-MeBT, 3-MeBT or 3,5-Me\textsubscript{2}BT) with UV light for 24 h produced the ring-opened BT\textsuperscript{*} complexes Re\textsubscript{2}(CO)\textsubscript{7}(\mu-BT\textsuperscript{*}) (1a-d) in moderate yields (20-40%) (Scheme 1). Complexes 1a-d are air-stable, orange solids that are soluble in most organic solvents including CH\textsubscript{2}Cl\textsubscript{2}, benzene and hexanes. In solution, 1a-d are stable for days at room temperature if stored under an inert atmosphere such as N\textsubscript{2}.

Complexes 1a-d contain a ring-opened BT\textsuperscript{*} ligand that has been cleaved regioselectively at the C\text{\textit{vinyl}}-S bond and bridges the Re\textsubscript{2}(CO)\textsubscript{7} backbone through the S atom
Scheme 1. Reaction scheme for the preparation of \( \text{Re}_2(\text{CO})_7(\mu-\text{BT}^*) \) (1a-d).

and also \( \eta^1, \eta^2 \)-through the vinyl group. The cleavage of C-S bonds in the BT* ligands the 2-position. This is in contrast to the results reported by Jones, et al.\(^8\) for the reaction of 2-MeBT with \( \text{Cp}^*\text{Rh(PMe}_3)(\text{Ar})(\text{H}) \) (\( \text{Ar} = \text{Ph} \) or 3,5-xylyl). In this system, Rh metal insertion into the \( \text{C}_{\text{vinyl}}\)-S bond of 2-MeBT gave, as the kinetic product, \( \text{Cp}^*\text{Rh(PMe}_3)(\text{C}_{\text{vinyl}},\text{S}-2\text{-MeBT}) \) which readily converted into the \( \text{C}_{\text{aryl}}\)-S cleaved complex \( \text{Cp}^*\text{Rh(PMe}_3)(\text{C}_{\text{aryl}},\text{S}-2\text{-MeBT}) \) upon heating (74 °C, 38 h) in \( \text{C}_6\text{D}_{12} \) solution. The complexes 1a-d were not converted into a \( \text{C}_{\text{aryl}}\)-S metal-inserted isomer even when heated in refluxing toluene for 2 d.
In the $^1$H NMR spectra for 1a-d (in CD$_2$Cl$_2$), the chemical shift for the terminal vinyl proton of 1a ($\delta$ 8.63, d, $J = 11.4$), 1c ($\delta$ 8.22, s) and 1d ($\delta$ 8.20, s) is shifted to low field compared to that in the free BT* molecules (in the range of $\delta$ 7.95-7.00). This significant downfield shift of the vinyl protons in 1a, 1c and 1d is consistent with C-S cleavage of the BT* ligands and $\eta^1$-binding of the terminal vinyl carbon to a Re metal center. An example of such proton chemical shifts was observed in the iron complex Fe$_2$(CO)$_6$(μ-BT), which is spectroscopically and structurally similar to 1a, and also exhibits a similar downfield shift for the terminal BT vinyl proton ($\delta$ 8.99 in CDCl$_3$). The chemical shift for the methyl protons of the 2-MeBT ligand (in CD$_2$Cl$_2$) in 1b ($\delta$ 3.16, s) was observed downfield of that in free 2-MeBT ($\delta$ 2.60) and is also consistent with the vinyl proton shifts in 1a, 1c and 1d. Signals for the aromatic protons in 1a-d are shifted upfield by 0.4-0.5 ppm compared to those of the unbound BT* molecules ($\delta$ 7.95-7.00).

**Proposed Mechanism for the Formation of 1a-d.** A possible mechanism for the formation of complexes 1a-d according to reaction (a) in Scheme 1 is shown in Scheme 2 and is similar to that proposed by Brown and coworkers for the formation of the alkenyl complexes of type Re$_2$(CO)$_8$(μ-alkenyl)(μ-H). The first step likely involves photochemically induced cleavage of the Re-Re bond in Re$_2$(CO)$_{10}$ to generate •Re(CO)$_5$ radicals (eq. 1).

$$\text{Re}_2(\text{CO})_{10} \xrightarrow{\text{hv}} 2 \text{Re}(\text{CO})_5 \quad (1)$$

$$\text{Re}(\text{CO})_5 + \text{BT*} \xrightarrow{\text{SS}} \text{Re}(\text{CO})_4(\text{BT*}) + \text{CO} \quad (2)$$

$$\text{Re}(\text{CO})_4(\text{BT*}) + \text{Re}(\text{CO})_5 \xrightarrow{\text{SS}} \text{Re}_2(\text{CO})_9(\text{BT*}) \quad (3)$$
Scheme 2. Mechanistic scheme for the formation of complexes 1a-d.

These radicals could undergo thermal substitution in the presence of BT* molecules to produce •Re(CO)$_4$(η$^1$(S)-BT*) radicals (eq. 2). Cross-coupling of the •Re(CO)$_4$(η$^1$(S)-BT*) radicals with •Re(CO)$_5$ (eq. 3) or other •Re(CO)$_4$(η$^1$(S)-BT*) radical fragments would produce complexes 2a-d or Re$_2$(CO)$_8$(η$^1$(S)-BT*)$_2$ in the first step (Step 1, Scheme 2). The resulting Re$_2$(CO)$_8$(η$^1$(S)-BT*) or Re$_2$(CO)$_8$(η$^1$(S)-BT*)$_2$ complexes could undergo further photochemical loss of a ligand (L = CO or BT*) at the adjacent Re(CO)$_4$(L) moiety with subsequent η$^2$-binding of the BT vinyl group to form a bridging BT* species Re$_2$(CO)$_8$(μ$_2$-
\[ \eta^1(S),\eta^2\text{-}BT^* \] (Step 2, Scheme 2). Subsequent CO loss and oxidative addition of the vinyl C-S bond of BT* would produce 1a-d (Step 3, Scheme 2) in the final step. None of the proposed intermediates, including \( \text{Re}_2(\text{CO})_9(\eta^1(S)\text{-}BT^*) \) (2a-d) and \( \text{Re}_2(\text{CO})_8(\eta^1(S)\text{-}BT^*)_2 \), were observed during the formation of 1a-d; however irradiation of \( \text{Re}_2(\text{CO})_9(\eta^1(S)\text{-}3-\text{MeBT}) \) (2e) in hexanes solvent for 1-5 h did produce 1e in high yield (>50%) as illustrated in reaction (b) of Scheme 1. This conversion of 2e into 1e supports the proposal that 2a-d and possibly \( \text{Re}_2(\text{CO})_8(\eta^1(S)\text{-}BT^*)_2 \) are precursors to 1a-d.

If \( \text{Re}_2(\text{CO})_9(\eta^1(S)\text{-}BT^*) \) or \( \text{Re}_2(\text{CO})_8(\eta^1(S)\text{-}BT^*)_2 \) complexes are produced as intermediates during the photolysis of \( \text{Re}_2(\text{CO})_{10} \) and BT*, then the formation of these complexes should be inhibited in the presence of excess CO or by a radical scavenger such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical), and complexes 1a-d should not be formed. Indeed, complex 1a was not observed spectroscopically (IR) when \( \text{Re}_2(\text{CO})_{10} \) and excess BT were irradiated with UV light under a CO atmosphere (in hexanes solution at 10 °C for 24 h) and only the bands corresponding to \( \text{Re}_2(\text{CO})_{10} \) were observed. Complex 1a also did not form when \( \text{Re}_2(\text{CO})_{10} \) and BT were irradiated in hexanes solution with UV light under a nitrogen atmosphere in the presence of the radical scavenger TEMPO. TEMPO is a known radical trapping agent that reacts with \( \cdot\text{M}(\text{CO})_3 \) (M = Mn or Re) radicals to produce the neutral complexes (TEMPO)M(\text{CO})_3 during UV photolysis of M_2(\text{CO})_{10} (M = Mn or Re).\textsuperscript{24} The results of both the CO and TEMPO experiments are consistent with a mechanism (eq. 1-3) involving Re(CO)_5 radicals in the formation of 1a-d.\textsuperscript{25}

**Preparation of \( \text{Re}_2(\text{CO})_9(\eta^1(S)\text{-}BT^*) \) (2a-d).** The S-bound complexes, \( \text{Re}_2(\text{CO})_9(\eta^1(S)\text{-}BT^*) \) (2a-d) were prepared by two different synthetic routes (method A and
B). In method A, a dry THF solution of \( \text{Re}_2(\text{CO})_{10} \) was irradiated in a quartz tube for 1-1.5 h (10 °C) until the formation of \( \text{Re}_2(\text{CO})_9(\text{THF}) \) was observed (IR in THF: 2101 (w), 2047 (m), 1987 (s), 1954 (m) and 1917 (m) cm\(^{-1} \)). Excess BT* was then added to the THF solution containing the \( \text{Re}_2(\text{CO})_9(\text{thf}) \) complex with stirring for 15-20 h as described in the experimental section. Method B is similar to that reported\(^{26,27} \) for the preparation of \( \text{Re}_2(\text{CO})_9(\text{CH}_3\text{CN}) \). Both methods produced \( 2a-d \) in comparably yields (10-40%).

Complexes \( 2a-d \), are moderately air stable in the solid state and each complex is soluble in \( \text{CH}_2\text{Cl}_2 \), benzene and hexanes solvents. The BT* ligand in each complex is labile and was replaced by CO (1 atm) to form \( \text{Re}_2(\text{CO})_{10} \) in less than 2 min in toluene solution. Complexes \( 2a-d \) were characterized by IR and \(^1\text{H} \) NMR spectroscopy and an X-ray structure of \( 3c \) was determined.

The \(^1\text{H} \) NMR spectrum of \( 2a-d \) indicates S-binding of the BT* ligands with chemical shifts within ±0.05-0.30 ppm of those of the free BT*. Similar chemical shifts were observed in the \(^1\text{H} \) NMR spectra of \( \text{CpRe}(\text{CO})_2(\eta^1(\text{S})-\text{BT})^{28,29} \), \( \text{M}(\text{CO})_5(\eta^1(\text{S})-\text{BT}) (\text{M} = \text{Cr or W})^{30} \) and \( \text{[CpFe}(\text{CO})_2(\eta^1(\text{S})-\text{BT})]^+ \)^{31}. If binding of the BT* ligands were in an \( \eta^2 \)-fashion, the olefinic protons would be expected to shift to high field as observed in \( \text{Cp}^*\text{Re}(\text{CO})_2(2,3-\eta^2-\text{BT})^{29} \) (δ 4.25 and 3.96 ppm in CDCl\(_3 \)). The bis-BT* complexes of type \( \text{Re}_2(\text{CO})_8(\eta^1(\text{S})-\text{BT*})_2 \) were not observed during the reactions using either Method A or B.

**Photolysis Reaction of \( \text{Re}_2(\text{CO})_{10} \) and 3,5-Me\(_2\)BT with \( \text{H}_2 \).** When \( \text{Re}_2(\text{CO})_{10} \) and a 3-5 fold excess of 3,5-Me\(_2\)BT were irradiated with UV light in a \( \text{H}_2 \)-saturated decane solution (24-36 h, 10 °C) the complexes \( \text{H}_2\text{Re}_2(\text{CO})_8 \), \( \text{Re}_2(\text{CO})_7(\mu-3,5-\text{Me}_2\text{BT}) \) (1d), and the partially hydrogenated BT* complex \( \text{Re}_2(\text{CO})_7(\mu-3,5-\text{Me}_2\text{BT}-\text{H})(\mu-\text{H}) \) (3d) were produced (Scheme
3). Complex 3d contains a bridging, ring-opened 3,5-Me₂BT ligand similar to that in 1d; however in contrast to 1d only the BT* sulfur atom bridges the two Re centers and the \( \eta^2 \)-bound vinyl group has been protonated at the terminal vinyl carbon of 3d. A hydride ligand is also present in 3d as evidenced in the \(^1\text{H} \text{NMR} \) spectrum. In a related reaction, when

\[
\text{Re}_2(\text{CO})_{10} + \begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\end{array} \\
\xrightarrow{\text{UV}(\text{hv})} \\
+ \text{H}_2 \\
\downarrow \text{decane}
\]

complex 1e was irradiated with UV light under H₂ (1 atm) for 15-18 h in decane solution, the complex Re₂(\text{CO})₇(\text{μ-3-MeBT-H})(\text{μ-H}) (3e) was produced which is structurally analogous to 3d. Under the same reaction conditions, when complex 1e was irradiated in hexanes solution, 3e was produced.
Complexes 3c and 3d are colorless solids that are soluble in CH₂Cl₂, toluene and THF, but are moderately soluble in hexanes and decane. Both complexes are air-stable in the solid state and in solution if stored under N₂.

The ¹H NMR spectra of 3c and 3d are significantly different from that of 1c and 1d. The chemical shift of the protons on the η²-vinyl group of 3c (in CD₂Cl₂) are observed at δ 4.31 and 4.06 ppm which are shifted upfield compared to the proton on the terminal vinyl carbon of 1c (δ 8.22 ppm). Similar chemical shifts were observed in the ¹H NMR spectrum for the 3,5-Me₂BT ligand of 3d compared to 1d. Here, the vinyl protons are shifted upfield for 3d (in CDCl₃: δ 4.28 and 4.03 ppm) compared to 1d (δ 8.14 ppm). The hydride ligands in 3c (δ -12.60) and 3d (δ -12.62) were also observed in ¹H NMR spectra.

In the reaction of Re₂(CO)₁₀ and 3-MeBT or 3,5-Me₂BT with H₂, it is likely that complexes 3c and 3d are formed from the Re₂(CO)₇(μ-BT*) complexes 1c and 1d as illustrated in Scheme 4. In the first step, the Re-Re bond could dissociate in the presence of H₂ to produce an η²-bound dihydrogen complex. The η²-H₂ ligand could then undergo oxidative addition at the Re(CO)₃ metal center to form a dihydride species (step 2, Scheme 4) followed by hydrogen migration to the terminal vinyl carbon (step 3, Scheme 4) to give 3c or 3d. The addition of H₂ to complexes 1c and 1d is significant since the H-transfer is selectively and occurs at mild temperatures to form only one product (complex 3).

Reactions of 1a with Phosphines. In a recent communication²² we reported that Re₂(CO)₇(μ-BT) (1a) reacts with an excess of PMe₃ in toluene solution at room temperature to produce the further ring-opened BT complexes Re₂(CO)₇(PMe₃)₃(μ-BT) (4) and...
Re$_2$(CO)$_7$(PMe$_3$)$_2$(μ-BT) (5) in good yields (40% for 4 and 60% for 5) (Scheme 5). Complex 1a also reacts with P'Pr$_3$ (5 equivalents) and PCy$_3$ (2 equivalents) to produce the Re$_2$(CO)$_7$(PR$_3$)$_2$(μ-BT) complexes 6 (R = P'Pr) and 7 (R = Cy) which are structural analogs of 5. However, in contrast to the reaction of 1a with PMe$_3$, no evidence of complex analogs of 4 were observed for P'Pr$_3$ or PCy$_3$. The colorless complex 4 and the pale yellow 5-7 are soluble in CH$_2$Cl$_2$, toluene and benzene but sparingly soluble in hexanes. Each complex can be handled in air for short intervals of time (<1 h) and are moderately stable in solution.

The $^1$H NMR spectrum for 4 (in CD$_2$Cl$_2$) differs from that for 1a. The chemical shift for the proton in the 2-position of the BT ligand of 4 (δ 7.89, dd, J=13.5, 3.9 Hz) is shifted
upfield compared to that in 1a (δ 8.63, d, J=11.4 Hz). The proton in the 3-position (δ 7.43, dd, J=7.8, 1.2 Hz) is shifted downfield compared to that in the spectrum of 1a (δ 7.00, d, J=11.4 Hz). The dd pattern for the vinyl proton signals for 4 is due to coupling to the PMe3 phosphorus.

The BT aromatic protons for 4 are observed at δ 7.21-6.92 ppm and have a similar chemical shift as those for 1a (7.11-6.93 ppm). The protons corresponding to the three PMe3 ligands are observed as a multiplet at 1.62 ppm.

The ^1H NMR spectra (in CD2Cl2) of 5-7 are similar to each other, but significantly different from that of 1a (in CD2Cl2). The chemical shift for the proton in the 2-position of the BT ligand of 5 (δ 8.06, dd, J = 14.1, 2.4 Hz), 6 (δ 8.29, dd, J=14.4, 2.1 Hz) and 7 (δ 8.33,
dd, J=14.0, 2.0 Hz) is shifted upfield compared from that observed in the spectrum of 1a (δ 8.63 d, J=12.0 Hz). However, the chemical shift for the vinyl proton in the 3-position of the BT vinyl group in 5 (δ 7.44, dd, J=14.1, 3.6 Hz), 6 (δ 7.43, dd, J=14.4, 3.0 Hz) and 7 (δ 7.46, dd, J=14.4, 2.4 Hz) is shifted downfield from that of 1a (δ 7.00, d, J=12.0 Hz). The BT vinyl protons in the spectra of 5-7 in addition to being coupled to each other are also coupled to the phosphines and appear as a doublet of doublets with JHP coupling constants ranging from 2.1-3.0 Hz. The aromatic protons of 5-7 are observed as multiplets in the region δ 7.50-6.75 ppm while those in the spectrum of 1a are shifted upfield of these protons in the range δ 7.15-6.90 ppm. The methyl protons for the two distinct PMe₃ environments are shown at δ 1.87 and 1.19 ppm.

Scheme 6 shows a possible mechanism for the formation of 4 from the reaction of complex 1a with PMe₃. The first step of this mechanism could involve displacement of the η²-bound vinyl group by PMe₃ at the Re(CO)₃ moiety (Step 1, Scheme 6) to give an intermediate of the type Re₂(CO)₇(PMe₃)(μ-BT). Addition of a second PMe₃ ligand to the Re(CO)₃(PMe₃) unit would result in Re-Re bond cleavage (Step 2, Scheme 6) to produce an intermediate such as Re₂(CO)₇(PMe₃)₂(μ-BT). In the final step, an additional equivalent of PMe₃ could then displace the sulfur ligand to produce 4. Steps 1 and 2 could be interchanged and it is reasonable to assume that this is possible since there is no spectroscopic evidence (¹H NMR) for the existence of either intermediate. The proposed displacement of the BT sulfur as the final step in the formation of 4 is based on the observation that in complex 5, the S bridges the two Re centers thereby suggesting that the sulfur is rigid and is not easily displaced by PMe₃.
Scheme 6. Reaction scheme for the formation of Re$_2$(CO)$_7$(PMe$_3$)$_3$(μ-BT) (4).

A possible mechanism for the formation of the Re$_2$(CO)$_7$(PR$_3$)$_2$(μ-BT) complexes 5-7 from 1a-d is shown in Scheme 7. A distinguishing structural feature in these complexes is that the terminal BT vinyl carbon is $\eta^1$-bound to the Re(CO)$_3$ unit and not to the Re(CO)$_4$ unit as observed in 1a and also in 4. In order to propose a reasonable mechanism for the formation of 5-7, this change in vinyl coordination must be taken into account. The first step
in the proposed mechanism is the migration of a CO ligand from the Re(CO)$_4$ group in 1a to the Re(CO)$_3$ moiety to afford the isomer 1a' (Step 1, Scheme 7). Although 1a' has not been observed in the $^1$H NMR spectrum of 1a in solution, a variable temperature $^{13}$C NMR study of 1a (in CD$_2$Cl$_2$ solution) showed evidence for rapid CO migration between Re metal centers. The $^{13}$C NMR spectrum of 1a (−50.1 °C) exhibits a signal for each of the 7 carbonyl ligands which have chemical shifts at $\delta$ 193.4, 192.6, 189.9, 185.6, 184.7, 184.3 and 177.6 ppm. This spectrum is consistent with the static structure of 1a in the solid state which was
established by an X-ray diffraction study. However, at +20.1 °C, the 7 signals observed at 
−50.1 °C coalesce into three signals (at δ 189.1, 187.4 and 185.9 ppm) which suggests that 
the carbonyl ligands of the Re(CO)₃ unit and the Re(CO)₄ unit of 1a, are rapidly exchanging 
between Re centers.

Isomer 1a' could then react with a PR₃ ligand with dissociation of either the η²-vinyl 
group or the Re-Re bond. Since the Re(CO)₄ unit in 1a' is already saturated, substitution of 
the vinyl group for the PR₃ ligand would be unfavorable. However, if the Re-Re bond 
dissociates first, followed by addition of PR₃ to the Re(CO)₃ unit as proposed (Step 2, 
Scheme 7), then both Re centers would be 6-coordinate. Displacement of the vinyl group 
with addition of a PR₃ ligand to the Re(CO)₄ unit in the final step would produce the 
complex Re₂(CO)₇(PR₃)₂(μ-BT) (5-7). Although this proposed mechanism for the formation 
of 5-7 is appealing, none of the intermediates mentioned were directly observed 
spectroscopically.

The phosphines used in the preparation of complexes 6 and 7 were chosen based on 
their larger cone angles (PPr₃, 160°; PCy₃, 170°) and similar nucleophilic character 
compared to PMe₃ (118°). All three phosphines produce similar disubstituted phosphine 
complexes of the type Re₂(CO)₇(PR₃)₂(μ-BT) (5-7). However, complex 1a reacts with PMe₃ 
to produce the tri- and di-substituted phosphine complexes 4 and 5, respectively (Scheme 5).
It is reasonable to assume based on the complexes formed, that the di-substituted phosphine 
complexes 5-7 are formed when the reacting phosphine ligand has a large cone angle and that 
sterics is important. Since PMe₃ has a smaller cone angle compared to PPr₃ and PCy₃, both 4 
and 5 are produced when PMe₃ is reacted with 1a.
Although complexes 1a-d readily react with phosphines and H₂ under mild conditions, they are unreactive towards electrophiles such as Mel, methyl trifluoromethanesulfonate (MeOTf) and triflic acid even in refluxing benzene.

**Discussion of the Molecular Structure of Re₂(CO)₉(3-MeBT) (2c).** The molecular structure of 2c (Figure 1) contains a 3-MeBT ligand that is S-bound in the equatorial position to a Re₂(CO)₉ moiety. The carbonyl ligands on the two Re fragments are staggered with respect to each other. The Re-S bond distance is 2.5220(18) Å which is similar to that in the analogous DBT complex Re₂(CO)₉(S⁻¹(S)-DBT) (2.5375(8) Å)²¹ and the thietane complex Re₂(CO)₉(SCH₂CMe₂CH₂)³⁴ (2.485(4) Å). However, compared to Re complexes which have more electron density on the Re center such as Cp*Re(CO)₂(S⁻¹(S)-T) (2.360(3) Å)³⁵ and Cp*Re(CO)₂(S⁻¹(S)-3-MeBT)²⁹ (2.356(4) Å), the Re-S distance for 2c is significantly longer.

The tilt angle (θ) of the 3-MeBT ligand, which is defined as the angle between the Re-S bond and the vector from the sulfur to the midpoint between the C(11) and C(12) carbons of the 3-MeBT ligand, is used to describe the geometry around the thiophene sulfur atom. In complex 2c, the tilt angle is 116.9° which indicates that the 3-MeBT sulfur is pseudo-sp³ hybridized. The tilt angle for 2c is similar to that in the analogous DBT complex Re₂(CO)₉(S⁻¹(S)-DBT) (θ = 113.6°)²¹ and comparable to that in other complexes which contain electron deficient metal centers such as (CO)₅W(S⁻¹(S)-DBT)²⁰ (118.8°), (CO)₅Cr(S⁻¹(S)-DBT) (121.8°)³⁰, and [CpFe(CO)₂(S⁻¹(S)-DBT)]⁻ (119.4°)³¹. However, the tilt angle in 2c is much smaller compared to that in the electron-rich complexes Cp*Re(CO)₂(S⁻¹(S)-3-MeBT) (θ = 131.0°)²⁹ and Cp*Re(CO)₂(S⁻¹(S)-T) (θ = 140.4°)³⁵.

Harris³⁶ has proposed that the tilt angle in S-bound metal-thiophene complexes can be used
as an indicator of π-back donation from the metal to the thiophene ligand. More electron density on the metal center increases π-backbonding, which results in a larger tilt angle and also a shorter M-S bond distance. Therefore, the relatively electron deficient Re center in 2c leads to a smaller tilt angle and longer Re-S bond distance compared to these parameters in Cp*Re(CO)2(η1(S)-T*) (T* = T or 3-MeBT)29,35 complexes.

The C-S bonds in 2c (C(10)-S, 1.806(9) Å; C(17)-S, 1.685(9) Å) are slightly shorter than those in Cp*Re(CO)2(η1(S)-3-MeBT) (1.92(2) Å and 1.74(3) Å, respectively)29. The C-S-C angle in 2c (90.5(4)°) is similar to that found in the complex Cp*Re(CO)2(η1(S)-3-MeBT)29 (90(1)°). The Re-Re bond distance in the structure of 2c is 3.0343(4) Å and compares well with that in Re2(CO)9(η1(S)-DBT) (3.0389(2) Å)21 and Re2(CO)10 (3.0413(11) Å)37.

Comparison of the Molecular Structures of Re2(CO)7(µ-3,5-Me2BT) (1d) and Re2(CO)7(µ-3,5-Me2BT-H)(µ-H) (3d). The molecular structure of 1d (Figure 2) shows a 3,5-Me2BT ligand that is ring-opened at the C-vinyl-S bond and bridges the Re2(CO)7 moiety nearly symmetrically through the sulfur and both η1- and η2-through the terminal vinyl group. The molecular structure of 3d (Figure 3) shows a similar bridging 3,5-Me2BT ligand as in 1d, except that the Re in the Re-η1-vinyl bond has been replaced by a hydrogen. The bridging hydride ligand was observed in the 1H NMR spectrum of 3d, but was not located in the molecular structure.

The Re-sulfur distances in 1d are 2.4320(13) Å for Re(1)-S(1) and 2.4995(13) Å for Re(2)-S(1) and are similar to those in 3d which are 2.4444(14) Å for Re(1)-S and 2.4883(14) Å for Re(2)-S. The Re-S-Re angle for 3d (78.11(4)°) is larger than that in 1d (72.73(3)°) due
to the bridging hydride ligand which increases the distance between the Re atoms. The Re-Re bond (2.9245(3) Å) in 1d is short for a single bond compared to other Re-Re bonded complexes such as Re$_2$(CO)$_{10}$ (3.0413(11) Å)$^{37}$, Re$_2$(CO)$_9$(η$^1$(S)-DBT) (3.0389(2) Å)$^{21}$ and 2e (3.0343(4) Å) which are also formal single bonds. However, complex 3d (3.1083(3) Å) has a longer Re-Re bond distance than 1d (2.9245(3) Å) possibly due to the bridging hydride ligand, but this Re-Re distance is still smaller than that in the bridging DBT complex Re$_2$(CO)$_8$(μ-C$_{12}$H$_7$S)(μ-H) (3.345 Å)$^{21}$ which also contains a bridging hydride ligand.

The terminal vinyl group in 3d is bound in a η$^2$-fashion to the Re(CO)$_4$ moiety as evidenced by Re-C bond distances of 2.417(6) Å for Re(1)-C(4) and 2.532(6) Å for Re(1)-C(5). The analogous distances in 1d are 2.254(5) Å for Re(1)-C(4) and 2.463(5) Å for Re(1)-C(5) and are shorter than those observed in 3d which is likely due to the bridging nature of the vinyl group as indicated by the Re(2)-C(4) distance of 2.176(5) Å. The bond distance between the vinyl carbons in 1d (1.403(7) Å) is similar to that in 3d (1.379(8) Å). The C(4)-C(5)-C(7) angle for 1d is 122.9(5)° and does not differ much from that in 3d (120.3(5)°) despite the difference in binding modes of the vinyl group in each complex.

Furthermore, based on the structures of 1a$^{22}$ and 1d, the vinyl group in each complex is not likely to "flip-flop" as described for the structurally similar complexes Fe$_2$(CO)$_8$(μ-BT)$^{20}$, [Cp*Co]$_2$(μ-BT)$^{18}$ and [(dippe)Ni]$_2$(μ-BT)$^{19}$ due to the extra carbonyl group present on the Re(CO)$_4$ moiety which could act to block the coordination site needed for the vinyl group to migrate. Such is not the case in the for the Fe, Co and Ni complexes mentioned above which are symmetric.
Molecular structure of Re₂(CO)₇(P₃Pr₃)₂(μ-BT) (7). In the structure of 7 (Figure 4), a BT ligand that has been cleaved at the C_vinyly-S position bridges the two Re metal centers through the sulfur atom and the η¹-vinyl group is bonded to the Re(CO)₃(PMe₃) moiety. Each Re in 7 also contains one coordinated P₃Pr₃ group similar to that reported for the structurally analogous 4 which contains PMe₃ ligands. The sulfur in 7 bridges the two Re centers nearly symmetrically with distances of 2.5296(15) Å for Re(1)-S and 2.5499(15) Å for Re(2)-S. These distances are slightly larger than those observed in the structure of 1a (Re(1)-S, 2.506(2) Å; Re(2)-S, 2.431(3) Å) in which there is a Re-Re bond. The Re-S-Re angle in 7 (116.69(5)°) is also larger than that in complex 1a (71.77(7)°) and similar to that in 4 (116.76(3)°). The C=C distance for the vinyl group in 7 is 1.343(10) Å which is nearly identical to that in 4 (1.343(5) Å) and slightly shorter than that in 1a (1.370(14) Å). The Re(1)-C(13) distance of 2.173(6) Å is also similar to that observed in 4 (2.169(3) Å) but shorter than that in complex 1a (2.208(10) Å) which has a bridging vinyl group.

Conclusions. The UV-light promoted reaction of Re₂(CO)₁₀ and BT* molecules in hexanes solution to produce Re₂(CO)₇(μ-BT*) (1a-d) represents a novel method for regioselectively cleaving C-S bonds in benzothiophenes. In each case, the C_vinyly-S bond of the BT* molecule was cleaved preferentially over the C_arlyl-S bond regardless of the position of methyl groups on the BT* molecules.

When the UV photolysis of Re₂(CO)₁₀ was carried out in the presence of H₂ (1 atm), the partially hydrogenated complexes of the type Re₂(CO)₇(μ-BT*-H)(μ-H), 3c and 3d, were produced which are models for how hydrogen could be incorporated into BT* molecules at catalyst metal centers under commercial HDS conditions. Examples of H₂ addition to BT*
molecules at transition metal centers under such mild conditions (10-15 °C, 24 h) are rare. Complexes 1a-d were unreactive towards electrophiles such as Mel, MeOTf and triflic acid, but did react with nucleophiles such as phosphines to produce the further ring-opened BT* molecules in complexes 4-7.

The mechanism for the formation of complexes 1a-d during the photolytic reaction of Re₂(CO)₁₀ and BT* could involve the S-bound complexes Re₂(CO)₉(η¹(S)-BT*) (2a-d). Furthermore, complexes 2a-d did convert into 1a-d during photolysis in hexanes solution.

The thiophenes 2,5-dimethylthiophene (2,5-Me₂T), benzothiophenes (BT*) and dibenzothiophene (DBT) each react differently with Re₂(CO)₁₀ in hexanes solution during UV photolysis to give novel C-H and C-S cleaved thiophene complexes. The thiophenes 2,5-Me₂T and BT* react photolytically with Re₂(CO)₁₀ to give the C-S cleaved thiophene complexes Re₂(CO)₇(μ-2,5-Me₂T)²¹ and Re₂(CO)₇(μ-BT) (1a-d), while DBT reacts with Re₂(CO)₁₀ to afford both the S-bound and C-H cleaved DBT complexes Re₂(CO)₉(η¹(S)-DBT)²¹ and Re₂(CO)₈(μ-C₁₂H₇S)(μ-H)²¹. Therefore, the results of the reactions of thiophenes with Re₂(CO)₁₀ suggests that the C-S bonds in thiophenes and benzothiophenes are significantly weaker than those in dibenzothiophenes.

Experimental Procedures

General Considerations. All reactions were performed under a nitrogen or argon atmosphere in reagent grade solvents and using standard Schlenk techniques. The solvents hexanes, methylene chloride, toluene and tetrahydrofuran (THF) were dried using the Grubbs solvent purification system³⁸ (purification materials were purchased from Solv-Tek, Inc). Benzene and decane were dried and distilled over CaH₂ prior to use. Deutero-methylene chloride (Cambridge) and CDCl₃ (Cambridge) were stored over 4 Å molecular sieves.
Rhenium carbonyl was purchased from Strem Chemicals Inc. Benzothiophene (Aldrich Chemical Co.), 3-methylbenzothiophene (Maybridge Chemical Co.) and 3,5-dimethylbenzothiophene (Maybridge Chemical Co.) were used as received without further purification. 2-Methylbenzothiophene was prepared according to a literature procedure. Trimethylamine N-oxide (Me₃NO) (Aldrich) was dried by azeotropic distillation in dry benzene. Silica gel (40-140 mesh, J. T. Baker) was dried and degassed under vacuum for 14 hours at ambient temperature and stored under argon. TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) was purchased from Aldrich.

¹H NMR spectra for all complexes were recorded using either a Varian VXR-300 MHz, Bruker AC 200 MHz or an in-house 400 MHz spectrometer with the appropriate deuterated solvent used as both internal lock and internal reference. Solution infrared spectra were recorded on a Nicolet-560 spectrometer using NaCl cells with 0.1 mm spacers. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. All photochemical reactions were carried out in a 50 mL capacity quartz Schlenk photolysis tube fitted with a cold-finger which was immersed into the solution. All photolysis experiments were performed using a Hanovia 450 W Hg medium pressure lamp as the light source (inserted into a water-cooled quartz jacket). The reaction temperature was controlled using an Isotemp 1013P refrigerated circulating bath (Fisher Scientific) with circulation hoses connected to the cold-finger.

Preparation of Re₂(CO)₇(μ-BT*) (1a-d). Re₂(CO)₇(μ-BT) (1a). In a typical experiment, a hexanes (40 mL) solution of Re₂(CO)₁₀ (224 mg, 0.343 mmol) and BT (97.0 mg, 0.723 mmol) was prepared in a quartz Schlenk photolysis tube equipped with a Teflon-coated magnetic stir bar. A cold-finger (10 °C) was inserted into the solution and the tube
was fitted with an oil bubbler. The solution was then irradiated for 24 h with stirring and under a slow, but constant flow of N2, during which time the solution gradually became orange and an orange precipitate was present. The orange solution was then transferred to a column of silica gel (1 x 9 cm) packed in hexanes and an orange band was eluted using a mixture of hexanes and CH2Cl2 (10:1). This orange band was collected and the solvent was removed in vacuo to afford 1a as an orange solid (61.0 mg, 24% yield). 1H NMR (CD2Cl2, 300 MHz): δ 8.63 (d, 1 H, J = 11.4 Hz), 7.11 (m, 2 H), 7.05 (dt, 1 H, J = 7.5, 1.5 Hz), 7.00 (d, 1 H, J = 11.4 Hz), 6.93 (dt, 1 H, J = 7.2, 1.5 Hz). 13C NMR (300 MHz, -50.1 °C, CD2Cl2): δ 193.4 (CO), 192.6 (CO), 189.9 (CO), 185.6 (CO), 184.7 (CO), 184.3 (CO), 177.6 (CO), 150.0, 144.7, 135.6, 129.7, 129.5, 128.0, 127.7 and 115.8. IR (hexanes) νCO: 2099 (m), 2043 (s), 2027 (s), 1981 (s), 1977 (s), 1957 (m) and 1947 (s) cm⁻¹. Anal. Calcd (found) for C15H6O7Re2S: C, 25.64 (25.54); H, 0.86 (0.69).

Preparation of Re2(CO)7(µ-2-MeBT) (1b). Complex 1b was prepared in a similar fashion as 1a by irradiation of a hexanes (30 mL) solution of Re2(CO)10 (122 mg, 0.187 mmol) and 2-MeBT (61.0 mg, 0.412 mmol) with stirring for 29.5 h (15 °C). After further work-up as described for 1a, an orange solid was produced and characterized as 1b. Orange crystals of 1b were grown overnight (-20 °C) from a CH2Cl2 (1 mL) solution of 1b layered with hexanes (3 mL). The crystals of 1b were filtered and dried under vacuum (50.1 mg, 37% yield based on Re2(CO)10). 1H NMR (300 MHz, CD2Cl2): δ 7.09 (m, 2 H), 7.01 (dt, 1 H, J1 = 7.5 Hz, J2 = 1.2 Hz), 6.89 (dt, 1 H, J1 = 7.5 Hz, J2 = 1.5 Hz), 6.36 (s, 1 H), 3.16 (s, 3 H, Me). IR (hexanes): 2096 (m), 2041 (vs), 2026 (s), 1980 (s), 1974 (vs), 1956 (m), 1944 (s) cm⁻¹. Anal. Calcd (found) for C16H8O7Re2S: C, 26.81 (26.94); H, 1.13 (1.20).
Preparation of Re$_2$(CO)$_7$(µ-3-MeBT) (Ic). Complex Ic was prepared in a similar fashion as 1a from a hexanes solution (35 mL) of Re$_2$(CO)$_{10}$ (298 mg, 0.457 mmol) and 3-MeBT (282 mg, 1.90 mmol) that was irradiated for 24 h with stirring (10 °C). The orange complex Ic was purified and isolated as described for 1a by column chromatography on silica gel. Orange crystals of Ic were grown from a solution of CH$_2$Cl$_2$ (1 mL) that was layered with hexanes (5 mL) and stored overnight (at -20 °C) (159 mg, 49% yield based on Re$_2$(CO)$_{10}$).

$^1$H NMR (200 MHz, CD$_2$Cl$_2$): δ 8.22 (s, 1 H), 7.37 (d, 1 H, J = 7.6 Hz), 7.00 (m, 3 H), 2.58 (s, 3 H, Me). IR (hexanes): ν(CO) cm$^{-1}$ 2097 (m), 2040 (vs), 2024 (s), 1979 (vs), 1973 (s), 1954 (w), 1941 (m). Anal. Calcd (found) for C$_{16}$H$_8$O$_7$Re$_2$S: C, 26.81 (26.71); H, 1.13 (1.17).

Preparation of Re$_2$(CO)$_7$(3,5-Me$_2$BT) (Id). Complex Id was prepared and isolated from a photolytic reaction of Re$_2$(CO)$_{10}$ (238 mg, 0.365 mmol) and 3,5-Me$_2$BT (200 mg, 1.23 mmol) in hexanes (36 mL). The yield (112 mg) was 42% based on Re$_2$(CO)$_{10}$. $^1$H NMR (CD$_2$Cl$_2$) 300 MHz: δ 8.20 (s, 1 H), 7.20 (s, 1 H), 6.97 (d, 1 H, J = 7.8 Hz), 6.79 (d, 1 H, J = 7.8 Hz), 2.58 (s, 3 H, Me), 2.27 (s, 3 H, Me). IR (hexanes): ν(CO) cm$^{-1}$ 2097 (m), 2040 (vs), 2023 (s), 1978 (vs), 1972 (s), 1953 (m), 1940 (s). Anal. Calcd (found) for C$_{17}$H$_{10}$O$_7$Re$_2$S: C, 27.94 (27.85); H, 1.38 (1.17).

Preparation of Re$_2$(CO)$_9$(THF). In a typical experiment, a dry THF solution (30 mL) of Re$_2$(CO)$_{10}$ (204 mg, 0.313 mmol) was prepared in a quartz Schlenk photolysis tube equipped with a Teflon-coated magnetic stir bar. A cold-finger (10 °C) was inserted into the solution and an oil bubbler was then connected to the tube. The solution was then irradiated with stirring and monitored by IR spectroscopy until the ν$_{CO}$ bands were at a maximum (1.0-
1.5 h) for Re$_2$(CO)$_9$(THF). At this point the solution was ready for use in further experiments. IR (THF): cm$^{-1}$ 2101 (w), 2038 (m), 1988 (vs), 1956 (m), 1916 (m).

**Preparation of complexes Re$_2$(CO)$_9$(η$^1$(S)-BT$^*$) (2a-d).**

Re$_2$(CO)$_9$(η$^1$(S)-BT) (2a); **Method A.** Benzothiophene (79.0 mg, 0.589 mmol) was added to a freshly prepared THF (30 mL) solution of Re$_2$(CO)$_9$(THF) (0.313 mmol based on Re$_2$(CO)$_{10}$) with stirring at room temperature. The yellow-orange solution gradually became lemon yellow (1-2 h) and was stirred for an additional 12 h at which time the solvent was removed in vacuo to produce a yellow-brown oily residue. The residue was then dissolved in CH$_2$Cl$_2$ (1 mL) and layered with hexanes (5 mL) followed by cooling overnight (-20 °C) to give pale yellow crystals of 2a (45 mg, 19% yield based on Re$_2$(CO)$_{10}$) which were filtered and dried under vacuum. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.89 (m, 2 H), 7.57 (m, 2 H), 7.44 (d, 1 H, J=5.7 Hz), 7.32 (d, 1 H, J=5.7 Hz). IR (CH$_2$Cl$_2$): 2101(w), 2045(m), 1990 (s, br), 1967 (m) and 1931 (m) cm$^{-1}$. **Method B.** A THF (15 mL) solution of Re$_2$(CO)$_{10}$ (327 mg, 0.501 mmol) was prepared under an inert atmosphere in a 50 mL Schlenk flask equipped with a stir bar. Anhydrous Me$_3$NO (40 mg, 0.523 mmol) was then added with stirring to produce a yellow-orange solution that was stirred for an additional 1 h. The volatiles (THF and NMe$_3$) were then removed under vacuum, and the resulting yellow residue was again dissolved in THF (10 mL). Benzothiophene (258 mg, 1.92 mmol) was added and the yellow-orange solution was stirred for 15-18 h. During this time, the solution lightened to a pale yellow. The solvent was removed under vacuum and the yellow oily residue was dried further under reduced pressure. The crude residue was then dissolved in toluene (1 mL) and layered with hexanes (6-7 mL) followed by cooling to -20 ° until 2a precipitated as a yellow
solid. The precipitate of 2a was then filtered and dried *in vacuo* (42 mg, 11% yield based on Re₂(CO)₁₀). Complex 2a was characterized as described in Method A.

Re₂(CO)₉(η¹(S)-3-MeBT) (2c): Complex 2c was prepared and isolated in a similar fashion as 2a using both methods A and B. **Method A:** 3-MeBT (112 mg, 0.756 mmol) was added to a freshly prepared THF (30 mL) solution of Re₂(CO)₉(THF) (0.342 mmol based on Re₂(CO)₁₀) with stirring for 20 h. After solvent removal *in vacuo*, the yellow residue containing 2c was dissolved in CH₂Cl₂ (1 mL) and layered with hexanes (5 mL) (-20 °C for 2 d). The resulting yellow crystals of 2c were then filtered and dried *in vacuo* (72 mg, 27% yield based on Re₂(CO)₁₀). **Method B:** A THF solution (25 mL) of Re₂(CO)₁₀ (310 mg, 0.475 mmol) was prepared in a 50 mL Schlenk flask. Me₃NO (35 mg, 0.460 mmol) was then added with stirring for 1 h at which time 3-MeBT (215 mg, 1.45 mmol) was added with stirring for 15 h. The solvent was removed *in vacuo* from the yellow solution. The yellow residue was dissolved in CH₂Cl₂ and layered with hexanes (1:5 mL) (-20 °C for 1 d). The crystals of 2c were filtered and dried under vacuum (93 mg, 25% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.90 (m, 1 H), 7.80 (m, 1 H), 7.61 (m, 2 H), 6.96 (s, 1 H), 2.53 (s, 3 H, Me). IR (CH₂Cl₂): 2102 (w), 2043 (m), 1989 (s, br), 1967 (m), 1931 (m) cm⁻¹. Anal. Calcd for C₁₈H₁₈O₉Re₂S; C, 27.98 (27.76); H, 1.04 (1.00).

Re₂(CO)₉(η¹(S)-3,5-Me₂BT) (2d): Complex 2d was prepared in a similar fashion as 2a using methods A and B. **Method A:** 3,5-Me₂BT (505 mg, 3.08 mmol) was added to a freshly prepared THF (30 mL) solution of Re₂(CO)₉(THF) (0.314 mmol based on Re₂(CO)₁₀) in a quartz photolysis tube with stirring for 18 h. The solvent was removed from the yellow solution under vacuum to afford a yellow residue. The residue was dissolved in CH₂Cl₂ (1-2
mL) and layered with hexanes (5-6 mL) (-20 °C) until crystals formed (1 d). The yellow crystals of 2d were then filtered and dried \textit{in vacuo} (106 mg, 43% yield). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 7.74 (d, 1 H, J=8.1 Hz), 7.58 (s, 1 H), 7.38 (d, 1 H, J=8.1 Hz), 6.91 (s, 1 H), 2.53 (s, 3 H, Me), 2.47 (s, 3 H, Me). IR (CH$_2$Cl$_2$): 2102 (w), 2042 (m), 1989 (s, br), 1963 (m) and 1931 (m) cm$^{-1}$. Anal. Calcd (found) for C$_{19}$H$_{16}$O$_9$Re$_3$S: C, 29.01 (28.53); H, 1.28 (1.13). \textbf{Method B:} A THF solution (20 mL) of Re$_2$(CO)$_{10}$ (147 mg, 0.225 mmol) was prepared in a 50 mL Schlenk flask, followed by the addition of MesNO (27.0 mg, 0.360 mmol) with stirring for 1.5 h. The volatiles were then removed \textit{in vacuo} followed by addition of THF (10-15 mL) and 3,5-Me$_2$BT (112 mg, 0.691 mmol) with stirring (10 h). The solvent was then removed and the yellow oily residue was crystallized from CH$_2$Cl$_2$ and hexanes (1:4 mL) at -20 °C after 1 d to afford yellow crystals of 2d (62.4 mg, 35% based on Re$_2$(CO)$_{10}$).

\textbf{Photolysis reaction of Re$_2$(CO)$_{10}$ and BT with CO.} A hexanes solution (35 mL) of Re$_2$(CO)$_{10}$ (246 mg, 0.377 mmol) and BT (134 mg, 1.00 mmol) was prepared in a quartz photolysis tube equipped with a stir bar, cold-finger (inserted into solution) and oil bubbler. Carbon monoxide was then bubbled through the solution for 15 min followed by irradiation of the solution with UV light for 42-48 h (15 °C). The reaction was monitored by IR spectroscopy and only bands corresponding to Re$_2$(CO)$_{10}$ were observed in the v$_{CO}$ region (IR in hexanes: 2070(w), 2014(s), 1978(m) cm$^{-1}$) during the reaction time period.

\textbf{Photolysis reaction of Re$_2$(CO)$_{10}$ and BT with TEMPO.} A hexanes solution (35 mL) was prepared in a quartz reaction tube that contained Re$_2$(CO)$_{10}$ (155 mg, 0.238 mmol), BT (95.5 mg, 0.714 mmol) and TEMPO (74.0 mg, 0.474 mmol). The solution was then irradiated with
UV light with stirring for 2-3 h (10 °C). The solution gradually became dark with a dark precipitate, but the IR spectrum of a sample taken from solution after 3 h did not reveal bands corresponding to 1a or Re$_2$(CO)$_{10}$. No attempt was made to isolate the dark material present in the reaction solution.

**Photolysis of Re$_2$(CO)$_{10}$ and 3,5-Me$_2$BT in the presence of H$_2$.** A decane (30 mL) solution containing Re$_2$(CO)$_{10}$ (288 mg, 0.441 mmol) and 3,5-Me$_2$BT (226 mg, 1.39 mmol) was irradiated in a quartz reaction tube, equipped with a cold-finger (10-15 °C), for 24 h under a steady flow of H$_2$ which was bubbled through the solution. During the reaction period the solution became yellow, and an insoluble light brown residue formed. The solution was then transferred to a column of silica (1 x 10 cm) packed in hexanes and flushed twice with hexanes to remove decane and a yellow band corresponding to H$_2$Re$_2$(CO)$_8$ (12% based on Re$_2$(CO)$_{10}$) was eluted using CH$_2$Cl$_2$ and hexanes (1:10) and collected. After solvent removal under vacuum, an orange solid remained which contained 1d (based on IR and $^1$H NMR spectroscopies) and a second product. The orange solid containing both 1d and the new product was recrystallized from a toluene (1 mL) solution layered with hexanes (5 mL) (-20 °C). After 1 d, orange crystals of 1d and colorless crystals of the new product Re$_2$(CO)$_7$(μ-3,5-Me$_2$BT-H)(μ-H) (3d) were formed, isolated by filtration and separated by hand. The hand-picked crystals of 3d were then dissolved in toluene (1 mL) and layered with hexanes again followed by recrystallization at -20 °C to afford pure crystals of 3d (1-2 d) which were isolated by filtration and dried *in vacuo* (20-30 mg, 6-18% based on Re$_2$(CO)$_{10}$). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.20 (d, 1 H, J = 8.1 Hz), 7.00 (m, 1 H), 6.84 (s, 1 H), 4.24 (s, 1 H), 4.03 (d, 1 H, J = 2.1 Hz), 2.81 (s, 3 H, Me), 2.30 (s, 3 H, Me),
-12.62 (s, hydride). IR (hexanes): \( \nu_{\text{CO}} \) 2100(w), 2039(vs), 2003(s), 1992(vs), 1964(vs), 1955(w), 1943(m) cm\(^{-1}\).

**Photolysis Reaction of 1c with \( \text{H}_2 \).** A decane solution (30 mL) of 1c (125 mg, 0.174 mmol) was prepared in a quartz photolysis tube equipped with a magnetic stir bar. A cold-finger (10 °C) was inserted into the solution and an oil bubbler was connected to the tube. Hydrogen was then bubbled through the orange solution followed by irradiation for 15-18 h. During this time the solution became dark and formed a dark brown precipitate. The IR spectrum of a sample taken from solution showed several new \( \nu_{\text{CO}} \) bands. The solution was then filtered and chromatographed on silica gel (1 x 10 cm) packed in hexanes to remove the decane solvent. A solvent combination of \( \text{CH}_2\text{Cl}_2 \) and hexanes (1:10) was then used to elute the complex \( \text{Re}_2(\text{CO})_7(\mu-\text{3-MeBT-H})(\mu-\text{H}) \) (3c) with careful monitoring of the eluents by IR spectroscopy. The volatiles were removed under vacuum to produce 3c as a white solid. \(^1\)H NMR (300 MHz, \( \text{CD}_2\text{Cl}_2 \)): \( \delta \) 7.34 (td, 1 H, \( J_1=7.8 \text{ Hz} \), \( J_2=0.9 \text{ Hz} \)), 7.19 (m, 1 H), 7.09 (m, 2 H), 4.32 (s, 1 H), 4.06 (d, 1 H, \( J=2.1 \text{ Hz} \)), 2.81 (s, 3 H, Me), -12.60 (s, hydride). IR (hexanes): 2102(w), 2041(vs), 2005(s), 1994(vs), 1966(vs), 1958(m) and 1946(s) cm\(^{-1}\).

**Reaction of 1a with PMe\(_3\).** A toluene solution of 1a was prepared in a 50 mL Schlenk flask under inert atmosphere with stirring. A toluene solution of PMe\(_3\) was then added using a syringe, followed by an immediate color change from orange to light yellow. After 35-40 min, the volatiles were removed in vacuo and the resulting yellow oil was dissolved in \( \text{CH}_2\text{Cl}_2 \) (1 mL) and layered with hexanes (4-6 mL). Colorless crystals of \( \text{Re}_2(\text{CO})_7(\text{PMe}_3)_3(\mu-\text{BT}) \) (4) and yellow crystals of \( \text{Re}_2(\text{CO})_7(\text{PMe}_3)_2(\mu-\text{BT}) \) (5) were formed from the solution overnight at -20 °C. The crystals of 4 and 5 were filtered, dried in vacuo
and partially separated by hand-picking the crystals of each complex from the mixture (30-40 mg mixture). For 4: $^1$H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.89 (dd, 1 H, J = 13.5, 3.9 Hz), 7.43 (dd, 1 H, J = 7.8, 1.2 Hz), 7.21 (d, 1 H, J = 7.2 Hz), 6.99 (dt, 1 H, J = 7.5, 1.5 Hz), 6.92 (m, 2 H), 1.62 (m, 27 H, 3PMe$_3$). IR (CH$_2$Cl$_2$) ν$_{CO}$: 2079(w), 2018(s), 1978(s,sh), 1972(s), 1933(s) and 1893(s) cm$^{-1}$. For 5: $^1$H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.06 (dd, 1 H, J = 14.1, 2.4 Hz), 7.44 (dd, 1 H, J = 14.1, 3.6 Hz), 7.26 (d, 1 H, J = 7.8 Hz), 7.00 (m, 2 H), 6.87 (m, 1 H), 1.87 (d, 9 H, PMes, J = 9.3 Hz), 1.19 (d, 9 H, PMes, J = 8.4 Hz). IR (CH$_2$Cl$_2$) ν$_{CO}$: 2100(w), 2003(s), 1953(m, br), 1896(m, br) and 1873(m, br) cm$^{-1}$. Anal. Calcd (found) for C$_{21}$H$_{24}$O$_7$P$_2$Re$_2$S: C, 29.51 (29.24); H, 2.83 (2.78).

**Reaction of 1a with P$^i$Pr$_3$.** A CH$_2$Cl$_2$ solution (6 mL) of complex 1a (50 mg, 0.071 mmol) was prepared in a 50 mL Schlenk flask equipped with a stir bar. Next, P$^i$Pr$_3$ (0.069 mL) was added using a syringe. The solution lightened within 5 min and was stirred for 2 h, followed by removal of the solvent in vacuo to produce a pale yellow solid. The solid was then dissolved in benzene (1 mL) and layered with hexanes (3-4 mL) (5 °C) to afford crystals of Re$_2$(CO)$_7$(P$^i$Pr$_3$)$_2$(μ-BT) (6) after 1 d. The crystals of 6 (21-36 mg, 28-50% yield based on 1a) were filtered, washed with cold hexanes (0 °C) and dried in vacuo. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): δ 8.30 (dd, 1 H, J$_{HH}$=14.4 Hz, J$_{HP}$=2.1 Hz), 7.43 (dd, 1 H, J$_{HH}$=14.4 Hz, J$_{HP}$=3.0 Hz), 7.19 (d, 1 H, J=6.9), 6.94 (m, 2 H), 6.79 (m, 1 H), 2.77 (m, 3 H, CH), 2.08 (m, 3 H, CH), 1.42-0.86 (m, 36 H, Me). IR (hexanes): 2100(w), 2026(m), 2007(vs), 1949(m), 1905(m) and 1884(m) cm$^{-1}$.

**Reaction of 1a with PCy$_3$.** A toluene solution (5 mL) of complex 1a (40.2 mg, 0.057 mmol) was prepared in a 50 mL Schlenk flask with stirring at room temperature. A second
toluene solution (10 mL) containing PCy₃ (36.0 mg, 0.128 mmol) was prepared in a 25 mL Schlenk flask and subsequently transferred under inert atmosphere to the stirred solution of 1a using a teflon cannula. The color of the solution changed from orange to pale yellow within 1 h and was stirred for an additional 7 h. The solvent was then removed in vacuo and the yellow solid residue was dissolved in toluene (1 mL) and layered with hexanes (6 mL) followed by cooling (-20 °C) overnight which produced a yellow crystalline solid of Re₂(CO)₇(PCy₃)₂(μ-BT) (7). Crystals of complex 7 (33.8 mg, 0.026 mmol, 46%) were filtered, washed with hexanes (2 x 4 mL) and dried under vacuum. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.33 (dd, 1 H, J_HH=14.0 Hz, J_HP=2.0 Hz), 7.46 (dd, 1 H, J_HH=14.4 Hz, J_HP=2.4 Hz), 7.24 (m, 2 H), 6.98 (m, 2 H), 6.80 (m, 1 H), 2.41-0.88 (m, Cy). IR (CH₂Cl₂): 2096(w), 2016(m), 1999(vs), 1944(m), 1888(m) and 1868(m) cm⁻¹. Anal calcd. (found) for C₅₁H₇₂O₇P₂Re₂S: C, 48.48 (48.94); H, 5.74 (6.01).

Crystallographic structural determination for complexes 2c, 1d, 3d and 7.

The systematic absences in the diffraction data were uniquely consistent for space group Pbca for 1d and also for the space groups P1 and P1̅ for 2c, 3d, and 7. In the latter three cases the E-statistics strongly suggested the centrosymmetric space group P1̅ that yielded chemically reasonable and computationally stable results of refinement. In all cases the absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with
anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions.

In the case of 1d there are two symmetry independent molecules in the asymmetric unit however, only one molecule is presented in this dissertation chapter (Figure 2). In the case of 3d the Re-H bonds were constrained to ensure stable refinement.

Acknowledgement. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, under contract W-7405-Eng-82 with Iowa State University.

References.


(3) The traditional numbering scheme for benzothiophenes (BT) is shown below:


(13) Palmer, M. S.; Harris, S. *Organometallics* 2000, 19, 2114.


(21) Reynolds, M. A.; Guzei, I. A.; Angelici, R. J. manuscript submitted for publication.


(42) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, 1997, Bruker Analytical X-Ray Systems, Madison, WI).
Table 1. Crystalllographic Data for 2c and 1d.

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*a-quantity minimized = $R(wF^2) = \Sigma(W(F_o^2 - F_c^2)^2)/\Sigma(W(F_o^2)^2)^{1/2}$, $R=\Sigma\Delta(F_o)/\Sigma F_o$, $\Delta = |F_o - F_c|$
Table 2. Crystallographic Data for 3d and 7.

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\[ a-\text{quantity minimized} = R(ωF^2) = \frac{\sum[ω(F_o^2-F_c^2)^2]}{\sum (ωF_o^2)^2}]^{1/2}, R = \frac{\sum \Delta (F_o)}{\sum F_o}, \Delta = |(F_o-F_c)| \]
Figure 1. Molecular Structure of \(eq\)-Re\(_2\)(CO)\(_9\)(\(\eta^1\)(S)-3-MeBT) (2c). Selected Distances (Å) and Angles (°): Re(1)-Re(2), 3.0343(4); Re(2)-S, 2.5220(18); Re(2)-C(9), 1.927(7); S-C(10), 1.806(9); S-C(17), 1.685(9); C(10)-C(11), 1.268(12); Re(1)-Re(2)-S, 89.21(4); Re(2)-S-C(10), 106.3(3); Re(2)-S-C(17), 111.5(3); C(10)-S-C(17), 90.5(4); S-C(10)-C(11), 114.5(7); tilt angle = 116.9°.
Figure 2. Molecular Structure of Re₂(CO)₇(μ-3,5-Me₂BT) (1d). Selected bond distances (Å) and angles (°): Re(1)-Re(2), 2.9245(3); Re(1)-S(1), 2.4320(13); Re(2)-S(1), 2.4995(13); C(4)-C(5), 1.403(7); S(1)-C(12), 1.787(5); C(5)-C(7), 1.503(7); Re(1)-S(1)-Re(2), 72.73(3); C(4)-C(5)-C(7), 122.9(5); Re(1)-S(1)-C(12), 101.38(18); Re(2)-S(1)-C(12), 102.31(17); Re(2)-C(17)-O(7), 166.6(5); Re(1)-C(4)-Re(2), 82.60(18).
Figure 3. Molecular Structure of Re₂(CO)₇(μ-3,5-Me₂BT-H)(μ-H) (3d). Selected bond distances (Å) and angles (°): Re(1)-Re(2), 3.1083(3); Re(1)-S, 2.4444(14); Re(2)-S, 2.4883(14); Re(1)-C(4), 2.417(6); Re(1)-C(5), 2.532(6); S-C(12), 1.783(6); C(4)-C(5), 1.379(8); C(5)-C(7), 1.503(8); Re(1)-S-Re(2), 78.11(4); C(4)-Re(1)-S, 98.48(14); Re(1)-S-C(12), 104.6(2); Re(2)-S-C(12), 103.21(18); C(4)-C(5)-C(7), 120.3(5).
Figure 4. Molecular Structure of Re$_2$(CO)$_7$(P$^3$Pr$_3$)$_2$(μ-BT) (7). Selected bond distances (Å) and angles (°): Re(1)-S, 2.5296(15); Re(2)-S, 2.5499(15); Re(1)-C(13), 2.173(6); C(13)-C(14), 1.343(10); C(14)-C(15), 1.492(9); Re(1)-P(1), 2.5467(14), Re(2)-P(2), 2.5316(14); Re(1)-S-Re(2), 116.69(5); Re(1)-S-C(20), 108.8(2); Re(2)-S-C(20), 102.7(2); C(13)-Re(1)-S, 83.80(13), Re(1)-C(13)-C(14), 133.5(5).
GENERAL CONCLUSIONS

Organometallic modeling of the commercial hydrodesulfurization process using Re$_2$(CO)$_{10}$ has provided insights into the possible mechanistic steps of the commercial HDS process as it relates to thiophene adsorption and C-S bond cleavage. The use of UV light in cooperation with Re$_2$(CO)$_{10}$ was shown to produce a plethora of S-bound, C-S or C-H bond cleaved and partially hydrogenated thiophene and benzothiophene complexes. Based on the studies presented in this dissertation, it could be useful to incorporate Re –based catalysts into the HDS process for the desulfurization of thiophenic molecules which are present in petroleum feeds. Furthermore, the presence of two or more metal centers in organometallic complexes have proven to be useful in the activation of C-S and C-H bonds in thiophenes and could be useful models in the future for studying in the HDS process. Much more research is needed in the area of organometallic modeling of the the HDS process in order to develop better hydrotreating catalysts.
ACKNOWLEDGEMENTS

I would like to extend my thanks: to the U. S. Department of Energy, Office of Science, Office of Basic Sciences, Chemical Sciences Division, under contract W-7405-Eng-82 with Iowa State University for funding the work presented in this dissertation; to Professor R. J. Angelici for his guidance and helpful suggestions for the past 5 years on research, and particularly for helping me learn how to write more scientifically; to Dr. Ilia Guzei who conducted the X-ray diffraction studies and solved the crystal structures of all complexes mentioned in the dissertation; and also to the past and present group members for their contributions and helpful discussions on many topics including chemistry, particularly Dave Klein, Scott McKinley, Keith Stanger, Paul Vecchi, Seong, Max Ovchinnikov and Moon-Gun Choi.

A very special thanks is also deserved for my family and friends for tolerating my erratic behavior during my career at Iowa State University (and otherwise) including my mother (Toni) and father (Michael), sister and brothers (Erin, Kevin and Andrew), Julius and Becky. I also thank my girlfriend Erica Elliott, whom I love very much, for being so supportive these past couple of years (and for making me Mocha’s when I was writing late at night).

I have also appreciated knowing and learning from Professors Gordie Miller, Nenad Kostic, Valerie Sheares, Walter Trahanovsky and Victor Lin all of whom have contributed to my success here at Iowa State University.