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Organometallic Modeling of the Hydrodesulfurization (HDS)
Process: Rhenium Carbonyl-promoted C-S Bond Cleavage and
Hydrogenation of Thiophenes and Benzo thiophenes

by

Reynolds, Michael A.

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Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011-3020

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Michael Anthony Reynolds

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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 $\text{Re}_2(\text{CO})_{10}$ 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.

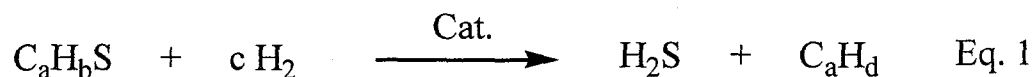
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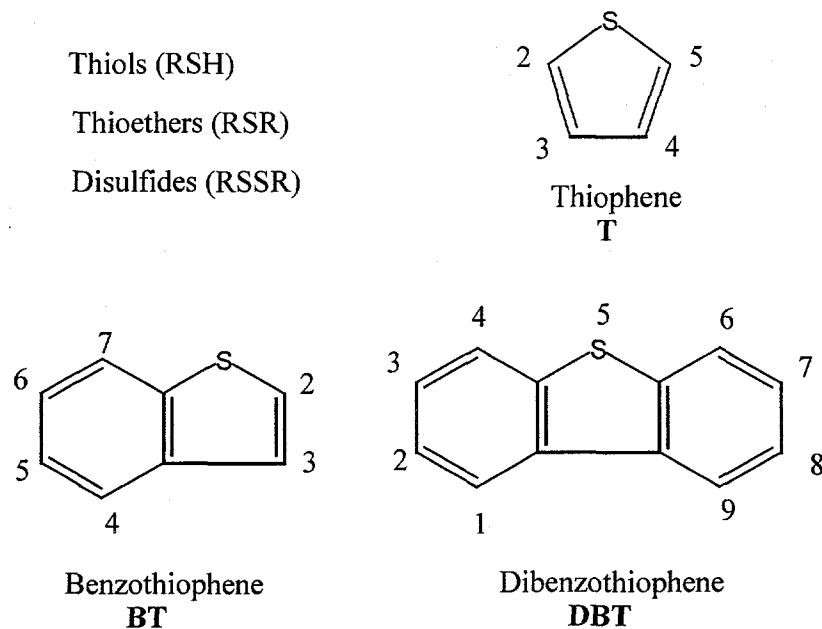
This dissertation consists of 4 main chapters: the first is an overview of current literature on metal clusters as HDS catalysts; subsequent chapters (2-4) are papers, submitted for publication, that discuss the role of $\text{Re}_2(\text{CO})_{10}$ in promoting binding, C-H and C-S bond cleavage and 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:^{1,2} 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.³ 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.^{4,5} 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_2S (eq. 1).¹ The catalysts typically used are MoS_2 or WS_2 that are promoted by Co or Ni and supported on alumina.^{1,2,6}





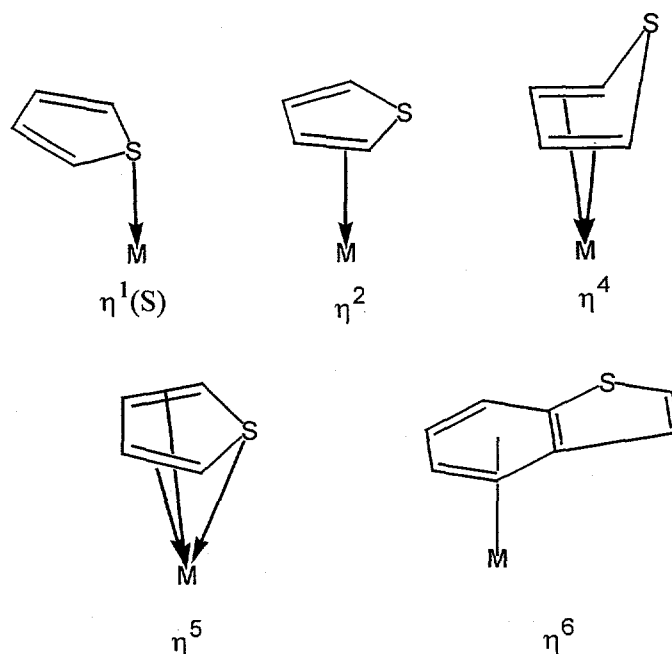
Scheme 1 Numbering system for thiophenic molecules.

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.^{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 $\eta^1(\text{S})$, η^2 , η^4 , η^5 and η^6 (Scheme 2) and many transition metal complexes containing thiophene ligands bound in several different ways have been

reported.^{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



Scheme 2 Thiophene binding modes.

transition metal complexes.^{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.

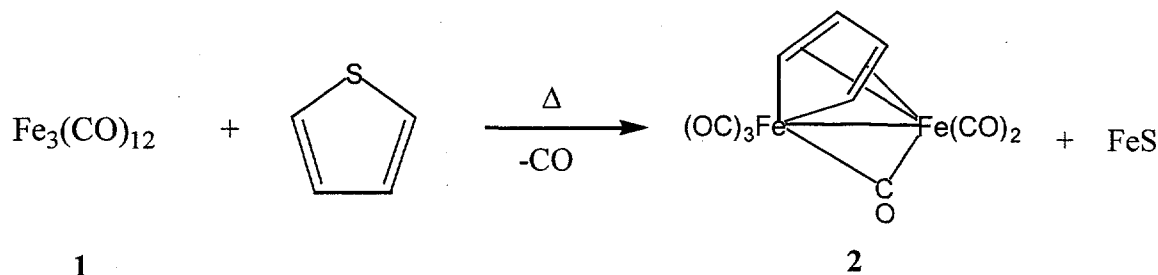
$M_3(CO)_{12}$ Clusters (M = Fe, Ru or Os) and $Co_4(CO)_{12}$

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 $M_2(CO)_9$ (for M = Fe or Os) or $M_3(CO)_{12}$ (where M = Fe, Ru or Os) with carbon monoxide. The $M_3(CO)_{12}$ 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 $M_2(CO)_8$ (where M = Co or Rh) and $M_4(CO)_{12}$ (M = Co, Rh, Ir). However, only the Co clusters, $Co_2(CO)_8$ and $Co_4(CO)_{12}$ 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

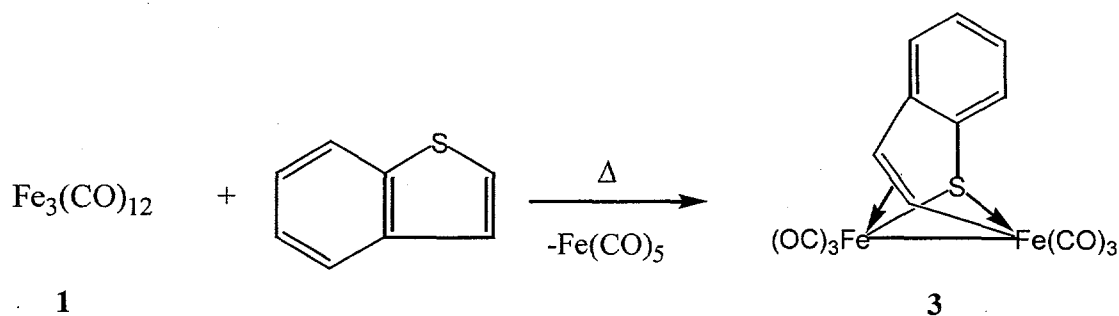
Stone and coworkers⁸⁻¹⁰ were the first to demonstrate the reactivity of organometallic clusters with thiophenic molecules, such as thiophene (T) and benzothiophene (BT), under thermal conditions to produce ring-opened or desulfurized thiophene-containing transition metal complexes. In these early studies it was found that when Fe₃(CO)₁₂ (**1**) 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

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



Scheme 4

complexes were observed during this reaction. The reaction of $\text{Fe}_3(\text{CO})_{12}$ with 2-methylthiophene (2-MeT) in refluxing heptane produced both the corresponding thiaferrole, $\text{Fe}_2(\text{CO})_6(\mu\text{-2-MeT})$ (**4**) in 0.7% yield, and also the desulfurized ferrole product $\text{Fe}_2(\text{CO})_6(2\text{-MeC}_4\text{H}_3)$ (**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 H_2 (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 $\text{Fe}(\text{CO})_5$; and also by heating **3** *in vacuo* to give Fe metal.

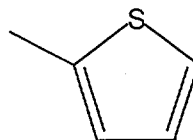
In summary, the first examples of ring-opened and desulfurized thiophenes by a metal-metal bonded cluster were demonstrated using $\text{Fe}_3(\text{CO})_{12}$ (**1**). Cluster **1** was shown to react with thiophenes and benzothiophenes to afford thiaferroles and ferroles as HDS model complexes. In some cases, reactions of these metal insertion products with H_2 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.

$\text{Ru}_3(\text{CO})_{12}$

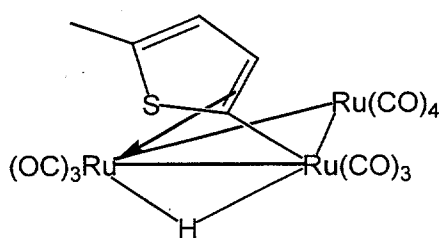
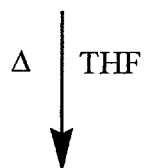
Recently, $\text{Ru}_3(\text{CO})_{12}$ (**6**) has been reported to react with thiophenes and benzothiophenes to afford both ring-opened and desulfurized thiophene-containing complexes, some of which are similar to those observed in the analogous reactions of $\text{Fe}_3(\text{CO})_{12}$. For instance, when $\text{Ru}_3(\text{CO})_{12}$ and 2-MeT are heated in refluxing THF, three Ru-based thiophene complexes are produced in low to moderate yields (Scheme 5).¹⁴

The first complex, $\text{Ru}_3(\text{CO})_{10}(\mu\text{-2-Me-C}_4\text{H}_4\text{S})(\mu\text{-H})$ (**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 $\text{Ru}(\text{CO})_4$ moiety. These isomers were not separated, but were characterized as a mixture using spectroscopic methods (IR and NMR). Complex **7** consists of a planar $\text{Ru}_3(\text{CO})_{10}$ unit in which the C-H cleaved 2-Me-5-thienyl species bridges the two $\text{Ru}(\text{CO})_3$ centers in an η^2 - and an η^1 -fashion with the hydride bridging the two $\text{Ru}(\text{CO})_3$ fragments.

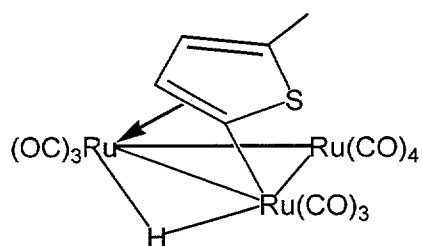
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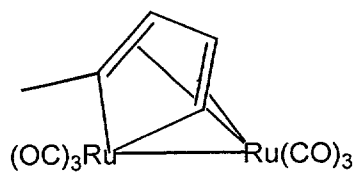
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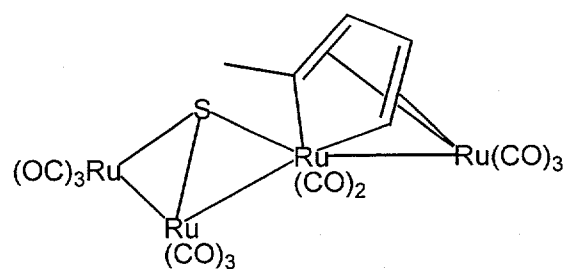
7a, (exo)



7b, (endo)



8



9

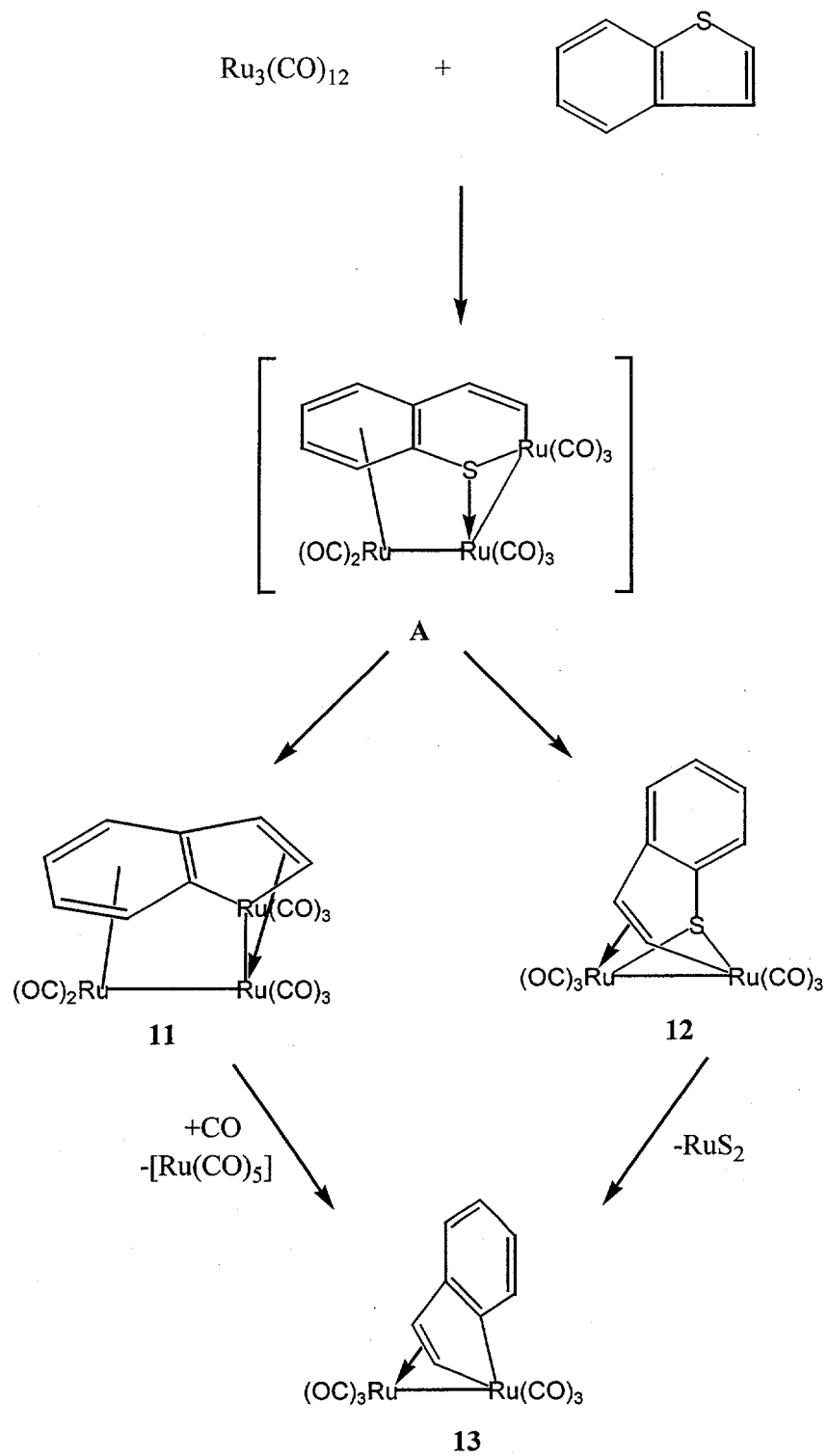
Scheme 5

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 $\text{Ru}_2(\text{CO})_6(\text{MeC}_4\text{H}_3)$ (**8**) is structurally analogous to the ferrole complexes previously reported, such as $\text{Fe}_2(\text{CO})_6(\text{C}_4\text{H}_4)$ ⁸ and $\text{Fe}_2(\text{CO})_6(\text{MeC}_4\text{H}_3)$ ¹³, which were prepared in a similar manner from $\text{Fe}_3(\text{CO})_{12}$. 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 $\text{Ru}_4(\mu_3\text{-S})(2\text{-MeC}_4\text{H}_3)(\text{CO})_{11}$ (**9**). The molecular structure of **9** reveals that the sulfur has been extruded from the thiophene ring and replaced by a $\text{Ru}(\text{CO})_2$ moiety to form a metallacyclopentadiene species. The extruded sulfur caps the $\text{Ru}(\text{CO})_2$ unit and two of the $\text{Ru}(\text{CO})_3$ moieties of the Ru_3 -plane. A third $\text{Ru}(\text{CO})_3$ unit is bonded to the $\text{Ru}(\text{CO})_2$ unit and is also η^4 -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 $\text{Ru}_2(\text{CO})_6(\text{C}_4\text{H}_4)$ (20% yield) and $\text{Ru}_4(\mu_3\text{-S})(\text{C}_4\text{H}_4)(\text{CO})_{11}$ (**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 $\text{Ru}_3(\text{CO})_8(\mu\text{-C}_8\text{H}_6)$ (**11**), $\text{Ru}_2(\text{CO})_6(\mu\text{-C}_8\text{H}_6\text{S})$ (**12**) and $\text{Ru}_2(\text{CO})_6(\text{C}_8\text{H}_6)$ (**13**)



Scheme 6

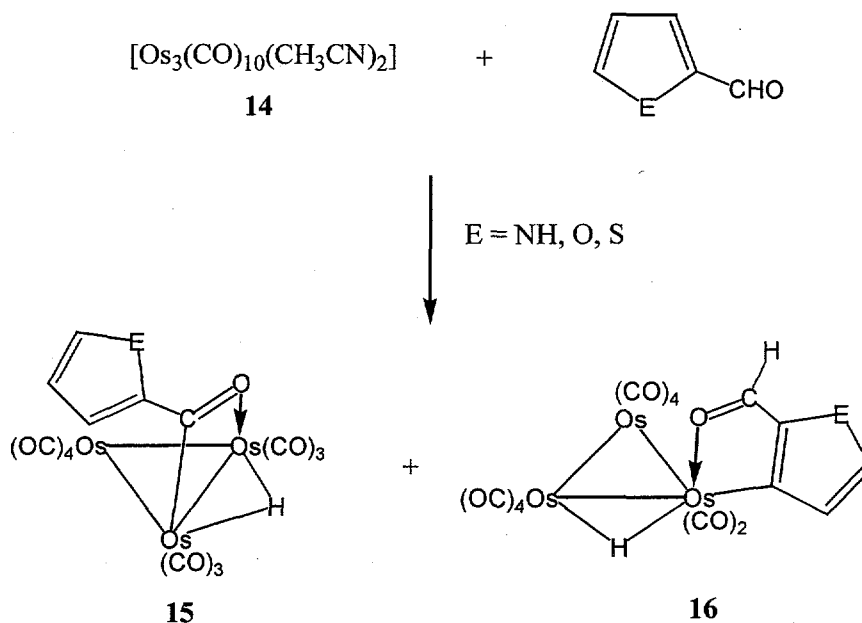
(Scheme 6)¹⁵ all of which contain ring-opened or desulfurized BT ligands. Complexes **11**, **12** and **13** were separated by TLC in yields of 28, 17 and 10% respectively and were characterized both spectroscopically (NMR and IR) and by their X-ray structures. These three complexes are proposed to 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 $\text{Ru}(\text{CO})_3$ group with the resulting $(\text{C}_8\text{H}_6)\text{Ru}(\text{CO})_3$ moiety acting as a π -ligand towards the $\text{Ru}_2(\text{CO})_5$ backbone. The formation of $\text{Ru}_3(\text{CO})_8(\mu\text{-C}_8\text{H}_6)$ (**11**) can be explained by the unobserved intermediate **A** undergoing desulfurization followed by ring closure. Complex **11** reacts further in CDCl_3 after 24 h at room temperature and under CO (1 atm) to afford the final desulfurized complex $\text{Ru}_2(\text{CO})_6(\text{C}_8\text{H}_6)$ (**13**) with proposed loss of $\text{Ru}(\text{CO})_5$. The complex $\text{Ru}_2(\text{CO})_6(\mu\text{-C}_8\text{H}_6\text{S})$ (**12**), which is a structural analog of the thiaferrole **3**, is also produced during the reaction of $\text{Ru}_3(\text{CO})_{12}$ with BT and occurs through the intermediate **A**, which eliminates RuS_2 to afford **13**. Complex **13** is similar to the ferrole complex **2**, in which one $\text{Ru}(\text{CO})_3$ unit forms a metallacycle with the desulfurized hydrocarbon and the other Ru binds η^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 $\text{Ru}_3(\text{CO})_{12}$ 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 $\text{Fe}_3(\text{CO})_{12}$. 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 $\text{Ru}_3(\text{CO})_{12}$ compared to $\text{Fe}_3(\text{CO})_{12}$ warrants further investigations into the reactivity of homoleptic and mixed metal with

thiophenic molecules. Such studies could lead to the preparation on new HDS models for thiophene activation which have not been observed in either Ru or Fe clusters alone.

$\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ and related clusters.

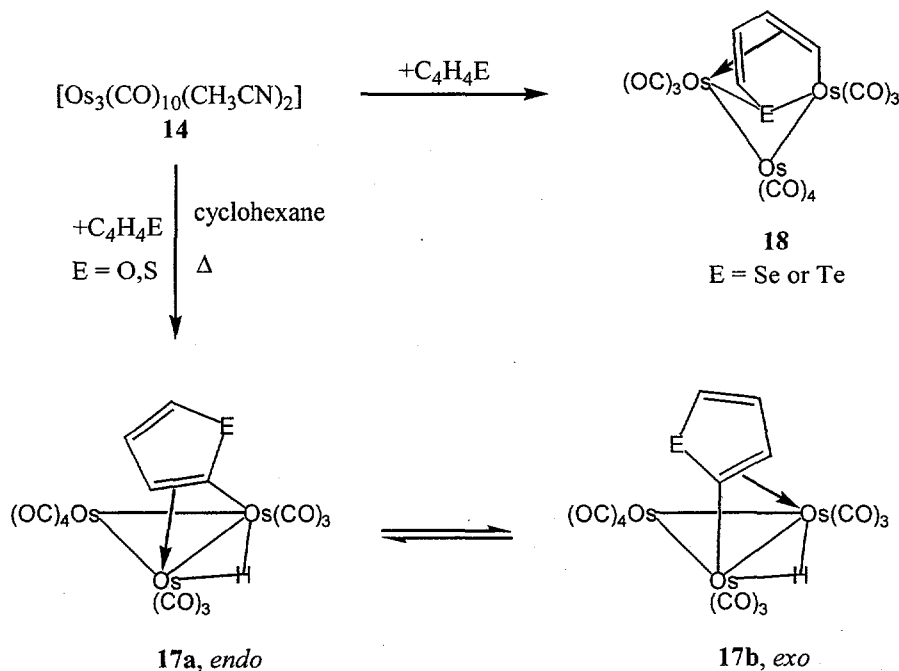
The osmium carbonyl cluster $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ (**14**) reacts with thiophenes and benzothiophenes to give a series of novel Os-thiophene complexes in which the thiophene has undergone bond cleavage. For example, **14** was first found to react with the 2-formyl derivatives of the heterocycles, $\text{C}_4\text{H}_3\text{X}(\text{CHO})$ ($\text{X} = \text{NH}, \text{S}$ or O), including 2-formylthiophene ($\text{X} = \text{S}$), to produce the triosmium hydride clusters $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu_2\text{-(CO)C}_4\text{H}_3\text{E})$ (**15**) and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu_2\text{-C}_4\text{H}_2\text{E}(\text{CHO}))]$ (**16**) ($\text{E} = \text{S}$ only) (Scheme 7).¹⁶ 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 $\text{Os}(\text{CO})_3$ units.



Scheme 7

The thiophene ligand in **16** behaves as a chelating ligand to a $\text{Os}(\text{CO})_3$ 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 $\text{E} = \text{NH}$ 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 $[\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_4\text{S})(\mu\text{-H})]$ (**17a,b**) (Scheme 8).

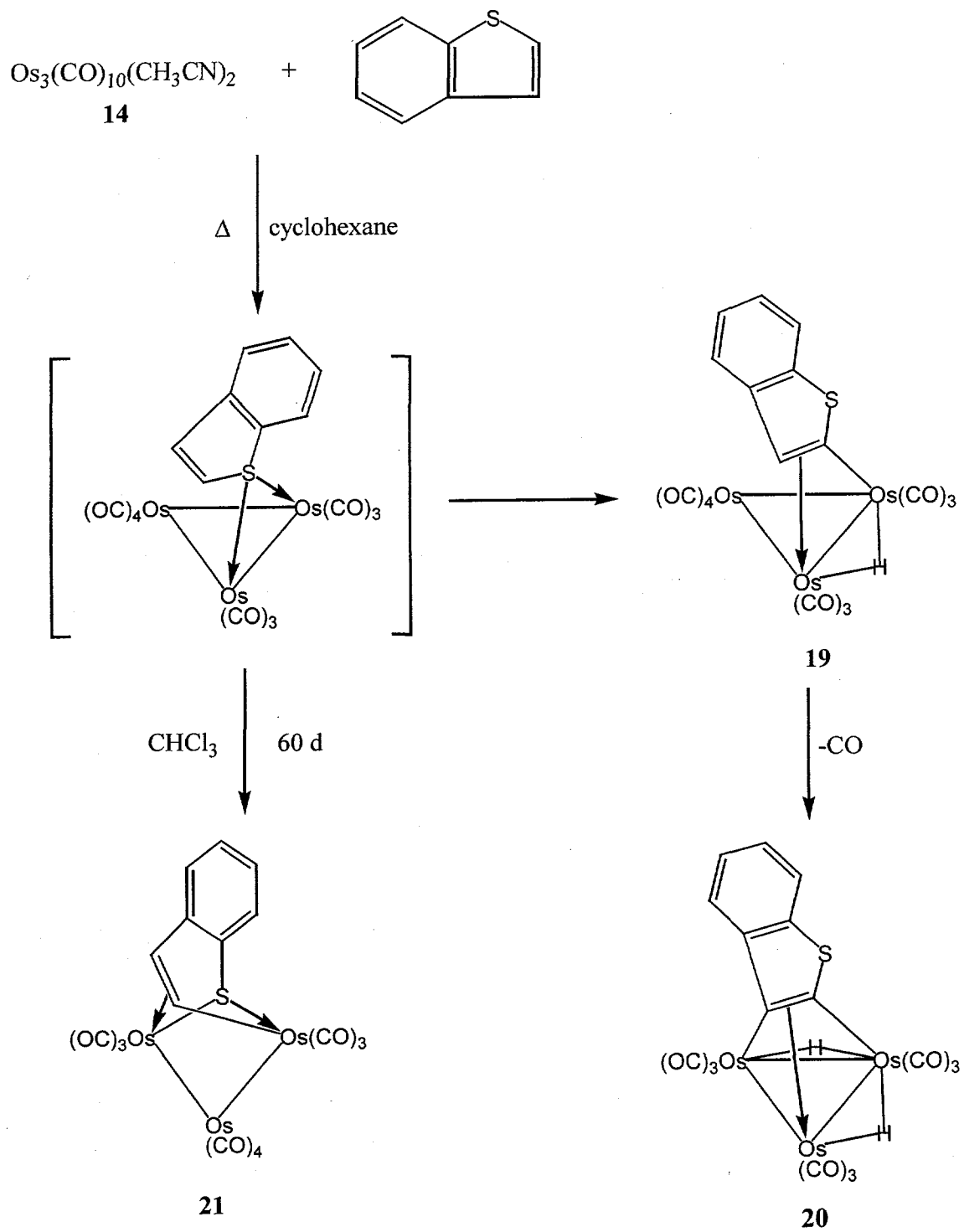


Scheme 8

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 $\text{Ru}_3(\text{CO})_{12}$ 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).¹⁷ 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-vinyl ligand.

The versatility of complex **14** has also been extended to C-S and C-H bond cleavage in BT and dibenzothiophene (DBT) compounds. Arce,¹⁸ 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

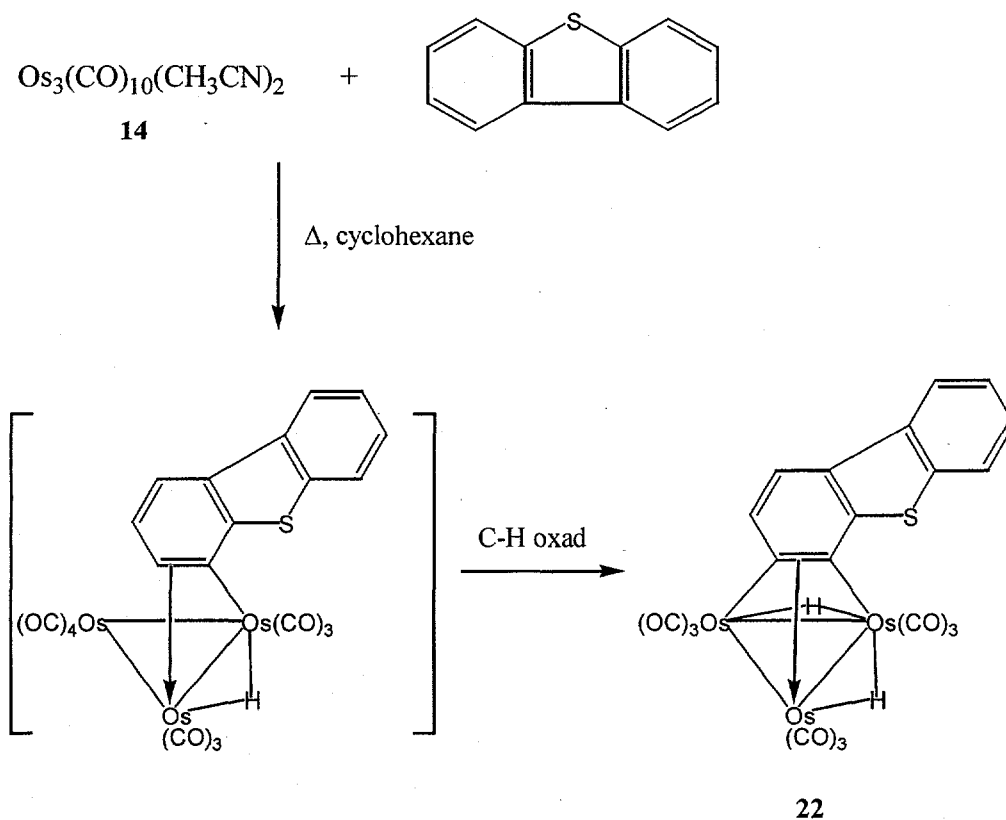


Scheme 9

can be described as a bridging "thiophyne" which is analogous to a benzyne ligand.

Dibenzothiophene reacts with **14** in refluxing cyclohexane to produce, $[\text{Os}_3(\text{CO})_9(\mu\text{-H})_2(\mu\text{-C}_{12}\text{H}_6\text{S})]$ (**22**) in 23% yield after separation by TLC on silica gel (Scheme 10).¹⁸

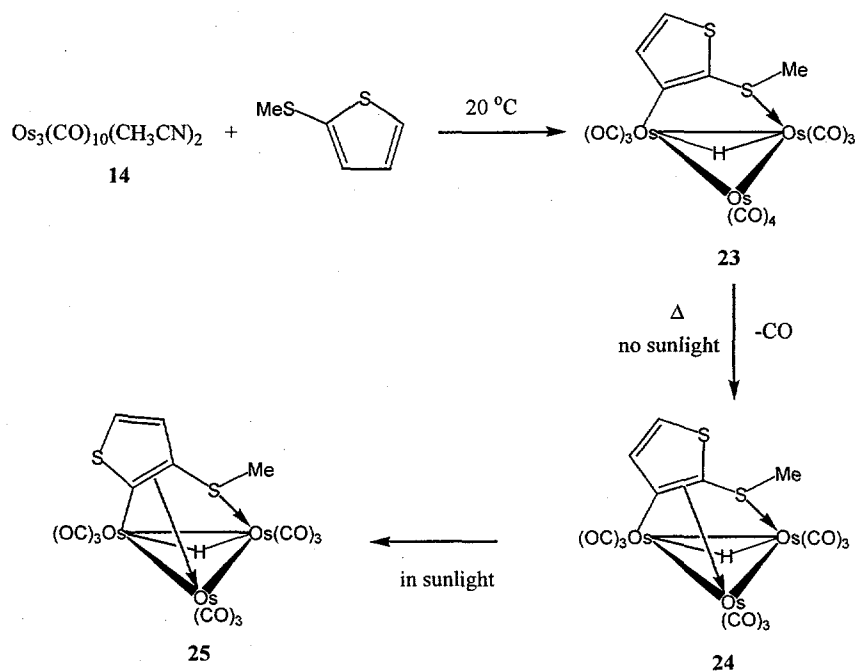
Complex **22** is bound to the Os_3 unit as a 'benzyne' type ligand as described for **20** in which two C-H bonds of the DBT ring have been oxidatively added to the Os_3 cluster unit resulting in two bridging hydride ligands. It is possible that complex **22** is formed via an intermediate species such as that shown in Scheme 8 by oxidative addition of a second C-H bond to another Os center of the proposed intermediate.



Scheme 10

The η^1, η^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.

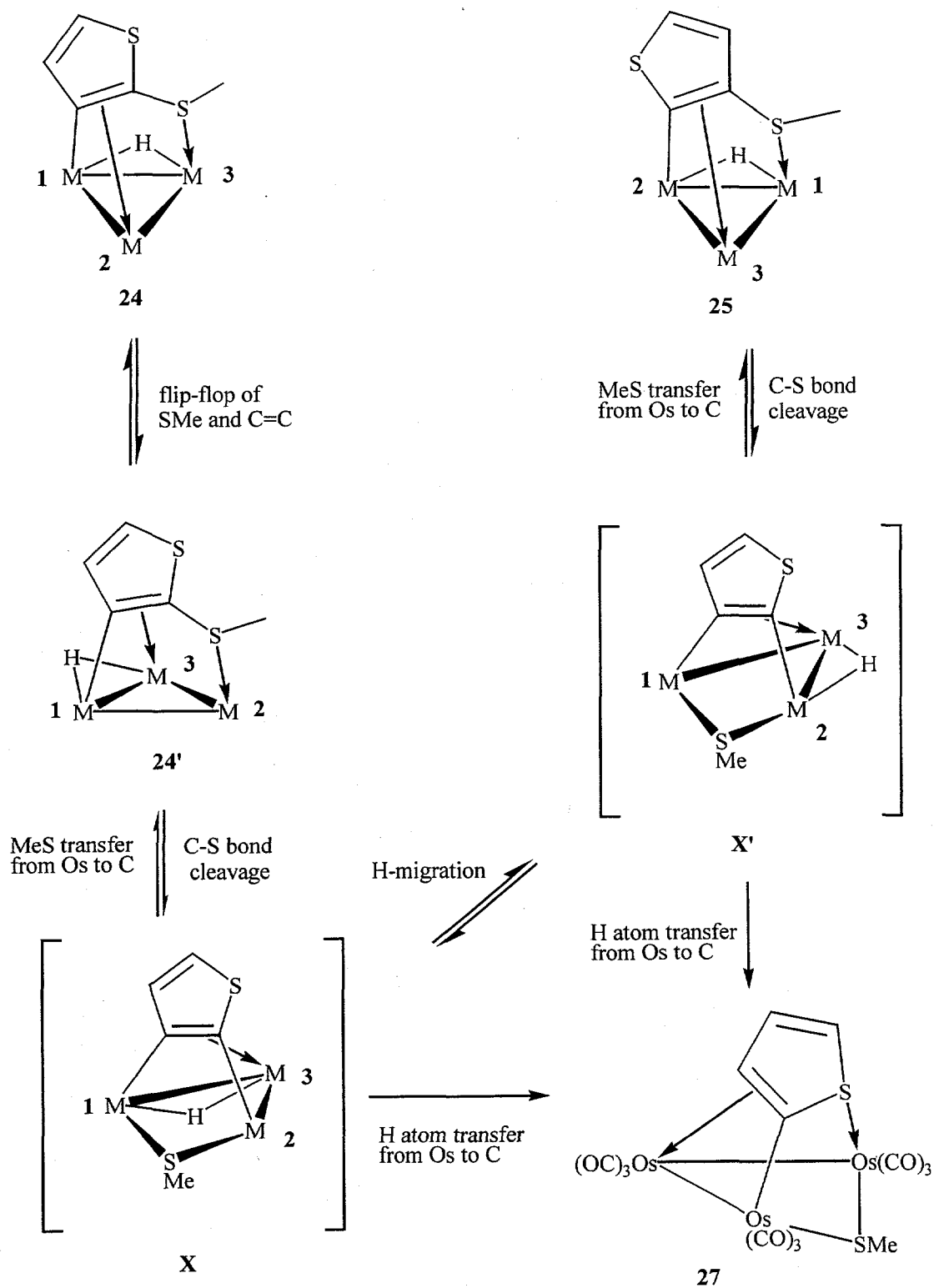
In yet another interesting HDS model study, complex **14** was found to react with 2-methylthiophene (2-MeS-T) at 20 °C to form the hydride complex $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-2-MeSC}_4\text{H}_2\text{S})]$ (**23**) in 68% isolated yield. The molecular structure of **23** was established and showed that the C-H bond in the 3-position of the thiophene has oxidatively added to a $\text{Os}(\text{CO})_3$ unit of the Os_3 cluster core with formation of a bridging hydride ligand (Scheme 11)¹⁹. The $\eta^1(\text{S})$ binding of -SMe group in **23** is to a $\text{Os}(\text{CO})_3$ 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

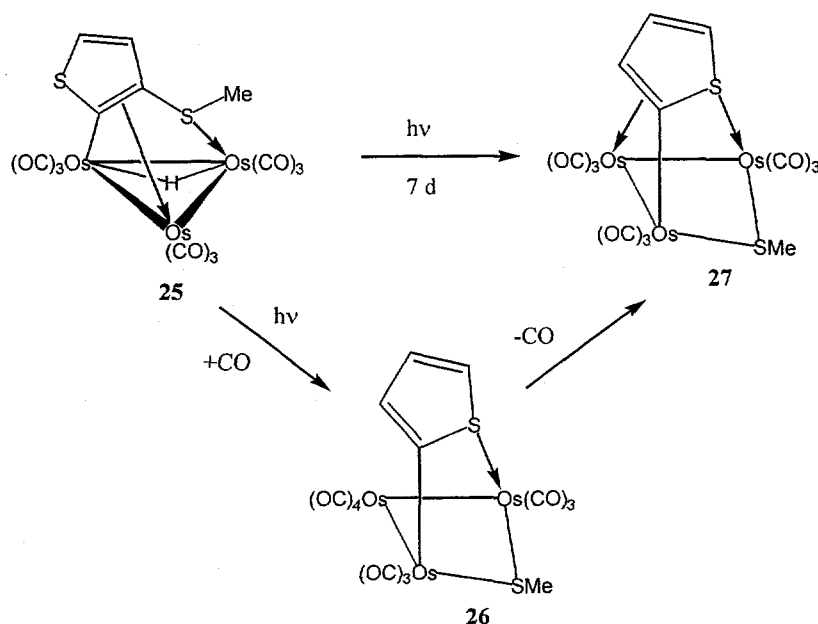
In refluxing octane, complex **23** loses CO from the Os(CO)₄ group with subsequent η^2 -binding of a C=C bond to the resulting Os(CO)₃, to afford the isomers **24** and **25** (36% mixture). The X-ray structures of single crystals of both isomers were determined. In the molecular structure of **24**, the thienyl ligand is μ_3 -bridging the Os₃ 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 Os₃ 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 [Os₃(CO)₁₀(μ -H)(μ -2-MeSC₄H₂S)] (**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 CD₂Cl₂ 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 $\eta^1(\text{S})$, η^2 - through the C2-C3 double bond and η^1 -at the 2-position to the Os metal centers. Complex **27** was characterized spectroscopically (^1H NMR), and is possibly a result of the pathway shown in Scheme 12. However, it was observed that when a CD_2Cl_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 -SMe ligand and a thienyl functionality that bridges the Os_3 core both η^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 η^2 -binding of the thienyl group at the vacant Os metal center (Scheme 13).

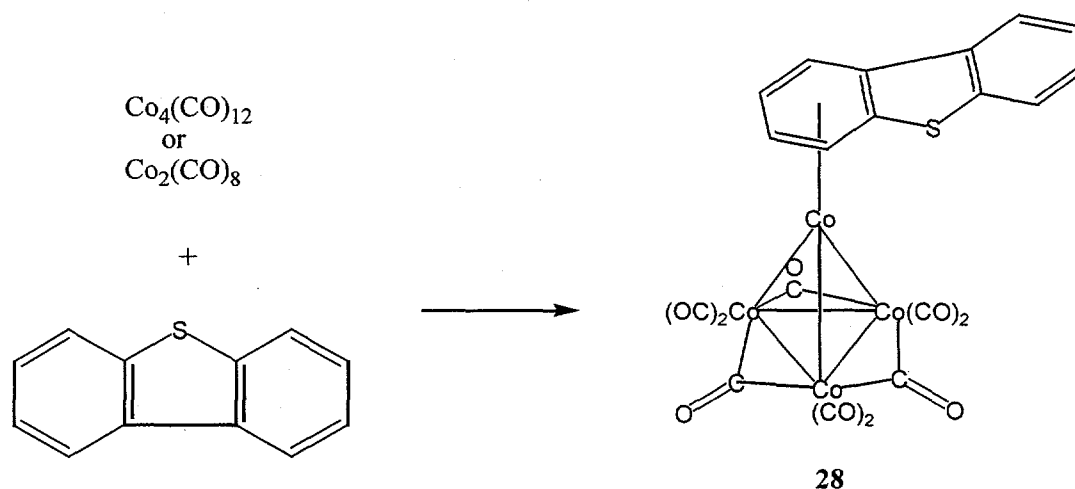


Scheme 13

In conclusion to this section, it has been demonstrated that both thermal and photochemical reactions of $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ (**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 $\text{Os}_3(\text{CO})_{12}$.

$\text{Co}_4(\text{CO})_{12}$

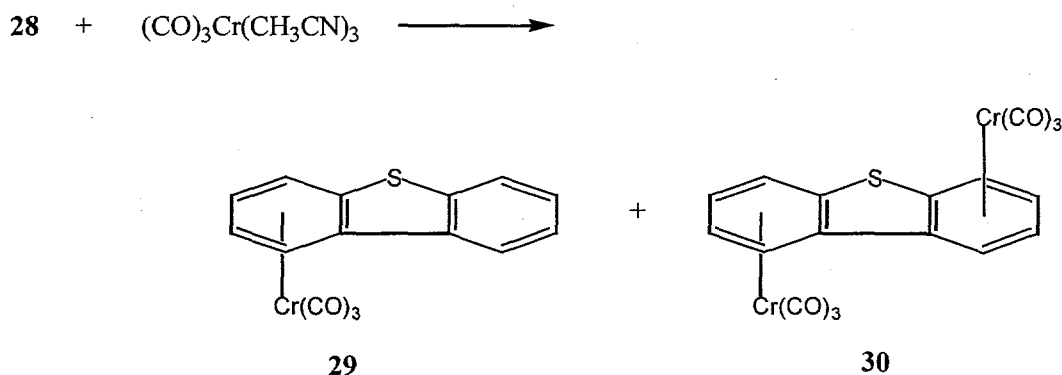
As a promoter, cobalt is an important component of the Co-Mo/ Al_2O_3 catalyst system used in the commercial HDS of petroleum feeds.¹ Despite its importance in this process, very few reactions have been reported for thiophenes and benzothiophenes with cobalt cluster complexes. Recently, Chen and Angelici²⁰ found that $\text{Co}_4(\text{CO})_{12}$ will react with DBT in refluxing hexanes to produce the π -bound complex $(\eta^6\text{-DBT})\text{Co}_4(\text{CO})_9$ (**28**) in moderate yield (44%) (Scheme 14).



Scheme 14

The molecular structure of **28** contains a $\text{Co}_4(\text{CO})_9$ 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 $\text{Cr}(\text{CO})_6$ to give the previously reported $(\eta^6\text{-DBT})\text{Cr}(\text{CO})_3$ (**29**)²¹ and the new complex $(\eta^6\text{-DBT})[\text{Cr}(\text{CO})_3]_2$ (**30**) in which both $\text{Cr}(\text{CO})_3$ units are on opposite sides of the DBT ring (Scheme 15).

Surprisingly, $(\eta^6\text{-DBT})\text{Co}_4(\text{CO})_9$ also reacts with $(\text{CO})_3\text{Cr}(\text{CH}_3\text{CN})_3$ to give an η^6 -benzene complex, $(\eta^6\text{-benzene})\text{Co}_4(\text{CO})_9$ (**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 $\text{Co}_4(\text{CO})_{12}$ to give **31** in 41% isolated yield with no evidence of an η^6 -bound BT intermediate complex such as that found for DBT.

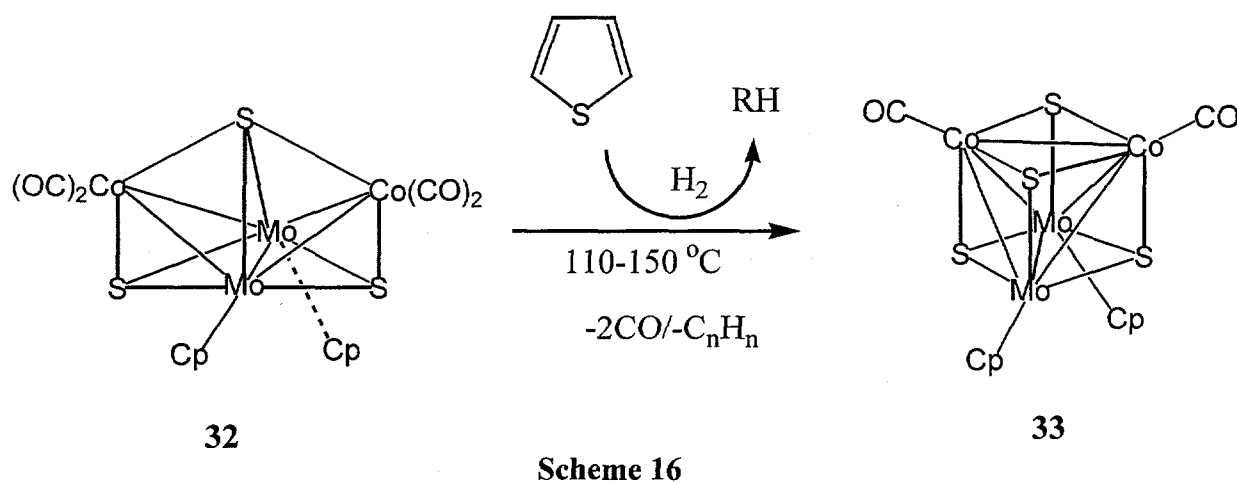


Scheme 15

Organometallic sulfide clusters

Curtis and coworkers^{22,23} prepared a series of mixed metal sulfido clusters that are similar in composition to commercial HDS catalysts. For example, the complex $\text{Cp}'_2\text{Co}_2\text{Mo}_2(\text{CO})_4\text{S}_3$ (**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

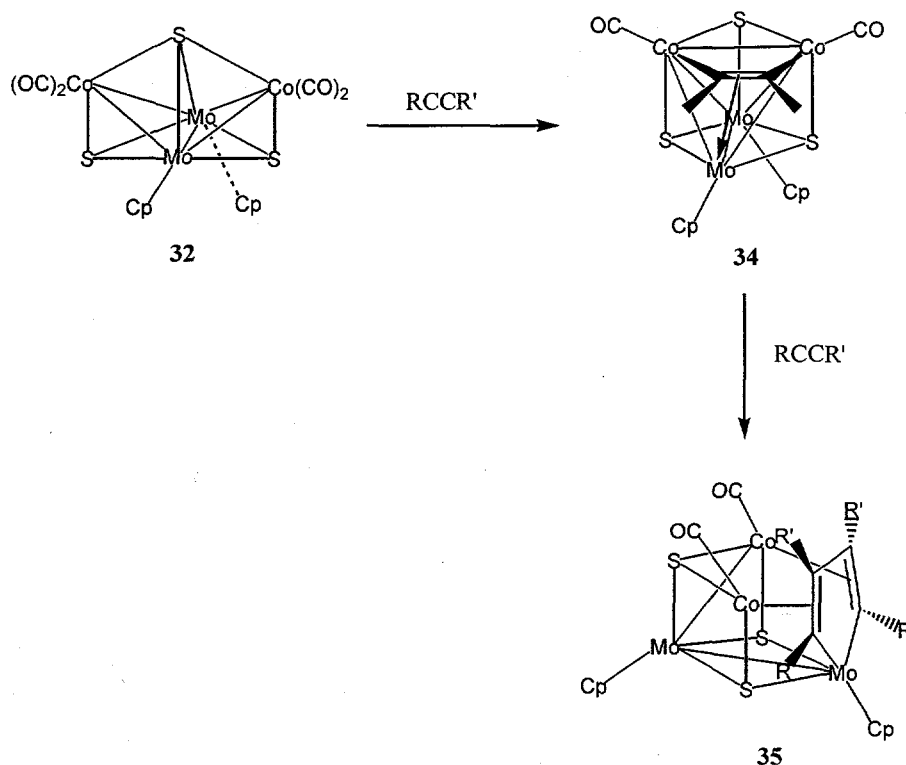
150 °C to produce the cubane cluster $\text{Cp}'_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ (**33**) quantitatively along with a carbon-based black residue following desulfurization of the thiophene (Scheme 16).²⁴ In the presence of H_2 (150 °C, 200 psi), complex **32** reacts with thiophene to 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 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 H_2 (150 °C, 500 psi) if thiophene is 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 *in situ*, **32** was reacted with alkynes such as PhCCH and RCCR ($\text{R} = \text{H}$, Pr or Ph);^{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 $\text{Cp}'_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_3$

$(\mu_3\text{-RCCR})_2$ (**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

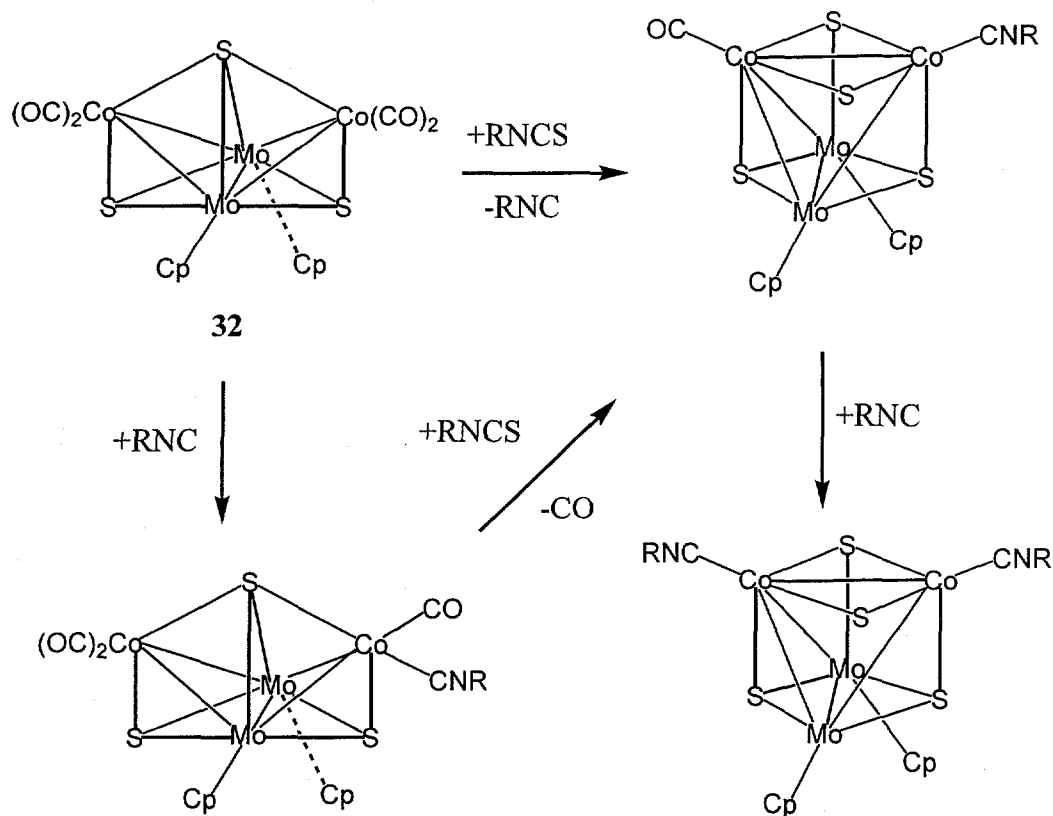


Scheme 17

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).²⁶ 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 characterized spectroscopically^{24,26} however, they were not characterized using X-ray diffraction studies.

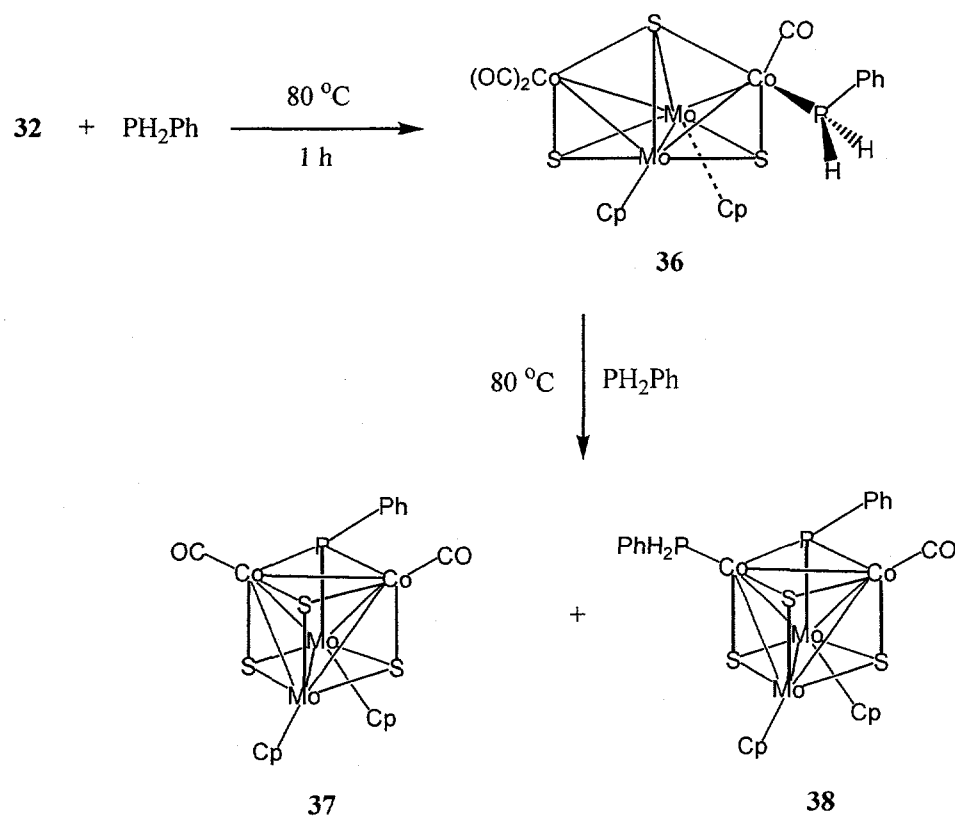


Scheme 18

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 H₂. While complex **33** did react with H₂ or CO/H₂ (50 psi, CO and 400 psi H₂, 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 H₂ 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.²⁶

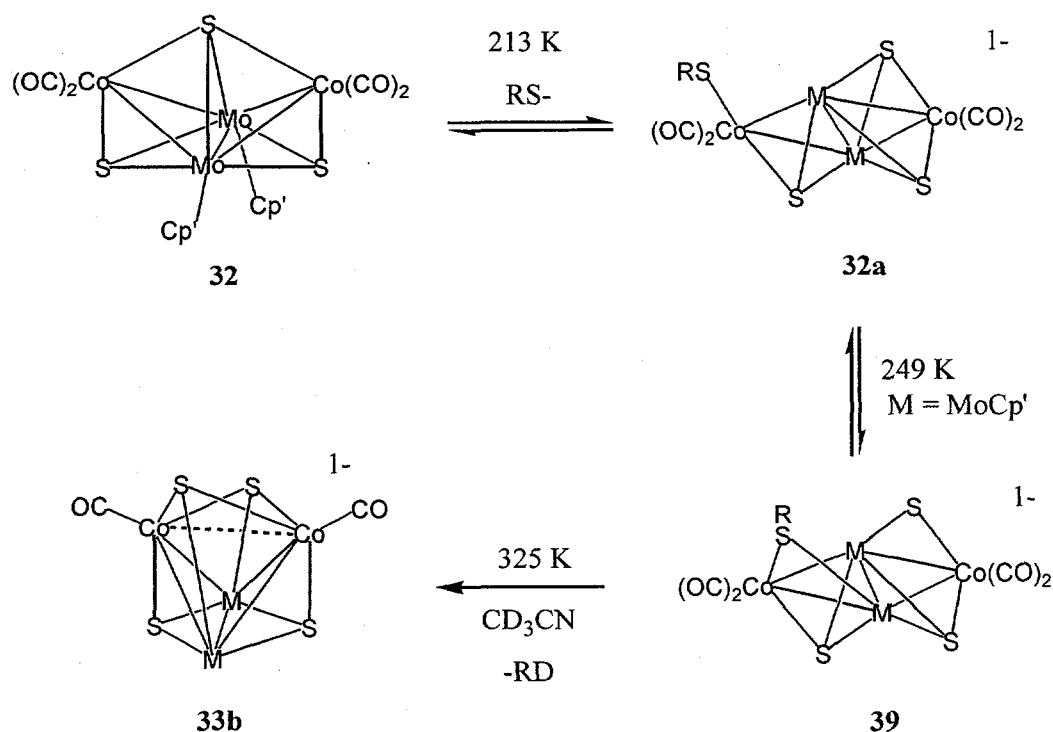
In an effort to support the possibility of a thiophene adduct of **32** as an intermediate in the thiophene desulfurization reaction presented in Scheme 16, complex **32** was reacted with isolobal analogs of H₂S, such as PH₂R to form P-bound clusters.^{26,27} Cluster **32** readily reacts with alkyl phosphines at 80 °C (1 h) to afford Cp₂Mo₂Co₂S₃(CO)₃(η¹(P)-PH₂R) (**36**) in 65% yield (Scheme 19) with loss of CO. The reaction of **36** with excess PH₂R in refluxing benzene produced the phosphinidene cluster **37** and the CO-substituted phosphinidene adduct **38**.



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 H_2S 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 ^1H 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



Scheme 20

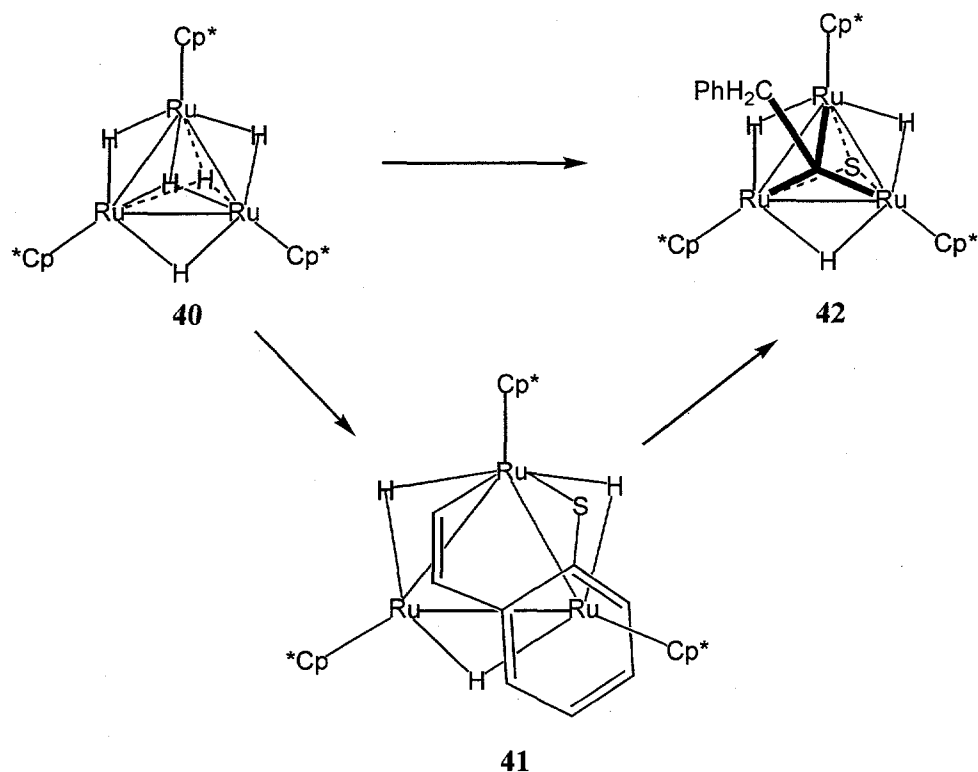
changed from red to green, CO was evolved, and a new complex, $\text{Cp}_2\text{Mo}_2\text{Co}_2\text{S}_3(\text{CO})_4(\text{SAr})^{1-}$ (**39**), was detected. Upon warming in CD_3CN solvent, **39** was converted into the radical anion **33b**. The only other detectable product in the reaction was 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 σ^* 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_2R 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 $\text{Cp}^*_3\text{Ru}_3\text{H}_3(\mu\text{-BT})$ (**41**) is formed as an intermediate which was characterized by ^1H 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 μ_3 -sulfido group and on the opposite face by a $\text{C-CH}_2\text{-Ph}$ moiety. The $\mu_3\text{-C-CH}_2\text{-Ph}$ 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 $[\text{Cp}^*\text{RuH}]_3(\mu_3\text{-S})$ (**43**) quantitatively with elimination of ethyl benzene.



Scheme 21

Dibenzothiophene reacts with cluster **41** in toluene (110 °C, 8 d) to also produce the sulfido cluster $[\text{Cp}^*\text{RuH}]_3(\mu_3\text{-S})$ **43** (67%) and biphenyl (64%).³⁰ 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 hydrides 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: $\text{Re}_2(\text{CO})_{10}$ -PROMOTED CLEAVAGE OF C-S BONDS IN BENZOTHIOPHENE

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

Michael A. Reynolds, Ilia A. Guzei[†] and Robert J. Angelici

Abstract

Ultraviolet photolysis of hexanes solutions containing $\text{Re}_2(\text{CO})_{10}$ and benzothiophene (BT) give the C-S cleavage product $\text{Re}_2(\text{CO})_7[\eta^2(\text{C}_2, \text{C}_3)-\mu_2(\text{C}_2, \text{S})\text{-BT}]$ (1) which reacts with PMe_3 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

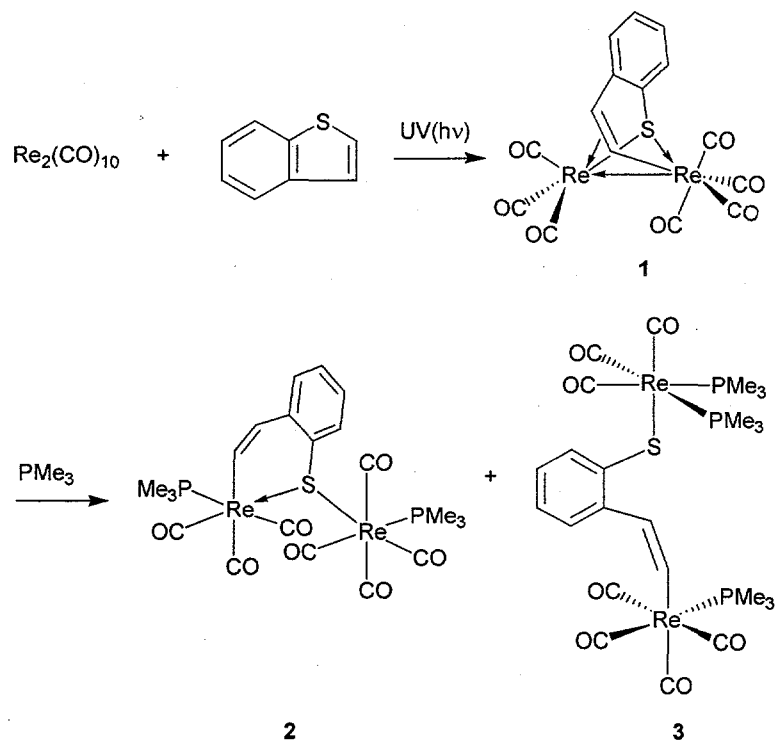
Heterogeneous catalytic hydrodesulfurization (HDS), the commercial process used for the removal of sulfur from organosulfur compounds present in petroleum-based feedstocks, is important in industry and for the environment.^{1,2} Typically, the sulfur in crude petroleum is present in the form of organic 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.³ 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 $\text{Re}_2(\text{CO})_{10}$ with BT under mild conditions to produce the C-S cleavage product (1) containing a Re-Re backbone.

Upon addition of PMe_3 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 $\text{Re}_2(\text{CO})_{10}$ and 2 eqv. of BT in a quartz reaction



Scheme 1

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 $\text{Re}_2(\text{CO})_{10}$ (ν_{CO} hexanes: 2071 (w), 2015 (s), 1977 (m) cm^{-1})⁴ were gradually replaced by those of **1** (ν_{CO} hexanes: 2099 (m), 2043 (s), 2027(s), 1981 (s), 1977 (s), 1957 (m), 1947(s) cm^{-1}). Solvent removal, followed by extraction with CH_2Cl_2 and column chromatography on silica gel packed in hexanes, produced orange **1** in 30-45% yield.^{8,*}

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 $\text{Re}_2(\text{CO})_{10}$. 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 η^1 -ligand to Re(1) and η^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 $\text{Re}_2(\text{CO})_{10}$ (3.0413(11) Å)⁵. Other previously reported dinuclear complexes, prepared by quite different methods, that contain a similar bridging BT ligand are $\text{Fe}_2(\text{CO})_5(\text{PPh}_3)(\text{C}_8\text{H}_6\text{S})$ ⁶ and $[\text{Cp}^*\text{Co}]_2(\mu\text{-C}_8\text{H}_6\text{S})$ ⁷.

The addition of PMe_3 (1-5 eqv) (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_2Cl_2 , and fractional crystallization of the crude residue produced yellow crystals of **2** and white **3**. Both complexes have been characterized spectroscopically^{§§} and by X-ray structure analysis of their single crystals.

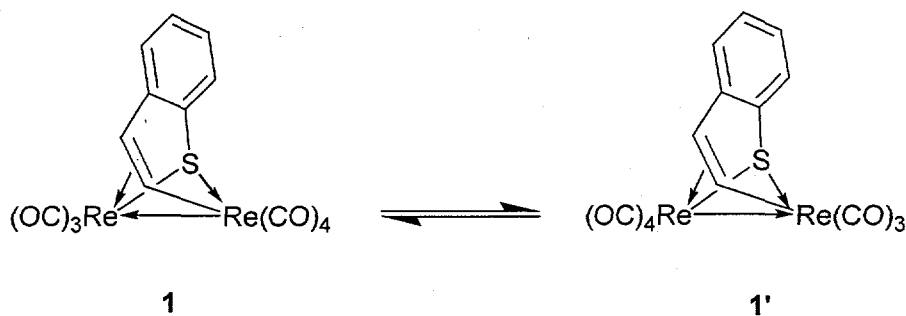
The X-ray structure of **2** (Figure 2)[§] shows that the C(1)-C(2) double bond is no longer η^2 -coordinated and the Re-Re bond has been cleaved. Both Re atoms are pseudo-octahedral and each contains a PMe_3 ligand. The S bridges both Re atoms almost symmetrically with distances of 2.5027(9) Å for Re(1)-S and 2.5320(9) Å for Re(2)-S.

A single crystal X-ray analysis of **3** (Figure 3)[§] 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 PMe_3 , the relative amounts of **2** and **3** formed are the same whether 1 or 5 equivalents of PMe_3 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 PMe_3 .

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 $\text{Re}(\text{CO})_3$ unit in **2** whereas in **3** it is coordinated to the $\text{Re}(\text{CO})_4$ 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

proposed for related bridging thiophene complexes $(\text{Fe}_2(\text{CO})_6(\text{C}_8\text{H}_6\text{S}))^6$, $[(\text{C}_5\text{Me}_5)\text{Co}]_2(\mu\text{-C}_4\text{H}_4\text{S})^8$, and $[(\text{dippe})\text{Ni}]_2(\mu\text{-C}_8\text{H}_6\text{S})^9$, or the migration of a CO group from one Re to the other.

The reaction of isomer **1'** with two equiv. of PMe_3 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 $\text{Re}(\text{CO})_3$ unit. On the other hand, the reaction of isomer **1** with three

equiv. of PMe_3 would lead to product **3** with the vinyl carbon bonded to the $\text{Re}(\text{CO})_4$ moiety while undergoing Re-olefin, Re-S and Re-Re bond cleavages. An attempt to detect the two isomers of **1** by low temperature ($-50\text{ }^\circ\text{C}$, CD_2Cl_2 solvent) ^1H NMR spectroscopy showed only the same isomer that is present in the room temperature spectrum.⁸ However, variable temperature ^{13}C NMR spectra of **1** ($-50\text{ }^\circ\text{C}$ to $+20\text{ }^\circ\text{C}$) 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 (CD_2Cl_2 , 300 MHz) δ 8.63 (d, 1 H, $J=11.4$ Hz), 7.11 (m, 2 H), 7.05 (dt, 1 H, $J_1=7.5$ Hz, $J_2=1.5$ Hz), 7.00 (d, 1 H, $J=11.4$ Hz), 6.93 (dt, 1 H, $J_1=7.2$ Hz, $J_2=1.5$ Hz). IR (hexanes) ν_{CO} : 2099 (m), 2043 (s), 2027 (s), 1981 (s), 1977 (s), 1957 (m), 1947 (s) cm^{-1} . For **2:** ^1H NMR (CD_2Cl_2 , 300 MHz): 8.06 (dd, 1 H, $J_1=14.1$ Hz,

$J_2=2.4$ Hz), 7.44 (dd, 1 H, $J_1=14.1$ Hz, $J_2=3.6$ 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, PMe_3 , $J=9.3$ Hz), 1.19 (d, 9 H, PMe_3 , $J=8.4$ Hz). IR (CH_2Cl_2) ν_{CO} : 2100 (w), 2003 (s), 1953 (m, br), 1896 (m, br), 1873 (m, br) cm^{-1} . For **3**: ^1H NMR (CD_2Cl_2 , 300 MHz): 7.89 (dd, 1 H, $J_1=13.5$ Hz, $J_2=3.9$ Hz), 7.43 (dd, 1 H, $J_1=7.8$ Hz, $J_2=1.2$ Hz), 7.21 (d, 1 H, $J=7.2$ Hz), 6.99 (dt, 1 H, $J_1=7.5$ Hz, $J_2=1.5$ Hz), 6.92 (m, 2 H), 1.62 (m, 27 H, 3PMe_3). IR (CH_2Cl_2) ν_{CO} : 2079 (w), 2018 (s), 1978 (s,sh), 1972 (s), 1933 (s), 1893 (s) cm^{-1} .

§ *Crystal data* for $\text{C}_{15}\text{H}_6\text{O}_7\text{Re}_2\text{S}$ **1**: $M = 702.66$, triclinic, $\text{P}\bar{1}$, $a = 9.167(1)$, $b = 12.544(1)$, $c = 16.019(2)$ Å, $V = 1668.3(2)$ Å³, $Z = 4$, $T = 293(2)$ K, $\mu = 14.659$ mm⁻¹, 5258 reflections collected, 4337 unique ($R_{\text{int}} = 0.0312$), $R1 = 0.0311$, $wR_2 = 0.0796$ [$I > 2\sigma(I)$]. 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.

ξ *Crystal data* for $\text{C}_{21}\text{H}_{24}\text{O}_7\text{P}_2\text{Re}_2\text{S}$ **2**: $M = 854.80$, monoclinic, $\text{P}2_1/\text{n}$, $a = 8.1110(4)$, $b = 27.1151(13)$, $c = 12.3490(6)$ Å, $V = 2655.7(2)$ Å³, $Z = 4$, $T = 173(2)$ K, $\mu = 9.344$ mm⁻¹, 23953 reflections collected, 6297 unique ($R_{\text{int}} = 0.0394$), $R1 = 0.0231$, $wR_2 = 0.0331$ [$I > 2\sigma(I)$]. 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 $\text{C}_{24}\text{H}_{33}\text{O}_7\text{P}_3\text{Re}_2\text{S}$ **3**: $M = 930.87$, orthorhombic, Pbca , $a = 9.6900(4)$, $b = 25.4267(12)$, $c = 25.8065(13)$ Å, $V = 6358.3(5)$ Å³, $Z = 8$, $T = 173(2)$ K, $\mu = 7.862$ mm⁻¹, 57303 reflections collected, 7716 unique ($R_{\text{int}} = 0.0583$), $R1 = 0.0242$, $wR_2 = 0.0327$.

[$I > 2\sigma(I)$]. Single crystals were grown from CH_2Cl_2 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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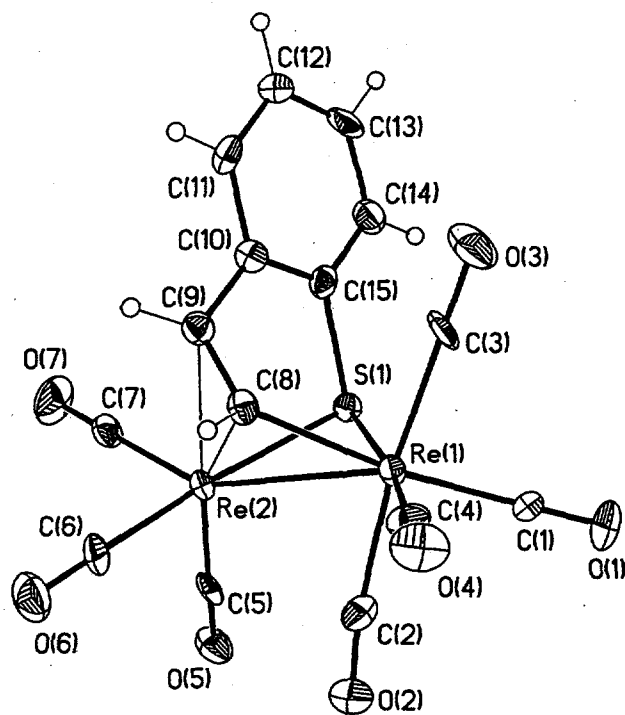


Figure 1. Molecular structure of **1** in the solid state. Selected bond lengths (Å) and angles (°): Re(1)-Re(2) 2.8945, Re(1)-S, 2.506(2), Re(2)-S 2.431(3), Re(1)-C(8) 2.142(10), Re(2)-C(8) 2.208(10), Re(2)-C(9) 2.413(11), C(8)-C(9) 1.370(14), S-C(15) 1.805(11), Re(2)-S-Re(1) 71.77(7), Re(1)-C(8)-Re(2) 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).

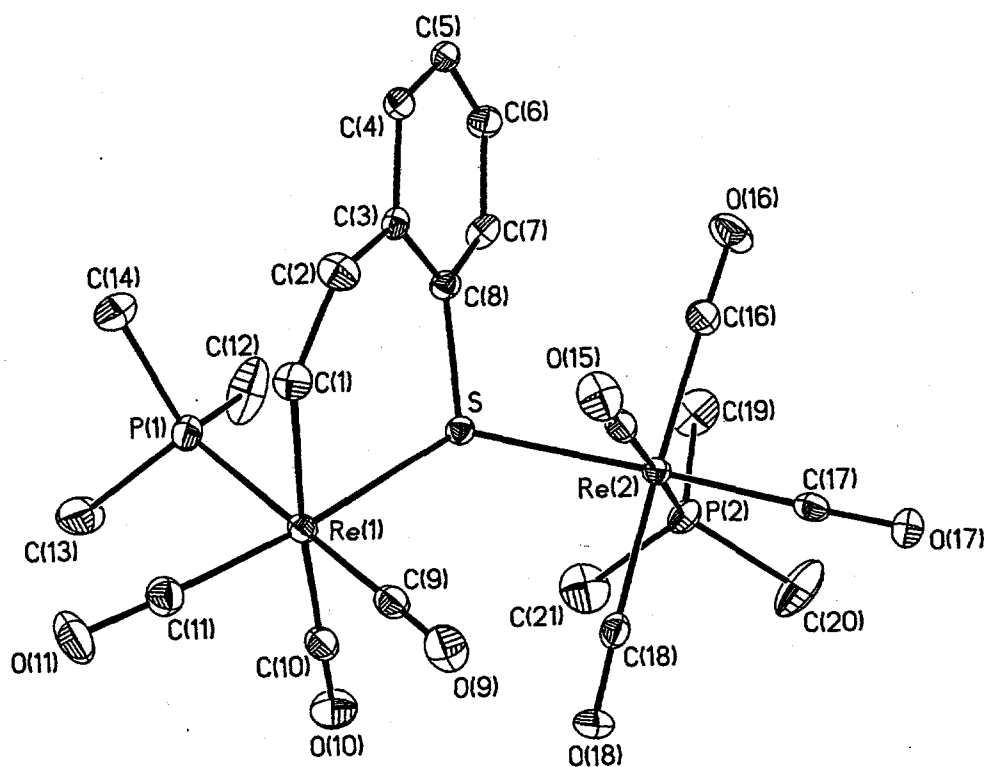


Figure 2. Molecular structure of complex **2** in the solid state. Selected bond distances (Å) and angles (°): Re(1)---Re(2) 4.2874(3), Re(1)-S 2.5027(9), Re(2)-S 2.5320(9), C(8)-S 1.796(3), Re(1)-C(1) 2.169(3), C(1)-C(2) 1.343(5), Re(1)-S-Re(2) 116.76(3), C(1)-Re(1)-S 86.51(10), Re(1)-S-C(8) 109.94(12), Re(2)-S-C(8) 105.40(12), P(1)-Re(1)-S 87.24(3), P(2)-Re(2)-S 88.04(3).

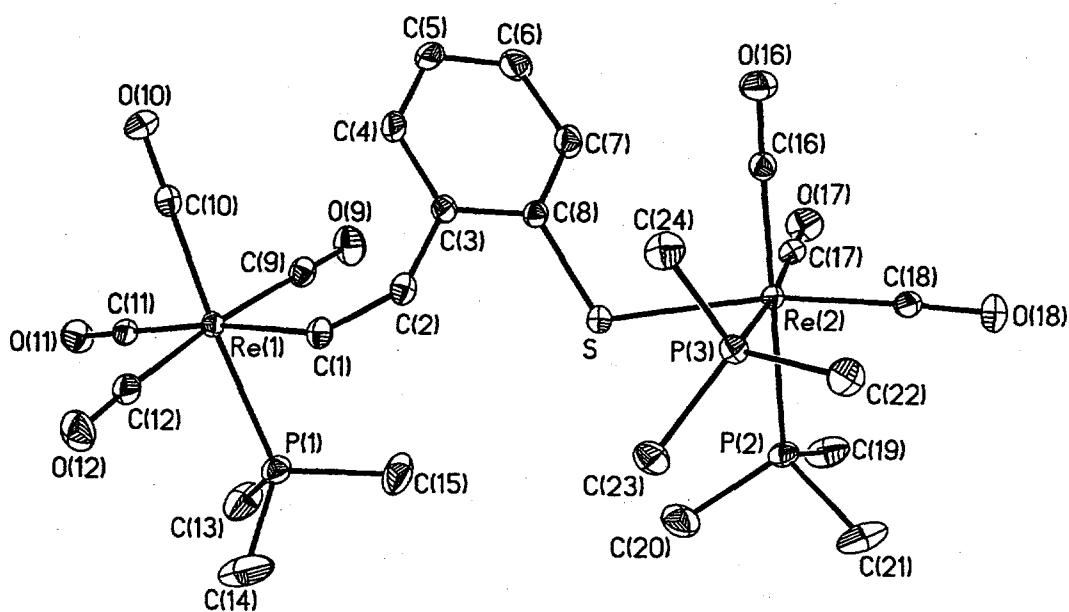


Figure 3. Molecular structure of **3** in the solid state. Selected bond distances (Å) and angles (°): Re(1)-C(1) 2.205(3), Re(2)-S 2.5086(9), C(1)-C(2) 1.327(4), S-C(8) 1.769(3), C(2)-C(3) 1.479(4), Re(1)-C(1)-C(2) 134.8(3), C(8)-S-Re(2) 113.18(12), P(2)-Re(2)-S 84.54(3), C(1)-C(2)-C(3) 129.8(3), C(1)-Re(1)-P(1) 82.44(8).

3. HOMOGENEOUS MODELS FOR CATALYTIC HYDRODESULFURIZATION: $\text{Re}_2(\text{CO})_{10}$ MEDIATED C-H AND C-S BOND CLEAVAGE IN DIBENZOTHIOPHENE AND 2,5-DIMETHYLTHIOPHENE

A paper to be submitted to the Journal *Organometallics*

Michael A. Reynolds, Ilia A. Guzei[†] and Robert J. Angelici*

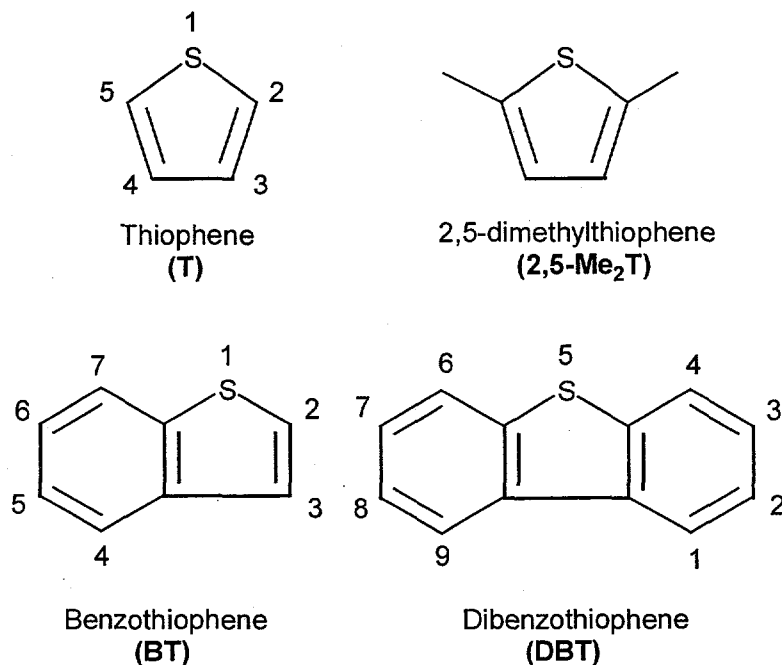
Abstract

Ultraviolet photolysis of $\text{Re}_2(\text{CO})_{10}$ and excess dibenzothiophene (DBT) in the non-coordinating solvent hexanes produces the S-bound *eq*- $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})$ (**1**) and the novel C-H cleaved DBT complex $\text{Re}_2(\text{CO})_8(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})$ (**2**). Under similar conditions, $\text{Re}_2(\text{CO})_{10}$ reacts with excess 2,5-dimethylthiophene (2,5- Me_2T) to give the interesting C-S cleaved 2,5- Me_2T complex $\text{Re}_2(\text{CO})_7(\mu\text{-2,5-}\text{Me}_2\text{T})$ (**3**) as the only product. The photolysis reactions of $\text{Re}_2(\text{CO})_{10}$ with DBT and 2,5- Me_2T 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 $\eta^1(\text{S})$ -bound thiophene complexes **1** and $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-2,5-}\text{Me}_2\text{T})$ (**5**) were prepared from $\text{Re}_2(\text{CO})_9(\text{THF})$ (**4**). The DBT ligand in **1** is labile and rapidly (< 2 min) reacts with CO (1atm) to form $\text{Re}_2(\text{CO})_{10}$ in 1,2-DCE. Based on its X-ray structure, complex **1** has one of the smallest tilt angles ($\theta = 113^\circ$) 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.¹⁻³ First, current US Federal regulations require refineries to reduce gasoline sulfur levels by as much as 300 ppm (by the year 2004³) in order to decrease the amount of sulfur oxides (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), benzothiophene (BT) and dibenzothiophene (DBT) (Scheme 1).

Scheme 1



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

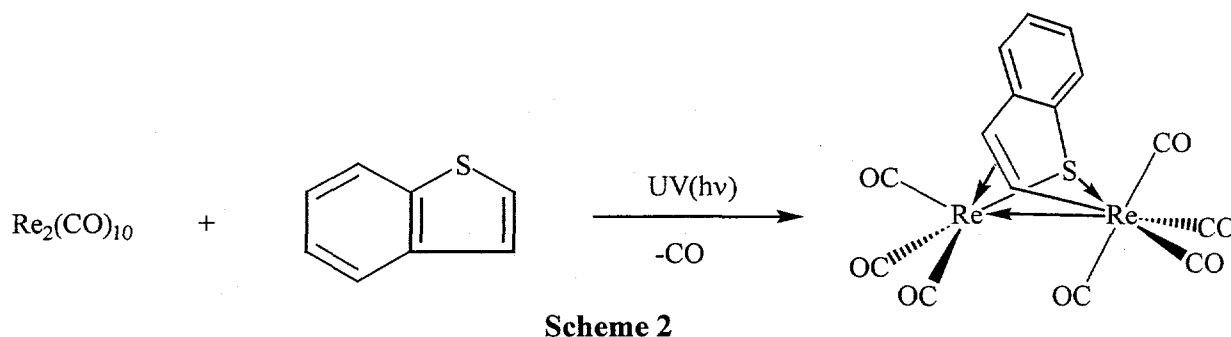
The common commercial HDS catalysts are typically MoS₂ or WS₂ promoted by Co or Ni on an alumina support, but several other metal sulfides, MS_x (M = Ru, Re, Os, Rh, and Ir) have demonstrated higher catalytic activity for the desulfurization of thiophenes and benzothiophenes under various hydrotreating 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.; $\eta^1(\text{S})$, η^2 , η^4 , η^5 and η^6)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 [$(\eta^5\text{-T})\text{Mn}(\text{CO})_3$]⁺ and [$(\eta^6\text{-BT})\text{Mn}(\text{CO})_3$]⁺. 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(η^2 -C,S-T) and (dippe)Ni(η^2 -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 C_{vinyl}-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 η^1 - and η^2 -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 process²² 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)₈(μ-C₁₂H₇S)(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 HRe₃(CO)₁₄²³ (<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, $\text{HRe}_3(\text{CO})_{14}$ 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 $\text{Re}_2(\text{CO})_9(\text{THF})$ and DBT. For **2**: ^1H NMR (CD_2Cl_2 , 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): ν_{CO} 2114 (w) 2087 (w), 2023 (vs), 2013 (s), 1995 (m), 1985 (s), 1958 (m). Anal. Calcd for $\text{C}_{20}\text{H}_8\text{O}_8\text{Re}_2\text{S}$: C, 30.77, H, 1.03; Found: C, 30.74, H, 1.03.

Preparation of $\text{Re}_2(\text{CO})_7(\text{C,S-Me}_2\text{T})$ (3**).** A hexanes solution (30 mL) of $\text{Re}_2(\text{CO})_{10}$ (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 CH_2Cl_2 and hexanes (1:5) and was collected. The volatiles were removed *in vacuo* leaving a yellow-orange oily residue which was then dissolved in CH_2Cl_2 (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 $\text{Re}_2(\text{CO})_{10}$) were dried under vacuum. ^1H NMR (CD_2Cl_2) 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): ν_{CO} 2093 (w), 2039 (s), 1993

(s), 1990 (s), 1963 (m), 1950 (vs) cm^{-1} . Anal calcd. for $\text{C}_{13}\text{H}_8\text{O}_7\text{Re}_2\text{S}$: C, 22.94; H, 1.18; S, 4.71; Found: C, 22.80; H, 1.20; S, 4.08.

Preparation of $\text{Re}_2(\text{CO})_9(\text{thf})$ (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 $\text{Re}_2(\text{CO})_{10}$ (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 ν_{CO} bands for 4 reached a maximum (1-1.5 h). The solution of 4, which contains some residual $\text{Re}_2(\text{CO})_{10}$, 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 $\text{Re}_2(\text{CO})_{10}$ (based on IR spectroscopy) and other unidentified impurities (based on ^1H 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_2Cl_2 or benzene solvents. ^1H NMR (CD_2Cl_2) 300 MHz: δ 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 $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-T}^*)$ complexes, 1 and 5, from 4. **Complex 1 (from Method A).** A solution of $\text{Re}_2(\text{CO})_9(\text{thf})$ (4) was prepared as described above (using Method A) from a THF (30 mL) solution of $\text{Re}_2(\text{CO})_{10}$ (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_2Cl_2 (1 mL) and layered

with hexanes (5 mL) followed by cooling to $-20\text{ }^{\circ}\text{C}$ 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 $\text{Re}_2(\text{CO})_{10}$). ^1H NMR (CD_2Cl_2 , 400 MHz): δ 8.17 (m, 2 H), 7.84 (m, 2 H), 7.61 (m, 4 H). IR (CH_2Cl_2): ν_{CO} 2102 (w), 2042 (m), 1988 (vs), 1963 (m), 1933 (m). Anal. Calcd. For $\text{C}_{21}\text{H}_8\text{O}_9\text{Re}_2\text{S}$: 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 $\text{Re}_2(\text{CO})_{10}$ (306 mg, 0.469 mmol) was prepared in a 100 mL Schlenk flask equipped with a magnetic stir bar. Anhydrous Me_3NO (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 ν_{CO} bands corresponding to complex **4**. The volatiles (THF and NMe_3) 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 CH_2Cl_2 (1-2 mL) and layered with hexanes (5-8 mL). Yellow crystals of **1** (128 mg, 34% based on $\text{Re}_2(\text{CO})_{10}$) were grown after 1 d ($-20\text{ }^{\circ}\text{C}$) and isolated after filtration, washing with hexanes (1 x 5 mL), and drying *in vacuo*.

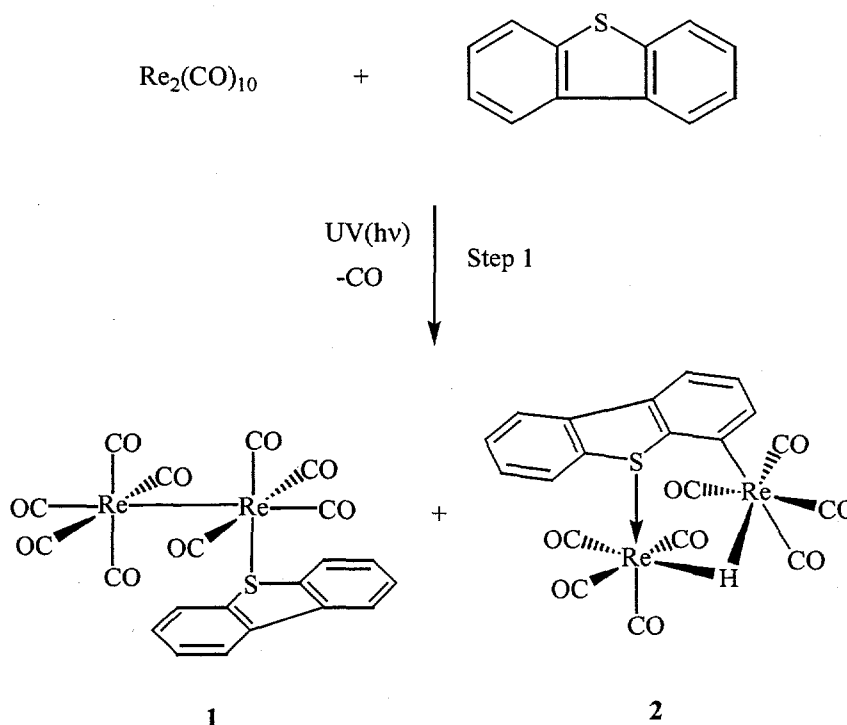
$\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-2,5-Me}_2\text{T})$ (5**).** Complex **5** was prepared in a similar manner as **1** (Method A) from a solution of $\text{Re}_2(\text{CO})_9(\text{thf})$ (0.222 mmol based on $\text{Re}_2(\text{CO})_{10}$). The freshly prepared $\text{Re}_2(\text{CO})_9(\text{thf})$ 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_2Cl_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 refinement²⁴. 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 SADABS²⁵ and by using program DIFABS²⁶ 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 PLATON²⁷ 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 \AA^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 $\text{Re}_2(\text{CO})_{10}$ with DBT. Irradiation of a stirred hexanes solution (10°C) containing $\text{Re}_2(\text{CO})_{10}$ and a 2-fold excess of DBT produced the bi- and tri-metallic Re complexes $eq\text{-Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})$ (**1**), $\text{Re}_2(\text{CO})_8(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})$ (**2**) and $\text{HRe}_3(\text{CO})_{14}$ after 18-24 h (Scheme 3).



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 $\text{Re}_2(\text{CO})_{10}$ and DBT under similar conditions in either benzene or ethyl ether. The photolysis reaction of DBT (2-4 fold excess) and $\text{Re}_2(\text{CO})_{10}$ in CH_2Cl_2 produced only $(\text{CO})_5\text{ReCl}^{29a}$ (<10%) and $\text{Re}_2(\text{CO})_8(\mu\text{-Cl})_2^{29b}$ (>90%) within 1 h, and no evidence for complexes **1** or **2** was observed. Although THF reacts with $\text{Re}_2(\text{CO})_{10}$ during photolysis to give

$\text{Re}_2(\text{CO})_9(\text{THF})$, no Re-DBT containing complexes were observed when $\text{Re}_2(\text{CO})_{10}$ 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_2Cl_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 $\text{Re}_2(\text{CO})_{10}$ 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 $\text{Re}_2(\text{CO})_9$ is common, and *eq*- $\text{Re}_2(\text{CO})_9(\text{L})$ complexes are known for $\text{L} = \text{CH}_3\text{CN}^{30}$, phosphines³¹ and pyridine³². When the donor ligand (L) is bulky, such as for $\text{L} = \text{PPh}_3$ ³¹ then axial substitution dominates. No evidence of a disubstituted DBT-Re complex of the type $\text{Re}_2(\text{CO})_8(\text{L})_2$ was observed although disubstituted complexes are known for $\text{L} =$ phosphines³¹ and pyridine³².

The ^1H 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 $\eta^1(\text{S})$ -bound DBT complexes such as $\text{CpRe}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})^{33}$, $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})^+]^{34}$, $\text{Cp}^*\text{Ir}(\text{Cl})_2(\eta^1(\text{S})\text{-DBT})^{35}$, $\text{CpMn}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})^{36}$, $(\text{CO})_5\text{W}(\eta^1(\text{S})\text{-DBT})^{36}$ and $(\text{CpSiMe}_2\text{Cp})\text{Mo}(\eta^1(\text{S})\text{-DBT})^{37}$.

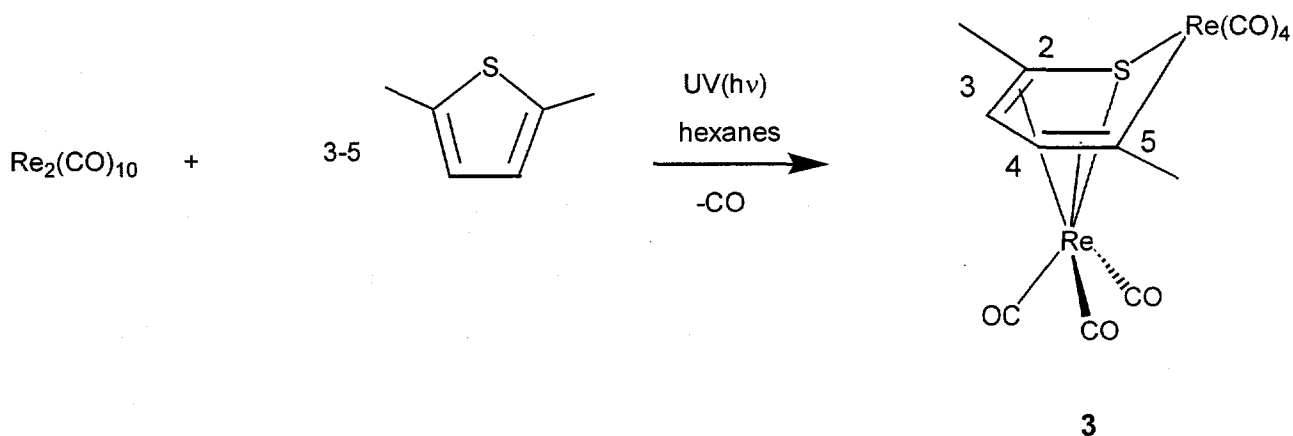
Complex **2** is a moderately air-stable yellow solid that is soluble in benzene, chloroform, CH_2Cl_2 and moderately soluble in hexanes. Crystals of **2**, hand-picked from the mixture of **1** and **2**, were characterized by elemental analysis, spectroscopic methods (^1H NMR and IR) and by X-ray diffraction studies. The IR spectrum for **2** is complicated and consists of 7 unique bands in the ν_{CO} 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, $\text{Re}_2(\text{CO})_{10}$ did not react with 4,6-dimethyldibenzothiophene (4,6-Me₂DBT) under photolysis conditions; only $\text{Re}_2(\text{CO})_{10}$ 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 $\text{Cp}^*\text{Rh}(\text{PMe}_3)$ which resulted from C-H bond cleavage of substituted dibenzothiophenes. These complexes were characterized spectroscopically (^{31}P and ^1H NMR) and subsequently converted into complexes with C-S cleaved DBT ligands. More recently⁴¹, $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ was reported to react with DBT to give the triosmium, benzyne cluster, $\text{Os}_3(\text{CO})_9(\mu\text{-C}_{12}\text{H}_6\text{S})(\mu\text{-H})_2$ 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,

$\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})$. Although it was not detected, the formation of such an intermediate is supported by the isolation and characterization of complex **2**.

Reactions of $\text{Re}_2(\text{CO})_{10}$ with Thiophenes. UV photolysis of a hexanes solution (10 °C) containing $\text{Re}_2(\text{CO})_{10}$ and a 3-5 fold excess of 2,5- Me_2T in a quartz photolysis tube produced the ring-cleaved thiophene complex $\text{Re}_2(\text{CO})_7(\mu\text{-2,5-}\text{Me}_2\text{T})$ (**3**) in 15-20% yield after 24 h (Scheme 4).



Scheme 4

Complex **3**, which is soluble in most organic solvents such as benzene, CH_2Cl_2 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 CH_2Cl_2 /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 ν_{CO} 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, $\text{Mn}_2(\text{CO})_7(\mu\text{-}2,5\text{-Me}_2\text{T})^{14}$ (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 CD_2Cl_2) 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, $\text{Mn}_2(\text{CO})_9(\mu\text{-}2,5\text{-Me}_2\text{T})^{14}$, which has proton signals at δ 7.05 and 5.62 ppm (in *d*₆-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 CD_2Cl_2). Complex **3** does not react with electrophiles such as triflic acid or methyl triflate ($\text{MeOSO}_2\text{CF}_3$). 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**, $\text{Mn}_2(\text{CO})_7(\mu\text{-}2,5\text{-Me}_2\text{T})$, 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 **3**^{14b}. However, in our hands, photolysis reactions of T, 2-MeT and 3-MeT with $\text{Re}_2(\text{CO})_{10}$ 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 $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-T}^*)$ ($\text{T}^* = \text{T}$, 2-MeT or 3-MeT) to the C-S cleaved product analogous to **3**.

Preparation and Characterization of $\text{Re}_2(\text{CO})_9(\text{THF})$ (4**).** Complex **4** was prepared using two separate methods (A and B). The first, Method A, involves irradiation of a dry THF solution containing $\text{Re}_2(\text{CO})_{10}$ 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 reported²⁴ and involves the removal of a CO ligand from $\text{Re}_2(\text{CO})_{10}$ using anhydrous Me_3NO . 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_2Cl_2 . The ^1H 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 ^1H 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 $\text{Re}_2(\text{CO})_9(\eta^1(\text{s})\text{-T}^*)$ (**1** and **5**, see below). The ^1H NMR spectrum (in CD_2Cl_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 $\text{Re}_2(\text{CO})_9(\text{NMe}_3)$ ²⁴ (δ 2.89 ppm) and unreacted Me_3NO (δ 3.04 ppm).

Synthesis and Characterization of $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-T}^*)$ Complexes (1 and 5). The S-bound thiophene complexes $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-T}^*)$ ($\text{T}^* = \text{DBT}$ (**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 $\text{Re}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_9(\text{NMe}_3)$ (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 ligands⁴² 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 $\text{Re}_2(\text{CO})_9$ 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.

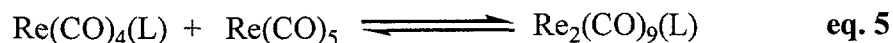
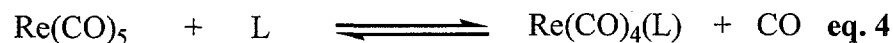
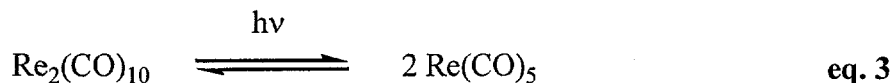
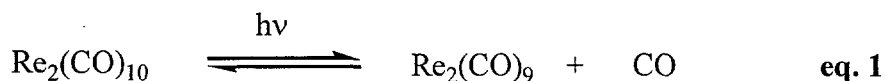
Complex **1**, prepared by both methods A and B, was characterized by elemental analyses, ¹H NMR and IR spectroscopies and also by its molecular structure which was determined by X-ray diffraction studies (Figure 2.). The yields of **1** were similar (27-34%) using both Methods A and B, which implies 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_2Cl_2). The methyl signal for the two chemically equivalent Me groups in **5** is also a singlet (δ 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 $\eta^1(\text{S})$ -bound 2,5-Me₂T ligands such as $\text{CpRe}(\text{CO})_2(\eta^1(\text{S})\text{-2,5-Me}_2\text{T})$ ³³ and $(\text{CO})_5\text{M}(\eta^1(\text{S})\text{-2,5-Me}_2\text{T})$ (M = Cr or W)³⁶. Notably, the S-bound thiophene ligand in **5** is labile and partially dissociates in solution (CD_2Cl_2 , 20 °C) at room temperature based on ¹H NMR studies. This is not surprising since the DBT ligand in **1**, which is expected to be a better donor⁴², 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 $\text{Re}_2(\text{CO})_{10}$ is activated by UV light to, [1] lose a CO group to generate $\text{Re}_2(\text{CO})_9$ species (eq. 1), or [2] to undergo metal-metal bond homolysis to produce the 17-electron $\bullet\text{Re}(\text{CO})_5$ radical species⁴³ (eq. 3). Such processes have been proposed for the formation of $\text{Re}_2(\text{CO})_9(\text{L})$ and $\text{Re}_2(\text{CO})_8(\text{L})_2$ complexes (L = phosphines and pyridine)⁴⁴⁻⁴⁵ during UV photolysis of $\text{M}_2(\text{CO})_{10}$ (M = Mn or Re) and L donor ligands (eq. 1-5). Complex **1** is also a $\text{Re}_2(\text{CO})_9(\text{L})$ 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 $\text{Re}_2(\text{CO})_{10}$ and DBT.

In an effort to understand how the photolysis reaction of $\text{Re}_2(\text{CO})_{10}$ and DBT (Scheme 3) occurs, a series of experiments were undertaken. When the UV-light promoted reactions of $\text{Re}_2(\text{CO})_{10}$ 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 $\text{Re}_2(\text{CO})_{10}$ remained. However, during UV photolysis of $\text{Re}_2(\text{CO})_{10}$ with a 3-fold excess of DBT under

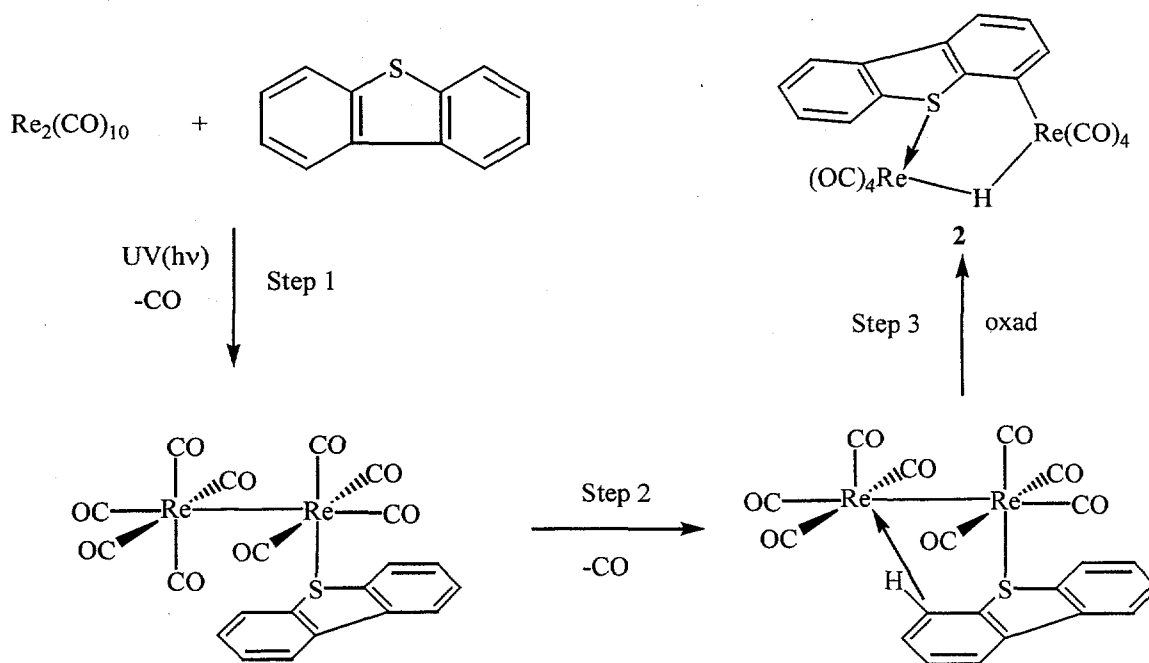


N_2 was performed in the presence of the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) (1 equiv. based on $\text{Re}_2(\text{CO})_{10}$) produced a modest yield of complex **2** after 8 h as detected by IR spectroscopy with no indication of the formation of **1**. Furthermore, when the ratio of $\text{Re}_2(\text{CO})_{10}$ to TEMPO was changed to 1:2, which is stoichiometric with respect to the formation of $\text{Re}(\text{CO})_5$ radicals, neither complex **1** nor **2** was observed after 10 h (10-15 °C). It is known⁴⁶ that TEMPO reacts with photochemically generated $\text{M}(\text{CO})_5$ ($\text{M} = \text{Mn}$ or Re) radicals to form neutral M-N-O cyclic complexes of type $(\text{TEMPO})\text{M}(\text{CO})_3$. In a related reaction, when $\text{Re}_2(\text{CO})_{10}$ and DBT (3 equiv.) were irradiated with UV light in CH_2Cl_2 solution, complexes **1** and **2** were not formed and both $\text{Re}_2(\text{CO})_8(\mu\text{-Cl})_2$ ^{29a} and $\text{Re}(\text{CO})_5\text{Cl}$ ^{29b} were produced as the only products after 1 h.

The observation that TEMPO and CH_2Cl_2 prevent the formation of **1** and **2** suggests that $\text{Re}(\text{CO})_5$ radicals are involved in the formation of both products. If decarbonylation of $\text{Re}_2(\text{CO})_{10}$ were a major pathway (eq. 1 and 2), then complex **1** should have been observed during the photolysis reactions of $\text{Re}_2(\text{CO})_{10}$, 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 $\text{Re}_2(\text{CO})_{10}$ to give $\text{Re}(\text{CO})_5$ radicals (eq.3-5). Some of these $\text{Re}(\text{CO})_5$ radicals

could undergo thermal substitution of CO with $\eta^1(\text{S})$ -binding of DBT to give $\text{Re}(\text{CO})_4(\eta^1(\text{S})\text{-DBT})$ radical species (eq. 4) which could then cross-couple with $\text{Re}(\text{CO})_5$ radical fragments to produce **1** (eq. 5).

Since complex **1** is formed during the UV photolysis reaction of $\text{Re}_2(\text{CO})_{10}$ and DBT, it is possible that **1** is also an intermediate in the formation of $\text{Re}_2(\text{CO})_8(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})$ (**2**). A possible mechanism (Scheme 5) for the conversion of **1** and **2** could involve loss of a CO ligand from the $\text{Re}(\text{CO})_5$ 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 $\text{Re}(\text{CO})_4$ unit resulting in the formation of the Re-C bond and a bridging hydride in **2**. However, $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})$ (**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.



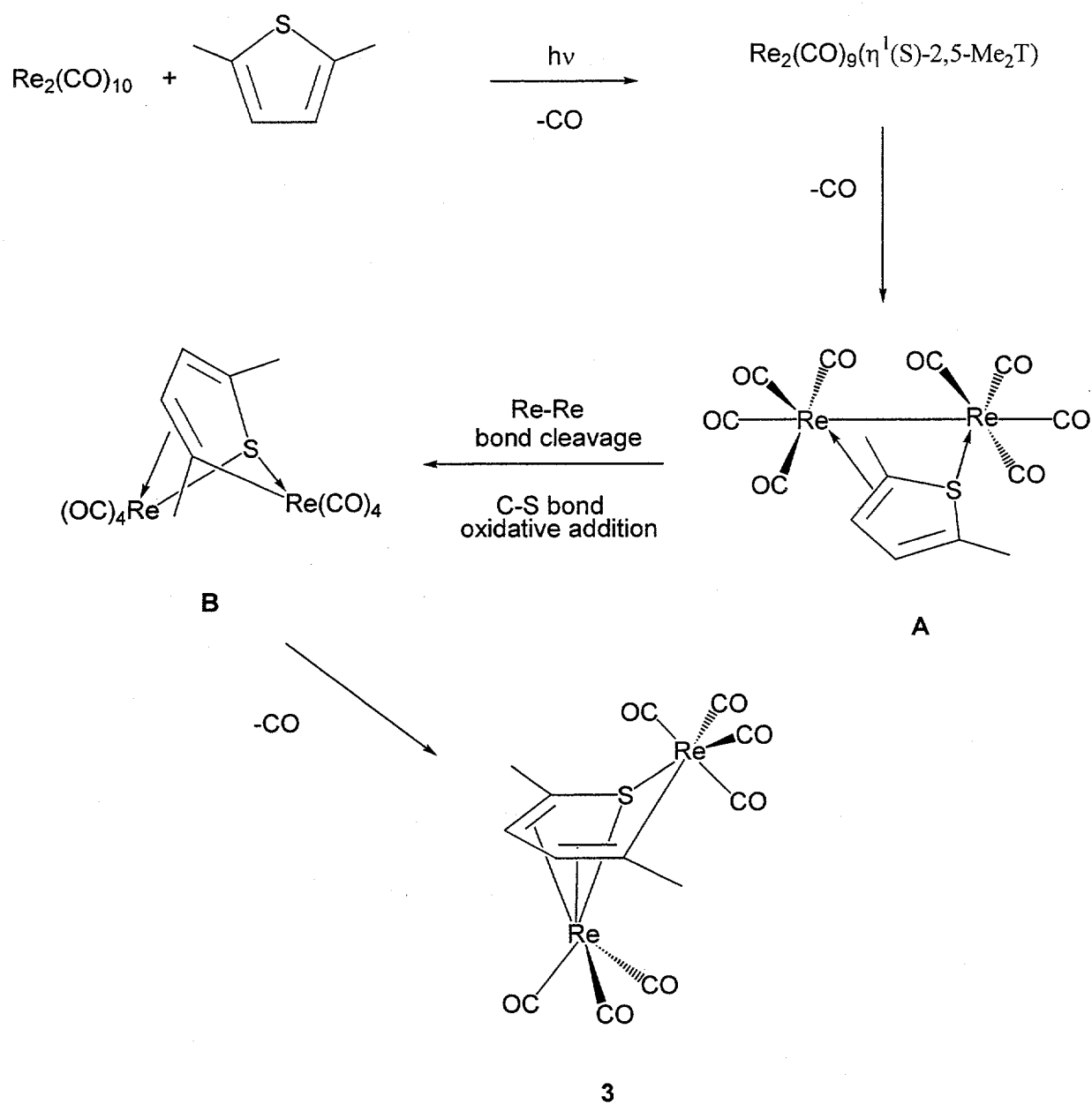
Scheme 5

Thermolysis of **1** in refluxing toluene produced only free DBT and unidentified Re decomposition products that did not contain DBT.

The cluster $\text{HRe}_3(\text{CO})_{14}$ was mentioned earlier as a minor product formed during the preparation of **1** and **2** by UV photolysis of $\text{Re}_2(\text{CO})_{10}$ and excess DBT. The $\text{HRe}_3(\text{CO})_{14}$ cluster likely forms from Re-Re bond cleavage of $\text{Re}_2(\text{CO})_{10}$ and cross-coupling of $\text{HRe}(\text{CO})_5$ and $\text{HRe}(\text{CO})_4$ radical fragments during photolysis although the exact mechanism is uncertain. $\text{HRe}_3(\text{CO})_{14}$, 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 $\text{HRe}_3(\text{CO})_{14}$ 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 $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})$ (**1**) with $\text{Re}_2(\text{CO})_8(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})$ (**2**) during the photolysis of $\text{Re}_2(\text{CO})_{10}$ 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 $\text{Re}_2(\text{CO})_7(\mu\text{-2,5-Me}_2\text{T})$ (**3**) could be formed from the S-bound complex $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-2,5-Me}_2\text{T})$ (**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 $\text{Re}_2(\text{CO})_{10}$ and 2,5-Me₂T, it is possible that it could convert into **3** via photochemically induced loss of CO from the $\text{Re}(\text{CO})_5$ unit, followed by η^2 -binding of a



Scheme 6

C=C double bond of the 2,5-Me₂T ligand to give an intermediate of type (CO)₄Re(μ-η¹(S),η²-2,5-Me₂T)Re(CO)₄ (**A**). Intermediate **A** could then undergo oxidative addition of a C-S bond to give a complex of type Re₂(CO)₈(μ-2,5-Me₂T) (**B**) followed by loss of an additional CO ligand and subsequent η²-binding of the second vinyl group to form **3**.

Although intermediates **A** and **B** were not observed during the photolysis of Re₂(CO)₁₀ and 2,5-Me₂T or during photolysis of **5**, thiophene complexes that are structurally similar to **B** are known for Ni, Co and Fe; Fe₂(CO)₆(μ-2-MeT)^{19b}, [Cp*Co]₂(μ-T)⁴⁷, and [(dippe)Ni]₂(μ-T)¹⁸.

Because of the very different route for the synthesis of the Mn analog of **3**, Mn₂(CO)₇(μ-2,5-Me₂T), it is not surprising that the proposed mechanism for the formation of **3** differs significantly from that proposed by Sweigart for the formation of Mn₂(CO)₇(μ-2,5-Me₂T). This complex was prepared by the chemical reduction of [(η⁵-2,5-Me₂T)Mn(CO)₃]⁺ with cobaltocene. The proposed mechanism^{14,15} involves electron transfer to [(η⁵-2,5-Me₂T)Mn(CO)₃]⁺ to generate a (η⁴-2,5-Me₂T)Mn(CO)₃⁻ species which then attacks the thiophene of a second molecule of [(η⁵-2,5-Me₂T)Mn(CO)₃]⁺ with subsequent formation of a bimetallic species which then converts into Mn₂(CO)₇(μ-2,5-Me₂T).

Comparison of the Structures of Re₂(CO)₉(η¹(S)-DBT) (1**) and Re₂(CO)₈(μ-C₁₂H₇S)(μ-H) (**2**).** The structure of **1** (Figure 1) shows an S-bound DBT ligand coordinated in an equatorial position to the Re₂(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 η¹-fashion. The hydride ligand which bridges the two Re centers, was not located, but was observed in the ¹H 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 $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CMe}_2\text{CH}_2)$ (2.485(4) Å)⁴⁸, $\text{Re}_2(\text{CO})_9[(\text{SCH}_2\text{CH}_2\text{CH}_2)_3]$ ⁴⁹ (2.498(3) Å) and $\text{Re}_2(\text{CO})_8(\mu\text{-SPh})(\mu\text{-H})$ ^{38a} (2.471(3) and 2.468(3) Å). However, the Re-S distances are much longer compared to the more electron-rich Re complexes $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-T})$ ³³ (2.360(3) Å) and $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-3-MeBT})$ ⁵⁰ (3-MeBT = 3-methylbenzothiophene) (2.356(4) Å) which contain the electron-donating π -donor ligand Cp* (Cp* = C₅Me₅).

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** ($\theta = 113.6^\circ$) is smaller than the analogous angle for **2** ($\theta = 124.8^\circ$). 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 $\eta^1(\text{S})$ -bound DBT complexes including $(\text{CO})_5\text{W}(\eta^1(\text{S})\text{-DBT})$ ³⁶ (118.8°), $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})^+]$ ³⁴ (119.4°), $(\text{CO})_5\text{Cr}(\eta^1(\text{S})\text{-DBT})$ ³⁶ (121.8°), and $\text{Cp}^*\text{Ir}(\text{Cl})_2(\eta^1(\text{S})\text{-DBT})$ 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 $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-T})$ (140.4°)³³ and $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-3-MeBT})$ ⁵⁰ (131.0°) in which the Re center is more electron-rich than **1**. The larger tilt angles suggest greater π -backbonding from the Re to the thiophene ligand in the $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-T}^*)$ complexes ($\text{T}^* = \text{T}$ and 3-MeBT) compared to complex **1**. This result is in agreement with Harris' proposal⁵¹ which suggests that the more electron-rich the metal center, the more π -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 $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-T})$ ³³ (2.360(3) Å) and $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-3-MeBT})$ ⁵⁰ (2.356(4) Å) than in **1**. We previously noted the smaller tilt angles ($^\circ$) and longer metal-sulfur distances (Å) in $[\text{CpFe}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})]^+$ ³⁴ as compared with those parameters for the more electron-rich $\text{CpMn}(\text{CO})_2(\eta^1(\text{S})\text{-DBT})$ 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 DBT⁵² (1.740 Å). The C-S-C angle in the DBT ligand for both **1** ($90.98(16)^\circ$) and **2** ($92.7(4)^\circ$) is similar to that for free DBT ($91.5(4)^\circ$).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 $\text{Re}_2(\text{CO})_7(\mu\text{-2,5-Me}_2\text{T})$ (3**).** In the structure of **3** (Figure 3) a $\text{Re}(\text{CO})_4$ fragment is inserted into a C-S bond of the 2,5-Me₂T ring and bent out of the thiophene plane; the resulting ring-opened thiophene is also η^5 -coordinated to the $\text{Re}(\text{CO})_3$ unit. The structure of **3** is very similar to that reported by Sweigart¹⁴ and coworkers for the 2-MeT

derivative, $\text{Mn}_2(\text{CO})_7(\mu\text{-2-MeT})$. 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 \AA which is out of bonding range compared to the reported Re-Re distance for both $\text{Re}_2(\text{CO})_{10}$ ($3.0413(11) \text{ \AA}$)⁵³ and complex **1** ($3.0389(2) \text{ \AA}$). The Re(1)-S distance of $2.5048(13) \text{ \AA}$ and the Re(2)-S distance of $2.4722(14) \text{ \AA}$ are nearly the same (difference of 0.03 \AA). In $\text{Mn}_2(\text{CO})_7(\mu\text{-2-MeT})$ this difference between Mn-S distances is also reported as 0.03 \AA .

Conclusion

In summary, we report that $\text{Re}_2(\text{CO})_{10}$ reacts with excess DBT in the presence of UV light and hexanes solvent to give the S-bound DBT complex $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})$ (**1**) and the C-H cleaved DBT complex $\text{Re}_2(\text{CO})_8(\mu\text{C}_{12}\text{H}_7\text{S})(\mu\text{-H})$ (**2**) (Scheme 3). These products were not expected since under similar conditions the reaction of $\text{Re}_2(\text{CO})_{10}$ with benzothiophene (BT) did not produce S-bound or C-H cleaved BT complexes, but rather the $\text{C}_{\text{vinyl}}\text{-S}$ bond was cleaved to give $\text{Re}_2(\text{CO})_7(\mu\text{-BT})$ as the only product (Scheme 2).²¹ However, irradiation of $\text{Re}_2(\text{CO})_{10}$ 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 $\text{Re}_2(\text{CO})_{10}$ during UV photolysis possibly due to electronic⁴² or steric⁴² effects. The pathway for the formation of **2** is proposed to occur through the isolable intermediates **1**. The S-bound complexes $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-T}^*)$ were prepared for $\text{T}^* = \text{DBT}$ (**1**) and 2,5-Me₂T (**5**) by substituting the THF ligand in the reactive species $\text{Re}_2(\text{CO})_9(\text{THF})$ (**4**). Although mechanistic pathways for the photolytic reactions between $\text{Re}_2(\text{CO})_{10}$ 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 Cp*Re(CO)₂(η^1 (S)-T)³³ and Cp*Re(CO)₂(η^1 (S)-3-MeBT)⁵⁰. 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 Cp*Re(CO)₂(η^1 (S)-T) (140.4°; 2.360(3) Å)³³ and Cp*Re(CO)₂(η^1 (S)-3-MeBT)⁵⁰ (131.0°; 2.356(4) Å).

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* Author to whom correspondence should be addressed.

† Iowa State University Molecular Structure Laboratory

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Table 1. Crystallographic Data for 1-3.

	1	2	3
Formula	C ₂₁ H ₈ O ₉ Re ₂ S.1/2CH ₂ Cl ₂	C ₂₀ H ₈ O ₈ Re ₂ S	C ₁₂ H ₈ O ₇ Re ₂ S
Formula weight	851.20	508.14	680.65
Space group	$P\bar{1}$	C2/c	$P\bar{1}$
<i>a</i> , Å	9.4152(4)	18.231(2)	8.5886(6)
<i>b</i> , Å	11.2600(5)	17.490(1)	9.2722(6)
<i>c</i> , Å	11.9289(6)	15.677(2)	12.4626(8)
α , °	95.972(1)		69.566(1)
β , °	109.303(1)	122.64(1)	87.392(1)
γ , °	93.279(1)		62.591(1)
<i>V</i> , Å ³	1181.41(9)	820.2(3)	3161.5(11)
<i>Z</i>	2	2	2
Crystal color, habit	Yellow block	Yellow block	Yellow block
<i>D</i> (calcd.), g cm ⁻³	2.393	2.058	2.765
μ (Mo K α), mm ⁻¹	10.49	11.62	14.95
Temperature, K	163(2)	293(2)	163(2)
Diffractometer	Bruker CCD-1000	Enraf-Nonius CAD4	Bruker CCD-1000
Absorption Correction	Empirical	Empirical	Empirical
<i>T</i> (max)/ <i>T</i> (min)	0.32/0.16	1.00/0.53	1.00/0.52

Table 1 continued

Reflections Collected	10433	4321	9606
Independent refl.	4795 (R(int)=0.020)	3475 (R(int)=0.064)	3338 (R(int)=0.031)
R(F), % ^a ($I \geq 2\sigma(I)$)	1.66	3.19	2.32
R(wF ²), % ^a	4.24	7.77	5.99

^a Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta / \Sigma(F_o)$, $\Delta = |(F_o - F_c)|$

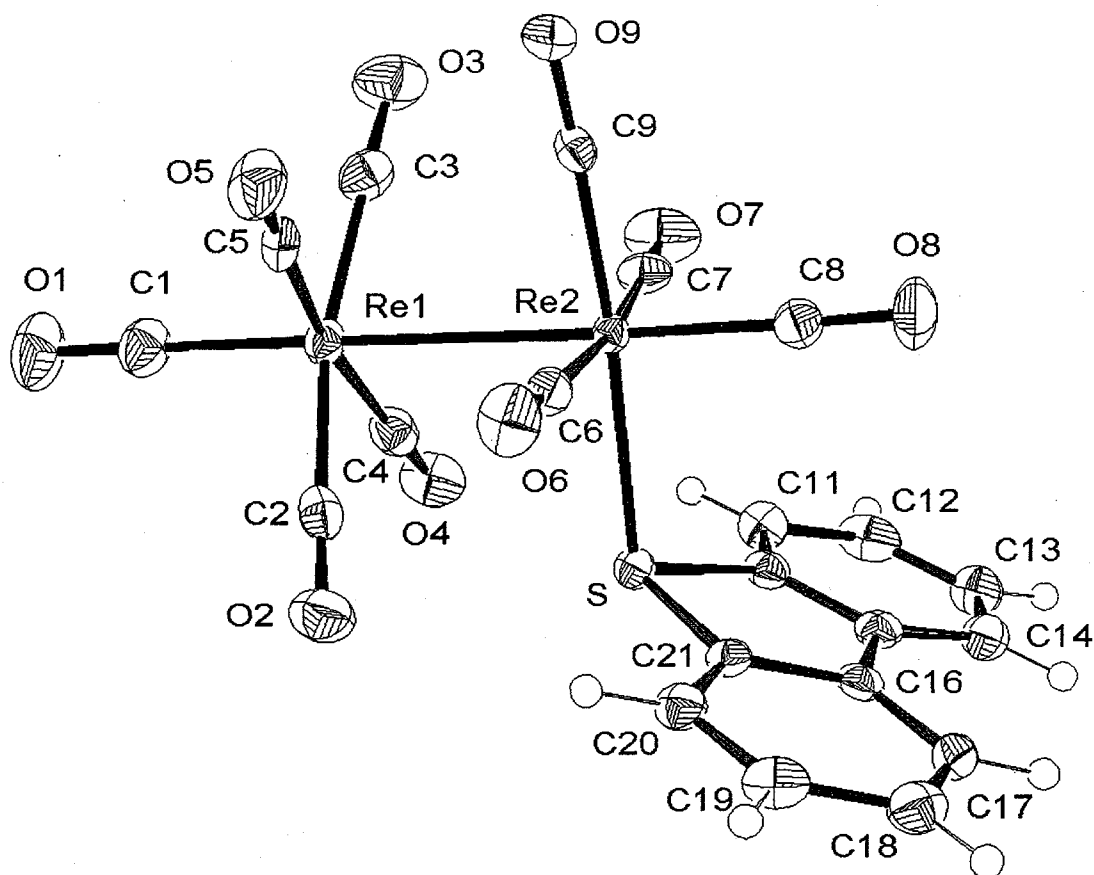


Figure 1. Molecular Structure of $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})$ (**1**). Selected bond distances (Å) and angles (°): $\text{Re}(1)\text{-Re}(2)$, 3.0389(2); $\text{Re}(2)\text{-S}$, 2.5375(8); $\text{S-C}(10)$, 1.781(3); $\text{S-C}(21)$, 1.782(3); $\text{Re}(1)\text{-C}(1)$, 1.933(4); $\text{Re}(2)\text{-C}(9)$, 1.926(3); $\text{C}(9)\text{-Re}(2)\text{-S}$ 174.69(10); $\text{Re}(2)\text{-S-C}(10)$, 107.08(11); $\text{Re}(2)\text{-S-C}(21)$, 106.60(11); $\text{C}(10)\text{-S-C}(21)$, 90.98(16); $\text{Re}(2)\text{-S-Midpt}$, 113.6.

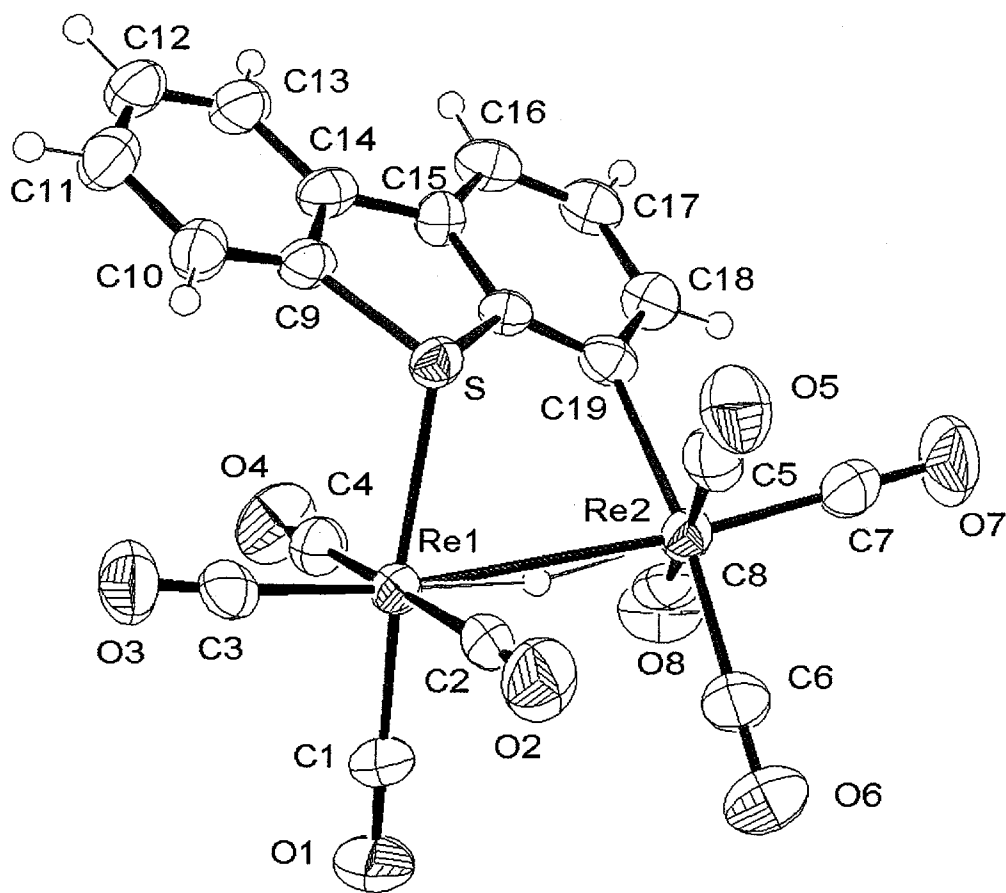


Figure 2. Molecular structure of $\text{Re}_2(\text{CO})_8(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})$ (**2**). Selected bond distances (Å) and angles ($^\circ$): $\text{Re}(1)\text{-S}$, 2.475(2); $\text{Re}(2)\text{-C}(19)$, 2.230(9); $\text{Re}(1)\text{---Re}(2)$, 3.345; $\text{S-C}(9)$, 1.765(8); $\text{S-C}(20)$, 1.768(7); $\text{Re}(1)\text{-C}(2)$, 1.996(10); $\text{Re}(1)\text{-C}(3)$, 1.961(10); $\text{Re}(1)\text{-C}(4)$, 2.002(10); $\text{Re}(2)\text{-C}(5)$, 1.981(11); $\text{Re}(2)\text{-C}(6)$, 1.962(10); $\text{Re}(2)\text{-C}(7)$, 1.897(11); $\text{Re}(2)\text{-C}(8)$, 2.009(12); $\text{C}(1)\text{-Re}(1)\text{-S}$, 173.5(3); $\text{C}(3)\text{-Re}(1)\text{-S}$, 94.5(3); $\text{C}(6)\text{-Re}(2)\text{-C}(19)$, 172.6(4); $\text{C}(7)\text{-Re}(2)\text{-C}(19)$, 87.8(4); $\text{Re}(1)\text{-S-C}(9)$, 116.0(3); $\text{C}(9)\text{-S-C}(20)$, 92.7(4); $\text{Re}(1)\text{-S-C}(20)$, 107.4(3); $\text{Re}(1)\text{-S-Midpt}$, 124.8.

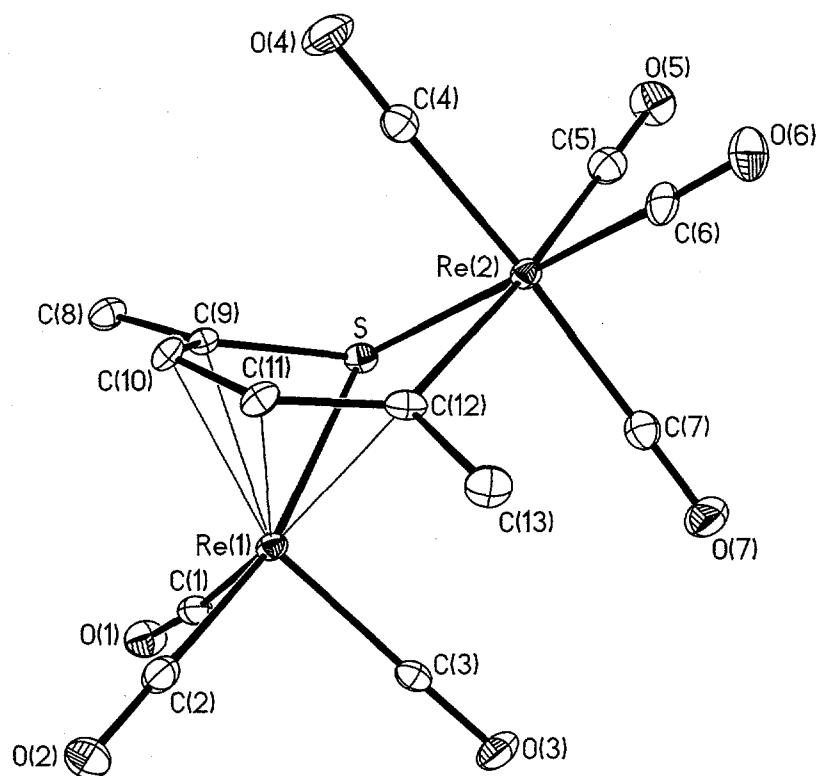


Figure 3. Molecular structure of $\text{Re}_2(\text{CO})_7(2,5\text{-Me}_2\text{T})$ (**3**). Selected bond distances (Å) and angles ($^\circ$): Re(1)-S, 2.5048(13); Re(2)-S, 2.4722(14); Re(1)-C(12), 2.554(5); Re(2)-C(12), 2.206(6); S-C(9), 1.773(5); C(9)-C(10), 1.382(8); C(10)-C(11), 1.473(7); C(11)-C(12), 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*

Michael A. Reynolds, Ilia A. Guzei[†] and Robert J. Angelici*

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 $\eta^1(\text{S})$ -bound BT^* complexes $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT}^*)$ (**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 $\eta^1(\text{S})$ -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 H_2 (10 °C, 24 h) in decane solution, complex **1d** and the partially hydrogenated BT^* complex $\text{Re}_2(\text{CO})_7(\mu\text{-3,5-Me}_2\text{BT-H})(\mu\text{-H})$ (**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 H_2 atmosphere (10°C) in decane solution also afforded the partially hydrogenated BT^* complexes $\text{Re}_2(\text{CO})_7(\mu\text{-3-MeBT-H})(\mu\text{-H})$ (**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 $\text{Re}_2(\text{CO})_7(\text{PMe}_3)_3(\mu\text{-BT})$ (**4**) and $\text{Re}_2(\text{CO})_7(\text{PR}_3)_2(\mu\text{-BT})$ ($\text{R} = \text{Me}$ (**5**), *iso*-Pr (**6**), and Cy (**7**)). Complexes **1-7** were characterized by spectroscopic methods (IR and ^1H 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

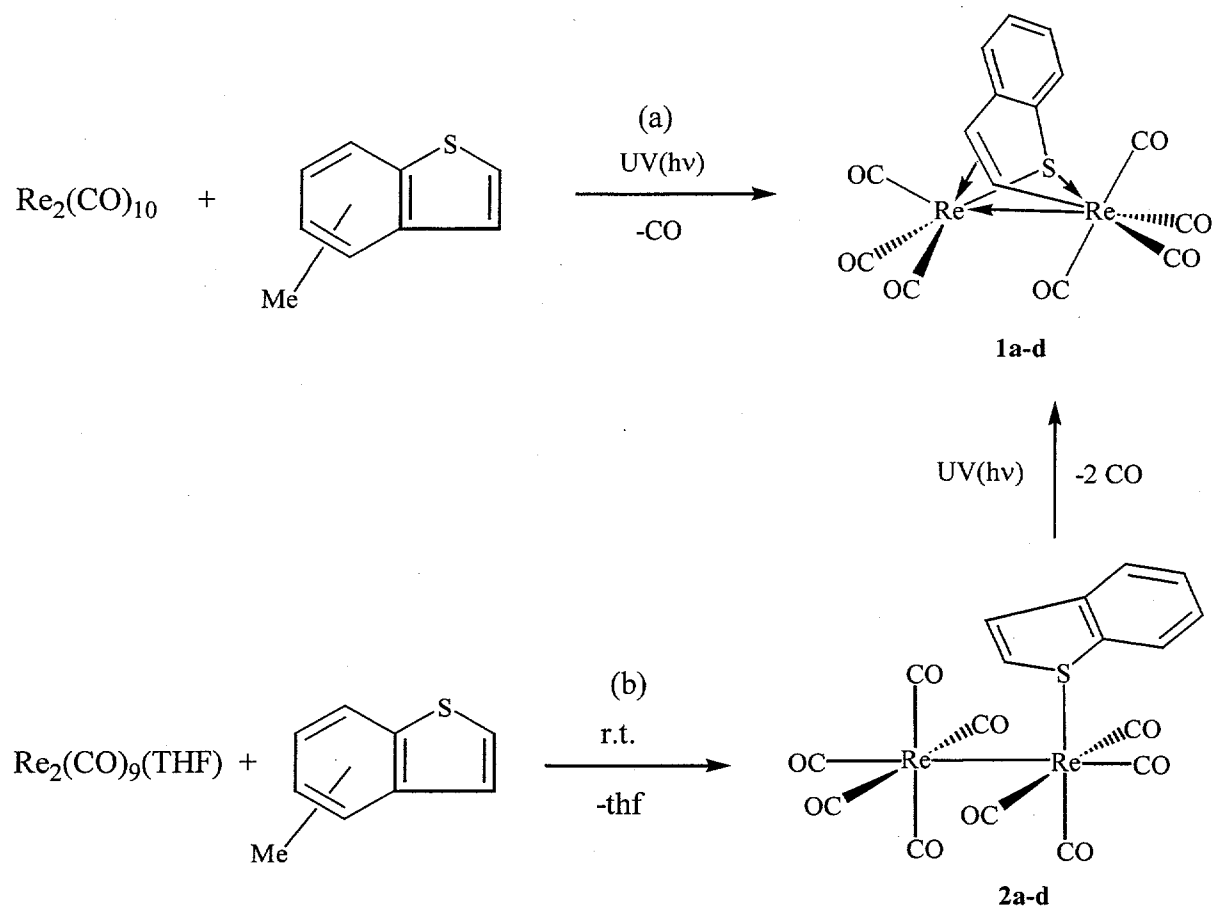
metal complexes in which the metal inserts into a C-S bond of a thiophene or benzothiophene compound.⁶⁻⁹ However, few examples of C-S bond cleavage of thiophenes in complexes that contain multiple metal centers have been reported.¹⁰⁻¹³ The complexes $\text{Mn}_2(\text{CO})_7(\mu\text{-T}^*)$ ¹⁴⁻¹⁷, $[\text{Cp}^*\text{Co}]_2(\mu\text{-T}^*)$ ¹⁸, $[(\text{dippe})\text{Ni}]_2(\mu\text{-T}^*)$ ¹⁹ and $\text{Fe}_2(\text{CO})_6(\mu\text{-T}^*)$ ²⁰ ($\text{T}^* = \text{T}$ and BT) represent some of the bimetallic complexes that contain bridging, ring-opened thiophenes. Recently, we reported the $\text{Re}_2(\text{CO})_{10}$ -promoted C-H cleavage of DBT to produce $\text{Re}_2(\text{CO})_8(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})$ and $\text{C}_{\text{vinyl}}\text{-S}$ cleavage in 2,5-Me₂T to afford $\text{Re}_2(\text{CO})_7(\mu\text{-2,5-Me}_2\text{T})$ during UV photolysis.²¹ We have also communicated our results for the preparation of $\text{Re}_2(\text{CO})_7(\mu\text{-BT})$ and its reactions with PMe_3 .²²

Herein we report further studies in the $\text{Re}_2(\text{CO})_{10}$ -promoted cleavage of the $\text{C}_{\text{vinyl}}\text{-S}$ bonds in alkyl-substituted benzothiophenes (BT^*) during UV photolysis to afford the BT^* complexes of type $\text{Re}_2(\text{CO})_7(\mu\text{-BT}^*)$. These complexes react with phosphines and H_2 to produce new dinuclear ring-opened and partially hydrogenated $\text{BT}^*\text{-Re}$ complexes.

Results and Discussion

Synthesis of $\text{Re}_2(\text{CO})_7(\mu\text{-BT}^*)$ complexes (1a-d). Irradiation of a hexanes solution containing $\text{Re}_2(\text{CO})_{10}$ and a 2-3 fold excess of BT^* ($\text{BT}^* = \text{BT}$, 2-MeBT, 3-MeBT or 3,5-Me₂BT) with UV light for 24 h produced the ring-opened BT^* complexes $\text{Re}_2(\text{CO})_7(\mu\text{-BT}^*)$ (**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_2Cl_2 , benzene and hexanes. In solution, **1a-d** are stable for days at room temperature if stored under an inert atmosphere such as N_2 .

Complexes **1a-d** contain a ring-opened BT^* ligand that has been cleaved regioselectively at the $\text{C}_{\text{vinyl}}\text{-S}$ bond and bridges the $\text{Re}_2(\text{CO})_7$ backbone through the S atom

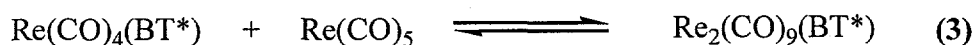
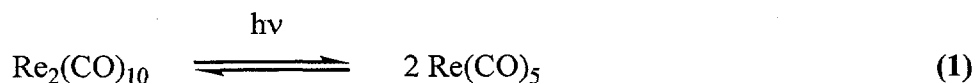


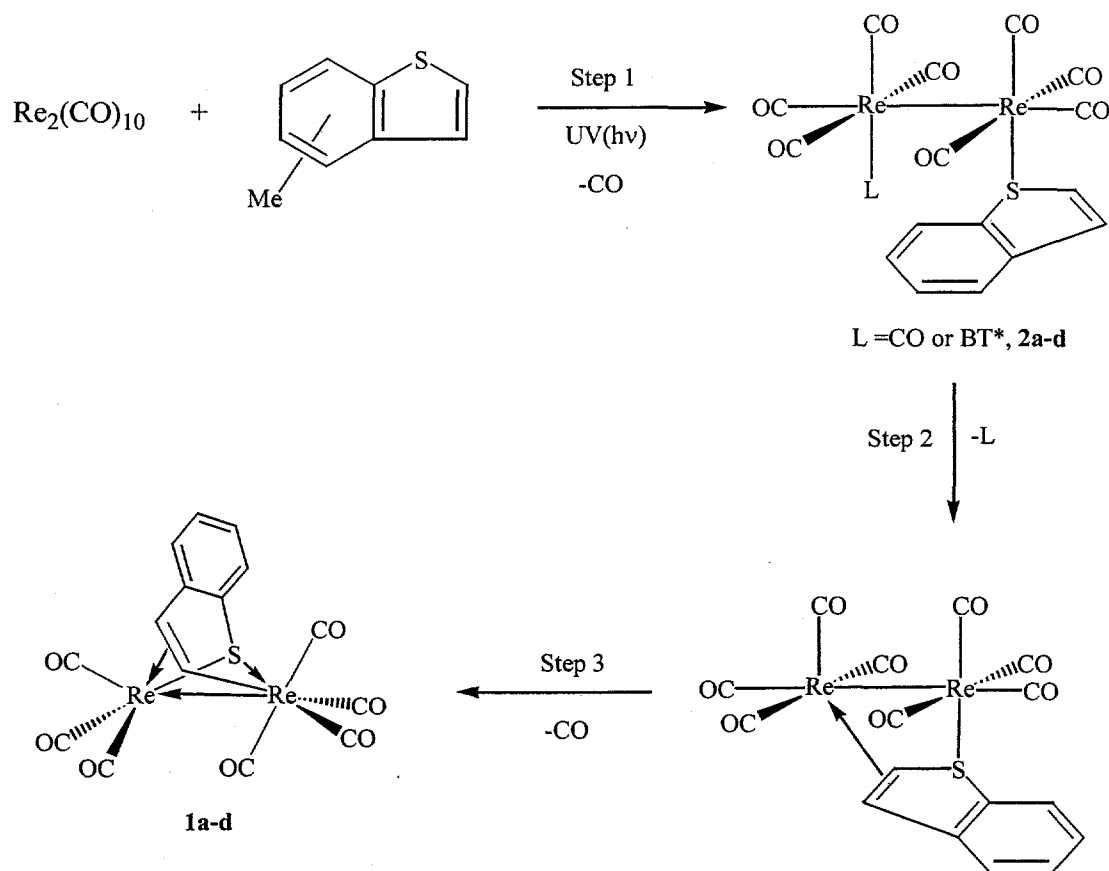
Scheme 1. Reaction scheme for the preparation of $\text{Re}_2(\text{CO})_7(\mu\text{-BT}^*)$ (1a-d).

and also η^1 , η^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.^{8c} for the reaction of 2-MeBT with $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{Ar})(\text{H})$ ^{8c} (Ar = Ph or 3,5-xylyl). In this system, Rh metal insertion into the $\text{C}_{\text{vinyl}}\text{-S}$ bond of 2-MeBT gave, as the kinetic product, $\text{Cp}^*\text{Rh}(\text{PMe}_3)\text{-(C}_{\text{vinyl}},\text{S-2-MeBT)}$ which readily converted into the $\text{C}_{\text{aryl}}\text{-S}$ cleaved complex $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{C}_{\text{aryl}},\text{S-2-MeBT})$ upon heating (74 °C, 38 h) in C_6D_{12} solution. The complexes **1a-d** were not converted into a $\text{C}_{\text{aryl}}\text{-S}$ metal-inserted isomer even when heated in refluxing toluene for 2 d.

In the ^1H NMR spectra for **1a-d** (in CD_2Cl_2), the chemical shift for the terminal vinyl proton of **1a** (δ 8.63, d, $J = 11.4$), **1c** (δ 8.22, s) and **1d** (δ 8.20, s) is shifted to low field compared to that in the free BT^* molecules (in the range of δ 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 η^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 $\text{Fe}_2(\text{CO})_6(\mu\text{-BT})$, which is spectroscopically and structurally similar to **1a**, and also exhibits a similar downfield shift for the terminal BT vinyl proton (δ 8.99 in CDCl_3).²⁰ The chemical shift for the methyl protons of the 2-MeBT ligand (in CD_2Cl_2) in **1b** (δ 3.16, s) was observed downfield of that in free 2-MeBT (δ 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 (δ 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 $\text{Re}_2(\text{CO})_8(\mu\text{-alkenyl})(\mu\text{-H})$.²³ The first step likely involves photochemically induced cleavage of the Re-Re bond in $\text{Re}_2(\text{CO})_{10}$ to generate $\bullet\text{Re}(\text{CO})_5$ radicals (eq. 1).





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 $\bullet\text{Re}(\text{CO})_4(\eta^1(\text{S})\text{-BT}^*)$ radicals (eq. 2). Cross-coupling of the $\bullet\text{Re}(\text{CO})_4(\eta^1(\text{S})\text{-BT}^*)$ radicals with $\bullet\text{Re}(\text{CO})_5$ (eq. 3) or other $\bullet\text{Re}(\text{CO})_4(\eta^1(\text{S})\text{-BT}^*)$ radical fragments would produce complexes **2a-d** or $\text{Re}_2(\text{CO})_8(\eta^1(\text{S})\text{-BT}^*)_2$ in the first step (Step 1, Scheme 2). The resulting $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT}^*)$ or $\text{Re}_2(\text{CO})_8(\eta^1(\text{S})\text{-BT}^*)_2$ complexes could undergo further photochemical loss of a ligand ($\text{L} = \text{CO}$ or BT^*) at the adjacent $\text{Re}(\text{CO})_4(\text{L})$ moiety with subsequent η^2 -binding of the BT vinyl group to form a bridging BT^* species $\text{Re}_2(\text{CO})_8(\mu_2\text{-$

$\eta^1(\text{S}), \eta^2\text{-BT}^*$) (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 $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT}^*)$ (**2a-d**) and $\text{Re}_2(\text{CO})_8(\eta^1(\text{S})\text{-BT}^*)_2$, were observed during the formation of **1a-d**; however irradiation of $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-3-MeBT})$ (**2c**) in hexanes solvent for 1-5 h did produce **1c** in high yield (>50%) as illustrated in reaction (b) of Scheme 1. This conversion of **2c** into **1c** supports the proposal that **2a-d** and possibly $\text{Re}_2(\text{CO})_8(\eta^1(\text{S})\text{-BT}^*)_2$ are precursors to **1a-d**.

If $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT}^*)$ or $\text{Re}_2(\text{CO})_8(\eta^1(\text{S})\text{-BT}^*)_2$ 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 $\bullet\text{M}(\text{CO})_5$ ($\text{M} = \text{Mn}$ or Re) radicals to produce the neutral complexes $(\text{TEMPO})\text{M}(\text{CO})_3$ during UV photolysis of $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}$ or Re).²⁴ The results of both the CO and TEMPO experiments are consistent with a mechanism (eq. 1-3) involving $\text{Re}(\text{CO})_5$ radicals in the formation of **1a-d**.²⁵

Preparation of $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT}^*)$ (2a-d**).** The S-bound complexes, $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT}^*)$ (**2a-d**) were prepared by two different synthetic routes (method A and

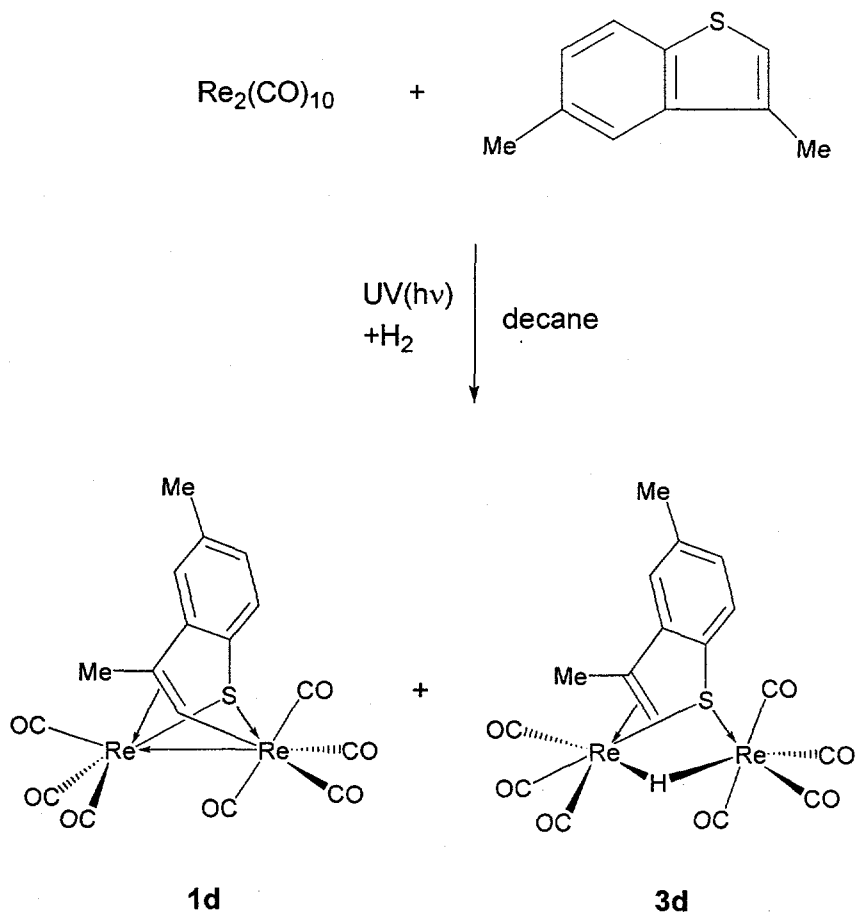
B). In method A, a dry THF solution of $\text{Re}_2(\text{CO})_{10}$ was irradiated in a quartz tube for 1-1.5 h (10°C) until the formation of $\text{Re}_2(\text{CO})_9(\text{THF})$ was observed (IR in THF: 2101 (w), 2047 (m), 1987 (s), 1954 (m) and 1917 (m) cm^{-1}). Excess BT^* was then added to the 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 CH_2Cl_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 ^1H NMR spectroscopy and an X-ray structure of **3c** was determined.

The ^1H 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 ^1H 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 η^2 -fashion, the olefinic protons would be expected to shift to high field as observed in $\text{Cp}^*\text{Re}(\text{CO})_2(2,3\text{-}\eta^2\text{-BT})$ 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_2BT with H_2 . When $\text{Re}_2(\text{CO})_{10}$ and a 3-5 fold excess of 3,5- Me_2BT were irradiated with UV light in a H_2 -saturated decane solution (24-36 h, 10°C) the complexes $\text{H}_2\text{Re}_2(\text{CO})_8$, $\text{Re}_2(\text{CO})_7(\mu\text{-}3,5\text{-Me}_2\text{BT})$ (**1d**), and the partially hydrogenated BT^* complex $\text{Re}_2(\text{CO})_7(\mu\text{-}3,5\text{-Me}_2\text{BT-H})(\mu\text{-H})$ (**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 η^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 ¹H NMR spectrum. In a related reaction, when



Scheme 3.

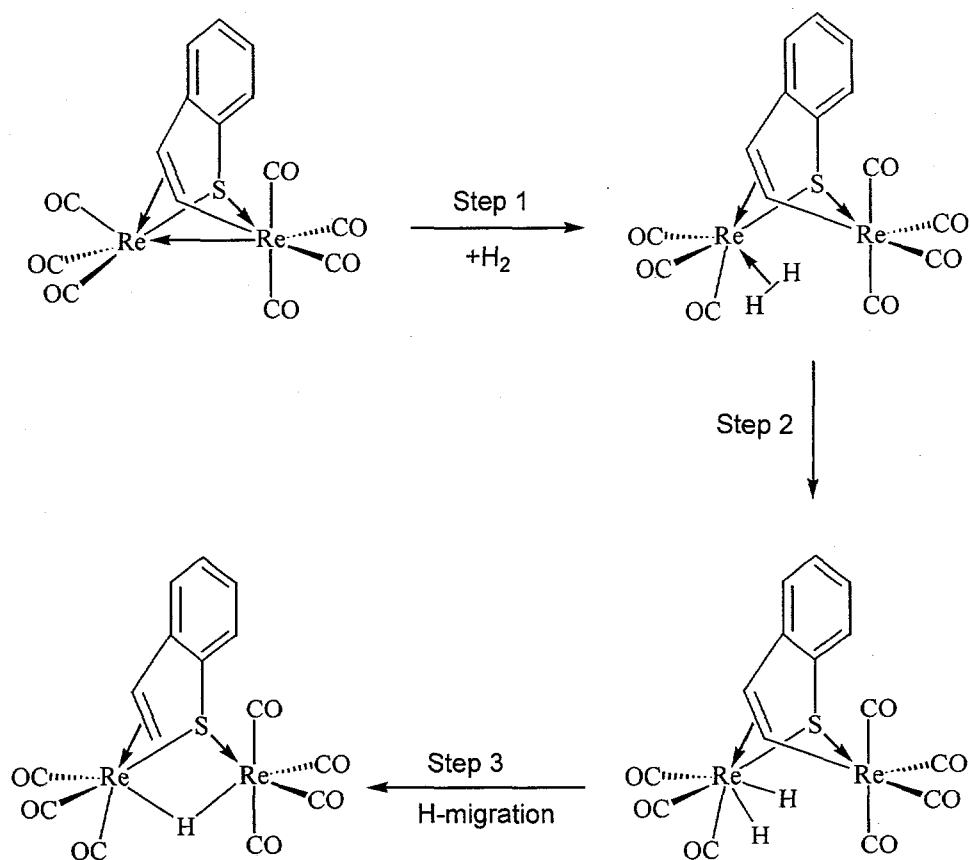
complex **1c** was irradiated with UV light under H_2 (1 atm) for 15-18 h in decane solution, the complex $\text{Re}_2(\text{CO})_7(\mu\text{-3-MeBT-H})(\mu\text{-H})$ (**3c**) was produced which is structurally analogous to **3d**. Under the same reaction conditions, when complex **1c** was irradiated in hexanes solution, **3c** was produced.

Complexes **3c** and **3d** are colorless solids that are soluble in CH_2Cl_2 , 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 N_2 .

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 η^2 -vinyl group of **3c** (in CD_2Cl_2) 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- Me_2BT ligand of **3d** compared to **1d**. Here, the vinyl protons are shifted upfield for **3d** (in CDCl_3 : 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 $\text{Re}_2(\text{CO})_{10}$ and 3-MeBT or 3,5- Me_2BT with H_2 , it is likely that complexes **3c** and **3d** are formed from the $\text{Re}_2(\text{CO})_7(\mu\text{-BT}^*)$ complexes **1c** and **1d** as illustrated in Scheme 4. In the first step, the Re-Re bond could dissociate in the presence of H_2 to produce an η^2 -bound dihydrogen complex. The $\eta^2\text{-H}_2$ ligand could then undergo oxidative addition at the $\text{Re}(\text{CO})_3$ 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 H_2 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 $\text{Re}_2(\text{CO})_7(\mu\text{-BT})$ (**1a**) reacts with an excess of PMe_3 in toluene solution at room temperature to produce the further ring-opened BT complexes $\text{Re}_2(\text{CO})_7(\text{PMe}_3)_3(\mu\text{-BT})$ (**4**) and

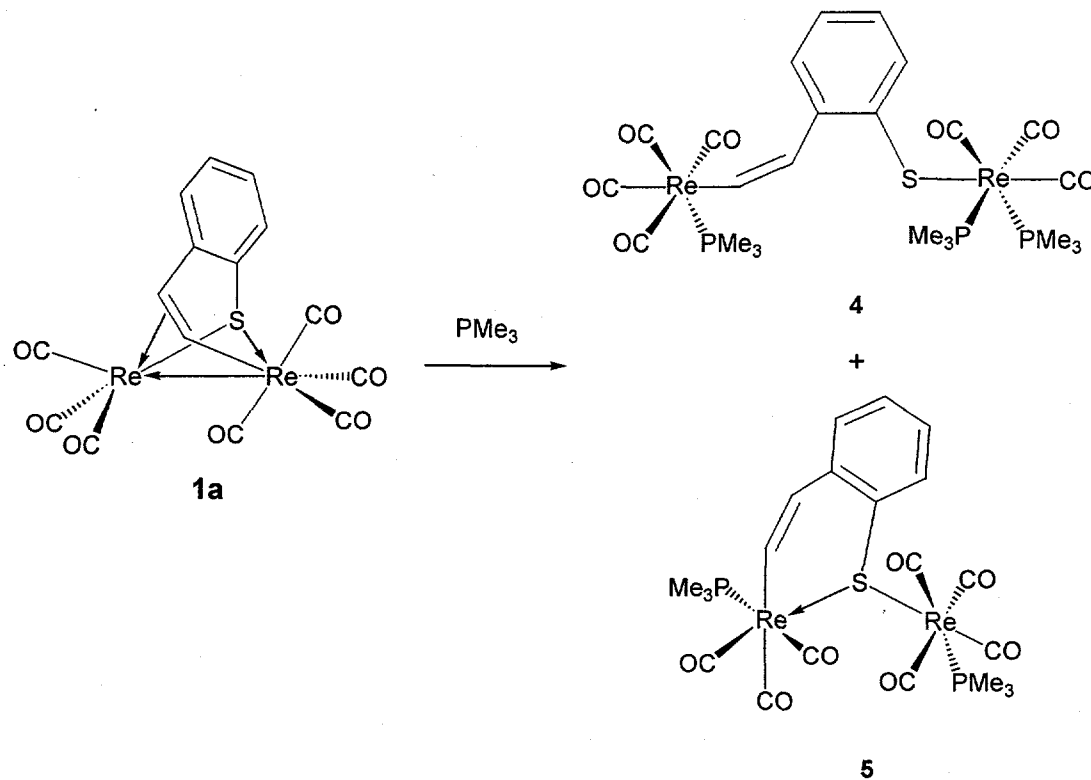


Scheme 4.

$\text{Re}_2(\text{CO})_7(\text{PMe}_3)_2(\mu\text{-BT})$ (**5**) in good yields (40% for **4** and 60% for **5**) (Scheme 5). Complex **1a** also reacts with P^iPr_3 (5 equivalents) and PCy_3 (2 equivalents) to produce the $\text{Re}_2(\text{CO})_7(\text{PR}_3)_2(\mu\text{-BT})$ complexes **6** ($\text{R} = ^i\text{Pr}$) and **7** ($\text{R} = \text{Cy}$) 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^iPr_3 or PCy_3 . The colorless complex **4** and the pale yellow **5-7** are soluble in CH_2Cl_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 ^1H NMR spectrum for **4** (in CD_2Cl_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 PMe_3 phosphorus.



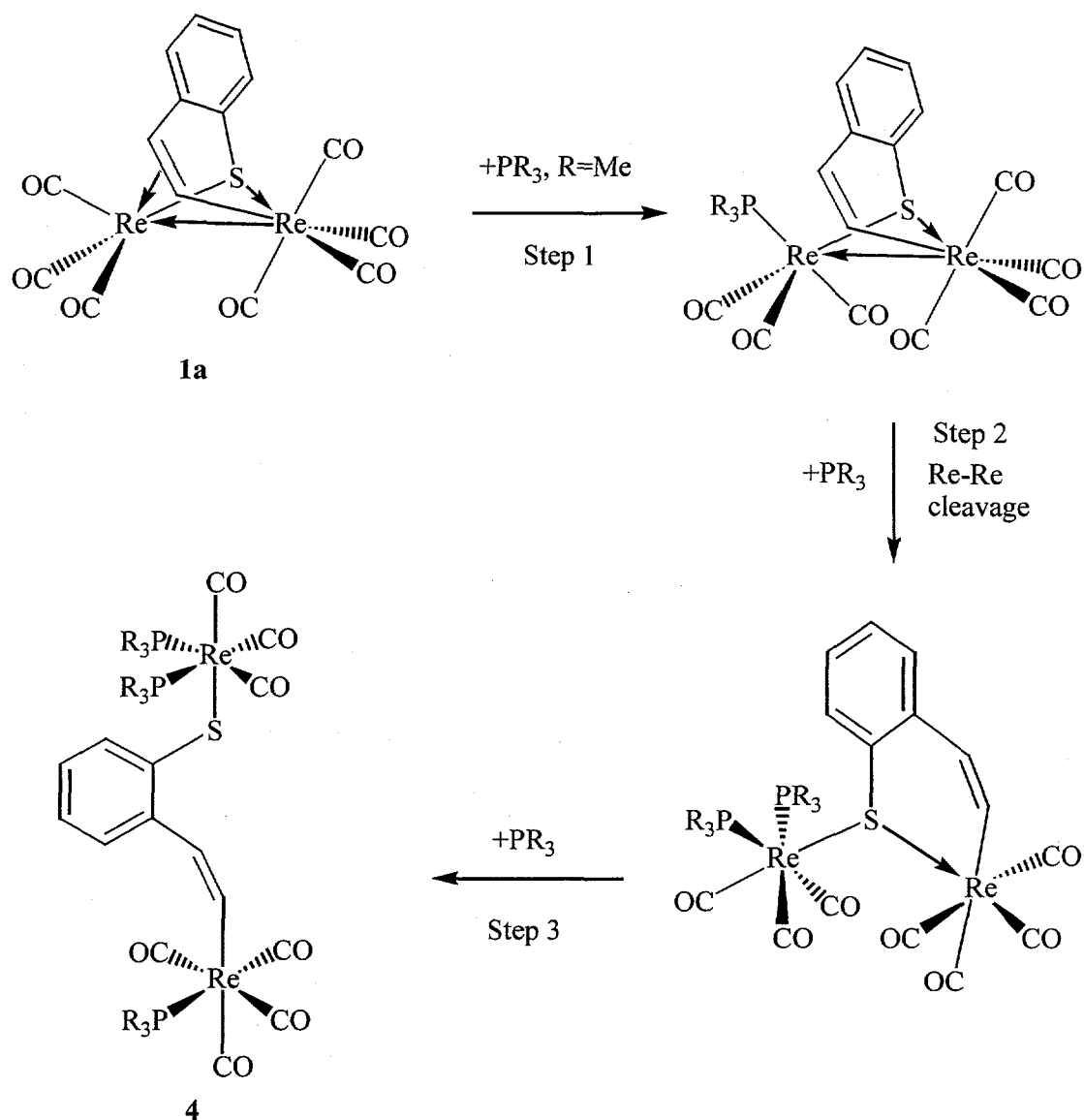
Scheme 5

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 PMe_3 ligands are observed as a multiplet at 1.62 ppm.

The ^1H NMR spectra (in CD_2Cl_2) of **5-7** are similar to each other, but significantly different from that of **1a** (in CD_2Cl_2). The chemical shift for the proton in the 2-position of the BT ligand of **5** (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,

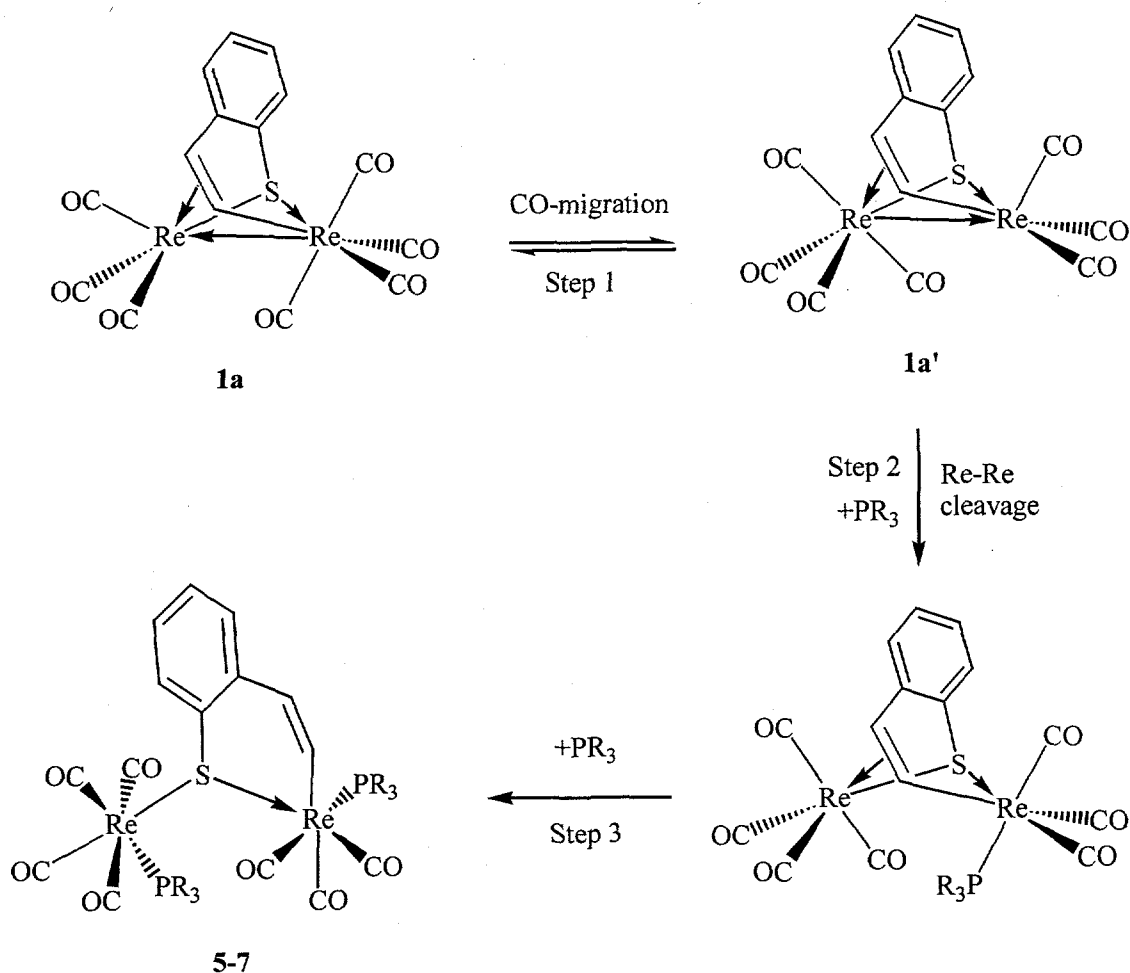
dd, $J=14.0, 2.0$ Hz) is shifted upfield compared from that observed in the spectrum of **1a** (δ 8.63 d, $J=12.0$ Hz). However, the chemical shift for the vinyl proton in the 3-position of the BT vinyl group in **5** (δ 7.44, dd, $J=14.1, 3.6$ Hz), **6** (δ 7.43, dd, $J=14.4, 3.0$ Hz) and **7** (δ 7.46, 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 J_{HP} 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 PMe_3 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 PMe_3 . The first step of this mechanism could involve displacement of the η^2 -bound vinyl group by PMe_3 at the $\text{Re}(\text{CO})_3$ moiety (Step 1, Scheme 6) to give an intermediate of the type $\text{Re}_2(\text{CO})_7(\text{PMe}_3)(\mu\text{-BT})$. Addition of a second PMe_3 ligand to the $\text{Re}(\text{CO})_3(\text{PMe}_3)$ unit would result in Re-Re bond cleavage (Step 2, Scheme 6) to produce an intermediate such as $\text{Re}_2(\text{CO})_7(\text{PMe}_3)_2(\mu\text{-BT})$. In the final step, an additional equivalent of PMe_3 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 PMe_3 .



Scheme 6. Reaction scheme for the formation of $\text{Re}_2(\text{CO})_7(\text{PMe}_3)_3(\mu\text{-BT})$ (**4**).

A possible mechanism for the formation of the $\text{Re}_2(\text{CO})_7(\text{PR}_3)_2(\mu\text{-BT})$ 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 η^1 -bound to the $\text{Re}(\text{CO})_3$ unit and not to the $\text{Re}(\text{CO})_4$ 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



Scheme 7. Reaction scheme for the formation of $\text{Re}_2(\text{CO})_7(\text{PR}_3)_2(\mu\text{-BT})$ (**5-7**).

in the proposed mechanism is the migration of a CO ligand from the $\text{Re}(\text{CO})_4$ group in **1a** to the $\text{Re}(\text{CO})_3$ moiety to afford the isomer **1a'** (Step 1, Scheme 7). Although **1a'** has not been observed in the ^1H NMR spectrum of **1a** in solution, a variable temperature ^{13}C NMR study of **1a** (in CD_2Cl_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 δ 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.²² 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 $\text{Re}(\text{CO})_3$ unit and the $\text{Re}(\text{CO})_4$ unit of **1a**, are rapidly exchanging between Re centers.

Isomer **1a'** could then react with a PR_3 ligand with dissociation of either the η^2 -vinyl group or the Re-Re bond. Since the $\text{Re}(\text{CO})_4$ unit in **1a'** is already saturated, substitution of the vinyl group for the PR_3 ligand would be unfavorable. However, if the Re-Re bond dissociates first, followed by addition of PR_3 to the $\text{Re}(\text{CO})_3$ unit as proposed (Step 2, Scheme 7), then both Re centers would be 6-coordinate. Displacement of the vinyl group with addition of a PR_3 ligand to the $\text{Re}(\text{CO})_4$ unit in the final step would produce the complex $\text{Re}_2(\text{CO})_7(\text{PR}_3)_2(\mu\text{-BT})$ (**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 (P^iPr_3 , 160°; PCy_3 , 170°)³³ and similar nucleophilic character compared to PMe_3 (118°)³³. All three phosphines produce similar disubstituted phosphine complexes of the type $\text{Re}_2(\text{CO})_7(\text{PR}_3)_2(\mu\text{-BT})$ (**5-7**). However, complex **1a** reacts with PMe_3 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 PMe_3 has a smaller cone angle compared to P^iPr_3 and PCy_3 , both **4** and **5** are produced when PMe_3 is reacted with **1a**.

Although complexes **1a-d** readily react with phosphines and H₂ under mild conditions, they are unreactive towards electrophiles such as MeI, 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(η¹(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(η¹(S)-T) (2.360(3) Å)³⁵ and Cp*Re(CO)₂(η¹(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(η¹(S)-DBT) (θ = 113.6°)²¹ and comparable to that in other complexes which contain electron deficient metal centers such as (CO)₅W(η¹(S)-DBT)³⁰ (118.8°), (CO)₅Cr(η¹(S)-DBT) (121.8°)³⁰, and [CpFe(CO)₂(η¹(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(η¹(S)-3-MeBT) (θ = 131.0°)²⁹ and Cp*Re(CO)₂(η¹(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 $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})-\text{T}^*)$ ($\text{T}^* = \text{T}$ 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 $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-3-MeBT})$ (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 $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^1(\text{S})\text{-3-MeBT})$ ²⁹ (90(1)°). The Re-Re bond distance in the structure of **2c** is 3.0343(4) Å and compares well with that in $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})$ (3.0389(2) Å)²¹ and $\text{Re}_2(\text{CO})_{10}$ (3.0413(11) Å)³⁷.

Comparison of the Molecular Structures of $\text{Re}_2(\text{CO})_7(\mu\text{-3,5-Me}_2\text{BT})$ (1d**) and $\text{Re}_2(\text{CO})_7(\mu\text{-3,5-Me}_2\text{BT-H})(\mu\text{-H})$ (**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 $\text{Re}_2(\text{CO})_7$ moiety nearly symmetrically through the sulfur and both η^1 - and η^2 -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- η^1 -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 $\text{Re}_2(\text{CO})_{10}$ (3.0413(11) Å)³⁷, $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})$ (3.0389(2) Å)²¹ and **2c** (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 $\text{Re}_2(\text{CO})_8(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})$ (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 $\text{Re}(\text{CO})_4$ 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 $\text{Fe}_2(\text{CO})_6(\mu\text{-BT})$ ²⁰, $[\text{Cp}^*\text{Co}]_2(\mu\text{-BT})$ ¹⁸ and $[(\text{dippe})\text{Ni}]_2(\mu\text{-BT})$ ¹⁹ due to the extra carbonyl group present on the $\text{Re}(\text{CO})_4$ 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 $\text{Re}_2(\text{CO})_7(\text{P}^i\text{Pr}_3)_2(\mu\text{-BT})$ (7). In the structure of 7 (Figure 4), a BT ligand that has been cleaved at the $\text{C}_{\text{vinyl}}\text{-S}$ position bridges the two Re metal centers through the sulfur atom and the η^1 -vinyl group is bonded to the $\text{Re}(\text{CO})_3(\text{PMe}_3)$ moiety. Each Re in 7 also contains one coordinated P^iPr_3 group similar to that reported for the structurally analogous 4 which contains PMe_3 ligands. The sulfur in 7 bridges the two Re centers nearly symmetrically with distances of 2.5296(15) Å for $\text{Re}(1)\text{-S}$ and 2.5499(15) Å for $\text{Re}(2)\text{-S}$. These distances are slightly larger than those observed in the structure of 1a ($\text{Re}(1)\text{-S}$, 2.506(2) Å; $\text{Re}(2)\text{-S}$, 2.431(3) Å) in which there is a Re-Re bond. The Re-S-Re angle in 7 ($116.69(5)^\circ$) is also larger than that in complex 1a ($71.77(7)^\circ$) and similar to that in 4 ($116.76(3)^\circ$). 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 $\text{Re}(1)\text{-C}(13)$ 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 $\text{Re}_2(\text{CO})_{10}$ and BT^* molecules in hexanes solution to produce $\text{Re}_2(\text{CO})_7(\mu\text{-BT}^*)$ (1a-d) represents a novel method for regioselectively cleaving C-S bonds in benzothiophenes. In each case, the $\text{C}_{\text{vinyl}}\text{-S}$ bond of the BT^* molecule was cleaved preferentially over the $\text{C}_{\text{aryl}}\text{-S}$ bond regardless of the position of methyl groups on the BT^* molecules.

When the UV photolysis of $\text{Re}_2(\text{CO})_{10}$ was carried out in the presence of H_2 (1 atm), the partially hydrogenated complexes of the type $\text{Re}_2(\text{CO})_7(\mu\text{-BT}^*\text{-H})(\mu\text{-H})$, 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 H_2 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 MeI, 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 $\text{Re}_2(\text{CO})_{10}$ and BT* could involve the S-bound complexes $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT}^*)$ (**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 $\text{Re}_2(\text{CO})_{10}$ 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 $\text{Re}_2(\text{CO})_{10}$ to give the C-S cleaved thiophene complexes $\text{Re}_2(\text{CO})_7(\mu\text{-2,5-Me}_2\text{T})^{21}$ and $\text{Re}_2(\text{CO})_7(\mu\text{-BT})$ (**1a-d**), while DBT reacts with $\text{Re}_2(\text{CO})_{10}$ to afford both the S-bound and C-H cleaved DBT complexes $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-DBT})^{21}$ and $\text{Re}_2(\text{CO})_8(\mu\text{-C}_{12}\text{H}_7\text{S})(\mu\text{-H})^{21}$. Therefore, the results of the reactions of thiophenes with $\text{Re}_2(\text{CO})_{10}$ 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.^{8c} Trimethylamine *N*-oxide (Me_3NO) (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 $\text{Re}_2(\text{CO})_7(\mu\text{-BT}^*)$ (1a-d). $\text{Re}_2(\text{CO})_7(\mu\text{-BT})$ (1a). In a typical experiment, a hexanes (40 mL) solution of $\text{Re}_2(\text{CO})_{10}$ (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 N_2 , 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 CH_2Cl_2 (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 (CD_2Cl_2 , 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). ^{13}C NMR (300 MHz, -50.1 °C, CD_2Cl_2): 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) ν_{CO} : 2099(m), 2043(s), 2027(s), 1981(s), 1977(s), 1957(m) and 1947(s) cm^{-1} . Anal. Calcd (found) for $C_{15}H_6O_7Re_2S$: C, 25.64 (25.54); H, 0.86 (0.69).

Preparation of $Re_2(CO)_7(\mu-2-MeBT)$ (1b**).** Complex **1b** was prepared in a similar fashion as **1a** by irradiation of a hexanes (30 mL) solution of $Re_2(CO)_{10}$ (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 CH_2Cl_2 (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 $Re_2(CO)_{10}$). 1H NMR (300 MHz, CD_2Cl_2): δ 7.09 (m, 2 H), 7.01 (dt, 1 H, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz), 6.89 (dt, 1 H, $J_1 = 7.5$ Hz, $J_2 = 1.5$ 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 $C_{16}H_8O_7Re_2S$: C, 26.81 (26.94); H, 1.13 (1.20).

Preparation of $\text{Re}_2(\text{CO})_7(\mu\text{-3-MeBT})$ (1c**).** Complex **1c** was prepared in a similar fashion as **1a** from a hexanes solution (35 mL) of $\text{Re}_2(\text{CO})_{10}$ (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 **1c** was purified and isolated as described for **1a** by column chromatography on silica gel. Orange crystals of **1c** were grown from a solution of CH_2Cl_2 (1 mL) that was layered with hexanes (5 mL) and stored overnight (at -20 °C) (159 mg, 49% yield based on $\text{Re}_2(\text{CO})_{10}$). ^1H NMR (200 MHz, CD_2Cl_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): $\nu(\text{CO})$ cm^{-1} 2097 (m), 2040 (vs), 2024 (s), 1979 (vs), 1973 (s), 1954 (w), 1941 (m). Anal. Calcd (found) for $\text{C}_{16}\text{H}_8\text{O}_7\text{Re}_2\text{S}$: C, 26.81 (26.71); H, 1.13 (1.17).

Preparation of $\text{Re}_2(\text{CO})_7(3,5\text{-Me}_2\text{BT})$ (1d**).** Complex **1d** was prepared and isolated from a photolytic reaction of $\text{Re}_2(\text{CO})_{10}$ (238 mg, 0.365 mmol) and 3,5-Me₂BT (200 mg, 1.23 mmol) in hexanes (36 mL). The yield (112 mg) was 42% based on $\text{Re}_2(\text{CO})_{10}$. ^1H NMR (CD_2Cl_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): $\nu(\text{CO})$ cm^{-1} 2097 (m), 2040 (vs), 2023 (s), 1978 (vs), 1972 (s), 1953 (m), 1940 (s). Anal. Calcd (found) for $\text{C}_{17}\text{H}_{10}\text{O}_7\text{Re}_2\text{S}$: C, 27.94 (27.85); H, 1.38 (1.16).

Preparation of $\text{Re}_2(\text{CO})_9(\text{THF})$. In a typical experiment, a dry THF solution (30 mL) of $\text{Re}_2(\text{CO})_{10}$ (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 $\text{Re}_2(\text{CO})_9(\text{THF})$. 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 $\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT}^*)$ (2a-d).

$\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-BT})$ (2a); Method A. Benzothiophene (79.0 mg, 0.589 mmol) was added to a freshly prepared THF (30 mL) solution of $\text{Re}_2(\text{CO})_9(\text{THF})$ (0.313 mmol based on $\text{Re}_2(\text{CO})_{10}$) 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_2Cl_2 (1 mL) and layered with hexanes (5 mL) followed by cooling overnight ($-20\text{ }^\circ\text{C}$) to give pale yellow crystals of **2a** (45 mg, 19% yield based on $\text{Re}_2(\text{CO})_{10}$) which were filtered and dried under vacuum. ^1H NMR (300 MHz, CD_2Cl_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_2Cl_2): 2101(w), 2045(m), 1990 (s, br), 1967 (m) and 1931 (m) cm^{-1} . **Method B.** A THF (15 mL) solution of $\text{Re}_2(\text{CO})_{10}$ (327 mg, 0.501 mmol) was prepared under an inert atmosphere in a 50 mL Schlenk flask equipped with a stir bar. Anhydrous Me_3NO (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 $\text{Re}_2(\text{CO})_{10}$). Complex **2a** was characterized as described in Method A.

$\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-3-MeBT})$ (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 $\text{Re}_2(\text{CO})_9(\text{THF})$ (0.342 mmol based on $\text{Re}_2(\text{CO})_{10}$) with stirring for 20 h. After solvent removal *in vacuo*, the yellow residue containing **2c** was dissolved in CH_2Cl_2 (1 mL) and layered with hexanes (5 mL) ($-20\text{ }^\circ\text{C}$ for 2 d). The resulting yellow crystals of **2c** were then filtered and dried *in vacuo* (72 mg, 27% yield based on $\text{Re}_2(\text{CO})_{10}$). **Method B:** A THF solution (25 mL) of $\text{Re}_2(\text{CO})_{10}$ (310 mg, 0.475 mmol) was prepared in a 50 mL Schlenk flask. Me_3NO (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 CH_2Cl_2 and layered with hexanes (1:5 mL) ($-20\text{ }^\circ\text{C}$ for 1 d). The crystals of **2c** were filtered and dried under vacuum (93 mg, 25% yield). ^1H NMR (300 MHz, CD_2Cl_2): 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 (CH_2Cl_2): 2102 (w), 2043 (m), 1989 (s, br), 1967 (m), 1931 (m) cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_8\text{O}_9\text{Re}_2\text{S}$: C, 27.98 (27.76); H, 1.04 (1.00).

$\text{Re}_2(\text{CO})_9(\eta^1(\text{S})\text{-3,5-Me}_2\text{BT})$ (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 $\text{Re}_2(\text{CO})_9(\text{THF})$ (0.314 mmol based on $\text{Re}_2(\text{CO})_{10}$) 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 CH_2Cl_2 (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 *in vacuo* (106 mg, 43% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 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 (CH₂Cl₂): 2102 (w), 2042 (m), 1989 (s, br), 1963 (m) and 1931 (m) cm⁻¹. Anal. Calcd (found) for C₁₉H₁₀O₉Re₂S: C, 29.01 (28.53); H, 1.28 (1.13). **Method B:** A THF solution (20 mL) of Re₂(CO)₁₀ (147 mg, 0.225 mmol) was prepared in a 50 mL Schlenk flask, followed by the addition of Me₃NO (27.0 mg, 0.360 mmol) with stirring for 1.5 h. The volatiles were then removed *in vacuo* followed by addition of THF (10-15 mL) and 3,5-Me₂BT (112 mg, 0.691 mmol) with stirring (10 h). The solvent was then removed and the yellow oily residue was crystallized from CH₂Cl₂ and hexanes (1:4 mL) at -20 °C after 1 d to afford yellow crystals of **2d** (62.4 mg, 35% based on Re₂(CO)₁₀).

Photolysis reaction of Re₂(CO)₁₀ and BT with CO. A hexanes solution (35 mL) of Re₂(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 Re₂(CO)₁₀ were observed in the ν_{CO} region (IR in hexanes: 2070(w), 2014(s), 1978(m) cm⁻¹)³⁹ during the reaction time period.

Photolysis reaction of Re₂(CO)₁₀ and BT with TEMPO. A hexanes solution (35 mL) was prepared in a quartz reaction tube that contained Re₂(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 $\text{Re}_2(\text{CO})_{10}$. No attempt was made to isolate the dark material present in the reaction solution.

Photolysis of $\text{Re}_2(\text{CO})_{10}$ and 3,5-Me₂BT in the presence of H₂. A decane (30 mL) solution containing $\text{Re}_2(\text{CO})_{10}$ (288 mg, 0.441 mmol) and 3,5-Me₂BT (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 H₂ 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 $\text{H}_2\text{Re}_2(\text{CO})_8$ (12% based on $\text{Re}_2(\text{CO})_{10}$)⁴⁰. An orange band was eluted using CH₂Cl₂ and hexanes (1:10) and collected. After solvent removal under vacuum, an orange solid remained which contained **1d** (based on IR and ¹H 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 $\text{Re}_2(\text{CO})_7(\mu\text{-3,5-Me}_2\text{BT-H})(\mu\text{-H})$ (**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 $\text{Re}_2(\text{CO})_{10}$). ¹H NMR (300 MHz, CDCl₃): 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): ν_{CO} 2100(w), 2039(vs), 2003(s), 1992(vs), 1964(vs), 1955(w), 1943(m) cm^{-1} .

Photolysis Reaction of 1c with 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 ν_{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 CH_2Cl_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. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.34 (td, 1 H, $J_1=7.8$ Hz, $J_2=0.9$ Hz), 7.19 (m, 1 H), 7.09 (m, 2 H), 4.32 (s, 1 H), 4.06 (d, 1 H, $J=2.1$ 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 CH_2Cl_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**: ^1H NMR (CD_2Cl_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_2Cl_2) ν_{CO} : 2079(w), 2018(s), 1978(s,sh), 1972(s), 1933(s) and 1893(s) cm^{-1} . For **5**: ^1H NMR (CD_2Cl_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, PMe_3 , $J = 9.3$ Hz), 1.19 (d, 9 H, PMe_3 , $J = 8.4$ Hz). IR (CH_2Cl_2) ν_{CO} : 2100(w), 2003(s), 1953(m, br), 1896(m, br) and 1873(m, br) cm^{-1} . Anal. Calcd (found) for $\text{C}_{21}\text{H}_{24}\text{O}_7\text{P}_2\text{Re}_2\text{S}$: C, 29.51 (29.24); H, 2.83 (2.78).

Reaction of 1a with P^iPr_3 . A CH_2Cl_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^iPr_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 $\text{Re}_2(\text{CO})_7(\text{P}^i\text{Pr}_3)_2(\mu\text{-BT})$ (**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*. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.30 (dd, 1 H, $J_{\text{HH}}=14.4$ Hz, $J_{\text{HP}}=2.1$ Hz), 7.43 (dd, 1 H, $J_{\text{HH}}=14.4$ Hz, $J_{\text{HP}}=3.0$ 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 PCy_3 (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 ($-20\text{ }^\circ\text{C}$) overnight which produced a yellow crystalline solid of $\text{Re}_2(\text{CO})_7(\text{PCy}_3)_2(\mu\text{-BT})$ (**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, CD_2Cl_2): δ 8.33 (dd, 1 H, $J_{\text{HH}}=14.0\text{ Hz}$, $J_{\text{HP}}=2.0\text{ Hz}$), 7.46 (dd, 1 H, $J_{\text{HH}}=14.4\text{ Hz}$, $J_{\text{HP}}=2.4\text{ Hz}$), 7.24 (m, 2 H), 6.98 (m, 2 H), 6.80 (m, 1 H), 2.41-0.88 (m, Cy). IR (CH_2Cl_2): 2096(w), 2016(m), 1999(vs), 1944(m), 1888(m) and 1868(m) cm^{-1} . Anal calcd. (found) for $\text{C}_{51}\text{H}_{72}\text{O}_7\text{P}_2\text{Re}_2\text{S}$: 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 $\bar{P}1$ for **2c**, **3d**, and **7**. In the latter three cases the *E*-statistics strongly suggested the centrosymmetric space group $\bar{P}1$ that yielded chemically reasonable and computationally stable results of refinement⁴¹. In all cases the absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements⁴². 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

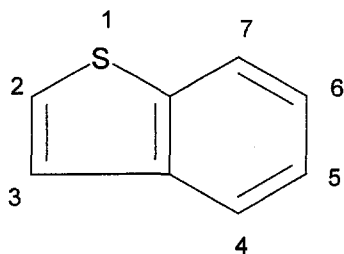
anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions.

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.

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Table 1. Crystallographic Data for **2c** and **1d**.

	2c	1d
Formula	C ₁₈ H ₈ O ₉ Re ₂ S	C ₁₇ H ₁₀ O ₇ Re ₂ S
Formula weight	772.71	730.71
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	9.3899(4)	9.5467(5)
<i>b</i> , Å	10.1350(5)	13.1048(7)
<i>c</i> , Å	11.3410(5)	13.6549(8)
α , °	79.066(1)	79.1811(10)
β , °	82.386(1)	88.0982(10)
γ , °	84.147(1)	74.7776(10)
<i>V</i> , Å ³	1047.07(8)	1855.97(17)
<i>Z</i>	2	4
<i>D</i> (calcd), g cm ⁻³	2.451	2.615
Temperature, K	173(2)	173(2)
Absorption correction	Empirical	Empirical
<i>T</i> (max)/(<i>T</i> Min)	1.00/0.607	0.1780/0.0768
Reflections collected	11136	16567
Independent refl..	4250 <i>R</i> (int)=0.0564	7537 <i>R</i> (int)=0.0302
<i>R</i> (<i>F</i>), % ^a (<i>I</i> ≥2σ(<i>I</i>))	3.78	2.62
<i>R</i> (<i>wF</i> ²), % ^a	4.12	3.12

^a- quantity minimized = $R(wF^2) = \Sigma[W(F_o^2 - F_c^2)^2] / \Sigma[(wF_o^2)^2]^{1/2}$, $R = \Sigma \Delta / \Sigma(F_o)$, $\Delta = |F_o - F_c|$

Table 2. Crystallographic Data for **3d** and **7**.

	3d	7
Formula	C ₁₇ H ₁₂ O ₇ Re ₂ S	C ₃₃ H ₄₈ O ₇ P ₂ Re ₂ S
Formula weight	732.73	1023.11
Space group	$P\bar{1}$	P2 ₁
<i>a</i> , Å	8.5211(4)	8.8458(4)
<i>b</i> , Å	9.3409(4)	14.7313(6)
<i>c</i> , Å	13.0690(6)	14.4311(6)
α , °	72.9212(10)	90
β , °	85.1222(10)	90.037(1)
γ , °	86.7596(4)	90
<i>V</i> , Å ³	990.21(8)	1880.52(14)
<i>Z</i>	2	2
<i>D</i> (calcd), Mg cm ⁻¹	2.458	1.807
Temperature, K	173(2)	173(2)
Absorption correction	Empirical	Empirical
<i>T</i> (max)/(<i>T</i> Min)	0.1914/0.1190	0.2055/0.1773
Reflections collected	8809	15554
Independent refl..	4016 <i>R</i> (int)=0.0246	7666 <i>R</i> (int)=0.0362
<i>R</i> (<i>F</i>), % ^a (<i>I</i> ≥2σ(<i>I</i>))	3.05	1.88
<i>R</i> (<i>wF</i> ²), % ^a	3.38	1.90

a- quantity minimized = $R(wF^2) = \Sigma[W(F_o^2 - F_c^2)^2] / \Sigma[(wF_o^2)^2]^{1/2}$, $R = \Sigma\Delta / \Sigma(F_o)$, $\Delta = |F_o - F_c|$

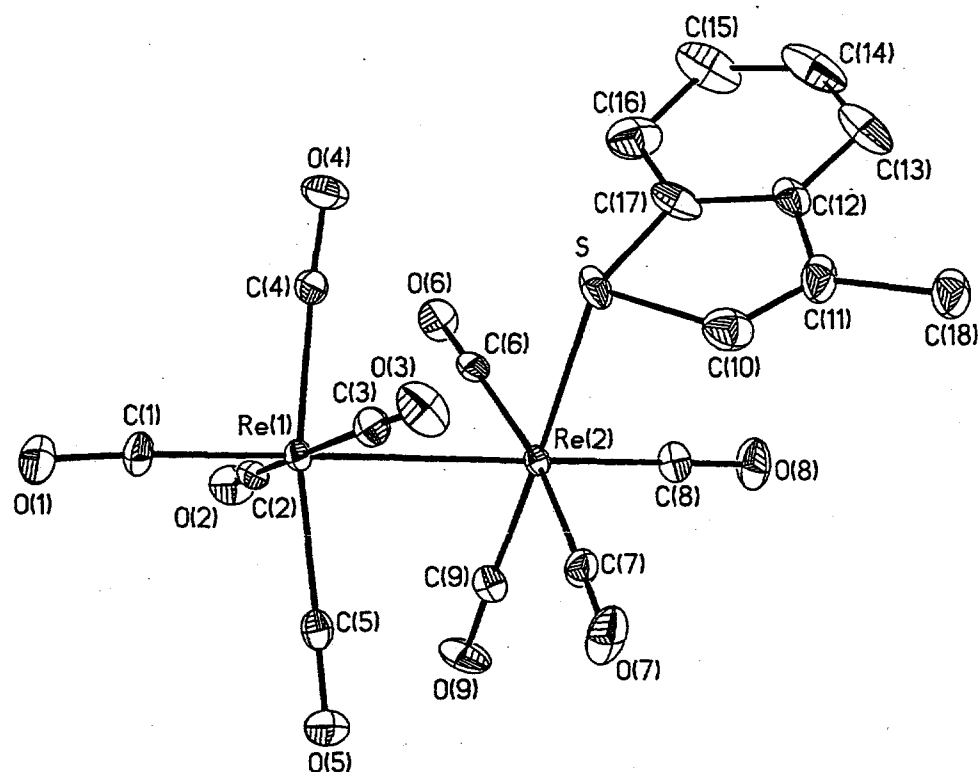


Figure 1. Molecular Structure of *eq*-Re₂(CO)₉(η¹(S)-3-MeBT) (**2c**). Selected Distances (Å) and Angles (°): Re(1)-Re(2), 3.0343(4); Re(2)-S, 2.5220(18); Re(2)-C(9), 1.927(7); S-C(10), 1.806(9); S-C(17), 1.685(9); C(10)-C(11), 1.268(12); Re(1)-Re(2)-S, 89.21(4); Re(2)-S-C(10), 106.3(3); Re(2)-S-C(17), 111.5(3); C(10)-S-C(17), 90.5(4); S-C(10)-C(11), 114.5(7); tilt angle = 116.9°.

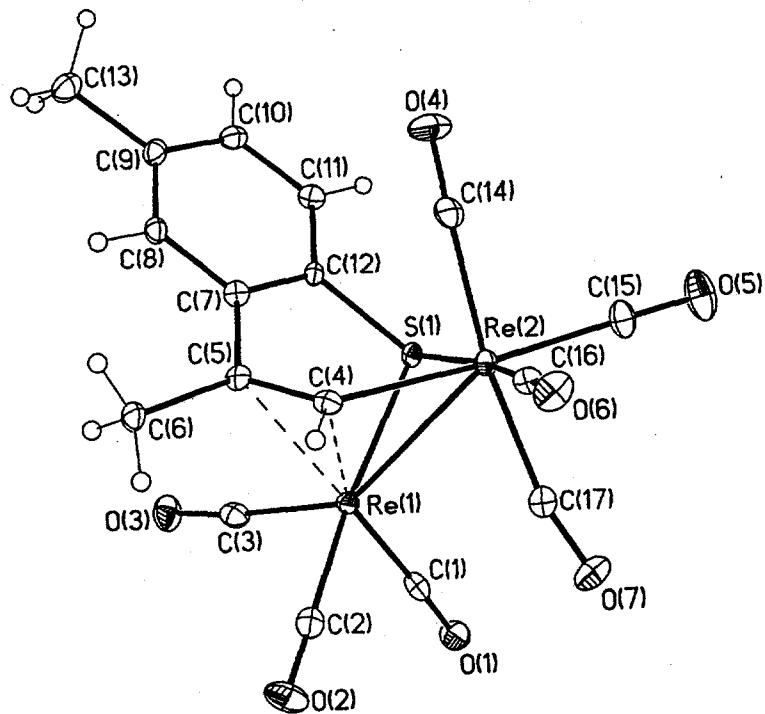


Figure 2. Molecular Structure of $\text{Re}_2(\text{CO})_7(\mu\text{-}3,5\text{-Me}_2\text{BT})$ (**1d**). Selected bond distances (Å) and angles (°): $\text{Re}(1)\text{-Re}(2)$, 2.9245(3); $\text{Re}(1)\text{-S}(1)$, 2.4320(13); $\text{Re}(2)\text{-S}(1)$, 2.4995(13); $\text{C}(4)\text{-C}(5)$, 1.403(7); $\text{S}(1)\text{-C}(12)$, 1.787(5); $\text{C}(5)\text{-C}(7)$, 1.503(7); $\text{Re}(1)\text{-S}(1)\text{-Re}(2)$, 72.73(3); $\text{C}(4)\text{-C}(5)\text{-C}(7)$, 122.9(5); $\text{Re}(1)\text{-S}(1)\text{-C}(12)$, 101.38(18); $\text{Re}(2)\text{-S}(1)\text{-C}(12)$, 102.31(17); $\text{Re}(2)\text{-C}(17)\text{-O}(7)$, 166.6(5); $\text{Re}(1)\text{-C}(4)\text{-Re}(2)$, 82.60(18).

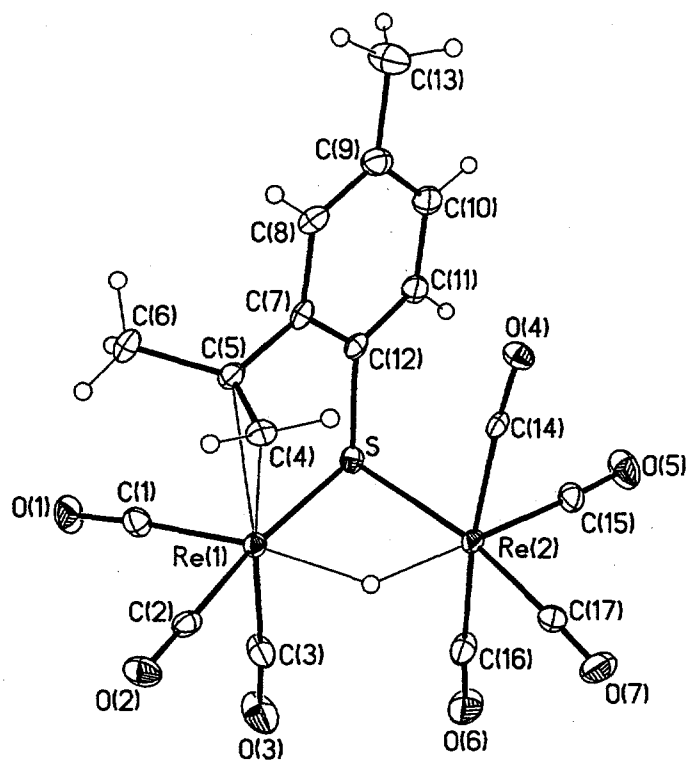


Figure 3. Molecular Structure of $\text{Re}_2(\text{CO})_7(\mu\text{-}3,5\text{-Me}_2\text{BT-H})(\mu\text{-H})$ (**3d**). Selected bond distances (Å) and angles (°): Re(1)-Re(2), 3.1083(3); Re(1)-S, 2.4444(14); Re(2)-S, 2.4883(14); Re(1)-C(4), 2.417(6); Re(1)-C(5), 2.532(6); S-C(12), 1.783(6); C(4)-C(5), 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).

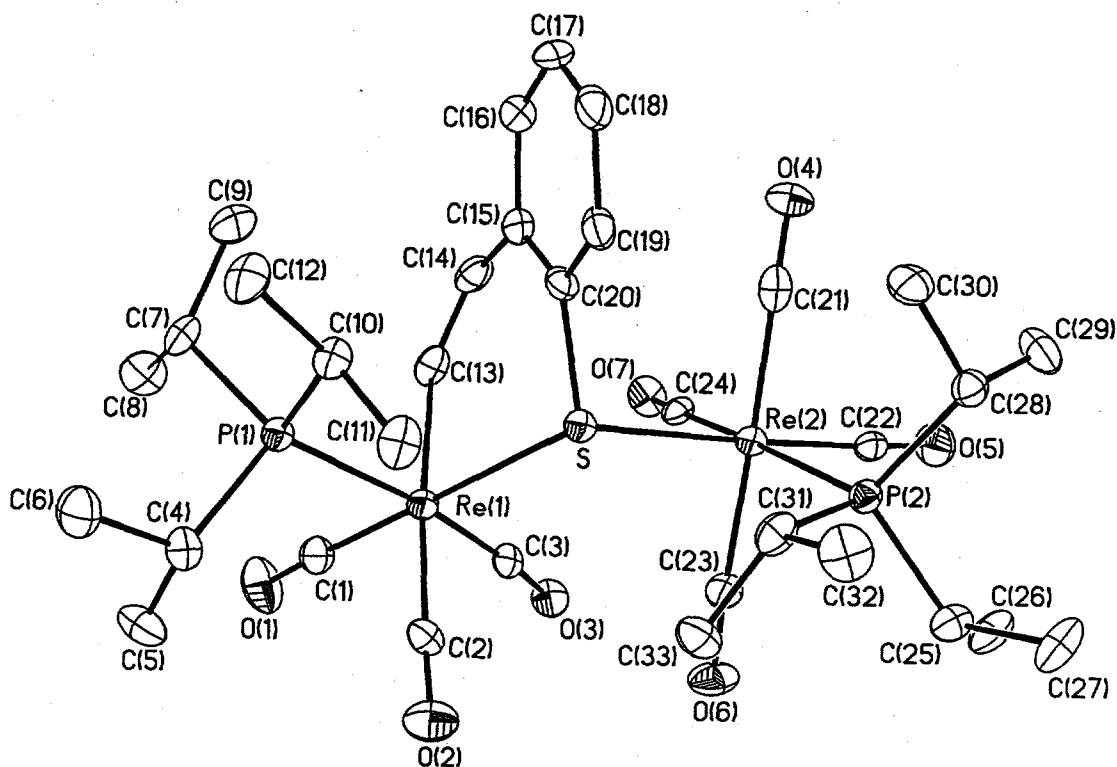


Figure 4. Molecular Structure of $\text{Re}_2(\text{CO})_7(\text{P}^i\text{Pr}_3)_2(\mu\text{-BT})$ (7). Selected bond distances (Å) and angles (°): $\text{Re}(1)\text{-S}$, 2.5296(15); $\text{Re}(2)\text{-S}$, 2.5499(15); $\text{Re}(1)\text{-C}(13)$, 2.173(6); $\text{C}(13)\text{-C}(14)$, 1.343(10); $\text{C}(14)\text{-C}(15)$, 1.492(9); $\text{Re}(1)\text{-P}(1)$, 2.5467(14), $\text{Re}(2)\text{-P}(2)$, 2.5316(14); $\text{Re}(1)\text{-S-Re}(2)$, 116.69(5); $\text{Re}(1)\text{-S-C}(20)$, 108.8(2); $\text{Re}(2)\text{-S-C}(20)$, 102.7(2); $\text{C}(13)\text{-Re}(1)\text{-S}$, 83.80(13), $\text{Re}(1)\text{-C}(13)\text{-C}(14)$, 133.5(5).

GENERAL CONCLUSIONS

Organometallic modeling of the commercial hydrodesulfurization process using $\text{Re}_2(\text{CO})_{10}$ 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 $\text{Re}_2(\text{CO})_{10}$ 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.

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