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Transition Metal complexes of Cr, Mo, W and Mn Containing
{eta}**1**(S)-2,5-dimethylthiophene, benzothiophene and
debenzothiophene ligands.

by

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Major Professor

J. Kraus
For the Major Program

For the Graduate College

Dedicated to my parents Toni and Michael.

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ABBREVIATIONS

HDS, hydrodesulfurization

R, any organic functional group

Me, methyl, -CH₃

Ph, phenyl, -C₆H₅

Cy, cyclohexyl, -C₆H₁₁

^tBu, *tert*-butyl, -C(CH₃)₃

T*, any thiophene

T, thiophene, C₄H₄S

Me₂T, 2,5-dimethylthiophene

BT, benzothiophene, C₈H₆S

2- or 3-MeBT, 2- or 3-methylbenzothiophene

DBT, dibenzothiophene, C₁₂H₈S

Cp, cyclopentadienyl, η^5 -C₅H₅

Cp', any functionalized cyclopentadienyl ligand

Cp*, pentamethylcyclopentadienyl, η^5 -C₅(CH₃)₅

PCy₃, tricyclohexylphosphine

py, pyridine, C₅H₅N

THF, tetrahydrofuran, C₄H₈O

Thi, thienyl, -C₄H₃S

Nu, nucleophile

GENERAL INTRODUCTION

Catalytic heterogeneous hydrodesulfurization (HDS) is the important commercial process for removing sulfur from organosulfur compounds, such as thiophenes, which are present in petroleum-based feedstocks. The catalysts involved in this industrial process consist primarily of Co- or Ni-promoted WS_2 or MoS_2 on alumina. However, despite their activity as HDS catalysts, not much is known about how W and Mo react with thiophenes on the sulfided-metal surface prior to desulfurization. A key step in the HDS process is the adsorption of thiophenes to a metal site. Therefore, in order to know how thiophenes bind to W and Mo metal centers, organometallic complexes of these metals containing coordinated thiophenes are desirable as molecular models for the HDS process.

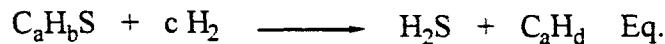
Thesis Organization

This thesis consists of two chapters: the first is a review of the known coordination modes and reactivities of thiophenes with metal centers in organometallic complexes containing group 6 and 7 transition metals.; the second contains the results of my research as it will be submitted for publication. In both chapters, the literature citations, schemes, tables and figures correspond only to the chapters in which they appear.

AN OVERVIEW OF THE MODES OF BINDING AND REACTIVITY OF THIOPHENES WITH GROUP 6 AND 7 TRANSITION METAL COMPLEXES

Introduction

Hydrodesulfurization (HDS) is the important industrial process whereby sulfur is removed from organosulfur compounds present in petroleum-based feedstocks by treatment with hydrogen gas (>200 atm) at high temperatures (300 - 400 °C) and in the presence of a catalyst to form H₂S and hydrocarbons (Eq 1).¹



This process is known as hydrotreating and the preferred catalysts currently used in this process are Co- or Ni-promoted MoS₂ or WS₂ on alumina.^{2,3} The process of removing sulfur from petroleum-based feedstocks is crucial for two main reasons: first, sulfur is known to poison precious metal-based reforming catalysts used for making high octane fuels which ultimately makes the processing of petroleum more costly and; secondly, to prevent the formation and release of sulfur oxides (SO)_x (x = 2, 3) into the atmosphere during the combustion process.¹

The types of organosulfur compounds found in petroleum distillates include thiols (RSH), sulfides (RSR), disulfides (RSSR) and thiophenes (T*). However, the thiophenes, including thiophene (T), benzo[b]thiophene (BT), dibenzo[b,d]thiophene (DBT) and their substituted derivatives (Figure 1), are the hardest to desulfurize industrially under current hydrotreating conditions. This is primarily due to aromatic stabilization of these ring systems.^{1d,e}

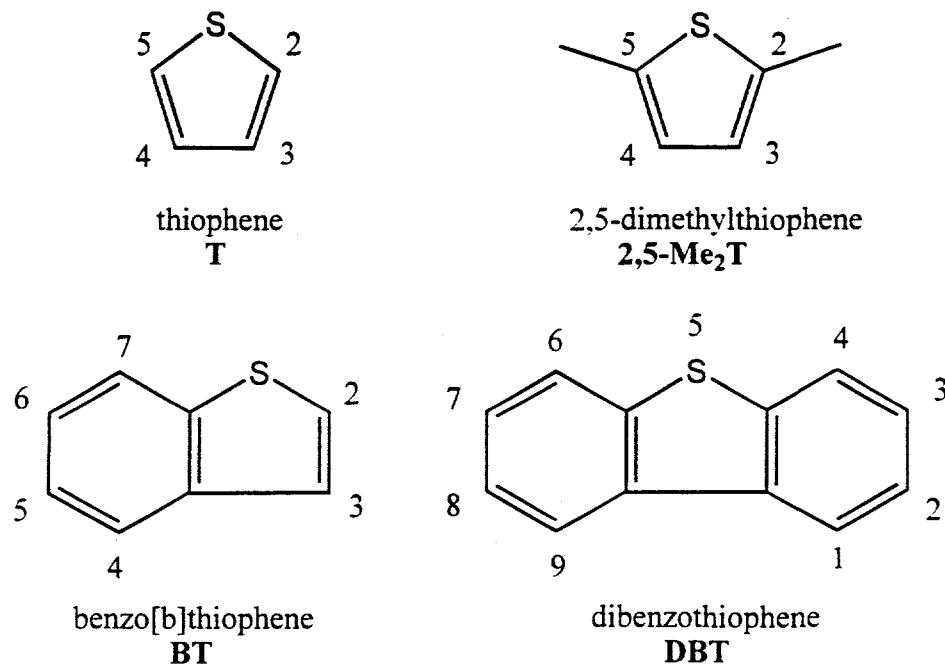


Figure 1 Numbering system for thiophenes.

A key step in the hydrodesulfurization of thiophenes is the adsorption of the thiophene to a metal site. Therefore, it is important to know how thiophenes can bind to metal centers on catalyst surfaces.^{2,3} One way of determining thiophene binding modes is by modelling this adsorption using organometallic complexes. Thiophenes, in principle, can bind to a metal center in several ways including: $\eta^1(S)$ through the sulfur, η^2 through a C-C double bond, η^4 through both C-C double bonds, and η^5 through the entire 6 π electron system (Figure 2). Binding in the benzothiophenes can occur $\eta^1(S)$ through the sulfur, η^2 through the C2-C3 double bond (for BT only), or η^6 through one (BT, DBT) or both benzene rings (DBT) (Figure 2).

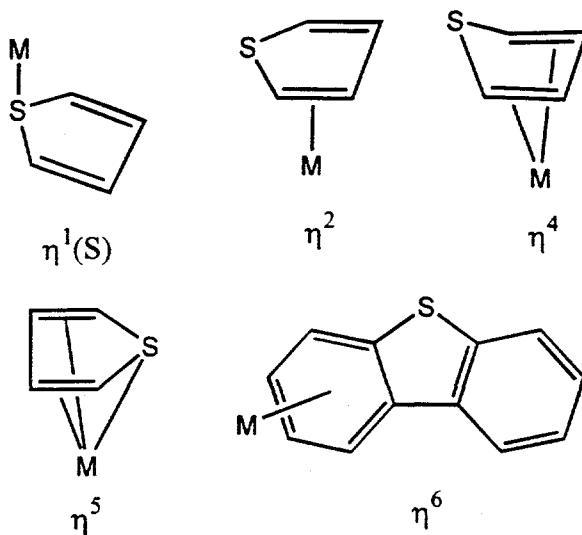


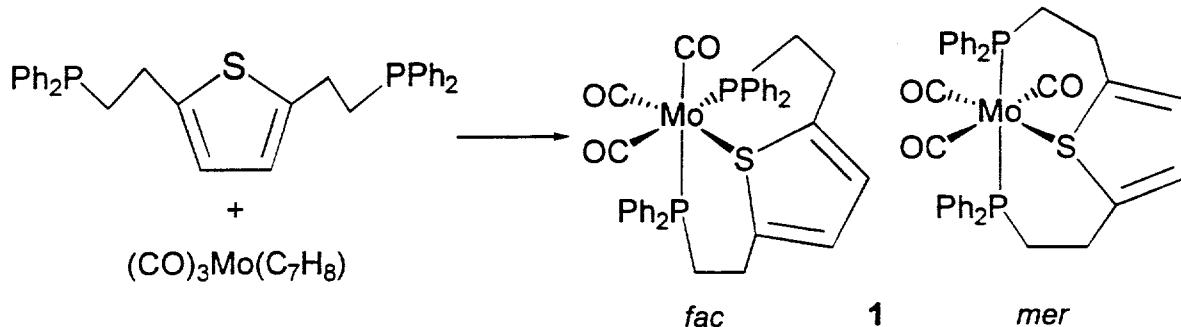
Figure 2 Thiophene binding modes.

Since the industrial scale HDS process uses primarily MoS_2 and WS_2 as the active catalysts, organometallic complexes modelling these catalysts with respect to thiophene binding modes, C-S and C-H bond activation and desulfurization is of great importance.¹

Group 6 Transition Metal-Thiophene Complexes

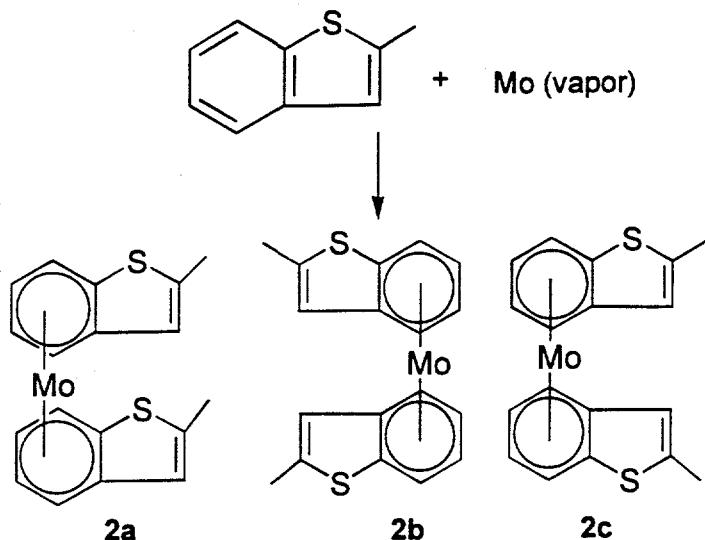
Despite the fact that Mo and W in their sulfided forms (MoS_2 and WS_2) play a major role in the commercial HDS process, very few organometallic complexes containing coordinated or activated thiophenes have been reported for these metals. The Mo complexes, $(\text{CO})_5\text{Mo}(\eta^1\text{S}-\text{T})$ and $(\text{CO})_3\text{Mo}(\eta^5\text{-T})$ have been proposed to be theoretically possible based on MO calculations;⁴ however, neither complex has been prepared. Two types of molybdenum complexes containing coordinated thiophenes that have been reported are the *mer* and *fac*- $\text{Mo}(\text{CO})_3[2,5-(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{C}_4\text{H}_2\text{S}]^5$ **1** and the sandwich complex $\text{Mo}(\eta^6\text{-2-$

MeBT)₂⁶ **2**. In the former, both the *fac* and *mer* isomers were prepared from (CO)₃Mo(C₇H₈) and 2,5-(PPh₂CH₂CH₂)₂C₄H₂S in hexanes or CH₂Cl₂ at 25 °C (Scheme 1).



Scheme 1

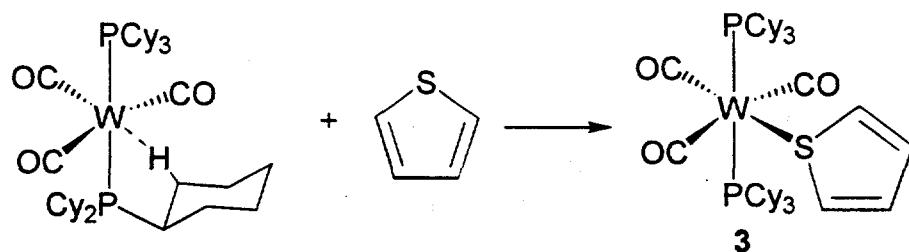
In both isomers, the thiophene was observed to act as a tridentate ligand by binding to the Mo center through both phosphines and the sulfur atom. A molecular structure was obtained for the *fac* isomer confirming its ligand configuration and both isomers were fully characterized spectroscopically (IR, ¹H, ³¹P NMR). In the presence of carbon monoxide, the thiophene of *fac*-**1** was not observed to be labile when reacted at atmospheric pressure. This is presumably due to the forced S-coordination facilitated by the chelating phosphines. The sandwich complex **2** is prepared by co-condensation of Mo atoms with 2-MeBT at 77 K (Scheme 2).



Scheme 2

A mixture of diasteriomers with both mesomeric (eclipsed) **2a** and racemic (staggered) **2b,c** forms was observed in the ratio of 1:2 and confirmed spectroscopically (^1H and ^{13}C NMR). These complexes in the solid state decompose within minutes in air to form intractable products. Both **1** and **2** represent the first reported $\eta^1(\text{S})$ and η^6 thiophene complexes of Mo.

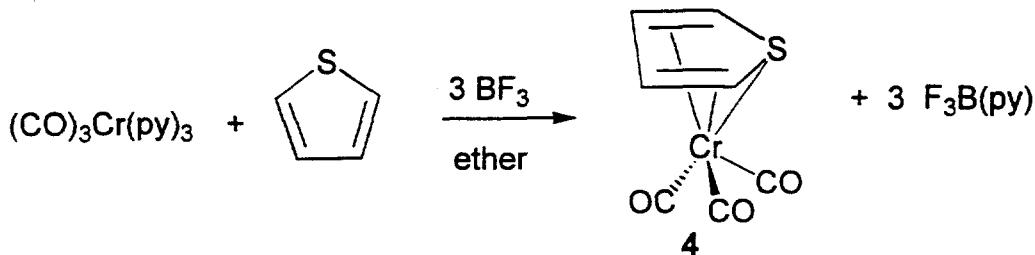
There are relatively few examples of W complexes containing coordinated thiophene ligands. The complex $\text{W}(\text{CO})_3(\text{PCy}_3)_2(\eta^1(\text{S})\text{-T})^7$ **3** is a stable $\eta^1(\text{S})\text{-T}^*$ complex which is prepared from a toluene solution of $(\text{CO})_3\text{W}(\text{PCy}_3)_2$ and excess thiophene (Scheme 3).



Scheme 3

The weak agostic interaction between the W and a C-H of a cyclohexyl group in $(CO)_3W(PCy_3)_2$ is reversible in the presence of excess thiophene or donor ligand. This allows the thiophene ligand to bind through the sulfur to the W metal center. The 1H NMR spectrum indicated that **3** exhibits a high degree of dissociation of the T ligand in solution. This implies that the thiophene is also a weakly coordinated ligand in this particular W complex. IR spectroscopic evidence for the complex $(CO)_5W(\eta^1(S)-T)$ has been reported based on 3 observed bands in the CO stretching region, but it was not isolated from solution and no other supporting evidence was given.⁸ The assignment of an $\eta^1(S)$ coordination to $(CO)_5W(T)$ was made based on IR assignments of similar W complexes with heterocyclic ligands. The bimetallic complex $Cp^*(CO)_2Re(2,3-\eta^2:\eta^1(S)-\mu_2-BT)W(CO)_5$ ⁹ has been prepared and contains a $(CO)_5W$ - moiety bound to the sulfur of BT. This is possible since the $Cp^*(CO)_2Re$ moiety acts as an electron donating group towards the C2-C3 double bond of the BT ligand, thus making the BT sulfur more nucleophilic towards the $W(CO)_5$ species. No η^5 or $\eta^6\pi$ complexes of thiophenes or benzothiophenes are known for tungsten.

Unlike Mo or W, π -complexes of Cr and thiophenes of the type $(\eta^5-T^*)Cr(CO)_3$ (**4**) ($T^* \neq BT$ or DBT) are much more common while $\eta^1(S)$ binding modes are not. The more commonly reported synthetic route to **4** involves refluxing $Cr(CO)_6$ with a large excess of T^* ligand in a high boiling solvent such as butyl ether¹⁰, or in neat ligand.¹¹ A route which gives reportedly higher yields (>80%) involves the reaction of $(CO)_3Cr(py)_3$ with excess T^* in the presence of BF_3 etherate (Scheme 4).¹²

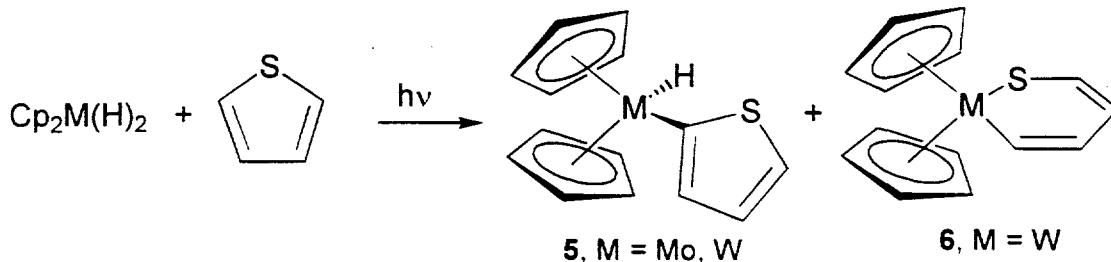


Scheme 4

In most cases, these complexes are moderately stable in solution and in air but the yields tend to be quite low (< 40%).¹⁰⁻¹¹ Complexes of type **4** have a piano-stool configuration with a planar thiophene ligand as evidenced by X-ray crystallography and spectroscopy.^{11,13}

The preparation of $(\eta^6\text{-BT})Cr(CO)_3$ ¹⁴ and $(\eta^6\text{-DBT})Cr(CO)_3$ ^{14,15} complexes have also been reported using similar methods as those reported for the preparation of the $\eta^5\text{-T}^*$ complexes. The reaction of $(CO)_3Cr(\eta^6\text{-BT})$ ¹⁴ (**7**) with $Cp'(CO)_2Re(\text{thf})$ to give the bimetallic complex $Cp'(CO)_2Re(\eta^2\text{:}\eta^6\text{-}\mu_2\text{-BT})Cr(CO)_3$ has been demonstrated.⁹ Coordination of the $Cr(CO)_3$ moiety presumably enhances the π -acidity of the C2-C3 olefin double bond of BT. The electron rich $Cp'(CO)_2Re$ - moiety therefore prefers η^2 coordination over S-coordination of the $(CO)_3Cr(BT)$ complex. Other reactivity of these $(\eta^6\text{-T}^*)Cr(CO)_3$ complexes has been reported. The only reported S-bound T^* complex for Cr is $(\eta^1(S)\text{-}2\text{-}R_2BT)Cr(CO)_5$ ¹⁶ which was prepared by reacting a 2-diorganoborothiophene ($R = \text{Me}$ or Et) with $(CO)_5Cr(\text{thf})$ at room temperature. In this specific example the thiophene displaces the THF ligand and binds to the Cr through the sulfur. The coordination of sulfur to Cr is proposed to be stabilized by a weak B-CO π -interaction.

Organometallic complexes resulting from C-H or C-S bond activation of T* are not very common for any of the group 6 metals. While Mo and W exhibit a few examples, none are known for Cr. Probably the best example of both C-H and C-S bond activation in thiophenes with both Mo and W was reported by Jones, et al.¹⁷ They found that irradiation of a solution of Cp₂MH₂ (M = Mo or W) with excess T gave Cp₂M(C₄H₃S)H (**5**) with C-H bond activation in the 2-position of the thiophene. For W, the metallacycle **6** (Scheme 5) results from cleavage of the C-S bond followed by metal insertion which occurs competitively with C-H bond cleavage. No C-S bond activation products were observed when M = Mo.

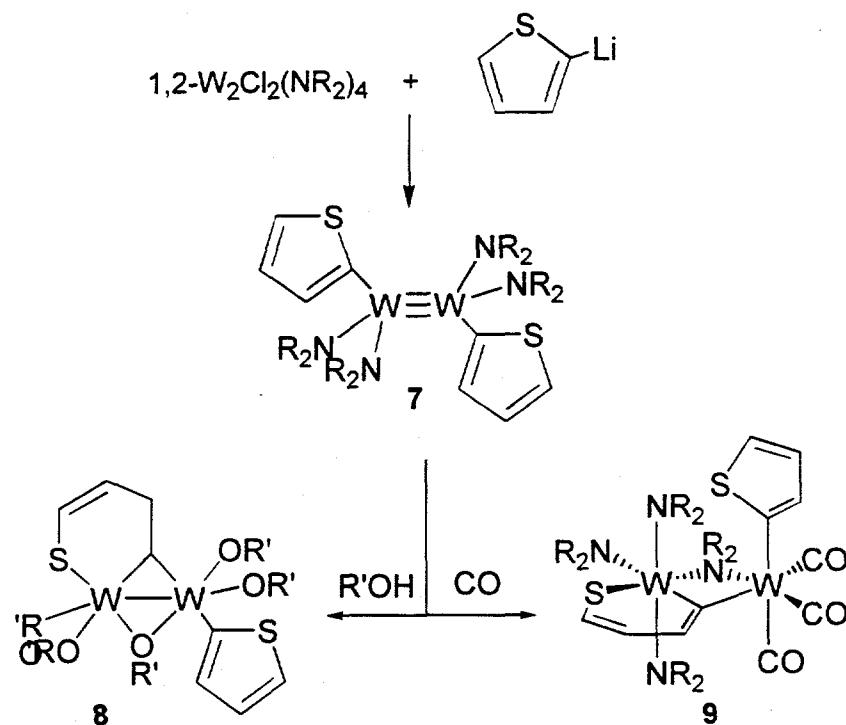


Scheme 5

The ratio of the C-H and C-S bond cleavage products of the W complexes (**5:6**) is a function of the total irradiation time, i.e. a longer irradiation time gives a ratio for **5:6** of approximately 1:1 whereas shorter irradiation times (approximately 2 h) give a 1:4 ratio of products.

Chisholm, et al has recently reported W≡W complexes which react with 2-thienyl ligands in toluene solution to give a variety of complexes which eventually lead to C-S cleavage products.^{18,19} For example, the complex 1,2-W₂Cl₂(NMe₂)₄ reacts with 2-thienyllithium (2 equiv.) to give the air-sensitive and thermodynamically stable dithienyl

product $1,2\text{-W}_2(\sigma\text{-2-T})_2(\text{NR}_2)_4$ (**7**) ($\text{R} = \text{Me}$).¹⁹ This product reacts with excess $^t\text{BuOH}$ or CO to give the ring-opened products **8** and **9**, respectively (Scheme 6). Complexes **8** and **9** are thermally robust, but very air-sensitive.



Scheme 6

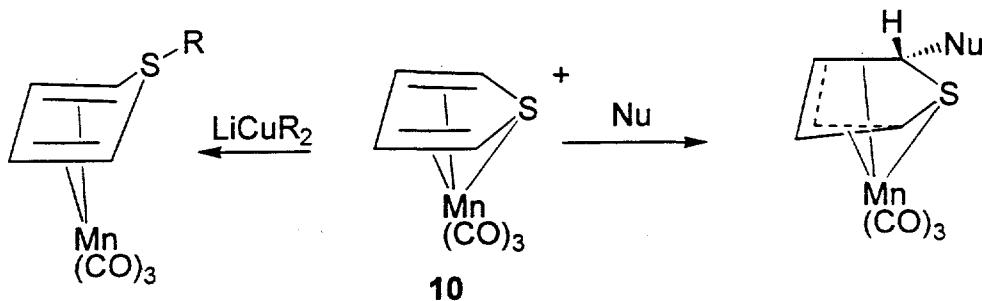
Group 7 Transition Metal-Thiophene Complexes

Several group 7 (Mn and Re) metal complexes have been reported with T^* ligands.

Manganese tends to form η^5 and η^6 complexes with thiophenes and benzothiophenes, respectively, while only $\eta^2\text{-BT}$ and $\eta^1(\text{S})\text{-T}^*$ complexes are known for Re.

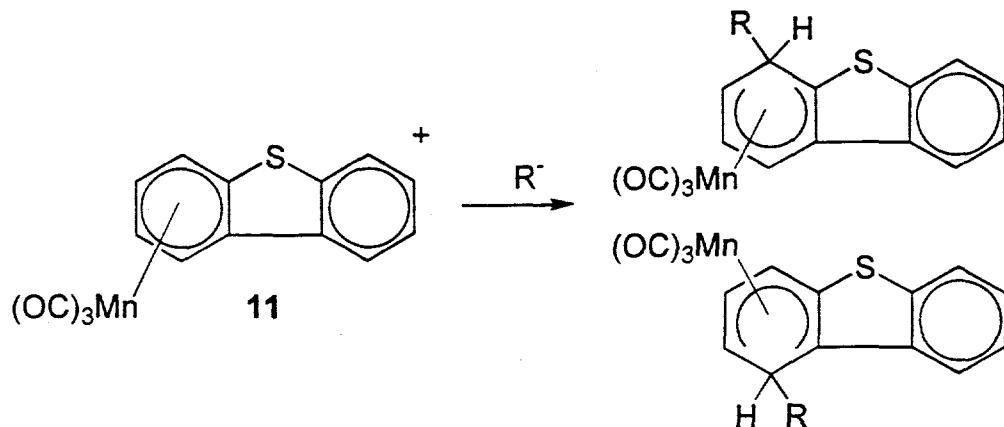
The Mn- T^* complexes of type $(\eta^5\text{-T}^*)\text{Mn}(\text{CO})_3^+$ **10** are well known.²⁰⁻²² They are best prepared by halide abstraction from $(\text{CO})_5\text{MnX}$ ($\text{X} = \text{halide or OSO}_2\text{CF}_3$) with Ag^+ salts

in the presence of excess T^* ligand in refluxing CH_2Cl_2 .²² They readily undergo nucleophilic attack at the 2-position of the T^* ligand upon reaction with nucleophiles (Nu) such as hydrides (BH_4^- or $HFe(CO)_4^-$), PR_3 (R = alkyl) or CN^- to give stable allyl sulfide products (Scheme 7).²⁰



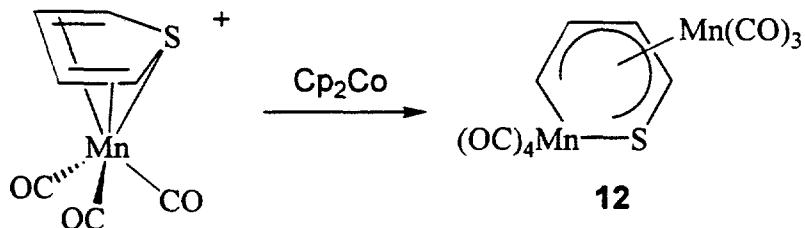
Scheme 7

When complex **10** ($T^* = T$ or substituted T) is reacted with $LiCuR_2$ (R = alkyl) in THF, the η^4 -Thi * complex (η^4 - T^* -R) $Mn(CO)_3$ results in 33-55% yield. Here, the sulfur bends out of the thiophene plane as a result of alkylation as observed in both the crystal structure and spectroscopically (NMR, IR).²² Nucleophilic attack occurs in the 1 and/or 4 positions of DBT when (η^6 -DBT) $Mn(CO)_3^+$ (**11**)^{23,24} is reacted with hydrides or alkylating agents to give η^5 -cyclohexatrienyl products of DBT (Scheme 8).²³ These complexes were only characterized by spectroscopic methods since separation of the isomers was not possible.



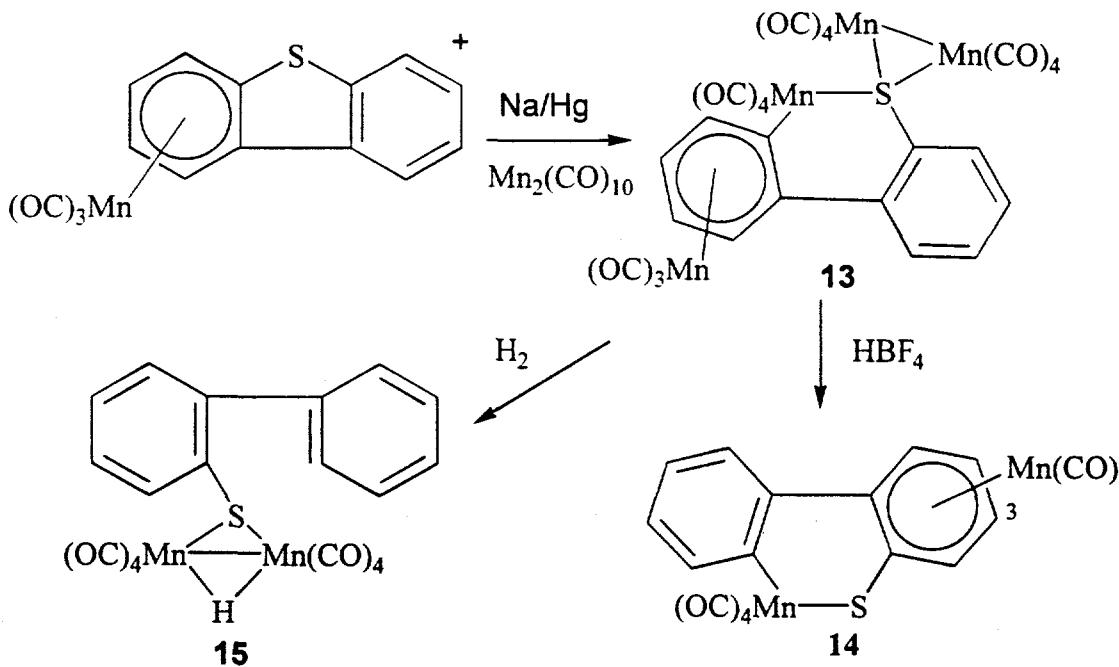
Scheme 8

Manganese insertion into the C-S bonds of thiophenes and benzothiophenes has become quite common recently.²⁵⁻²⁸ This metal insertion into the aromatic thiophene ring(s) occurs during the reduction of cationic $(\eta^5\text{-T}^*)\text{Mn}(\text{CO})_3^+$ or $(\eta^6\text{-T}^*)\text{Mn}(\text{CO})_3^+$ complexes with Cp_2Co (cobaltocene) or Na/Hg to give Mn metallathiacyclic complexes such as **12** (Scheme 9) and **14** (Scheme 10).^{25,28} The metallathiacycle **12** has a $\text{Mn}(\text{CO})_4$ moiety inserted into a C-S bond and a $\text{Mn}(\text{CO})_3$ moiety bonded through the four thiophene carbons and the sulfur atom in a π fashion. The single crystal X-ray structure has been reported for **12**.²⁵ Complex **12** is resistant to electrophilic attack at the sulfur when reacted with methyl triflate or HBF_4 . No desulfurization products were reported.

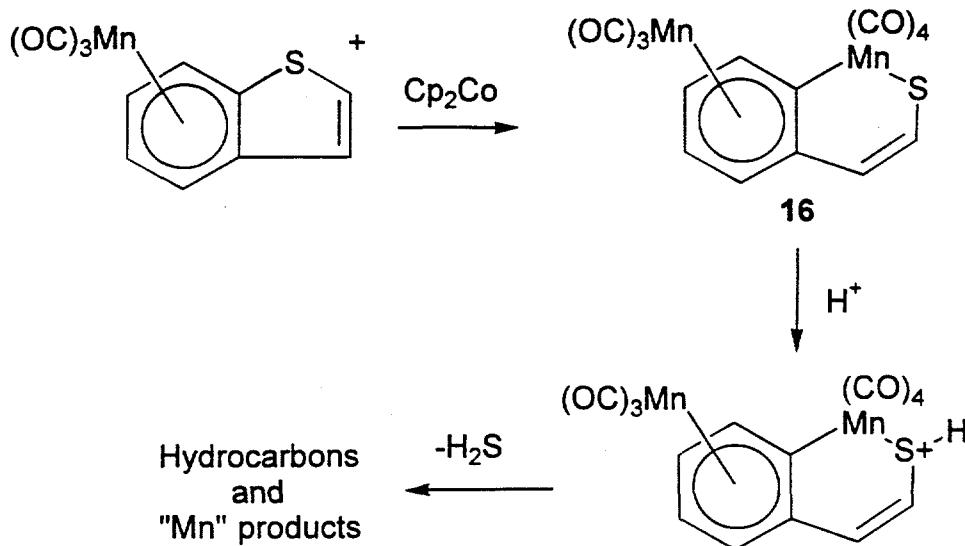


Scheme 9

Reduction of $(\eta^6\text{-DBT})\text{Mn}(\text{CO})_3^+$ in the presence of $\text{Mn}_2(\text{CO})_{10}$ affords the structurally interesting complex **13** in 20% yield. In this complex, the sulfur is coordinated to three Mn metal centers, one of which has inserted into a C-S bond of the DBT. The other two are bridged by the sulfur. When **13** is reacted with a solution of HBF_4 in CH_2Cl_2 , it can be converted into the thermodynamically unstable, bimetallic Mn complex **14** (17% yield). As illustrated in Scheme 6, treatment of complex **13** with H_2 (500 psi, 97 °C, 3 h) facilitates conversion to the bridging biphenyl thiolate complex **15** (87% yield).²⁸ The complex $(\eta^6\text{-DBT})\text{Mn}(\text{CO})_3^+$ also undergoes reduction with Cp_2Co to give the thiametallacycle **16**, which is (Scheme 11) structurally similar to the analogous DBT complex **14**. However, **16** readily undergoes protonation and desulfurization to afford H_2S , hydrocarbons and intractable products.²⁶ This is in contrast to **14** in which no protonated intermediates were observed.

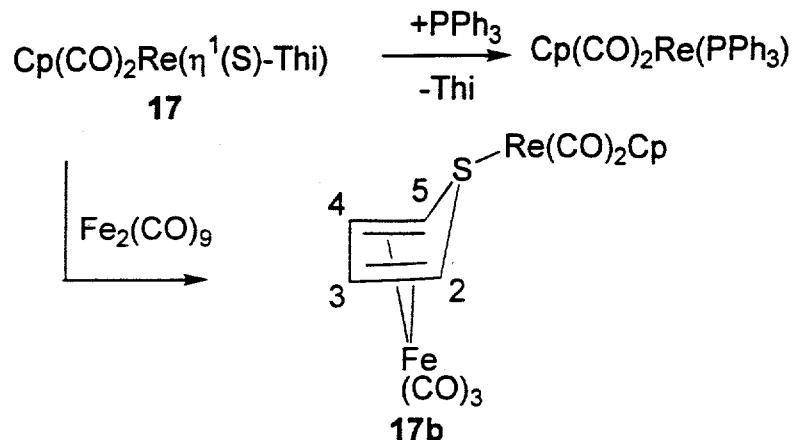


Scheme 10



Scheme 11

Surprisingly few Re complexes containing coordinated thiophene ligands have been reported in the literature. The most commonly reported Re-T^{*} complexes are those which contain an S-bound T^{*} ligand as in Cp'(CO)₂Re(η¹(S)-T^{*})^{9,29,30} **17** and [Cp(NO)(PPh₃)Re(η¹(S)-Thi^{*})]⁺³¹ **18**. The T^{*} complexes of **17** are prepared by adding excess T^{*} ligand to a stirred THF solution of Cp'(CO)₂Re(thf) which undergoes displacement of the THF ligand followed by T^{*} substitution. The Cp'(CO)₂Re(η¹(S)-T^{*}) complexes are known to undergo T^{*} ligand displacement in the presence of PPh₃ to give the more kinetically stable phosphine complex Cp'(CO)₂Re(PPh₃) (Scheme 12).²⁹ It was concluded from these studies that adding methyl groups to the thiophene ring decreased the rate of thiophene dissociation from the Re complex. When T^{*} = T, complex **17** also reacts with Fe₂(CO)₉ in THF to give the bimetallic complex Cp'(CO)₂Re(μ₂-η⁴-(S)-T)Fe(CO)₃ **17b** which is interesting since the S

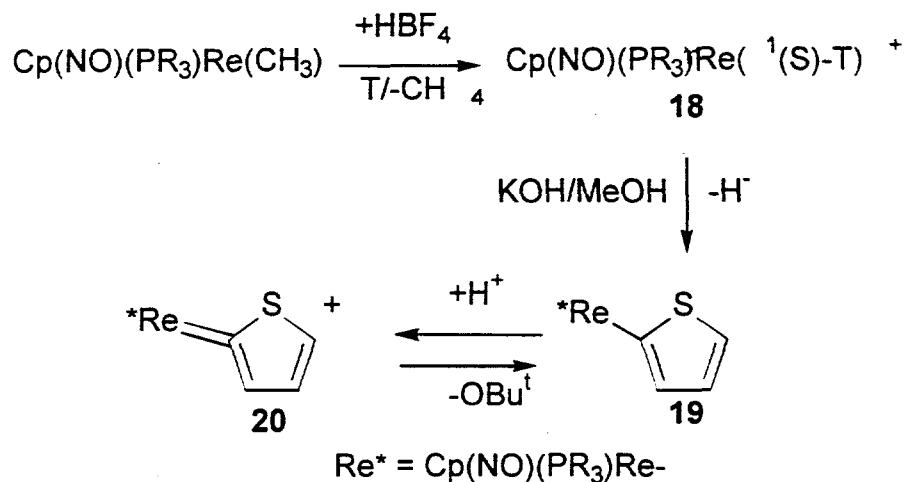


Scheme 12

bends out of the thiophene plane. The thiophene ring is folded with an angle of 143° between the C2-C3-C4-C5 and C2-S-C5 planes (Scheme 12).³⁰ One particularly interesting example of an $\eta^2\text{-T}^*$ complex is $\text{Cp}'(\text{CO})_2\text{Re}(\eta^2\text{-BT})$,⁹ which occurs as one of two isomers in equilibrium with the S-bound isomer $\text{Cp}'(\text{CO})_2\text{Re}(\eta^1\text{S-BT})$. Although the exact reason for the isomers is not known, it was proposed that the Cp' ligand influences the electronic effects of Re with respect to how it binds the BT ligand. For example, when $\text{Cp}' = \text{Cp}^*$, the equilibrium strongly favors $\eta^2\text{-BT}$ coordination to the Re metal center due to enhanced electron density on the Re donated from the Cp^* ligand. When $\text{Cp}' = \text{Cp}$, the $\eta^1\text{S-BT}$ isomer is favored in the equilibrium.

Complex **18** also has a S-bound thiophene and is prepared from the reaction of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{CH}_3)$ with HBF_4 etherate in CH_2Cl_2 and in the presence of T^* .³¹ It is proposed that $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{ClCH}_2\text{Cl})^+$ is generated as an intermediate and dissociates the weakly coordinated CH_2Cl_2 ligand in the presence of free T^* . Complex **18** can be readily converted to a 2-thienyl complex $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(2\text{-Thienyl})^+$ **19** by reaction with base.

Further conversion to the carbene complex **20** occurs when **19** is exposed to a strong acid (Scheme 13) such as triflic acid. Complex **20** could not be isolated due to its instability in solution but was characterized spectroscopically (^{13}C , ^1H NMR).³¹ No examples of η^4 -, η^5 - or $\eta^6\text{-T}^*$ complexes with Re have been reported which is surprising when considering the vast number of Mn-T* complexes found in the literature as described earlier.



Scheme 13

In conclusion, the complexes mentioned in this chapter are products of homogeneous reactions with organometallic complexes. These complexes, may or may not be representative of the actual mechanisms associated with the commercial catalytic heterogeneous HDS process with respect to thiophene binding modes, bond activation and desulfurization. However, each reported complex can lead to a better understanding of how thiophenes can react at metal centers. Hopefully the work in this field will lead to the design of better catalysts for the future as well as a better understanding of how the heterogenous systems work.

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**TRANSITION METAL COMPLEXES OF Cr, Mo, W AND Mn
CONTAINING $\eta^1(S)$ -2,5-DIMETHYLTIOPHENE,
BENZOTIOPHENE, AND DIBENZOTIOPHENE LIGANDS**

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Abstract

The UV photolysis of hexanes solutions containing the complexes $M(CO)_6$ ($M = Cr, Mo, W$) or $CpMn(CO)_3$ ($Cp = \eta^5-C_5H_5$) and excess thiophene (T^*) ($T^* = 2,5$ -dimethylthiophene (2,5-Me₂T), benzothiophene (BT), and dibenzothiophene (DBT)) produces the $\eta^1(S)$ - T^* complexes $(CO)_5M(\eta^1(S)-T^*)$ **1-8** or $Cp(CO)_2Mn(\eta^1(S)-T^*)$ **9-11**, respectively. However, when $T^* = DBT$, and $M = Mo$, a mixture of two products result which includes the $\eta^1(S)$ -DBT complex $(CO)_5Mo(\eta^1(S)-DBT)$ **4a** and the unexpected π -complex $(CO)_3Mo(\eta^6-DBT)$ **4b** as detected by ¹H NMR. The lability of the $\eta^1(S)$ - T^* ligands is illustrated by the rapid displacement of DBT in the complex $(CO)_5W(\eta^1(S)-DBT)$ (**1**) by THF, and also in the complexes $(CO)_5Cr(\eta^1(S)-DBT)$ (**5**) and $CpMn(CO)_2(\eta^1(S)-DBT)$ (**9**) by CO (1 atm) at room temperature. Complexes **1-11** have been characterized spectroscopically (¹H NMR, IR) and when possible isolated as analytically pure solids (elemental analysis, EIMS). Single crystal, X-ray structural determinations are reported for $(CO)_5W(\eta^1(S)-DBT)$ and $Cp(CO)_2Mn(\eta^1(S)-DBT)$.

Introduction

Hydrodesulfurization (HDS), the process whereby sulfur is removed from organosulfur compounds present in petroleum-based feedstocks, is an important commercial process for many environmental and industrial reasons.^{1,2} Petroleum feedstocks vary in their sulfur content (0.2 - 4%)³⁻⁵ and contain many different types of organosulfur compounds. Among these, the most difficult to desulfurize are the thiophenes (T*) including thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and their derivatives (Figure 1).

A necessary first step in commercial HDS is the adsorption of thiophenes to a sulfided metal catalyst surface such as Co- or Ni-promoted MoS₂ or WS₂ on alumina.^{6,7} Thus, organometallic modelling of thiophene adsorption to metal centers has become a topic of interest in recent years. In fact, the literature is rich with transition metal-thiophene complexes containing T* ligands bound in many ways (Figure 2).⁸⁻¹³ However, complexes of group 6 and 7 metals are still relatively rare. Despite the central role of Mo and W in the commercial HDS process, very few organometallic examples of these metals containing coordinated T* ligands have been reported. The complexes (CO)₅Mo(η^1 (S)-T) and (CO)₃Mo(η^5 -T) have been proposed to be theoretically possible by F. Ruette, et. al.¹⁴ based on MO calculations, but neither complex has been prepared. In fact, only two different Mo complexes containing thiophenes have been reported. The first is the stable (CO)₃Mo[2,5-(Ph₂PCH₂CH₂)₂C₄H₂S]¹⁵ complex which exists as a pair of isomers (*mer* and *fac*) in which the thiophene is part of a chelating ligand that binds to the Mo center, in both isomers, through the phosphine groups and the sulfur. The second complex, Mo(η^6 -2-MeBT)₂¹⁶, is a

weakly stable sandwich complex consisting of a Mo coordinated to two 2-methylbenzothiophene (2-MeBT) ligands through the arene rings in an η^6 fashion. Tungsten-thiophene complexes reported in the literature include $\text{W}(\text{PCy}_3)_2(\text{CO})_3(\eta^1(\text{S})\text{-T})^{17}$ and $(\text{CO})_5\text{W}(\eta^1(\text{S})\text{-T})^{18}$. Both presumably have $\eta^1(\text{S})$ - coordinated thiophene ligands which are largely dissociated in solution. The former was isolated and fully characterized spectroscopically, while the latter was only evidenced by IR spectroscopy. In both examples, the thiophenes were observed to dissociate in solution. In the bimetallic complex $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^2:\eta^1(\text{S})\text{-}\mu_2\text{-BT})\text{W}(\text{CO})_5^{19}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), the $\text{W}(\text{CO})_5$ - moiety is coordinated to the BT ligand through the sulfur. The reason for this sulfur binding to the $\text{W}(\text{CO})_5$ fragment is due to the enhanced nucleophilicity of the sulfur. The sulfur becomes more nucleophilic due to the presence of the electron rich $\text{Cp}^*\text{Re}(\text{CO})_2$ fragment which is coordinated η^2 to the BT ligand. The η^5 - and η^6 - π -thiophene complexes of group 6 metals have been mostly limited to those of chromium including: $(\eta^5\text{-T})\text{Cr}(\text{CO})_3^{20}$, $(\eta^6\text{-BT})\text{Cr}(\text{CO})_3^{21}$, and $(\eta^6\text{-DBT})\text{Cr}(\text{CO})_3^{21}$.

Group 7 metal complexes containing coordinated thiophene ligands include $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-T}^*)^{19,22}$, $[(\eta^5\text{-T})\text{Mn}(\text{CO})_3]^+^{23}$, $[(\eta^6\text{-DBT})\text{Mn}(\text{CO})_3]^+^{24}$ and $[(\eta^6\text{-BT})\text{Mn}(\text{CO})_3]^+^{25}$, as well as several C,S-cleaved products.^{26,27}

We now report the preparation of group 6 and 7 metal complexes of 2,5-Me₂T, BT and DBT obtained by UV photolysis of hexanes solutions containing $\text{M}(\text{CO})_6$ or $\text{CpMn}(\text{CO})_3$ and excess T* ligands. The complexes are characterized by their IR, NMR and

mass spectra, as well as X-ray determined molecular structures in two cases. Stabilities and labilities of the complexes are also described.

Experimental Section

General Procedure. All reactions were performed under a nitrogen atmosphere in reagent grade solvents, using standard Schlenk techniques. Hexanes, methylene chloride and 1,2-DCE were dried and distilled over CaH_2 prior to use. Deutero-methylene chloride (Cambridge) was stored over 4 \AA molecular sieves. The complexes $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{CpMn}(\text{CO})_3$ were purchased from Pressure Chemical Co. The complex $\text{CpMn}(\text{CO})_3$ was chromatographed on a neutral alumina column (2.5 x 32 cm) packed in hexanes and using hexanes as the eluent. The volume of the fraction containing the yellow $\text{CpMn}(\text{CO})_3$ was reduced and cooled (-20 °C) to give the crystalline product. The complex $\text{W}(\text{CO})_6$ was purchased from Strem Chemicals, Inc. Dibenzothiophene, benzothiophene, and 2,5-dimethylthiophene were purchased from Aldrich Chemical Co. The ligand 3-methylbenzothiophene (3-MeBT) was purchased from Maybridge Chemical Co. Unless otherwise mentioned all complexes and ligands were used without further purification.

The ^1H NMR spectra for all complexes were recorded on a Varian VXR-300 spectrometer using CD_2Cl_2 as the solvent, internal lock and internal reference (δ 5.32 ppm for ^1H). Solution infrared spectra were recorded on a Nicolet-560 spectrometer using NaCl cells with 0.1 mm spacers and hexanes, CH_2Cl_2 , or 1,2-DCE as the solvent. Electron-ionization mass spectra (EIMS) were recorded on a Finnigan TSQ700 instrument. Elemental analyses were performed on a Perkin Elmer 2400 series II CHNS/O analyzer. All photochemical

reactions were carried out in a 60 mL quartz Schlenk photolysis tube (24/40 inner joint). A Hanovia 450 watt mercury UV lamp was used as the light source. The temperature of each reaction was controlled using an Isotemp 1013P refrigerated circulating bath (Fisher Scientific) with the circulation hoses connected to a 230 mm cold finger condenser with a 24/40 outer joint. The cold finger was inserted into the quartz Schlenk tube to cool the solutions to the desired temperature.

Synthesis of $(CO)_5W(\eta^1S)$ -DBT (1). A quartz Schlenk photolysis tube, equipped with a teflon coated magnetic stir bar, was charged with $W(CO)_6$ (262 mg, 0.745 mmol) and DBT (276 mg, 1.50 mmol). Hexanes (40 mL) was added and the reaction tube was then fitted with a cold finger (10 °C) and an oil bubbler. The actual solution temperature varied by ± 5 °C. A slow, continuous flow of nitrogen was maintained through the tube while the solution was irradiated with stirring for 8 h. During this time the solution turned light yellow and a yellow solid precipitated. The solution was allowed to settle and then filtered via cannula. The remaining yellow solid residue was washed with cold hexanes (2 x 5 mL) to remove excess DBT and $W(CO)_6$ and then dried *in vacuo*. The remaining yellow solid was then extracted with methylene chloride and layered with hexanes (1:6). Slow cooling overnight (-20 °C) yielded yellow, air-stable, X-ray quality crystals of **1** (110 mg, 0.217 mmol, 29% based on $W(CO)_6$). Mp 114-116 °C (dec). 1H NMR (CD_2Cl_2): δ 8.17 (m, 2 H), 7.91 (m, 2 H), 7.62 (m, 4 H). IR (hexanes): (ν_{CO}) 2078 (w), 1951 (s), 1946 (sh), 1935 (m) cm^{-1} . EIMS (70eV): *m/e* 508 (M^+ for ^{184}W), 452 ($M^+ - 2CO$), 424 ($M^+ - CO$), 368 ($M^+ -$

2CO), 184 (M⁺ - W(CO)₅) Anal Calcd for C₁₇H₈O₅SW: C, 40.18; H, 1.58; Found: C, 40.12, H, 1.71.

Preparation of (CO)₅W(η^1 (S)-BT) (2): Complex **2** was prepared in a similar fashion as **1** by irradiation of a hexanes (40 mL) solution of W(CO)₆ (254 mg, 0.722 mmol) and BT (190 mg, 1.42 mmol) for 9 h at 0 °C. After filtration and solvent evaporation, a yellow-brown, air-sensitive oil characterized as impure **2** remained. Due to the instability of **2**, its purification was not possible. ¹H NMR (CD₂Cl₂): δ 7.94 (m, 2 H), 7.52 (d, 1 H, J = 5.4 Hz), 7.45 (m, 3 H). IR (hexanes): (ν_{CO}) 2079 (w), 1952 (s), 1947 (sh), 1935 (m) cm⁻¹.

Preparation of (CO)₅W(η^1 (S)-2,5-Me₂T) (3): Complex **3** was prepared in a similar manner as **1** by irradiating a hexanes (40 mL) solution of W(CO)₆ (204 mg, 0.580 mmol) and 2,5-dimethylthiophene (0.41 mL, 3.6 mmol) for 13 h at 10 °C with stirring. Removal of solvent and excess ligand *in vacuo* resulted in a yellow-brown, air-sensitive, oily residue characterized as **3**. ¹H NMR (CD₂Cl₂): δ 6.65 (s, 2 H), 2.47 (s, 6 H, Me). IR (hexanes): (ν_{CO}) 2079 (w), 1949 (s), 1934 (m) cm⁻¹.

Preparation of (CO)₅Mo(η^1 (S)-DBT) (4a) and (CO)₃Mo(η^6 -DBT) (4b): Compounds **4a** and **4b** were prepared following the same procedure as **1** from Mo(CO)₆ (321 mg, 1.22 mmol) and DBT (454 mg, 2.46 mmol) dissolved in hexanes (40 mL). The solution was irradiated for 8 h at 10 °C. Filtration and washing with hexanes yielded 83 mg of an air-sensitive, yellow-green mixture of solids **4a** and **4b**. The two complexes could not be separated, but were identified spectroscopically. For **4a**, ¹H NMR (CD₂Cl₂): δ 8.18 (m, 2 H), 7.88 (m, 2 H), 7.62 (m, 4 H). IR (hexanes): (ν_{CO}) 2080 (w), 1958 (s), 1937 (m) cm⁻¹. For **4b**,

¹H NMR (CD₂Cl₂): δ 8.03 (m, 1 H), 7.79 (m, 1 H), 7.53 (m, 2 H), 6.83 (d, 1 H, J= 6.9 Hz), 6.54 (d, 1 H, J= 6.9 Hz), 5.93 (t, 1 H, J=6.0 Hz), 5.67 (t, 1 H, J= 6.0 Hz).

Preparation of (CO)₅Cr(η^1 (S)-DBT) (5): Compound 5 was prepared in the same manner as 1 by irradiation of a hexanes (40 mL) solution of Cr(CO)₆ (246 mg, 1.12 mmol) and DBT (408 mg, 2.21 mmol) for 12 h at 10 °C. Golden brown, air-sensitive crystals of 5 were grown from a CH₂Cl₂/hexanes solution (1:6) of the crude complex at -20 °C (120 mg, 0.319 mmol, 28.5% yield). Mp 110-112 °C dec. ¹H NMR (CD₂Cl₂): δ 8.16 (m, 2 H), 7.91 (m, 2 H), 7.61 (m, 4 H). IR (hexanes): (ν_{CO}) 2073 (w), 1948 (s), 1937 (m) cm⁻¹. EIMS: *m/e* 376 (M⁺), 320 (M⁺ - 2CO), 264 (M⁺ - 4CO), 236 (M⁺ - 5CO), 184 (M⁺ - Cr(CO)₅). Anal Calcd for C₁₇H₈CrO₅S: C, 54.26; H, 2.14. Found: C, 54.01; H, 2.21.

Preparation of (CO)₅Cr(η^1 (S)-3-MeBT) (6): Compound 6 was prepared in a manner similar to 1 by irradiation of a hexanes (35 mL) solution of Cr(CO)₆ (250 mg, 1.14 mmol) and 3-MeBT (236 mg, 1.59 mmol) for 8 h at 10 °C. Filtration and solvent evaporation *in vacuo* yielded a dark yellow, air-sensitive, oily residue containing 6, which was characterized spectroscopically. ¹H NMR (CD₂Cl₂): δ 8.01 (d, 1 H), 7.78 (d, 1 H), 7.59 (m, 2 H), 6.99 (s, 1 H), 2.47 (s, 3 H, Me). IR (hexanes): (ν_{CO}) 2073 (w), 1947 (s), 1936 (m) cm⁻¹.

Preparation of (CO)₅Cr(η^1 (S)-BT) (7): Complex 7 was prepared in a similar fashion as 1 by irradiation of Cr(CO)₆ (250 mg, 1.14 mmol) and BT (307 mg, 2.29 mmol) in hexanes (30 ml) for 9 h at 10 °C. The removal of solvent *in vacuo* produced 7 as a yellow,

air-sensitive, oily residue. Attempts at further purification by both chromatography and crystallization were not successful. IR (hexanes): (ν_{CO}) 2073 (w), 1947 (s), 1934 (m) cm^{-1} .

Preparation of $(CO)_5\text{Cr}(\eta^1(\text{S})\text{-2,5-Me}_2\text{T})$ (8): Complex **8** was prepared in a similar manner to **1** by irradiation of a hexanes (38 mL) solution of $\text{Cr}(\text{CO})_6$ (197 mg, 0.895 mmol) and 2,5-Me₂T (0.61 ml, 5.36 mmol) for 12 h at 10 °C. The solvent and excess ligand were removed *in vacuo* affording an air sensitive, yellow oil containing **8**. ¹H NMR (CD₂Cl₂): δ 6.64 (s, 2 H), 2.45 (s, 6 H, Me). IR (hexanes): (ν_{CO}) 2073 (w), 1951 (s), 1936 (m) cm^{-1} .

Preparation of $\text{Cp}(\text{CO})_2\text{Mn}(\eta^1(\text{S})\text{-T}^*)$ complexes 9-11 ($\text{T}^* = \text{DBT, BT, 2,5-Me}_2\text{T}$):

Cp(CO)₂Mn(η¹(S)-DBT) (9) A quartz reaction tube equipped with a teflon coated stir bar was charged with CpMn(CO)₃ (300 mg, 1.47 mmol) and DBT (547 mg, 2.97 mmol) under a nitrogen atmosphere. Hexanes (45 mL) was added via syringe affording a yellow solution. An oil bubbler was connected to the quartz reaction tube using Tygon tubing and a cold finger was inserted into the reaction tube for controlling the solution temperature. The solution was kept under a continuous flow of nitrogen and irradiated for 5 h at 10 °C. During this time the solution became orange and a precipitate formed. The solution was filtered and the orange precipitate was washed with hexanes (3x10 mL) to remove residual DBT and CpMn(CO)₃. Orange-brown, air-stable, X-ray quality crystals of **9** were grown overnight at -20 °C in a CH₂Cl₂/hexanes solution (1:5) (207 mg, 0.574 mmol, 39% based on CpMn(CO)₃). Mp 118-120 dec. ¹H NMR (CD₂Cl₂): δ 8.07 (m, 2 H), 7.97 (m, 2 H), 7.55 (m, 4 H), 4.09 (s, 5 H, Cp). IR (hexanes): (ν_{CO}) 1952 (s), 1890 (s) cm^{-1} . EIMS: 360 (M⁺), 304

(M⁺ - 2CO), 184 (M⁺ - Cp(CO)₂Mn), 120 (M⁺ - (2CO + DBT)). Anal. Calcd for C₁₉H₁₃MnO₂S: C, 63.34; H, 3.64; Found: C, 63.19; H, 3.61.

Preparation of Cp(CO)₂Mn(η¹(S)-BT) (10): Complex **10** was made in the same manner as **9** by irradiation of a hexanes (35 mL) solution of CpMn(CO)₃ (201 mg, 0.986 mmol) and BT (398 mg, 2.97 mmol) for 10 h at 0 °C. The dark orange solution was then filtered and the solvent was removed *in vacuo* giving an oily residue characterized as **10**. ¹H NMR (CD₂Cl₂): δ 8.2-7.6 (m, 2 H), 7.5-7.2 (m, 4 H, br), 4.22 (s, 5 H, Cp). IR (hexanes): (ν_{CO}) 1953 (s), 1893 (s) cm⁻¹.

Preparation of Cp(CO)₂Mn(η¹(S)-2,5-Me₂T) (11): Complex **11** was also prepared in a similar fashion to **9** by irradiation of a hexanes solution (40 mL) of CpMn(CO)₃ (278 mg, 1.36 mmol) and 2,5-Me₂T (0.60 mL, 5.27 mmol) for 6.5 h at 5 °C. Complex **11** was obtained as an orange oil after removal of solvent and excess 2,5-Me₂T *in vacuo*. ¹H NMR (CD₂Cl₂): δ 6.54 (s, 2 H), 4.23 (s, 5 H, Cp), 2.39 (s, 6 H, 2CH₃). IR (hexanes): (ν_{CO}) 1954 (s), 1892 (s) cm⁻¹.

Reaction of (CO)₅W(η¹(S)-DBT) (1) with THF. A 25 mL Schlenk flask equipped with a stirbar was charged with (CO)₅W(η¹(S)-DBT) (28 mg, 0.06 mmol) and dissolved in degassed THF (10 ml) at room temperature. IR spectra of aliquots taken from the reaction solution showed that in less than 1 min complete displacement of the DBT ligand by THF occurred giving quantitative conversion to the (CO)₅W(THF)⁴⁰ complex (ν_{CO} 2074 (w), 1930 (s), 1892 (m) cm⁻¹).

Reaction of $(CO)_5Cr(\eta^1(S)\text{-DBT})$ (5) with CO. A 50 mL Schlenk flask equipped with a teflon coated stirbar was charged with $(CO)_5Cr(\eta^1(S)\text{-DBT})$ (40 mg, 0.11 mmol) dissolved in degassed hexanes (15 ml) with stirring. Carbon monoxide was bubbled into the Schlenk flask slowly; an aliquot of the solution taken after 5 min at room temperature showed quantitative conversion of complex 5 to $Cr(CO)_6$ ($\nu_{CO} = 1974 \text{ cm}^{-1}$)⁴⁰.

Reaction of $CpMn(CO)_2(\eta^1(S)\text{-DBT})$ with CO. A 50 mL Schlenk flask was charged with 9 (31 mg, 0.09 mmol) and dissolved in 8-10 ml of 1,2-dichloroethane which was added by syringe. Carbon monoxide (1 atm) was introduced with stirring for 48 h. During the reaction, aliquot samples were taken periodically for IR studies. After 36 h, the two bands in the CO stretching region corresponding to $CpMn(CO)_2(\eta^1(S)\text{-DBT})$ (IR (1,2-DCE): 1940 and 1871 cm^{-1}) were completely replaced by those of $CpMn(CO)_3$ (IR (1,2-DCE): 2021 and 1930 cm^{-1}).

X-ray Structural Determinations of $(CO)_5W(\eta^1(S)\text{-DBT})$ (1) and $Cp(CO)_2Mn(\eta^1(S)\text{-DBT})$ (9). Single crystals of both yellow 1 and orange-brown 9 suitable for X-ray diffractional studies were obtained by recrystallization from a CH_2Cl_2 /hexanes solution and slow cooling overnight (-20 °C). For 1, a single crystal of the compound was mounted on a glass fiber on an Enraf-Nonius CAD4 diffractometer for a data collection at 293(2) ± 1 K. Pertinent data collection and reduction information for 1 are given in Table 1.

Lorentz and polarization corrections and a nonlinear correction based on the dacay in the standard reflections was applied to the data. A series of azimuthal reflections was collected for 1. A Semi-empirical absorption correction was applied to the data. The space

group P1 was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful direct-methods solution²⁸ and subsequent refinement. All non-hydrogen atoms were placed directly from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. Final refinements were done with SHELXL-93.^{29,30} Data collection and structure solution were conducted at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Zenith Data Systems Pentium computer using SHELXL-93.²⁹ Selected bond distances and angles for **1** are given in Table 2.

For **9**, the clear orange-brown, parallelepiped shaped crystal of **9** was mounted on a glass capillary. All measurements were made on a Siemens P4 diffractometer at 296 K. Pertinent data collection and reduction information for **9** are given in Table 1. The space group was determined to be P 2₁/n based on systematic absences and by successful structural refinement. All data were collected using an ω -scan technique. Variable scan rates were employed dependent on peak intensity. The intensities of three standard reflections showed no appreciable change throughout the data collection period. The data were corrected for Lorentz and polarization effects. No absorption correction was done due to the small value of μ . The structure was solved using direct method techniques. Initial positions of the non-hydrogen atoms were found using SHELXS-86. Hydrogens were placed in the calculated positions and all non-hydrogen atoms were refined anisotropically. Each asymmetric unit for **9** contains two independent molecules which are designated as (A) and (B) with selected bond distances and angles given in Tables 3 and 4. Neutral atomic scattering factors were

taken from X-ray tables³¹, including corrections for anomalous dispersion³². All calculations were performed on a Pentium PC using locally developed crystallographic software.³³

Results and Discussion

Synthesis and Characterization of $(CO)_5M(\eta^1(S)-T^*)$ Complexes (1-8).

Ultraviolet irradiation of $M(CO)_6$ ($M = Cr, Mo, W$) complexes and excess T^* (2-5 equiv.) in hexanes solution affords $\eta^1(S)-T^*$ complexes in low yields (<30%). IR spectroscopy serves as a useful tool for monitoring the progress of the reactions since none of the corresponding bands due to ν_{CO} stretching frequencies of the $M(CO)_6$ starting materials overlap with those of the S-bound T^* complexes. The $(CO)_5M(\eta^1(S)-DBT)$ complexes $(CO)_5W(\eta^1(S)-DBT)$ and $(CO)_5Cr(\eta^1(S)-DBT)$ are isolated as moderately air-stable, analytically pure solids, while the analogous $(CO)_5M(\eta^1(S)-T^*)$ complexes of BT, 3-MeBT or 2,5-Me₂T, **2-4** and **6-8**, are only moderately stable in hexanes solution and quite difficult to isolate. Attempted isolations of complexes **2-4** and **6-8** by solvent removal led to complete decomposition of the oily complexes within 50-60 minutes. Column chromatography (silica, Celite or alumina) was also unsuccessful. Complexes **1-7** are all soluble in CH_2Cl_2 , however dissociation of the T^* ligand occurs (15-20 min) at room temperature with decomposition.

Complexes **1-8** were characterized by ¹H NMR and IR spectroscopy. The ¹H NMR chemical shifts for the protons of the S-bound thiophene ligands in complexes **1-8** are similar to those of the free thiophene ligands (± 0.15 ppm). These chemical shifts, are also similar to those of other known $\eta^1(S)-DBT$ and $\eta^1(S)-BT$ complexes: $Cp(CO)_2Re(\eta^1(S)-BT)$,¹⁹ $Cp(CO)_2Re(\eta^1(S)-DBT)$,²² and $[Cp(CO)_2Fe(\eta^1(S)-DBT)]^+$ ³⁴. The IR spectra in the CO

region for all the S-bound complexes **1-8** are similar. Each complex has a weak a_1 band in the 2070 cm^{-1} region, a strong e band ($1947\text{-}1958\text{ cm}^{-1}$) and a medium a_1 band ($1934\text{-}1937\text{ cm}^{-1}$) in hexanes solution which are typical for group 6 $(\text{CO})_5\text{M}(\text{L})$ complexes such as $(\text{CO})_5\text{Cr}(\text{THF})^{35}$ and $(\text{CO})_5\text{W}(\text{NC}_5\text{H}_5)^{36}$.

Synthesis of $(\text{CO})_5\text{Mo}(\eta^1(\text{S})\text{-DBT})$ (4a) and $(\text{CO})_3\text{Mo}(\eta^6\text{-DBT})$ (4b). The complexes **4a** and **4b** were prepared in the same way as **1-8** by UV irradiation of a hexanes solution of $\text{Mo}(\text{CO})_6$ with excess DBT under inert atmosphere. The two complexes (**4a** and **4b**) are equally soluble in hexanes but decompose rapidly upon exposure to air in both the solid state and in solution; Although they could not be isolated as pure compounds, the ^1H NMR spectra of the mixture strongly supports their formation. ^1H NMR spectra were obtained for **4a** and **4b** in CD_2Cl_2 but slow, yet complete decompositon of both complexes occurs within 1-2 h. under inert atmosphere. Isolation of either **4a** or **4b** by column chromatography (alumina, silica gel or Celite) was unsuccessful as was attempted fractional crystallization at low temperature ($-20\text{ }^\circ\text{C}$) in CH_2Cl_2 /hexanes (1:4). Attempts were made to determine the ratio of the two complexes using ^1H NMR spectroscopy; however due to their instability, such attempts were unsuccessful. The ^1H NMR spectra of the DBT proton signals assigned to **4a** are similar to those observed in **1** and **5** ($\pm 0.03\text{ ppm}$). The proton resonances assigned to complex **4b** were based on those of the analogous Cr complex ($\eta^6\text{-DBT})\text{Cr}(\text{CO})_3$).²⁰ The coordinated benzo-ring of **4b** has well resolved splittings of the ring protons which consist of a pair of doublets ($\delta 6.83$ and 6.54) from the 1,4 protons and a pair of triplets ($\delta 5.93$ and 5.67) corresponding to the 2,3 protons of the DBT ligand (see Fig. 1). The uncoordinated ring of DBT has chemical shifts that are similar to those in free DBT

between 8.2-7.4 ppm. The IR bands in the CO region are assigned to **4a** based on similar assignments for complexes **1** and **5**. However, the e and $a_1(2)$ bands corresponding to **4a** appear to be broad indicating that the two bands expected for **4b** may be overlapping with those for **4a**. The EIMS of the mixture of **4a** and **4b** shows a Mo isotope pattern (*m/e* 366 for ^{98}Mo) corresponding to either an M^+ for the $(\eta^6\text{-DBT})\text{Mo}(\text{CO})_3$ complex, or a fragment corresponding to **4a** with a loss of two CO ligands such as those observed in the spectra of $(\text{CO})_5\text{Cr}(\eta^1\text{(S)-DBT})$ and $(\text{CO})_5\text{W}(\eta^1\text{(S)-DBT})$. No M^+ was observed for complex **4a**.

Synthesis and Characterization of $\text{Cp}(\text{CO})_2\text{Mn}(\eta^1\text{(S)-T}^*)$ (9-11). Irradiation of a hexanes solution of freshly sublimed $\text{CpMn}(\text{CO})_3$ with excess T^* (2-4 equiv.) leads to the formation of $\text{Cp}(\text{CO})_2\text{Mn}(\eta^1\text{(S)-T}^*)$ complexes. Complex **9** is stable for months in the solid state while **10** and **11** are stable only in hexanes solution under inert atmosphere for a short time, and are not isolable in a pure form. Complexes **9-11** are soluble in most hydrocarbons and chloronated solvents. Only complex **9** is stable in chloronated solvents for any length of time.

Complexes **9-11** were characterized by ^1H NMR and IR spectroscopies. The ^1H NMR chemical shifts of the T^* protons for **9-11** were similar to those of the analogous $\text{Cp}(\text{CO})_2\text{Re}(\text{T}^*)$ ^{19,22} ($\text{T}^* = \text{DBT, BT, 2,5-Me}_2\text{T}$) complexes (± 0.4 ppm) and the cationic complex $\text{Cp}(\text{CO})_2\text{Fe}(\text{DBT})^+$.³⁴ In the IR spectra for **9-11**, two bands with similar intensities are observed in the ν_{CO} region. The positions of these signals are essentially the same for each complex of the series **9-11** ($\pm 3.0 \text{ cm}^{-1}$). Comparably small differences are observed in the ν_{CO} bands between the analogous $\text{Cp}(\text{CO})_2\text{Re}(\text{T}^*)$ complexes which differ from each

other by ± 4.0 cm^{-1} depending on the thiophene ligand. For complex **10**, sulfur coordination of the BT ligand is assigned instead of 2,3- η^2 -BT coordination since the IR bands for **10** (ν_{CO} 1953, 1893 cm^{-1}) are more indicative of those observed in $\text{Cp}(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-BT})^{19}$ (ν_{CO} 1947, 1885 cm^{-1}) rather than those of $\text{Cp}(\text{CO})_2\text{Re}(2,3\text{-}\eta^2\text{-BT})^{19}$ (ν_{CO} 1977, 1907 cm^{-1}).

Comparison of the Structures of $(\text{CO})_5\text{W}(\eta^1(\text{S})\text{-DBT})$ (1) and $\text{Cp}(\text{CO})_2\text{Mn}(\eta^1(\text{S})\text{-DBT})$ (9). In the structure of **1** (Figure 3) the coordinated DBT ligand is S-bound to the W metal center with trigonal-pyramidal geometry about the sulfur (pseudo- sp^3 hybridization). The sum of the angles around S (309.7°) in **1** is similar to those in the complex $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$ (309.8°)³⁴ and significantly smaller than those observed in $\text{Cp}^*\text{IrCl}_2(\eta^1(\text{S})\text{-DBT})^{39}$ (317.9°). The W has octahedral geometry with angles of nearly 90° formed between adjacent carbonyls and the central W atom (see Table II). The C-W-C angles defined by trans carbonyl ligands with the central W are nearly 180° . The W-S bond distance is 2.580 (2) \AA which is longer than both the Fe-S distance in $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$ (2.289 (1) \AA)³⁴ and the Ir-S distance in $\text{Cp}^*\text{IrCl}_2(\eta^1(\text{S})\text{-DBT})^{39}$ (2.375 (2) \AA). The W lies out of the DBT ring plane with the angle between the W-S bond and the vector from the S to the midpoint of the C6 and C7 ring carbons of 118.8° . This angle is slightly smaller than that reported for $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$ (119.4°)³⁴ and much smaller than in $\text{Cp}^*\text{IrCl}_2(\eta^1(\text{S})\text{-DBT})^{39}$ (128.0°) which were defined similarly. The mean C-S bond in the DBT ligand of **1** is 1.763 \AA which is slightly longer than that in free DBT (1.740 \AA).³⁷ The C1-S-C12 angle of the DBT ligand in **1** is 90.7° which decreased slightly from that in free DBT (91.5°). The

DBT ligand is essentially planar with the sulfur deviating 0.02 Å out of the least squares plane which is defined by the C1, C6, C7 and C12 carbon atoms.

In the structure of **9** (Figure 4)[†] the DBT ligand is S-bound to the Mn metal center. The structure of **9** is very similar to that of $\text{Cp}^*\text{IrCl}_2(\eta^1(\text{S})\text{-DBT})^{39}$ with the DBT ligand oriented syn to the Cp ring. This is contrary to the observed ligand orientation in the structure of $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$ in which the DBT ligand is anti to the Cp ring.³⁴ The sulfur has trigonal-pyramidal geometry with pseudo-sp³ hybridization. This geometry is assigned based on the sum of the angles around the S atom in **9** (317°) which is smaller than the sum (360°) one would expect if the sulfur was planar. In comparison to other reported thiophene complexes the sum of the angles around the S atom in **9** is similar to that in $\text{Cp}^*\text{IrCl}_2(\eta^1(\text{S})\text{-DBT})^{39}$ (317.9°), but greater than those of $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$ (309.8 Å)³⁴ and $(\text{CO})_5\text{W}(\eta^1(\text{S})\text{-DBT})$ (**1**) (309.7°). The angle between the Mn-S vector and the vector from the S to the midpoint of the line between C(2) and C(8) of the DBT ring is 125.6°. This angle is larger in comparison to similar angles in the complexes $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$ (119.4°)³⁴, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{2-MeT})^+$ (119.11°)³⁸ and **1** (118.8°). The Mn-S distance (2.255 (1) Å) in **9** is similar to that of $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$ (2.289 (1) Å) and slightly smaller in comparison to the Ir-S distance of 2.375 (2) Å in $\text{Cp}^*\text{IrCl}_2(\eta^1(\text{S})\text{-DBT})^{39}$. The mean C-S bond length in **9** is 1.770 Å which is longer than that in free DBT³⁷ (1.740 Å). The C1-S-C7 angle is 90.8° in complex **9** which is quite similar to free DBT³⁷ (91.5°). The DBT ligand is essentially planar, with the sulfur deviating only 0.07 Å out of

the least squares plane in the opposite direction of the Mn as defined by the C1, C2, C7 and C8 atoms.

Reactions of $(CO)_5W(\eta^1S\text{-DBT})$ (1) with THF, and $(CO)_5Cr(\eta^1S\text{-DBT})$ (5) and $CpMn(CO)_2(\eta^1S\text{-DBT})$ (9) with CO. Complex 1 is dissolved in THF at room temperature. The solution IR spectroscopy shows displacement of the DBT ligand by THF within seconds. The observed signals (2074 (w), 1930 (s), 1892 (m) cm^{-1}) correspond similarly with those for the complex $(CO)_5W(\text{THF})^{40}$. When $W(CO)_6$ is irradiated in THF with stirring for 7-8 h at -20 °C, the same signals are observed in the CO stretching region after 1 h.

A similar displacement of the DBT ligand is observed when complex 5 is stirred in hexanes solution with CO (1 atm). The quantitative formation of $Cr(CO)_6$ was determined by monitoring the reaction by IR spectroscopy. The CO stretching region showed only one broad band at 1974 cm^{-1} corresponding to $Cr(CO)_6^{40}$ within minutes. When 5 was stirred in hexanes solution at room temperature under inert atmosphere, no decomposition was observed for several hours. Therefore, it is apparent that the DBT ligand is very labile even in the presence of weak donor ligands (such as CO).

When complex 9 is dissolved in DCE under CO (1 atm) for 48 h, the complex $CpMn(CO)_3$ forms as the only product. This ligand exchange was observed using IR spectroscopy to monitor the ν_{CO} stretching region of aliquot samples taken periodically over the course of 2 d.

Conclusion

UV photolysis of metal carbonyls in the non-coordinating solvent hexanes is a useful method for preparing $(CO)_5M(\eta^1(S)-T^*)$ and $Cp(CO)_2Mn(\eta^1(S)-T^*)$ complexes. The complex $(CO)_5W(\eta^1(S)-DBT)$ is the first example of a fully characterized thiophene complex of the HDS-active metal tungsten. It is evident from the stabilities of the complexes that DBT ligands bind more strongly than BT or Me_2T . The same trend was observed in the preparation of $Cp^*IrCl_2(\eta^1(S)-T^*)$ complexes³⁹ and in equilibrium studies³⁸ of several $Cp(CO)(PPh_3)Ru(\eta^1(S)-T^*)^+$ complexes. The complex $CpMn(CO)_2(\eta^1(s)-DBT)$ binds the DBT ligand more strongly than either W or Cr in complexes **1** and **5**. Finally, the structures of complexes **1** and **9** are good examples of S-binding of thiophenes in W and Mn complexes.

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‡ For the structure of $\text{Cp}(\text{CO})_2\text{Mn}(\eta^1\text{-DBT})$ (**9**), the bond distances and angles refer only to molecule (A) (Table 3). The bond distances and angles for (B) are given in Table 4 and will not be discussed since they are very similar with only slight deviations from those of (A).

Table 1. Crystal and Data Collection Parameters for $(CO)_5W(\eta^1(S)\text{-DBT})$ (1) and $Cp(CO)_2Mn(\eta^1(S)\text{-DBT})$

	1	9
formula	$C_{17}H_8O_5SW$	$C_{19}H_{13}MnO_2S$
formula weight	508.14	360.31
space group	$P\bar{1}$	$P\bar{2}_1/n$
a, Å	9.576 (2)	13.076 (3)
b, Å	10.143 (2)	10.309 (2)
c, Å	10.420 (2)	23.484 (5)
α , deg.	71.24 (3)	-----
β , deg.	63.03 (3)	92.92 (3)
γ , deg	67.58 (3)	-----
V , Å ³	820.2 (3)	3161.5 (11)
Z	2	8
D_{calc} , g/cm	2.058	1.514
$\mu(\text{Mo K}\alpha)$, mm ⁻¹	7.193	0.973
diffractometer	Enraf-Nonius CAD4	Siemens P4
temp, K	293	296
reflections collected	4452	12,361
independent reflections	3773 ($R(int)=0.049$)	5268 ($R(int)=0.026$)
$R(F)$, % ^a ($I \geq 2\sigma(I)$)	3.93	3.63
$R(wF^2)$, % ^a	8.53	9.43

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

Table 2. Selected bond distances (Å) and Angles (deg.) for (CO)₅W(η^1 (S)-DBT) (1)

distances			
W-S	2.580 (2)	C(1)-C(2)	1.381 (10)
W-C(13)	2.006 (8)	C(1)-C(6)	1.387 (10)
W-C(14)	2.039 (8)	C(2)-C(3)	1.394 (11)
W-C(15)	2.060 (8)	C(3)-C(4)	1.383 (12)
W-C(16)	2.020 (8)	C(4)-C(5)	1.370 (12)
W-C(17)	1.962 (8)	C(5)-C(6)	1.380 (10)
S-C(1)	1.762 (7)	C(6)-C(7)	1.443 (10)
S-C(12)	1.764 (7)	C(7)-C(8)	1.384 (10)
O(1)-C(13)	1.156 (9)	C(7)-C(12)	1.382 (10)
O(2)-C(14)	1.132 (9)	C(8)-C(9)	1.376 (12)
O(3)-C(15)	1.131 (9)	C(9)-C(10)	1.383 (13)
O(4)-C(16)	1.162 (9)	C(10)-C(11)	1.384 (12)
O(5)-C(17)	1.157 (9)	C(11)-C(12)	1.385 (10)
angles			
W-S-midpoint	118.8	C(13)-W-C(16)	90.9 (3)
C(1)-S-W	110.8 (2)	C(17)-W-C(15)	90.9 (3)
C(12)-S-W	108.2 (2)	C(16)-W-C(15)	88.0 (3)
C(17)-W-S	177.1 (2)	C(14)-W-C(15)	90.4 (3)
C(13)-W-C(15)	178.9 (3)	C(13)-W-S	88.6 (2)
C(16)-W-C(14)	175.1 (3)	C(16)-W-S	92.3 (2)
C(17)-W-C(13)	89.3 (3)	C(14)-W-S	92.4 (2)
C(17)-W-C(16)	89.7 (3)	C(15)-W-S	91.2 (2)
C(17)-W-C(14)	85.7 (3)	C(1)-S-C(12)	90.7 (3)

Table 3. Selected bond distances (Å) and angles (deg.) for the complex $\text{Cp}(\text{CO})_2\text{Mn}(\eta^1(\text{S})\text{-DBT})$ (9) molecule (Å).

distances			
Mn-S	2.2557(8)	S-C(8A)	1.773(3)
Mn-C(1A)	2.121(3)	S-C(19A)	1.765(3)
Mn-C(2A)	2.109(3)	C(6A)-O(6A)	1.159(4)
Mn-C(3A)	2.130(3)	C(7A)-O(7A)	1.159(4)
Mn-C(4A)	2.148(3)		
Mn-C(5A)	2.151(3)		
Mn-C(6A)	1.772(3)		
Mn-C(7A)	1.770(3)		
angles			
S-Mn-C(1A)	145.81(9)	Mn-S-C(8A)	113.33(9)
S-Mn-C(2A)	147.65(10)	Mn-S-C(19A)	112.90(9)
S-Mn-C(3A)	108.42(11)	C(8A)-S-C(19A)	90.45(12)
S-Mn-C(4A)	89.59(9)	C(6A)-Mn-C(7A)	92.6(1)
S-Mn-C(5A)	107.54(8)		
S-Mn-C(6A)	92.80(11)		
S-Mn-C(7A)	93.17(10)		

Table 4. Selected bond distances (Å) and angles (deg.) for the complex $\text{Cp}(\text{CO})_2\text{Mn}(\eta^1\text{S}-\text{DBT})$ (9) molecule (B).

distances			
Mn-S(1)	2.2553(8)	S-C(8)	1.771(3)
Mn-C(1)	2.115(3)	S-C(19)	1.772(3)
Mn-C(2)	2.121(3)	C(6)-O(6)	1.165(3)
Mn-C(3)	2.143(3)	C(7)-O(7)	1.163(3)
Mn-C(4)	2.145(3)		
Mn-C(5)	2.135(3)		
Mn-C(6)	1.767(3)		
Mn-C(7)	1.767(3)		
angles			
Mn-S-Midpt	125.6	C(6)-Mn-C(7)	92.88(1)
S-Mn-C(1)	147.71(9)	Mn-S-C(8)	112.70(8)
S-Mn-C(2)	145.56(9)	Mn-S-C(19)	113.52(8)
S-Mn-C(3)	107.02(8)	C(8)-S-C(19)	90.80(12)
S-Mn-C(4)	89.48(8)		
S-Mn-C(5)	108.75(9)		
S-Mn-C(6)	92.41(9)		
S-Mn-C(7)	93.34(9)		

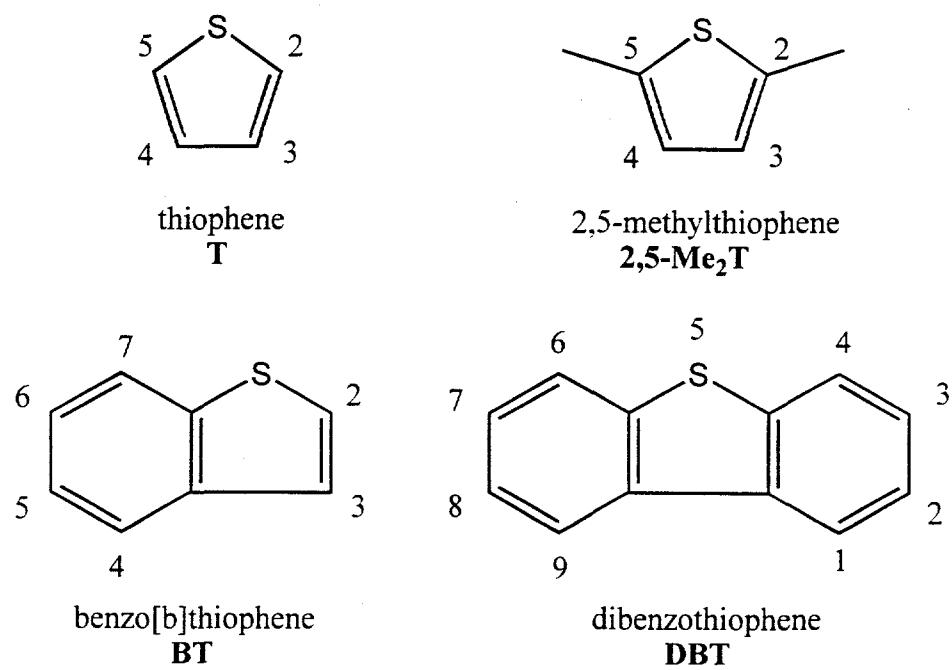


Figure 1. Thiophene and its derivatives

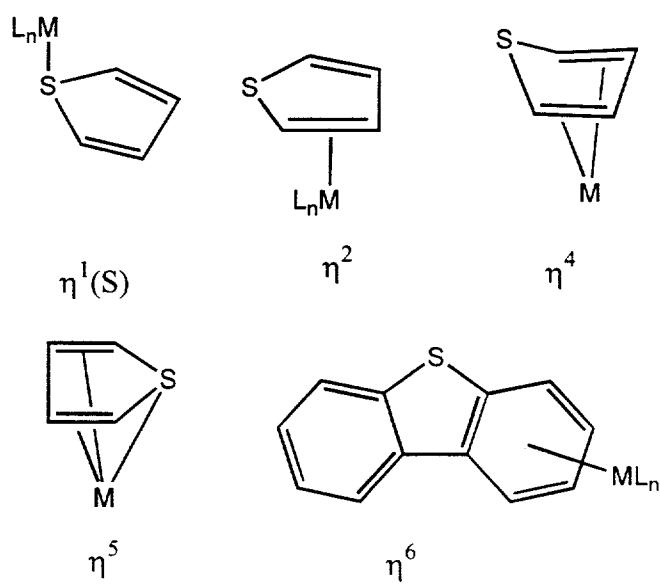


Figure 2. Thiophene binding modes.

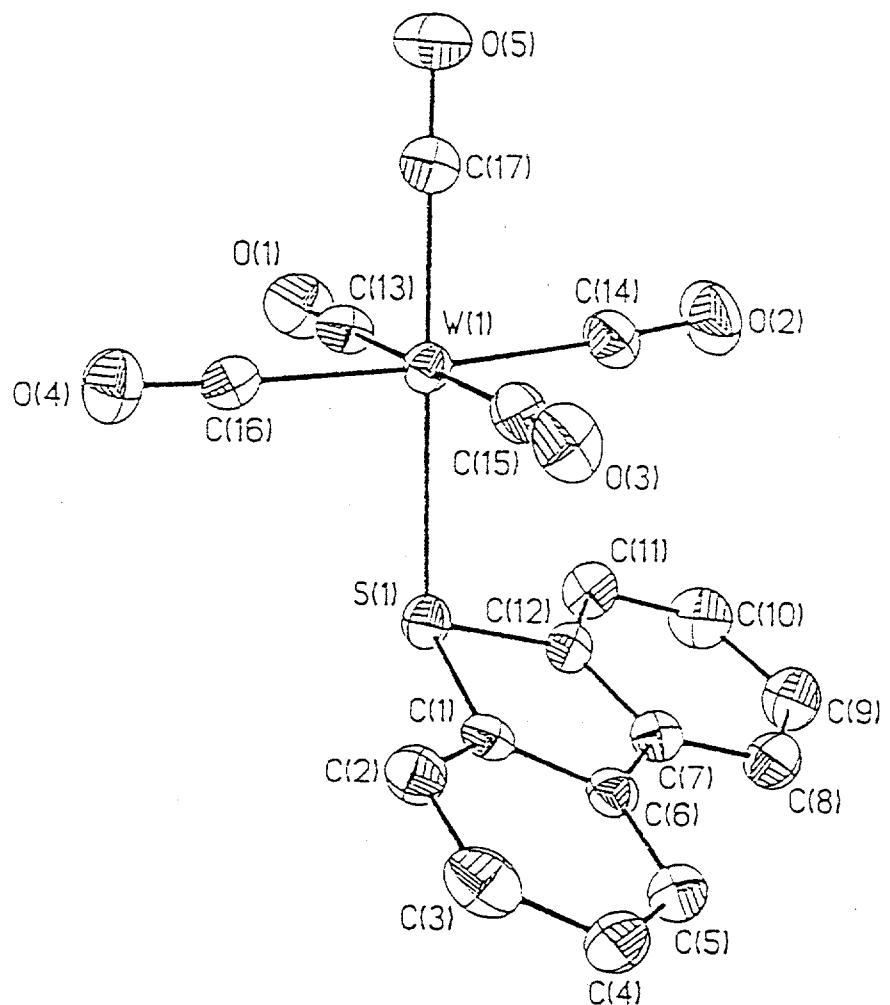


Figure 3 Thermal ellipsoid drawing of $(CO)_5W(\eta^1(S)-DBT)$ (1).

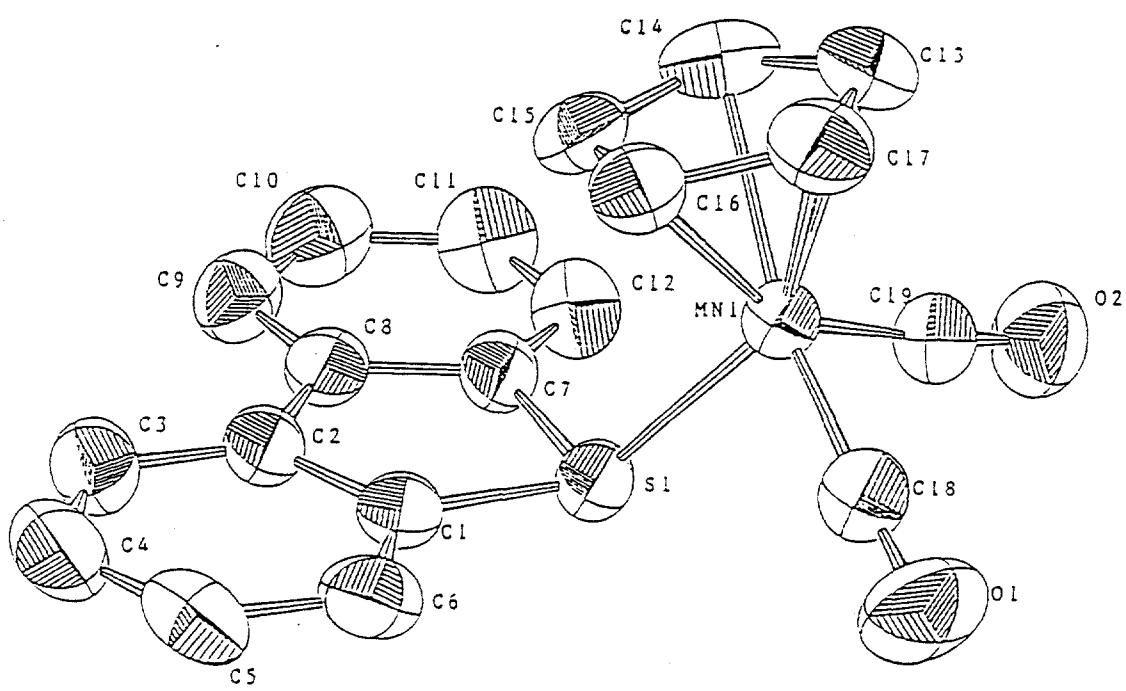


Figure 4 Thermal ellipsoid drawing of $\text{Cp}(\text{CO})_2\text{Mn}(\eta^1(\text{S})\text{-DBT})$ (9).

GENERAL CONCLUSIONS

Organometallic complexes of transition metals containing thiophene ligands have been very useful models for learning about how thiophenes and benzothiophenes can bind to metal centers. Some of the group 6 and 7 transition metal-thiophene complexes mentioned in the first chapter of this thesis have also proven to undergo C-H and C-S bond activation (cleavage) and in some cases complete desulfurization. The complexes and molecular structures mentioned in the second chapter illustrate how thiophenes can bind to the actual metals used in the HDS process (Mo and W). The complex $(CO)_5W(\eta^1(S)\text{-DBT})$ offers the first structural model of a W complex containing a coordinated thiophene ligand. All complexes mentioned and the reactions they have undergone may or may not be representative of how the commercial HDS catalysts behave with respect to thiophene binding. Molecular modelling only offers some insight into what might happen at a catalyst site. Much more needs to be learned about how the industrial catalysts work in order to create more effective and efficient heterogeneous catalysts in the future and molecular modelling contributes to this effort.

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