1990

Synthesis and reactions of thiophene, 2,5-dihydrothiophene, benzo[b]thiophene and selenophene transition metal complexes: models for catalytic hydrodesulfurization

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Recommended Citation

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Choi, Moon-Gun, Ph.D.

Iowa State University, 1990

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Synthesis and reactions of thiophene, 2,5-dihydrothiophene, benzo[b]thiophene and selenophene transition metal complexes: Models for catalytic hydrodesulfurization

by

Moon-Gun Choi

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemsitry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1990

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DEDICATION

To my family

PREFACE

Although recent organometallic model and catalytic reactor studies of thiophenes provide some mechanistic insight into the catalytic hydrodesulfurization (HDS) of organosulfur compounds, the initial mode of thiophene adsorption on the catalyst surface as well as the desulfurization pathway are still not well established. Therefore, the goal of this research is to synthesize new transition metal complexes of thiophene and its analogs, investigate their preferred modes of bonding and reactivity, and use the results to explain possible mechanism(s) for HDS. The research presented in this dissertation consists of the synthesis of thiophene, 2,5-dihydrothiophene, benzo[b]thiophene, and selenophene transition metal complexes and of studies their reactivity.

This dissertation contains seven sections. The first section is a review of different bonding modes of known thiophenes transition metal complexes and the following sections represent research as it was submitted for journal publication. Literature citations, tables and figures pertain only to the sections in which they are included. Following the final section is a general summary.

SECTION I. THE COORDINATION MODES OF THIOPHENE IN TRANSITION METAL COMPLEXES

INTRODUCTION

Hydrodesulfurization (HDS), the catalytic process by which sulfur is removed from crude oils by treatment with H_2 over a Mo-Co/γ-Al_2O_3 catalyst (eq 1), is one of the largest scale chemical processes practiced in the world.[1] There are several reasons for desulfurizing oil stocks: to prevent poisoning of sulfur-sensitive precious metal catalysts, to reduce corrosion during refining, to remove odor, and to reduce atmospheric pollution by sulfur oxides produced during the combustion of petroleum-based fuels.

$$C_X H_Y S_Z + H_2 \xrightarrow{\text{catalyst}} H_2S + \begin{array}{l}\text{Sulfur-free}\\ \text{Hydrocarbons}\end{array} \qquad (1)$$

It is known that petroleum feedstocks contain an incredibly complex mixture of organic sulfur compounds.[1a, 1d, 2] The classes of compounds include thiols, disulfides, sulfides and thiophenes. Among them, aromatic thiophenes are the most difficult to desulfurize. Therefore, most of HDS studies focus on thiophene chemistry. Despite the industrial and environmental importances of HDS, most aspects of the mechanism(s) including the mode of thiophene binding to the catalyst surface and the nature of the first steps in the process, are still not well established. One reason for this lack of information stems from the experimental difficulties associated with determining the nature of short-lived intermediates in the heterogeneous catalytic system. An alternative approach to understanding the mechanism(s) of thiophene HDS is to prepare well-characterizable organometallic model complexes, investigate preferred modes of bonding and reactivity, and use this knowledge to propose possible mechanisms.[3]

The first and the most fundamental question concerning the HDS mechanism is how thiophenes adsorb on the catalyst. The following is a review of previously known thiophene coordination modes in transition metal complexes and a summary of ^{13}C NMR data for different types of coordination.

COORDINATION MODES OF THIOPHENE

The most likely coordination sites in thiophene are at the unsaturated carbon-carbon double bonds and at the sulfur. Coordination at all of these sites is known in transition metal complexes[4] as shown in Figure 1.

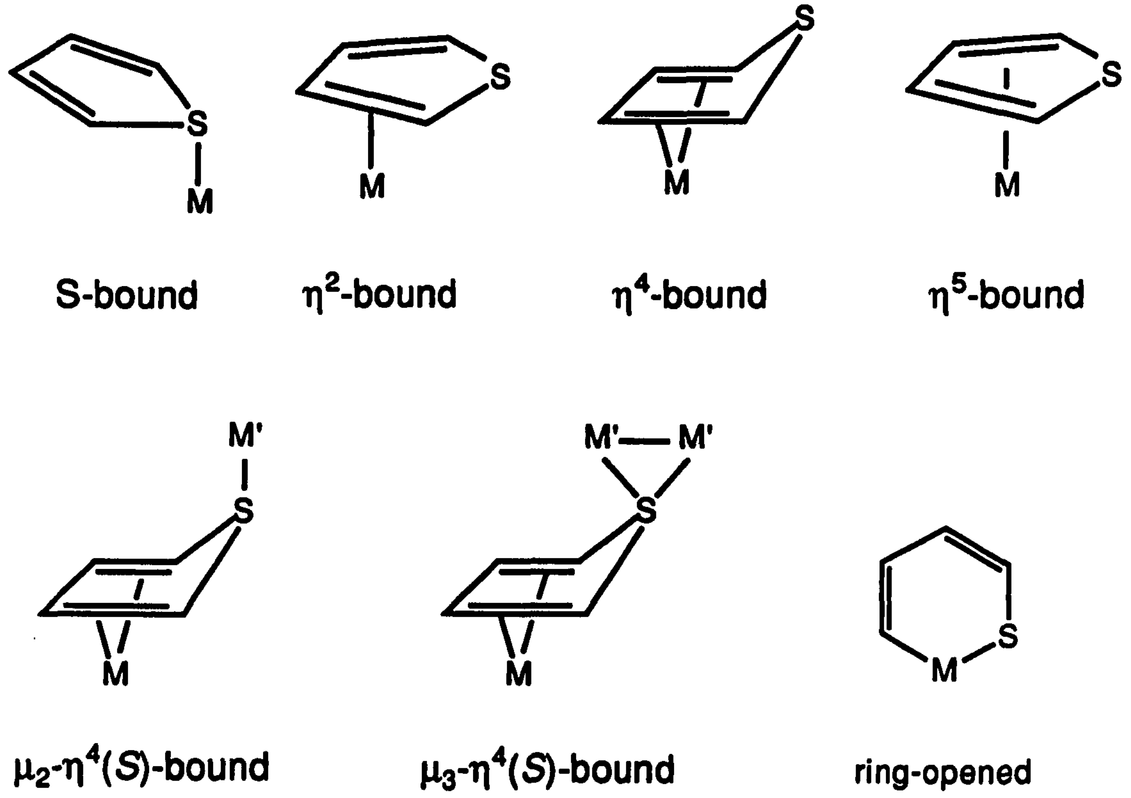
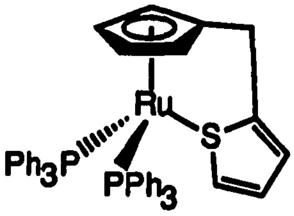
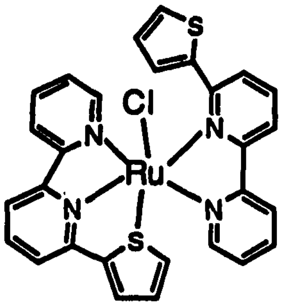


Figure 1. Known types of thiophene binding in transition metal complexes where M and M' are transition metal complex fragments

η^1(S)-Bound Thiophene Complexes

Thiophene is a very weak, sulfur-donor ligand compared to dialkyl or aryl-alkyl sulfides (R_2S) or partially and fully hydrogenated thiophene (dihydrothiophene, tetrahydrothiophene). Therefore, few S-bound thiophene complexes are known, and thiophene is very easily displaced by other weak ligands. Three of the earliest S-bound thiophene complexes in the literature are $W(CO)_5(T)$[5], $Ru(NH_3)_5(T)^{+2}$,[6] and $PdCl_2(TMT)_2$[7] which have been mentioned briefly without strong evidence. Several η^1(S)-bound thiophene complexes were reported later: $[CpFe(CH_3CN)_2(\eta^1(S)\text{-}2,5\text{-}Me_2T)]^+$,[8] $[CpFe(CO)_2(\eta^1(S)\text{-}T)]^+$,[9] $[CpFe(CO)_2(\eta^1(S)\text{-}2,5\text{-}Me_2T)]^+$,[10] $W(CO)_3(PCy_3)_2(\eta^1(S)\text{-}T)$.[11] Coordination by weakly donating S atom in thiophene can be promoted by chelation where thiophene is part of a multidentate ligand. Three stable, chelated, S-coordinated thiophene complexes have been isolated[12] and thiaporphyrin complexes are also known.[13] Well-characterized examples of S-coordinated thiophene complexes are $(PPh_3)_2Ru(C_5H_5CH_2\text{-}C_4H_3S)^+$,[12b] in which the S-bound thiophene is linked to the cyclopentadienyl ligand through a -CH_2-group, and $[RuClL_2]BF_4 \cdot CH_2Cl_2$,[12a] in which L is 6-(2-thienyl)-2,2'-bipyridine, and $Pd(\eta^3\text{-allyl})(L)^+$,[12c] in which L is 2,5,8-trithia[9](2,5)thiophenphane. The x-ray-determined structures of these compounds show that the sulfur has trigonal pyramidal geometry (roughly sp^3 hybridization). Previously, it was assumed that metals would bind to a lone pair of electrons in the plane of the thiophene.





Because of the weakly coordinating nature of S-bound thiophene, even as part of a chelate ligand, the only reported reactions of these complexes are displacement of the thiophene ligand from the metal.

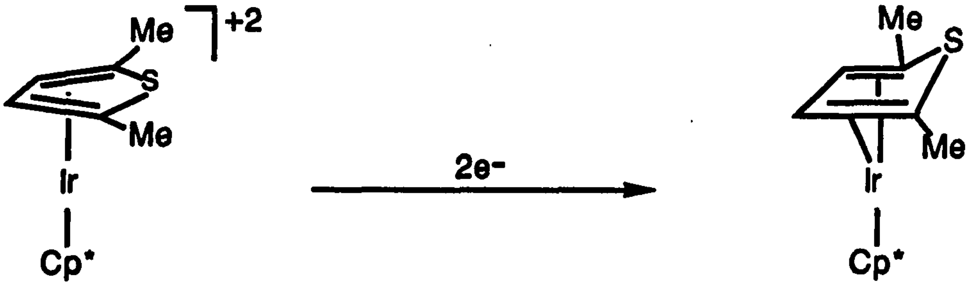
In related S-bound thiophene complexes, one S-bound benzo[b]thiophene (BT) and two dibenzothiophene (DBT) complexes are reported: $Cp(CO)_2Fe(\eta^1(S)\text{-}BT)^+$,[9a] $Cp(CO)_2Fe(\eta^1(S)\text{-}DBT)^+$,[9a] and $RuCl_2[4\text{-}(p\text{-}tolyl)_2P(DBT)]_2$,[14] in which the DBT contains a coordinating $(p\text{-}tolyl)_2P$ group in the 4-position. In the $Cp(CO)_2Fe$ moiety, the S-coordinated DBT ligand is kinetically more stable to displacement by CH_3CN or CD_3NO_2 than their BT and T analogs. In structures of both $Cp(CO)_2Fe(\eta^1(S)\text{-}DBT)^+$[9a] and $RuCl_2[4\text{-}(p\text{-}tolyl)_2P(DBT)]_2$,[14] the sulfur has a trigonal pyramidal geometry. In contrast to S-coordinated thiophene complexes, S-bound hydrogenated thiophene (dihydrothiophene or tetrahydrothiophene) transition metal complexes[15] are stable.

η^2-Thiophene Complexes

Coordination of thiophene in an η^2-mode occurs by binding through the unsaturated carbon-carbon π-bond to the metal. Recently, the η^2-T complex in $(NH_3)_5Os(T)^{2+}$[16] was proposed based on its ^1H NMR spectrum which shows four doublets of doublets shifted upfield as expected for η^2-binding. There are no other examples of η^2-thiophene complexes.

η^4-Thiophene Complexes

This is one of the more recently discovered coordination modes; in it four carbons coordinate to the metal but the sulfur does not. The first η^4-thiophene complex $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$[17] was prepared by a



two-electron reduction of $[Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)]^{+2}$. Similarly in the rhodium system, an analogous η^4-thiophene complex, $Cp^*Rh(\eta^4\text{-}Me_4T)$, where Me_4T = tetramethylthiophene, was also prepared a few month later.[18] The chemical reduction of $[Cp^*M(\eta^5\text{-}C_4R_4S)]^{+2}$ (M = Rh, Ir) results in major spectroscopic and geometry changes of thiophene. The NMR resonances for the η^4-thiophene move ~3 ppm upfield in the ^{1}H and ~50 ppm upfield in the ^{13}C NMR spectra upon reduction of the η^5-thiophene precursor.[17,18] A crystallographic study of Cp*Ir(η^4-2,5-Me$_2$T) shows[17] that the sulfur atom is bent out of the plane of the four carbons away from the Ir. The unusually high basicity of sulfur in η^4-thiophene complexes allows it to react with Lewis acids,[19] oxygen,[20] or other metal complexes.[21]

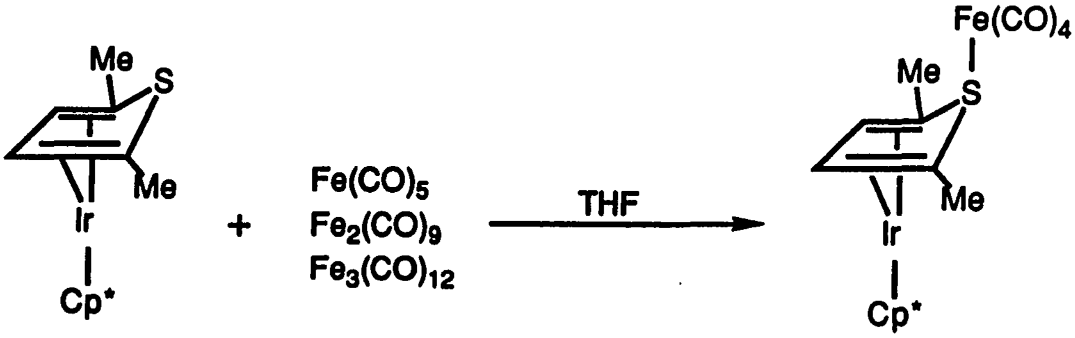
η^5-Thiophene Complexes

The η^5-coordination mode is the most common for thiophene in organometallic compounds. In general, η^5-thiophene shows higher stability than any of the other modes in thiophene complexes and coordinates more strongly as methyl groups are added to the ring. Each methyl group added to the ring increases the relative binding constant by a factor of approximately 6, stabilizing it by 1.2 Kcal/mole.[22] There are many known η^5-thiophene complexes: (η^5-T)Cr(CO)$_3$,[23] (η^5-T)Mn(CO)$_3^+$,[24] (η^5-T)MCp$^+$(M = Fe, Ru),[25] (η^5-T)M(PPh$_3$)$_2^{+2}$ (M = Rh, Ir),[26] (η^5-T)MCp^{*+2}(M = Rh, Ir),[27] (η^5-T)$_2$M^{2+} (M = Fe, Ru),[28] [(η^5-T)RuCl$_2$]$_2$,[28b] and {[(η^5-Me$_4$T)RuCl$_3$] S}$^+$.[28b] X-ray structure determination of (η^5-T)Cr(CO)$_3$, (η^5-T)Rh(PPh$_3$)$_2^+$, Ru(η^5-Me$_4$T)$_2^{+2}$ and {[(η^5-Me$_4$T)RuCl]$_3$S}$^+$ show that all five atoms of the thiophene ring are coordinated to the metal. The bond distances and angles in the thiophene ring are similar to those in free thiophene within experimental error. However, the ring is not exactly planar; the sulfur is slightly bent out of the four-carbon plane away from the metal.

Thiophene derivatives BT and DBT also form π-coordinated complexes. However, coordination occurs via the π-system of the benzene ring: $(\eta^6\text{-BT})Cr(CO)_3$,[29] $(\eta^6\text{-BT})RuCp^+$,[27] $(\eta^6\text{-BT})MCp^{*2+}$ (M = Rh, Ir),[27] $(\eta^6\text{-DBT})MCp^+$ (M = Fe, Ru).[30a,b]

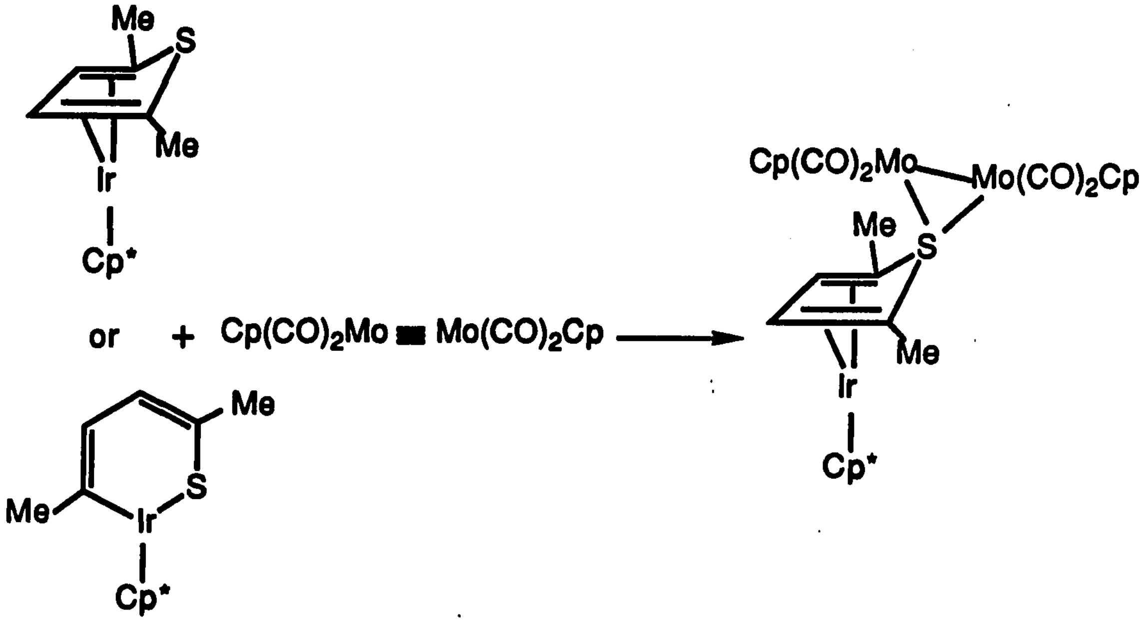
Bridging Thiophene Complexes

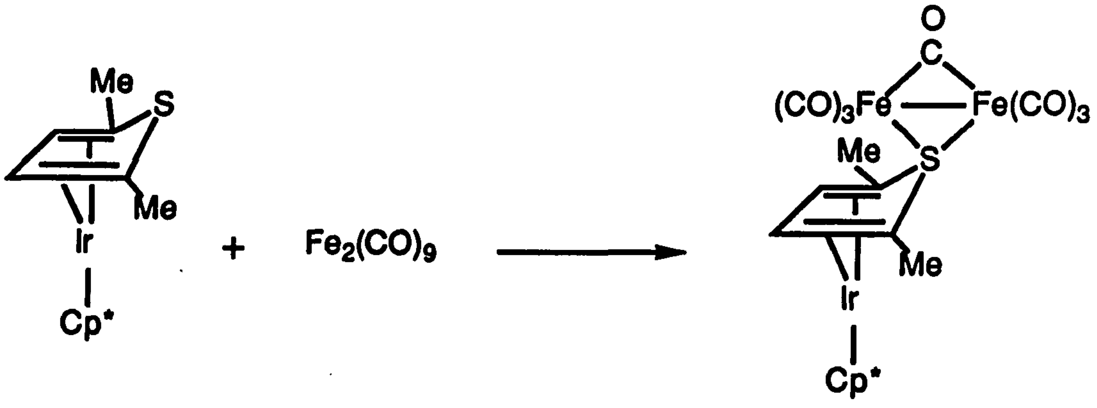
In contrast to that in η^5-thiophene, the unusually high basicity of the sulfur in η^4-thiophene complexes allows coordination with a second metal forming a bridging thiophene ligand. Reactions of $(\eta^4\text{-2,5-Me}_2T)IrCp^*$ with iron carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$) give $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-2,5-Me}_2T)Fe(CO)_4$[21b] in which thiophene is η^4-bound to Ir and S-bound to Fe.



Its structure is very similar to that of $Cp^*Ir(\eta^4\text{-2,5-Me}_2T)$[17b] and its BH_3 adduct.[17a] Thiophene can also bridge 3 metal centers in which there is η^4-coordination through the diene to one metal and S-coordination to two other metals. Two complexes $Cp^*Ir(\mu_3\text{-}\eta^4(S)\text{-2,5-Me}_2T)[Mo_2(CO)_4Cp_2]$[21a] and $Cp^*Ir(\mu_3\text{-}\eta^4(S)\text{-2,5-Me}_2T)$

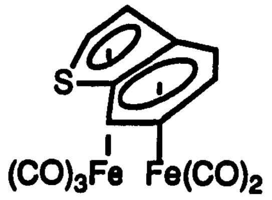
$[Fe_2(CO)_7]$[21b] were prepared from $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ by reaction with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ or iron carbonyls. The geometry around the four-coordinate sulfur ($4e^-$ donor) is approximately tetrahedral, and the M-M-S (M = Mo or Fe) plane is essentially perpendicular to the η^4-carbon plane. The basic structure of the thiophene in these complexes is very similar to that in the starting η^4-thiophene complex.

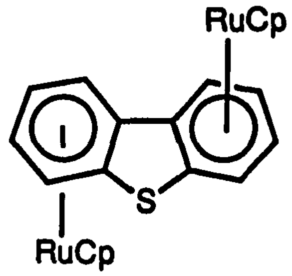




The sulfur atom of the hydrogenated thiophene, tetrahydrothiophene, has a much greater donor ability than that in thiophene. Like η^4-thiophene, tetrahydrothiophene bridges two metals: $[Cp(CO)_2Mo](\mu_2\text{-THT})[Cp(CO)_2Mo]^{31}$ and $Mn(CO)_4(\mu_2\text{-THT})Mn(CO)_4$.[32]

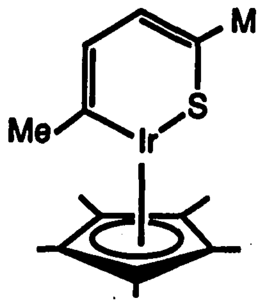
Only one complex has been proposed to have a structure in which BT acts as a bridging ligand. In $Fe_2(CO)_5BT$,[33] the $Fe(CO)_3$ and $Fe(CO)_2$ groups are suggested to be coordinated to both rings of the BT ligand. For the dibenzothiophene complexes, the crystal structures of $[(CpFe)(\mu_2\text{-}\eta^6,\eta^6\text{-DBT})(CpFe)]^{2+30a}$ and $CpRu(\mu_2\text{-}\eta^6,\eta^6\text{-DBT})CpRu^{30b}$ show that a planar DBT ligand is bonded on opposite sides by the two CpM units.





Ring-Opened Thiophene (Thiametallocycle) Complexes

The chemical reduction of $[Cp^*Ir(\eta^5\text{-}2,5\text{-}Me2T)]^{+2}$ gives not only $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ but also the ring-opened isomer, iridathiabenzene $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$,[17a] in which iridium inserts into a C-S bond of the η^4-thiophene. The ring-opened isomer is more stable than the η^4-isomer of $Cp^*Ir(2,5\text{-}Me_2T)$ and isomerization occurs by a basecatalyzed rearrangement. The structure of the ring-opened isomer consists of two planar rings which are perpendicular to each other. The cyclopentadienyl carbons of the Cp* ring lie in one plane, and the other plane is defined by Ir, S and the four carbons forming the six membered ring in which the π-system is delocalized. A related C-S cleavage of thiophene with Cp*Rh(PMe3)(Ph)H leads to the ring-opened thiametallacyclic compound Cp*(PMe3)Rh(C,S-T)[34] which is not a planar, delocalized ring; it is different than the Ir complex.



Another type of ring-opened thiophene complex is the thiaferrole. The reactions of thiophenes and benzo[b]thiophene with $Fe_3(CO)_{12}$ give thiaferrole[35,36] and benzothiaferrole[36] in which $Fe(CO)_3$ inserts into an S-C bond and another $Fe(CO)_3$ fragment coodinates the sulfur, the olefinic carbon-carbon bond and the iron of the S-C inserted $Fe(CO)_3$.

^{13}C NMR STUDIES OF DIFFERENT MODES OF THIOPHENE COORDINATION

Several studies have been reported[37] of thiophene adsorption on single-crystal surfaces using sulfur science techniques under ultrahigh vacuum. It would be desirable to study thiophene adsorption on supported catalyst which are used commercially. Modern solid stable NMR techniques allow one to study the orientation and structure of molecules adsorbed on the small metal particles in supported catalyst systems.[38] Solid state ^{13}C NMR should be an especially useful method for determining the initial adsorption modes of thiophene on heterogeneous catalysts. Thiophene ^{13}C chemical resonances are wide-spread depending on the nature of its coordination in organometallic compounds. Generally, the ^{13}C chemical shifts of $\eta^1(S)$-thiophene are shifted slightly downfield compared to free thiophene, but if carbon-carbon double bonds coordinate to the metal, the chemical shifts move upfield. The following table contains ^{13}C NMR data for the different coordination modes of thiophenes in transition metal complexes.

Mode	Free T	$\eta^1(S)$-T	η^4-T	η^5-T
ppm	124-140	120-140	15-90	80-120

Mode	Bridged T	Ring-Open T	Free BT	η^6-BT
ppm	50-90	120-183	121-141	80-150

Table 1. ^{13}C NMR data for the thiophene ring carbons in different thiophene coordination modes

Compound	Solvent	Chemical Shift(δ)	Reference
η^1(*S*)-Thiophene			
Re(T)Cp*(CO)$_2$	CDCl$_3$	138.9, 129.9	39
[Fe(T)Cp(CO)$_2$]BF$_4$	CD$_2$Cl$_2$	138.4, 134.4	9a
[Pd(η^3-2-MeC$_3$H$_4$)(TMT)$_2$](PF$_6$)	(CD$_3$)$_2$CO	128.7, 133.1	7
[Pd(TMT)$_2$Cl$_2$]	(CD$_3$)$_2$CO	119.1, 122.8	7
[Fe(BT)Cp(CO)$_2$]BF$_4$	CD$_2$Cl$_2$	143.1, 140.7, 132.9, 132.7, 129.8, 128.3, 127.2, 125.2	9a
[Fe(DBT)Cp(CO)$_2$]BF$_4$	CD$_3$NO$_2$	140.9, 138.8, 131.3, 130.8, 127.0, 124.9	9a
η^4-Thiophene			
Rh(TMT)Cp*	(CD$_3$)$_2$CO	42.9(C2,5), 88.4(C3,4)	18
Ir(2-MeT)Cp*	CDCl$_3$	14.2(C2), 67.1(C3), 65.9(C4), 30.1(C5)	17a
Ir(2,5-Me$_2$T)Cp*	CDCl$_3$	21.3(C2,5), 68.0(C3,4)	17a
Rh(TMTO)Cp*	(CD$_3$)$_2$CO	88.7, 75.5	20

Table 1. Continued

Compound	Solvent	Chemical Shift(δ)	Reference
η^5-Thiophene			
$Cr(TMT)(CO)_3$	$(CD_3)_2CO$	100.3, 100.7	7
$[Fe(TMT)Cp]PF_6$	CD_3CN	102.7, 95.9	25a
$[Fe(TMT)MeCp]PF_6$	CD_3CN	95.9, 95.7	25a
$Ru(TMT)(p\text{-}cymene)](PF_6)_2$	$(CD_3)_2CO$	107.9, 113.9	7
$[Ru(T)Cp]BF_4$	CD_2Cl_2	86.4, 79.1	25c
$[Ru(T)Cp]PF_6$	$(CD_3)_2CO$	87.1, 86.9	25c
$[Ru(2\text{-}MeT)Cp]BF_4$	$CDCl_3$	80.4(C2), 86.8, 86.2, 77.9(C3,4,5)	25e
$[Ru(3\text{-}MeT)Cp]BF_4$	$(CD_3)_2CO$	88.5, 79.7, 79.2 (C2,4,5), 69.1(C3)	25e
$[Ru(3\text{-}MeT)Cp^*]PF_6$	$(CD_3)_2CO$	78.5, 78.7(C2,5), 102.3(C3), 89.0(C4)	25f
$[Ru(2,5\text{-}Me_2T)Cp]BF_4$	$CDCl_3$	82.4(C2,5), 86.9(C3,4)	25e
$[Ru(TMT)_2](BF_4)_2$	$(CD_3)_2CO$	110.0, 107.7	28b
$[Ru(TMT)Cl_2]_2$	$CDCl_3$	92.1, 89.1	28b
$[Rh(TMT)(COD)]PF_6$	CD_2Cl_2	122.4, 103.5	7
$[Rh(TMT)(NBD)]PF_6$	$(CD_3)_2CO$	121.2, 103.2	7
$[Rh(2,5\text{-}Me_2T)(COD)]PF_6$	$(CD_3)_2CO$	108.2	7

Table 1. Continued

Compound	Solvent	Chemical Shift(δ)	Reference
$[Rh(T)Cp^*](PF_6)_2$	CD_3NO_2	107.1(C2,5), 110.3(C3,4)	27
$[Rh(TMT)Cp^*](PF_6)_2$	$(CD_3)_2CO$	118.6, 122.0	7
$[Ir(T)Cp^*](BF_4)_2$	CD_3NO_2	95.0(C2,5), 101.3(C3,4)	27
$[Ir(2,5\text{-}Me_2T)Cp^*](PF_6)$	$(CD_3)_2CO$	105.3	7
$[Ir(TMT)Cp^*](PF_6)_2$	$(CD_3)_2CO$	114.8, 107.3	7
η^6-Benzo[b]thiophene			
$[Ru(BT)Cp]BF_4$	$(CD_3)_2CO$	137.7(C2), 123.7(C3), 81.6(C4), 84.4(C5), 83.9(C6), 81.3(C7), 106.2(C8), 110.2(C9)	27
$[Ru(3\text{-}MeBT)Cp]PF_6$	$(CD_3)_2CO$	132.3(C2), 131.4(C3), 81.6(C4), 84.1(C5) 83.8(C6), 79.9(C7), 105.8(C8), 110.9(C9)	27
$[Rh(BT)Cp^*](PF_6)_2$	CD_3NO_2	147.7(C2), 122.4(C3), 103.3(C4), 103.6(C5), 102.4(C6), 102.6(C7), 122.4(C8), 126.4(C9)	27
$[Ir(BT)Cp^*](PF_6)_2$	CD_3NO_2	148.6(C2), 121.8(C3), 93.8(C4), 95.9(C5), 94.7(C6), 93.4(C7), 117.3(C8), 121.2(C9)	27
$[Ir(3\text{-}MeBT)Cp^*](BF_4)_2$	CD_3NO_2	141.8(C2), 131.6(C3), 94.0(C4), 95.5(C5) 94.6(C6), 91.8(C7), 116.7(C8), 121.3(C9)	27

Table 1. Continued

Compound	Solvent	Chemical Shift(δ)	Reference
$[Ir(2,3\text{-}Me_2BT)Cp^*](BF_4)_2$	CD_3NO_2	157.9(C2), 125.9(C3), 93.1(C4), 95.2(C5), 93.8(C6), 90.8(C7) 118.9(C8), 125.9(C9)	27
μ_2-Thiophene (Bridged)			
$ReCp^*(CO)_2(\mu_2\text{-}\eta^4(S)\text{-}T)$ $Fe(CO)_3$	$CDCl_3$	83.9, 57.1	39
$RhCp^*(\mu_2\text{-}\eta^4(S)\text{-}TMT)$ $Fe(CO)_4$	C_6D_6	90.3, 52.7	40
Ring-Opened Thiophene (Thiametallacycle)			
Ir(2-MeT)Cp*	$CDCl_3$	137.2(C2), 126.2(C3), 128.1(C4), 182.8(C5)	17a
Ir(2,5-MeT)Cp*	$CDCl_3$	140.8(C2), 125.7(C3), 132.3(C4), 181.0(C5)	17a
$Rh(T)Cp^*(PMe_3)$	C_6D_{12}	137.4, 126.5, 122.6, 122.4	34
$Rh(2\text{-}MeT)Cp^*(PMe_3)$	C_6D_{12}	137.5, 131.0, 129.0, 120.6	34
$Rh(2,5\text{-}Me_2T)Cp^*(PMe_3)$	C_6D_{12}	147.4, 129.2, 126.0, 120.4	34
$Fe_2(BT)(CO)_6$	CD_2Cl_2	173.5, 144.0, 131.1, 128.42, 128.38, 127.4 127.2, 95.6	36

Table 1. Continued

Compound	Solvent	Chemical Shift(δ)	Reference
Free Thiophene			
T	$(CD_3)_2CO$	125.6(C2,5) 127.3(C3,4)	41
2-MeT	$(CD_3)_2CO$	139.8(C2), 125.9(C3) 127.5(C4), 123.7(C5)	41
3-MeT	$(CD_3)_2CO$	121.3(C2), 138.2(C3) 130.1(C4), 126.1(C5)	41
2,5-Me_2T	$CDCl_3$	137.3(C2,5), 124.7(C3,4)	
Me_4T	$CDCl_3$	127.7, 132.9	7
BT	$CDCl_3$	126.2(C2), 123.8(C3), 123.6(C4), 124.1(C5), 124.2(C6), 122.4(C7), 139.6(C8), 139.7(C9)	42
2-MeBT	$CDCl_3$	140.8(C2), 121.6(C3), 122.5(C4), 124.0(C5), 123.3(C6), 122.0(C7), 140.8(C8), 139.7(C9)	42
3-MeBT	$CDCl_3$	121.4(C2), 132.0(C3), 121.6(C4), 123.7(C5), 124.0(C6), 122.7(C7), 139.6(C8), 140.2(C9)	42
2,3-Me2BT	$CDCl_3$	133.6(C2), 127.9(C3), 121.0(C4), 123.7(C5), 123.3(C6), 121.9(C7), 140.0(C8), 138.0(C9)	42
DBT	d_6-DMSO	121.9(C1,9), 124.6(C2,8) 127.0(C3,7), 122.9(C4,6) 138.5(C4a,4b) 134.9(C9a,9b)	43

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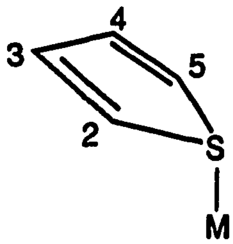
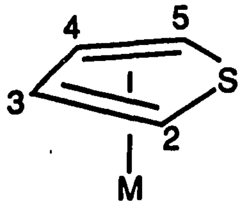
SECTION II. S-COORDINATED THIOPHENE AND DIBENZOTHIOPHENE IN Cp'(CO)$_2$Re(THIOPHENE) COMPLEXES[1]

INTRODUCTION

Thiophene and its derivatives, among the organosulfur compounds in petroleum, are the most difficult to desulfurize in the heterogeneous catalytic hydrodesulfurization (HDS) process.[2] In order to understand the mechanism(s) of HDS, it is important to know how thiophene adsorbs at metal sites on the catalyst surface. Thiophenes may coordinate through the sulfur and/or the unsaturated carbon-carbon double bonds. In its transition metal complexes, thiophene is known[3] to bind in various ways which involve the sulfur and unsaturated carbon-carbon bonds. Of these known thiophene coordination modes, the S- and η^5- bound forms are most often suggested for initial thiophene adsorption to catalyst surfaces.[4]



S-bound



η^5-bound

In a mechanism proposed in these Laboratories[4c,5] for the catalytic hydrodesulfurization (HDS) of thiophenes, the thiophene adsorbs via the entire π ring in the η5- mode.[6] Thiophenes coordinated in this manner in Mn and Ru complexes[7] are susceptible to attack by hydride sources, and this reactivity is the basis for the proposed HDS mechanism.[4c,5] Another mechanism[4a] assumes initial coordination of the thiophene through only the sulfur atom, and this coordination is presumed to activate the thiophene so as to give the H_2S and C_4 hydrocarbon products. However, in model complexes with S-bound thiophene (T) ligands such as $CpFe(CO)_2(T)^+$,[8] or even $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^{+2}$,[9] $[RuClL_2]BF_4$[10a] (L = 6-(2-thienyl)-2, 2'- bipyridine), and $Pd(\eta^3\text{-allyl})(L)^+$[10b] (L = 2,5,8-trithia[9](2,5)thiophenophane), where the thiophene is part of a chelate ligand, the thiophene is so weakly coordinated to the metal that all attempted reactions of the ligand have simply led to thiophene dissociation from the metal. Thus, there was no evidence that S-coordinated thiophene is activated to react until our preliminary report[11] of the reaction of $Cp^*Re(CO)_2(T)$ with $Fe_2(CO)_9$ to give the dinuclear thiophene-bridging complex, $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$. In this paper, we report the synthesis of a series of stable $Cp'(CO)_2Re(Th)$ (Cp'= C_5H_5 or C_5Me_5, Th = thiophene, 2-MeT, 3-MeT, 2,5-Me_2T, Me_4T, and dibenzothiophene (DBT)) and the X-ray structure determination of $Cp^*Re(CO)_2(T)$, which is the first structure of a simple non-chelated S-bound thiophene. Reactions of several of the $Cp'Re(CO)_2(Th)$ complexes with $Fe_2(CO)_9$ are also detailed.

EXPERIMENTAL

General Procedures

All reactions and reaction workups were carried out under an atmosphere of prepurified N_2 at room temperature using standard Schlenk techniques[12] unless otherwise stated. All solvents were reagent grade and dried following standard methods. Tetrahydrofuran (THF) was distilled under N_2 from Na/benzophenone. Hexanes and CH_2Cl_2 were distilled from CaH_2. The solvents were stored over 4 Å molecular sieves under N_2. The neutral alumina (Brockman, Activity I, 150 mesh) used for chromatography was deoxygenated at room temperature in high vacuum for 16 h and then deactivated with 5% w/w N_2-saturated water, shaken and stored under N_2.

The ^1H and ^{13}C NMR spectra were recorded on either a Nicolet NT-300 or a Varian VXR-300 spectrometer with $CDCl_3$ as the internal lock and internal reference (δ 7.25 for ^1H and δ 77.0 for ^{13}C). Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 instrument. Photochemical reactions (using a 450W mercury UV lamp) were carried out in a quartz tube which was maintained at -20 °C using a Lauda RK 20 constant temperature circulator. Infrared spectra were obtained on either a Digilab FTS-7 or a Nicolet 710 FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Thiophene was purified as previously described[7b] and 2-MeT, 3-MeT, 2,5-Me_2T, and dibenzothiophene (DBT) were purchased from Aldrich Chemicals and used without further purification. Me_4T was prepared by the literature method.[13] CpRe(CO)$_3$[14a] and Cp*Re(CO)$_3$[14b] were also prepared by reported methods.

Preparation of Cp*(CO)$_2$Re(T) (1)

A solution of Cp*(CO)$_2$Re(THF) was prepared by a modified literature method.[15] A solution of Cp*Re(CO)$_3$ (0.20 g, 0.49 mmol) in freshly distilled THF (30 mL) in a quartz photolysis tube equipped with a N$_2$ bubbler was irradiated with a mercury UV lamp (450W Canrad-Hanovia) for 3 h at -20 °C. An IR spectrum of the solution (ν(CO) 1890, 1820 cm^{-1}) showed a maximum conversion to the THF complex without too much subsequent decomposition.

This solution of Cp*(CO)$_2$Re(THF) was stirred with thiophene (5.0 mL, 62 mmol) at room temperature for 6-8 h, the progress of the reaction being monitored by IR spectroscopy. After removal of the solvent in vacuo, the residue was extracted with hexanes/CH$_2$Cl$_2$ (20:1). The extract was chromatographed on neutral alumina column (1 x 15 cm). After the unreacted Cp*Re(CO)$_3$ was eluted with hexanes, the yellow band containing the product was eluted with CH$_2$Cl$_2$/hexanes (1:4). The collected yellow band solution was concentrated under vacuum and slow cooling of the solution to -20 °C gave pale yellow crystals of 1 (0.098 g, 43%). IR (hexanes): ν(CO) 1934 (s), 1874 (s) cm^{-1}. EIMS(70 eV): m/e 462 (M$^+$), 404 (M$^+$-C$_2$H$_2$S), 376 (M$^+$-(C$_2$H$_2$S + CO)), 348 (M$^+$-(C$_2$H$_2$S + 2CO)), 84 (T$^+$), 58 (C$_2$H$_2$S$^+$). Anal. Calcd for C$_{16}$H$_{19}$O$_2$ReS: C, 41.63; H, 4.15. Found: C, 41.70; H, 4.14.

Preparation of Cp*(CO)$_2$Re(2-MeT) (2)

This compound was prepared from Cp*Re(CO)$_3$ (0.20 g, 0.49 mmol) and 2-MeT (1.0 mL, 10.3 mmol) using the same method as described for **1** giving pale yellow crystals (0.087 g, 37%). IR (hexanes) : υ(CO) 1932 (s), 1872 (s) cm^{-1}. EIMS (70 eV) m/e 476(M$^+$), 420 (M$^+$-2CO), 378 (M$^+$-MeT), 350 (M$^+$-(MeT+2CO)), 97 (MeT$^+$-H).

Preparation of Cp*(CO)$_2$Re(3-MeT) (3)

Compound **3** was prepared in the same manner as **1** using Cp*Re(CO)$_3$ (0.20 g, 0.49 mmol) and 3-MeT (1.0 mL, 10.3 mmol). Pale yellow crystals (0.082 g, 35%) of **3** were obtained. IR (hexanes) : υ(CO) 1931 (s), 1870 (s) cm^{-1}. EIMS (70eV) m/e 476 (M$^+$), 420(M$^+$-2CO), 378 (M$^+$-MeT), 350 (M$^+$-(MeT + CO)), 97 (MeT$^+$-H).

Preparation of Cp*(CO)$_2$Re(2,5-Me$_2$T) (4)

This synthesis proceeds as for **1** by using Cp*Re(CO)$_3$ (0.20 g, 0.49 mmol) and 2,5-Me$_2$T (3.0 mL, 26.3 mmol). Pale yellow crystals of **4** (0.085 g, 35%) were isolated. IR (hexanes) : υ(CO) 1929 (s), 1868 (s) cm^{-1}. EIMS(70 eV) m/e 490 (M$^+$), 434 (M$^+$-2CO), 378 (M$^+$-Me$_2$T), 350 (M$^+$- (Me$_2$T + CO)), 111(Me$_2$T$^+$-H). Anal Calcd for $C_{18}H_{23}O_2ReS$: C, 44.15; H, 4.73. Found : C, 44.29; H, 4.74.

Preparation of $Cp^*(CO)_2Re(Me_4T)$ (5)

This complex was prepared analogously to **1** from $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and Me_4T (0.5 mL, 3.5 mmol). Pale yellow crystals of **5** (0.053 g, 21%) were obtained. IR (hexanes) : υ(CO) 1926 (s), 1864 (s) cm^{-1}. EIMS (70 eV) m/e 518 (M^+), 462 (M^+-2CO), 378 (M^+-Me_4T), 350 (M^+-(Me_4T+CO)), 139(Me_4T^+-H).

Preparation of $Cp^*(CO)_2Re(DBT)$ (6)

Compound **6** was synthesized in the same manner as that for **1** using $Cp^*Re(CO)_3$ (0.25 g, 0.62 mmol) and DBT (0.85 g, 4.6 mmol). Pale yellow crystals of **6** (0.11 g, 32%) were obtained. IR (hexanes) : υ(CO) 1930 (s), 1869 (s) cm^{-1}. EIMS (70 eV) m/e 562 (M^+), 506 (M^+-2CO), 378 (M^+-DBT), 350 (M^+-(DBT + CO)), 184 (DBT^+). Anal. Calcd for $C_{24}H_{23}ReO_2S$: C, 51.32; H, 4.13. Found : C, 50.84; H, 4.09.

Preparation of $Cp(CO)_2Re(T)$ (7)

A THF solution (30 mL) of $CpRe(CO)_3$ (0.20 g, 0.60 mmol) was irradiated with a mercury UV lamp at -20 °C for 2 h until the concentration of $Cp(CO)_2Re(THF)$ was at a maximum as indicated by intensities of the υ(CO) bands at 1910 and 1837 cm^{-1}. Thiophene (4.0 mL, 50 mmol) was added and the solution was stirred at room temperature for 6-8 h. After chromatography and crystallization as described for **1**, pale yellow crystals of **7** (0.094 g, 40%) were obtained. IR (hexanes) : υ(CO) 1951 (s), 1888 (s) cm^{-1}. EIMS (15 eV) m/e 392 (M^+), 336 (M^+-2CO), 308 (M^+-T), 208 (M^+-(T + CO)), 84

(T^+). Anal. Calcd for $C_{11}H_9ReO_2S$: C, 33.75; H, 2.32. Found : C, 33.67; H, 2.31.

Preparation of Cp(CO)$_2$Re(2-MeT) (8)

This complex was prepared analogously to **7** from CpRe(CO)$_3$ (0.25 g, 0.75 mmol) and 2-MeT (1.0 mL, 10.3 mmol) to give pale yellow crystals (0.11 g, 36%) of **8**. IR (hexanes): υ(CO) 1949 (s), 1885 (s) cm^{-1}. EIMS (16 eV): m/e 406 (M^+), 350 (M^+-2CO), 308 (M^+-MeT), 280 (M^+-(MeT+CO)), 97 (MeT^+-H). Anal. Calcd for $C_{12}H_{11}ReO_2S$: C, 35.55; H, 2.73. Found : C, 35.69; H, 2.73.

Preparation of Cp(CO)$_2$Re(3-MeT) (9)

This synthesis proceeds as for **7** using CpRe(CO)$_3$ (0.20 g, 0.60 mmol) and 3-MeT (1.0 mL, 10.3 mmol). Pale yellow crystals of **9** (0.085 g, 35%) were isolated. IR (hexanes) : υ(CO) 1948 (s), 1885 (s) cm^{-1}. EIMS (16 eV) m/e 406 (M^+), 350 (M^+-2CO), 308 (M^+-MeT), 280 (M^+-(MeT + CO)), 98 (MeT^+). Anal. Calcd for $C_{12}H_{11}ReO_2S$: C, 35.55; H, 2.73. Found : C, 35.54; H, 2.77.

Preparation of Cp(CO)$_2$Re(2,5-Me$_2$T) (10)

Complex **10** was synthesized in the same manner as **7** using CpRe(CO)$_3$ (0.25 g, 0.75 mmol) and 2,5-Me$_2$T (2.0 mL, 17.6 mmol) to give the product (0.14 g, 45%). IR (hexanes); υ(CO) 1948 (s), 1886 (s) cm^{-1}. EIMS (16 eV) m/e 420 (M^+), 364 (M^+-2CO), 308 (M^+-Me$_2$T), 280 (M^+-(Me$_2$T + CO)), 111 (Me$_2$T$^+$-H).

Preparation of $Cp(CO)_2Re(Me_4T)$ (11)

This complex was prepared analogously to **7** from $CpRe(CO)_3$ (0.20 g, 0.60 mmol) and Me_4T (0.5 mL, 3.5 mmol). After chromatography and recrystallization as described above, pale yellow crystals of **11** (0.041 g, 15%) were obtained. IR (hexanes): ν(CO) 1942 (s), 1879 (s) cm^{-1}. EIMS (16 eV) m/e 448 (M^+), 392 (M^+-2CO), 308 (M^+-Me_4T), 139 (Me_4T^+-H).

Preparation of $Cp(CO)_2Re(DBT)$ (12)

The dibenzothiophene complex **12** was synthesized analogously to **7** from $CpRe(CO)_3$ (0.25 g, 0.75 mmol) and DBT (1.0 g, 5.4 mmol). The product **12** was isolated in 26% yield (0.095 g). IR (hexanes): ν(CO) 1945 (s), 1883 (s) cm^{-1}. EIMS (70 eV): m/e 492(M^+), 436(M^+-2CO), 308(M^+-DBT), 280(M^+-(DBT+CO)), 184(DBT^+). Anal. Calcd for $C_{19}H_{13}ReO_2S$: C, 46.42; H, 2.67. Found: C, 46.29; H, 2.80.

Reaction of 1 with $Fe_2(CO)_9$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (13)

To a solution of **1** (0.035 g, 0.076 mmol) in 15 mL of THF was added $Fe_2(CO)_9$ (0.10 g, 0.27 mmol). While the reaction mixture was stirred for 1.5 days, the solution color changed from orange-yellow to dark purple. After evaporating the solvent in vacuo, the residue was extracted with 20 mL of a hexanes/CH_2Cl_2 mixture (10:1). The extract was chromatographed over neutral alumina (1 x 10 cm) in CH_2Cl_2/hexanes (1:3) to give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (**13**) as a yellow band. The intractable red-purple band remained at the top of the column. Slow cooling of the concentrated yellow band solution to -20 °C gave air-stable, yellow crystals of **13** (0.027 g, 59%). IR (hexanes): υ(CO) 2064 (s), 2002 (s), 1988 (s), 1922(s), 1862 (s) cm^{-1}. CIMS (methane): m/e 603 (M^++H), 574 (M^+-CO), 546 (M^+-2CO), 519 (M^++H-3CO), 419 (M^++H-4CO), 462 (M^+-5CO). Anal. Calcd for $C_{19}H_{19}FeO_5ReS$: C, 37.94; H, 3.18. Found: C, 38.08; H, 3.16.

Reaction of 2 with $Fe_2(CO)_9$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}2\text{-}MeT)Fe(CO)_3$ (14)

This reaction proceeds as described for **13** using **2** (0.045 g, 0.095 mmol) and $Fe_2(CO)_9$ (0.10 g, 0.27 mmol). The product **14** was isolated as air-stable yellow crystals (0.032 g, 55%). IR (hexanes): υ(CO) 2056 (s), 1996 (s), 1987 (s), 1922(s), 1862 (s) cm^{-1}. CIMS (methane): m/e 617 (M^++H), 588 (M^+-CO), 560 (M^+-2CO), 533 (M^++H-3CO), 476 (M^++H-4CO).

Reaction of 3 with $Fe_2(CO)_9$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}3\text{-}MeT)Fe(CO)_3$ (15)

This reaction was performed as for **13** starting with **3** (0.050 g, 0.11 mmol) and $Fe_2(CO)_9$ (0.10 g, 0.27 mmol). Air-stable yellow crystals of **15** (0.036 g, 56%) were obtained. IR (hexanes): υ(CO) 2058(s), 1990(s), 1986(s), 1921(s), 1859(s) cm^{-1}. CIMS (methane): m/e 617 (M^++H), 588 (M^+-CO), 560 (M^+-2CO), 533 (M^++H-3CO), 477

(M$^+$+H-5CO). Anal. Calcd for $C_{20}H_{21}FeO_5ReS$: C, 39.03; H, 3.44. Found: C, 39.29; H, 3.41.

Reaction of 7 with $Fe_2(CO)_9$ To Give $Cp(CO)_2Re(\mu_2$-$\eta^4(S)$-T$)Fe(CO)_3$ (16)

This reaction was performed in the same manner as for **13** using **7** (0.040 g, 0.10 mmol) and $Fe_2(CO)_9$ (0.10 g, 0.27 mmol). Air-stable yellow crystals of **16** (0.031 g, 57%) were obtained. IR (hexanes): υ(CO) 2064(s), 2005(s), 1995(s), 1938(s), 1877(s) cm^{-1}. CIMS (methane): m/e 533 (M$^+$+H), 504 (M$^+$-CO), 476 (M$^+$-2CO), 449 (M$^+$+H-3CO). Anal. Calcd for $C_{14}H_9FeO_5ReS$: C, 31.65; H, 1.71. Found: C, 31.60; H, 1.63.

X-ray Structure Determination of 1 and 13

Single crystals of complexes **1** and **13** suitable for X-ray diffraction study were obtained by recrystallization from hexane solution at -80 °C. Single crystals of **1** and **13** were mounted on the end of a glass fiber. Pertinent data collection and reduction information for **1** and **13** are given in Table 1. The cell constants of both complexes were determined from a list of reflections found by an automated search routine. The empirical absorption corrections for both complexes were made on the basis of a series of psi scans. For **1**, the position of the Re and S atoms were given by direct methods.[16] The remainder of the non-hydrogen atoms were located in difference Fourier maps following least-squares refinement of the known atoms.

Hydrogen atoms were not included in the model. In the final cycles of refinement, all of the atoms were given anisotropic temperature factors;[17] the refinement included 181 variable parameters and converged with unweighted and weighted agreement factors of R = 0.0363 and R_w = 0.0461.

The structure of **13** was also solved by direct methods.[16] After the positions of the Re and Fe atoms were located, least-squares refinement and a different Fourier map indicated the positions of all of the remaining non-hydrogen atoms, all of which were refined with anisotropic thermal parameters in the final cycles.[17] Hydrogen atoms were not included in the calculations. The final cycle included 244 variable parameters and converged with unweighted and weighted agreement factors of R = 0.0263 and Rw = 0.0372. Selected bond distances and angles are presented in Tables 4 and 5, and ORTEP drawings of **1** and **13** are given in Figures 1 and 2, respectively. The final positional and thermal parameters are listed in Tables 6. and 7, respectively.

Table 1. Crystal and data collection parameters for Cp*(CO)$_2$Re(T) (**1**) and Cp*(CO)$_2$Re(μ_2-η^4(S)T)Fe(CO)$_3$ (**13**)

	1	**13**
Formula	$C_{16}H_{19}O_2ReS$	$C_{19}H_{19}FeO_5ReS$
Formula weight	461.60	601.47
Space Group	$P2_1/m$	$P2_1/c$
a, Å	9.388(2)	11.395(2)
b, Å	14.346(2)	13.310(1)
c, Å	12.601(3)	14.636(3)
β, deg	99.63(1)	109.151(8)
V, Å^3	1673.1(6)	2096.8(8)
Z	4	4
d_{calc}, g/cm^3	1.832	1.905
Crystal size, mm	0.20 x 0.35 x 0.50	0.10 x 0.30 x 0.30
$\mu(MoK_\alpha)$, cm^{-1}	74.8	66.59
Data collection instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	$MoK_\alpha(\lambda=0.71073Å)$	$MoK_\alpha(\lambda=0.71073Å)$
Orientation reflections, number, range (2θ)	25, 20° < 2θ < 32°	25, 21° < 2θ < 32°
Temperature, °C.	22(1)	22(1)
Scan method	θ-2θ	θ-2θ
Data col. range, 2θ, deg	4.0-50.0	4.0-50.0

Table 1. Continued

	1	**13**
Total unique reflections	3064	3684
Unique reflections observed ($F_o^2 > 3\sigma(F_o^2)$)	2099	2850
Number of parameters refined	181	244
Trans. factors, max., min. (psi-scans)	0.995, 0.557	0.993, 0.417
R^a	0.0363	0.0263
$R_w{}^b$	0.0461	0.0372
Quality-of-fit indicator[c]	1.142	0.964
Largest shift/esd, final cycle	0.01	0.01
Largest peak, e/Å^3	1.829	0.827

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

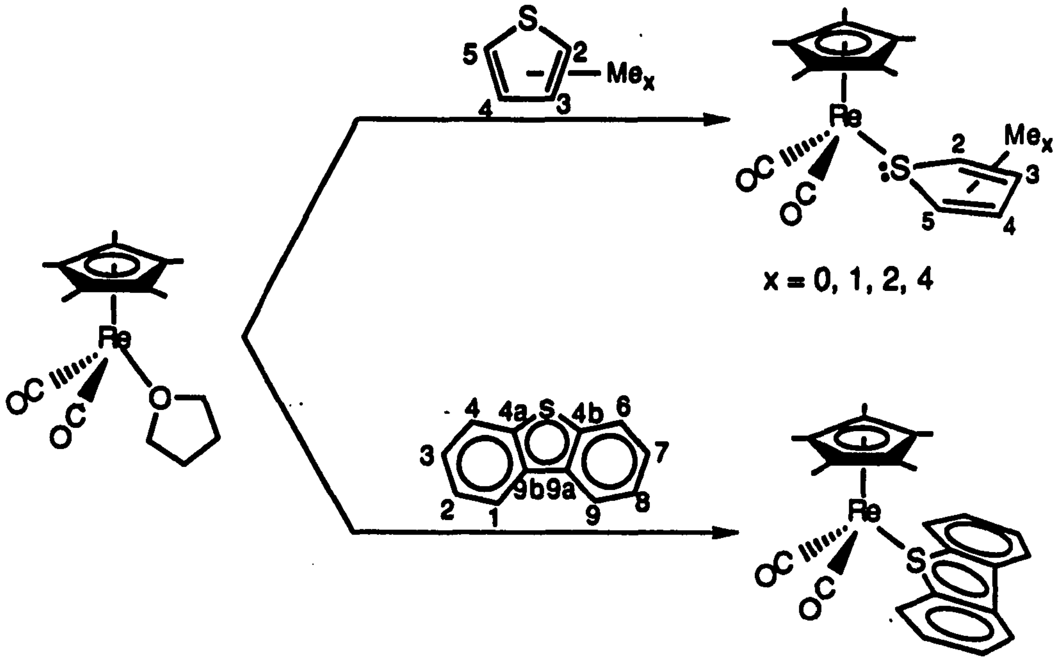
[b] $R_w = [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$; $\omega = 1/\sigma^2(|F_o|)$.

[c] Quality-of-fit $= [\Sigma\omega(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.

RESULTS AND DISCUSSION

Preparation of the S-Coordinated Thiophene Complexes

Substitution reactions of the weakly coordinated THF ligand in Cp'(CO)$_2$Re(THF) (Cp' = C_5H_5 or C_5Me_5) with excess thiophenes or dibenzothiophene give moderately air-stable S-bound thiophene complexes in 20-45% yield (eq 1).



(1)

The ^{1}H NMR chemical shifts of the thiophene protons in **1-12** are nearly the same (±0.2 ppm) as those of the free ligand (Table 2). Similar small changes were also observed for other S-bound thiophene complexes: Cp(CO)$_2$Fe(T)$^+$,[8] Cp(CO)$_2$Fe(2,5-Me$_2$T)$^+$,[18] Cp(CH$_3$CN)$_2$Fe(2,5-Me$_2$T)$^+$,[19] and Cp(CO)$_2$Fe(DBT)$^+$.[8a] If, on the other hand, the thiophenes in **1-12** were η^2-coordinated as in $(NH_3)_5Os(2,3\text{-}\eta^2\text{-}T)^{+}$[20] and the selenophene in $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}Sel)$,[21] the coordinated olefinic proton resonances would be expected to move to substantially higher field. Such upfield shifts are also well-known in η^2-bound olefins and arenes.[22]

The small (3-15 ppm) downfield ^{13}C NMR chemical shifts (Table 3) of the thiophene carbons in **1-12** as compared with those in the free thiophene also support sulfur coordination of the ligand. Similar small downfield ^{13}C NMR shifts were also observed for $Cp(CO)_2Fe(T)^+$ [8a] and $Cp(CO)_2Fe(DBT)^+$.[8a] The X-ray crystal study of **1** (Figure 1), which is discussed below, confirms the S-coordination of the thiophene.

Comparisons of the IR spectra of the Cp and Cp* analogs show the $\upsilon(CO)$ bands in the Cp* analogs to be about 15 cm^{-1} lower than those of the Cp complexes. The methyl groups of the Cp* ligand provide more electron density to the metal, thereby increasing π back bonding from the metal to the CO π^* orbitals and weakening the $C{\equiv}O$ bond thus accounting for the lower $\upsilon(CO)$ bands in the Cp* complexes. The electron-donating ability of methyl groups in the methyl-substituted thiophenes also adds more electron-density to the Re by enhancing the donor character of the thiophene sulfur. For example, in the Me_4T complexes, the $\upsilon(CO)$ bands (1926, 1864 cm^{-1} for Cp*; 1942, 1879 cm^{-1} for Cp) are about 8 cm^{-1} lower than those in the thiophene complexes (1934, 1874 cm^{-1} for Cp*; 1951, 1888 cm^{-1} for Cp). Methyl substitution in the thiophene ring also appears to

Table 2. ^{1}H NMR data (δ) for the complexes in CDCl$_3$

Complex	Thiophene	Cp* or Cp	other
Cp*(CO)$_2$Re(T) (1)	7.19(br. s, 2H), 7.11(br. s, 2H)	1.95(s, 15H)	
Cp*(CO)$_2$Re(2-MeT) (2)	6.98(br. m, 1H), 6.91(br. m, 1H) 6.86(br. m, 1H)	1.95(s, 15H)	2.28(s, 3H)
Cp*(CO)$_2$Re(3-MeT) (3)	7.10(br. m, 1H), 6.91(br. m, 1H), 6.74(br. m, 1H)	1.96(s, 15H)	2.25(s, 3H)
Cp*(CO)$_2$Re(2,5-Me$_2$T)(4)	6.63(s, 2H)	1.96(s, 15H)	2.22(s, 6H)
Cp*(CO)$_2$Re(Me$_4$T) (5)		1.95(s, 15H)	2.10(s, 6H), 1.99(s, 6H)
Cp*(CO)$_2$Re(DBT) (6)	8.01(m, 2H), 7.80(m, 2H), 7.50(m, 4H)	1.62(s, 15H)	
Cp(CO)$_2$Re(T) (7)	7.28(br. s, 2H), 7.03(br. s, 2H)	4.92(s, 5H)	
Cp(CO)$_2$Re(2-MeT) (8)	7.08(br. m, 1H), 6.83(br. m, 1H), 6.77(br. m, 1H)	4.92(s, 5H)	2.35(s, 3H)
Cp(CO)$_2$Re(3-MeT) (9)	7.19(br. m, 1H), 6.83(br. m, 2H)	4.92(s, 5H)	2.24(s, 3H)
Cp(CO)$_2$Re(2,5-Me$_2$T) (10)	6.56(s, 2H)	4.89(s, 5H)	2.28(s, 6H)
Cp(CO)$_2$Re(Me$_4$T) (11)		4.88(s, 5H)	2.17(s, 6H), 1.98(s, 6H)

Cp(CO)$_2$Re(DBT) **(12)**	8.00(m, 2H), 7.89(m, 2H), 7.51(m, 4H)	4.71(s, 5H)	
Cp*(CO)$_2$Re(μ_2-η^4(S)-T)Fe(CO)$_3$ **(13)**	5.95(m, 2H), 3.56(m, 2H)	1.98(s, 15H)	
Cp*(CO)$_2$Re(μ_2-η^4(S)-2-MeT)Fe(CO)$_3$ **(14)**	5.78(m, 1H), 5.39(m, 1H), 3.53(m, 1H)	1.99(s, 15H)	1.64(s, 3H)
Cp*(CO)$_2$Re(μ_2-η^4(S)-3-MeT)Fe(CO)$_3$ **(15)**	5.98(m, 1H), 3.59(m, 1H), 3.41(m, 1H)	1.98(s, 15H)	2.16(s, 3H)
Cp(CO)$_2$Re(μ_2-η^4(S)-T)Fe(CO)$_3$ **(16)**	5.97(m, 2H), 3.55(m, 2H)	4.94(s, 5H)	
T	7.48(m, H2,5), 7.14(m, H3,4)		
2-MeT	7.18(dd, H5), 6.88(dd, H4), 6.78(m, H3)		2.46(s)
3-MeT	7.34(dd, H5), 7.02(m, H2), 6.95(d, H4)		2.25(s)
2,5-Me$_2$T	6.54(s, H3,4)		2.37(s)
Me$_4$T			2.23(s), 1.92(s)
DBT	8.30(m, H1,9), 7.49(m, H2,8), 7.50(m, H3,7), 7.95(m, H4,6)		

Table 3. ^{13}C NMR data (δ) for the complexes in $CDCl_3$

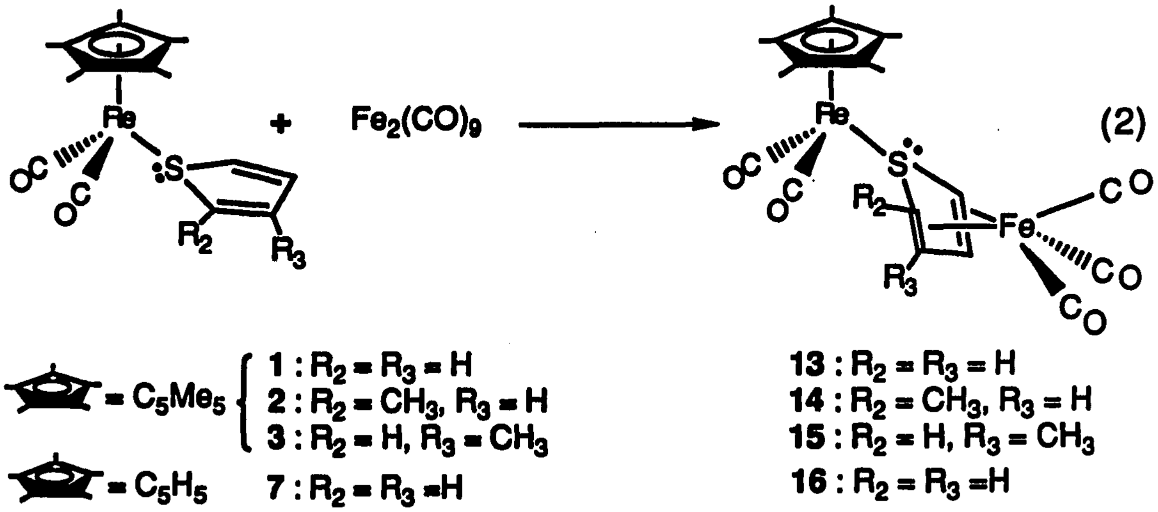
Complex	Thiophene	Cp* or Cp	CO	other
$Cp^*(CO)_2Re(T)$ (1)	138.9, 129.9	96.0, 10.5	205.2	
$Cp^*(CO)_2Re(2\text{-}MeT)$ (2)	150.8, 136.3, 129.3, 126.8	95.7, 10.3	205.2	13.3
$Cp^*(CO)_2Re(3\text{-}MeT)$ (3)	140.6, 139.6, 133.3, 132. 8	95.8, 10.5	205.4	16.1
$Cp^*(CO)_2Re(2,5\text{-}Me_2T)$ (4)	147.8, 126.6	95.4, 10.5	205.0	13.7
$Cp^*(CO)_2Re(Me_4T)$ (5)	138.6, 135.3	95.2, 10.5	205.5	13.6. 11.5
$Cp^*(CO)_2Re(DBT)$ (6)	145.4, 137.1, 127.6, 127.3, 124.4, 121.6	96.0, 10.2	205.7	
$Cp(CO)_2Re(T)$ (7)	143.9, 129.0	82.4	201.2	
$Cp(CO)_2Re(2\text{-}MeT)$ (8)	155.9, 141.0, 128.5, 125.6	82.5	201.4	13.8
$Cp(CO)_2Re(3\text{-}MeT)$ (9)	144.0, 139.7, 137.6, 132.0	82.4	201.5	16.2
$Cp(CO)_2Re(2,5\text{-}Me_2T)$ (10)	152.5, 125.2	82.7	201.4	14.3
$Cp(CO)_2Re(Me_4T)$ (11)	142.1, 134.7	82.7	201.9	13.6, 12.1
$Cp(CO)_2Re(DBT)$ (12)	149.3, 135.5, 128.0, 127.7, 124.9, 121.9	83.6	202.0	

Cp*(CO)$_2$Re(μ_2-η^4(*S*)-T)Fe(CO)$_3$ (**13**)	83.9, 57.1	95.5, 10.5	208.5, 207.0	
Cp*(CO)$_2$Re(μ_2-η^4(*S*)-2-MeT)Fe(CO)$_3$ (**14**)	85.9, 83.8, 75.1, 56.0	95.6, 10.6	209.5, 206.9 206.4	16.1
Cp*(CO)$_2$Re(μ_2-η^4(*S*)-3-MeT)Fe(CO)$_3$ (**15**)	104.2, 85.0, 61.4, 54.5	95.5, 10.5	208.7, 206.9	15.5
Cp(CO)$_2$Re(μ_2-η^4(*S*)-T)Fe(CO)$_3$ (**16**)	83.7, 57.3	82.7	208.0, 202.6	
T	127.3(C3,4), 125.6(C2,5)			
2-MeT	139.8(C2), 125.9(C3), 127.5(C4), 123.7(C5)			14.9
3-MeT	121.3(C2), 138.2(C3), 130.1(C4), 126.1(C5)			15.5
2,5-Me$_2$T	137.3(C2,5), 124.7(C3,4)			15.1
Me$_4$T	133.0(C2,5), 127.7(C3,4)			13.0 12.7
DBT	121.9(C1,9), 124.6(C2,8), 127.0(C3,7), 122.9(C4,6), 138.5(C4a,4b), 134.9(C9a,9b)			

strengthen the Re-S bond as indicated by kinetic studies of thiophene substitution by PPh_3 in the reaction, $Cp'(CO)_2Re(Th) + PPh_3 \rightarrow Cp'(CO)_2Re(PPh_3) + Th$.[23] Rate constants ($10^7 k_1$, s^{-1}) for thiophene dissociation from $Cp(CO)_2Re(Th)$ in this reaction decrease with increasing methyl substitution: T (3,000) > 3-MeT (1,200) > 2-MeT (91) > 2,5-Me_2T (13) > Me_4T (2.7). It has been generally assumed that methyl groups in the 2- and 5- positions (α to the S) sterically hinder S-coordination to the metal. However, this assumption was based on a coordination geometry in which the metal atom lies in the plane of the thiophene. The crystal structure of **1** (discussed in detail later) shows that Re lies out of the thiophene plane and the sulfur has a trigonal pyramidal geometry. Therefore, methyl groups in the 2,5-positions pose much less of a steric problem than supposed, but their electronic effect does enhance S-coordination of methyl-substituted thiophenes to the metal.

Reactions of $Cp'(CO)_2Re(Th)$ With $Fe_2(CO)_9$

Reactions of S-bound thiophene complexes **1**, **2**, **3** and **7** with $Fe_2(CO)_9$ in THF at room temperature give the thiophene-bridged dinuclear complexes **13**, **14**, **15** and **16**, respectively (55-60% yield, eq 2).



(2)

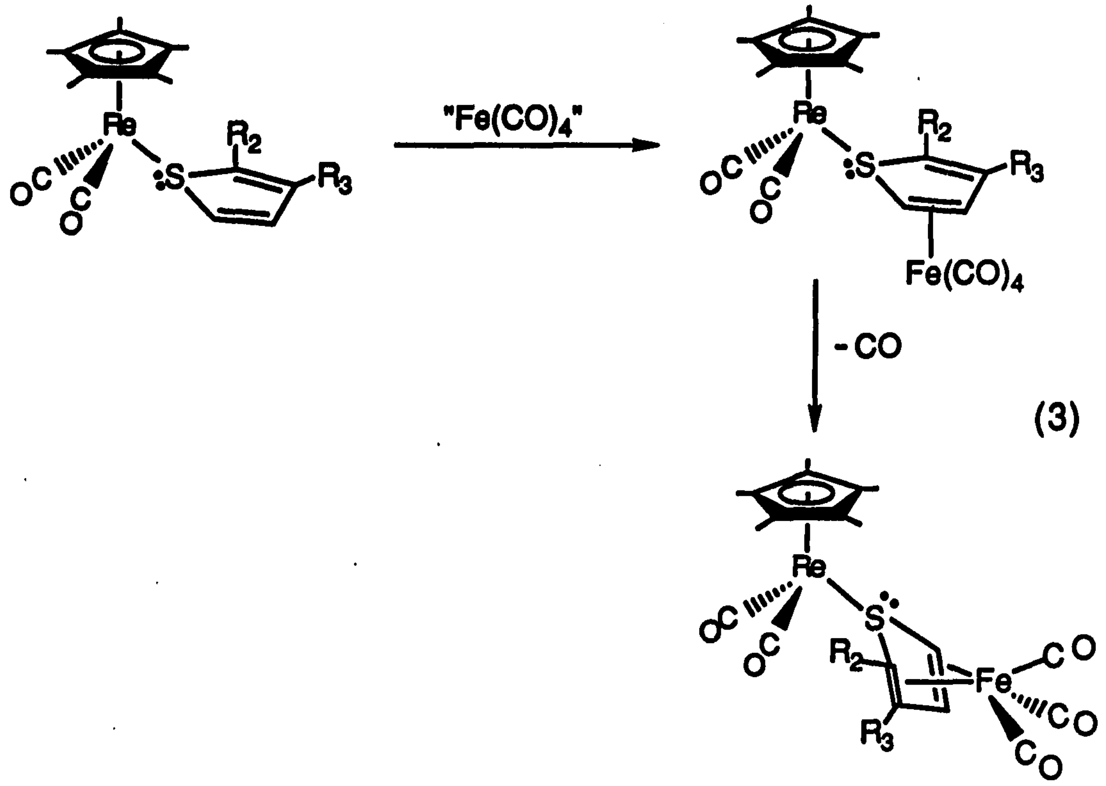
$= C_5Me_5$ $\left\{ \begin{array}{l} 1 : R_2 = R_3 = H \\ 2 : R_2 = CH_3, R_3 = H \\ 3 : R_2 = H, R_3 = CH_3 \end{array} \right.$

$= C_5H_5$ $7 : R_2 = R_3 = H$

$13 : R_2 = R_3 = H$
$14 : R_2 = CH_3, R_3 = H$
$15 : R_2 = H, R_3 = CH_3$
$16 : R_2 = R_3 = H$

Complex **13** was identified by its elemental analysis, IR, MS (Experimental Section) and ^1H and ^{13}C NMR (Table 2,3) spectra. The ^1H NMR spectrum of **13** shows two multiplets for the thiophene protons (5.95, 3.56 ppm) which are far upfield compared to those in **1** (7.19, 7.11 ppm). In the ^{13}C NMR spectrum, the two signals (83.9, 57.1 ppm) for the ring carbon atoms in **13** are shifted upfield by 50-70 ppm from those in **1** (138.9, 129.9 ppm) and those in free thiophene (127.3, 125.6 ppm). This characteristic upfield ^{13}C NMR shift is also well known in η^4-diene complexes.[24] The ^1H and ^{13}C NMR spectra of complexes **14**, **15**, **16** show similar upfield shifts of the thiophene ^1H and ^{13}C signals indicating the same type of μ_2-η^4(S)- bonding in these complexes.

While the reactions of complexes **2**, **3** and **7** with $Fe_2(CO)_9$ yield the thiophene-bridged complexes **14**, **15** and **16**, the α,α'-dimethyl-substituted thiophene (2,5-Me_2T and Me_4T) complexes **4**, **5** do not react with $Fe_2(CO)_9$ under the same conditions. This difference



in reactivity can be explained by assuming that the reaction (eq 2) occurs in two steps (eq 3). The first presumably involves η^2-coordination of $Fe(CO)_4$ to the diene part of the ring; subsequent loss of CO leads to η^4-coordination of the diene system. In **4** and **5**, the steric and electron-donating properties of the α-methyl groups at both double bonds in the thiophene would inhibit formation of the η^2-intermediate. In the $Cp'(CO)_2Re(Th)$ complexes which react with $Fe_2(CO)_9$, one of the thiophene double bonds does not contain a methyl group and therefore forms an η^2-complex. While this step-by-step mechanism (eq 3) accounts for the reactivity pattern, it is possible that the reaction (eq 2) proceeds by a concerted mechanism in which all four diene carbons coordinate to iron simultaneously. In this case two or more methyl groups must deactivate the diene to the extent that complexes **4** and **5** do not react.

Although thiophene reacts with $Fe_2(CO)_9$ to give thiaferroles and ferroles under vigorous conditions,[25] it does not react with $Fe_2(CO)_9$ in THF-d_8 at room temperature for 24 h as dtermined by 1H NMR spectrometry. Therefore, it appears that S-coordination in these complexes disrupts the aromaticity of the thiophene ligand in a way that allows the diene section of it to react with $Fe_2(CO)_9$.

Complexation of $Fe(CO)_3$ to the diene significantly affects the rhenium center in the thiophene-bridged complexes. This is evident in the ν(CO) values for the $Cp^*(CO)_2Re$ group in **13** (1922, 1862 cm^{-1}) which are lower than those in **1** (1934, 1874 cm^{-1}), implying that the sulfur atom in the $(\eta^4\text{-T})Fe(CO)_3$ ligand is a better donor to Re than thiophene itself. This is consistent with previous observations that the sulfur of the η^4-thiophene in $Cp^*Ir(\eta^4\text{-2,5-}Me_2T)$ is an unusually strong donor as indicated by its reactions with Lewis acids (BH_3, R^+),[26] or metal complexes,[27] to form sulfur adducts.

Comparison of the Structures of $Cp^*(CO)_2Re(T)$ (1) and $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-T})Fe(CO)_3$ (13)

The structure of **1** (Fig. 1) shows that the coordinated thiophene sulfur has a trigonal pyramidal geometry (i.e., is roughly sp^3 hybridized). The Re-S distance of 2.360(3) Å is somewhat shorter than those (2.396(4), 2.425(5), 2.400(5) Å) in $ReBr_3(tetrahydrothiophene)_3$[28]

and significantly shorter than that (2.480(2) Å) in $Re(S_2CNEt_2)_3(CO)$.[29] The Re lies out of the thiophene plane such that the angle between the Re-S vector and the vector from S to the midpoint of the (C3)-(C4) bond is 140.4°, which is somewhat larger than that in $(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)^+$ (126°),[9] and those in the S-coordinated DBT of $[RuCl_2\{P(4\text{-}MeC_6H_4)_2(SC_{12}H_7)\}_2]$ (131°)[30] and $Cp(CO)_2Fe(DBT)^+$ (119.4 °).[8a] The thiophene ring is planar within experimental error; the dihedral angle between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes is 6.1(±4.5°). The C(2)-S and C(5)-S bond the distances and angles within the thiophene ring are essentially the same within experimental error as those in $(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)^{+}$[9] and free thiophene.[31]

In the structure of **13** (Figure 2),[11] the bridging thiophene ligand that is coordinated to the Re atom via sulfur and to the Fe through the four carbons of the diene system, is no longer planar. The thiophene ring is folded with an angle of 143.1(4)° between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes. This angle is very similar to those in other η^4-thiophene complexes such as $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-}2,5\text{-}Me_2T)Fe(CO)_4$ (142.1(4)°)[27b] and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (138°).[32] The Re-S distance (2.330(1) Å) is 0.03 Å shorter than that (2.360(1) Å) in **1**, which is consistent with the sulfur being a better donor in **13** as in the discussion of the υ(CO) frequencies. The sulfur in **13** is pyramidal as indicated by the angle (125°) between the Re-S vector and the vector from S to the midpoint of the line from C(2) to C(5). The longer distances for C(2)-C(3) (1.458(8) Å) and C(4)-C(5) (1.427(8) Å) as

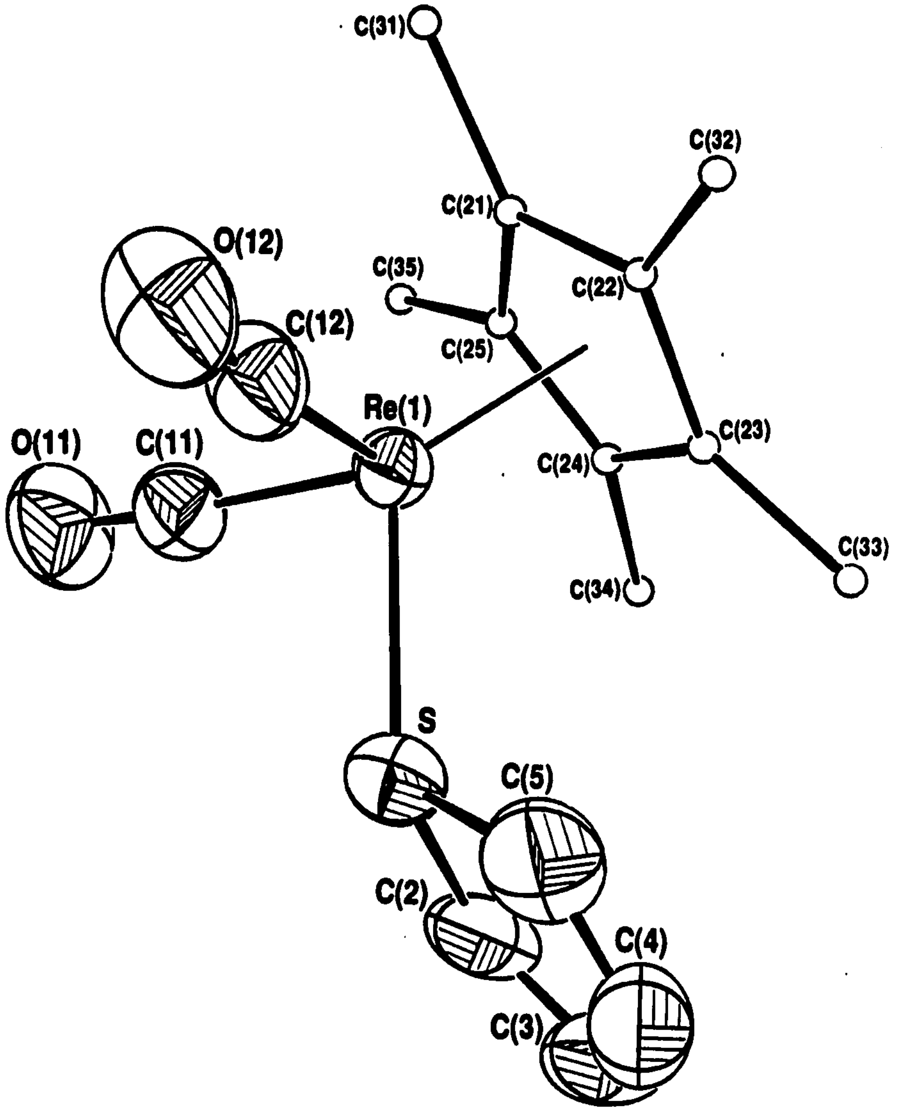


Figure 1. ORTEP drawing of Cp*(CO)$_2$Re(T) (1)

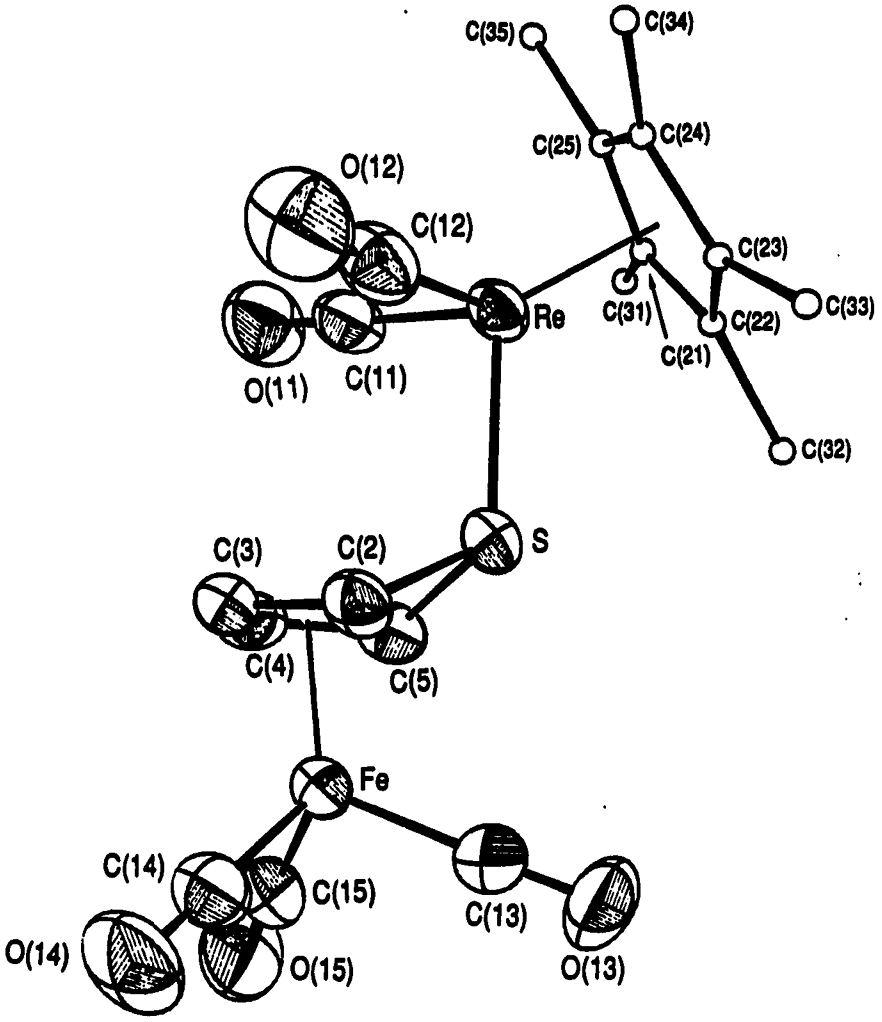


Figure 2. ORTEP drawing of Cp*(CO)$_2$Re(μ_2-η^1(*S*)-T)Fe(CO)$_3$ (**13**)

Table 4. Bond distances (Å)[a] for **1** and **13**

	1	**13**
Re - S	2.360(3)	2.330(1)
Re - C(11)	1.86(1)	1.883(6)
Re - C(12)	1.90(1)	1.884(7)
Re - C(21)	2.227(9)	2.307(7)
Re - C(22)	2.275(9)	2.296(6)
Re - C(23)	2.313(8)	2.281(7)
Re - C(24)	2.290(8)	2.266(8)
Re - C(25)	2.249(8)	2.255(7)
Fe - C(2)		2.086(6)
Fe - C(3)		2.044(6)
Fe - C(4)		2.048(6)
Fe - C(5)		2.099(6)
Fe - C(11)		1.769(8)
Fe - C(12)		1.789(7)
Fe - C(13)		1.798(6)
S - C(2)	1.72(1)	1.807(6)
S - C(5)	1.73(1)	1.802(5)
O(11)- C(11)	1.16(1)	1.157(9)

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4. Continued

	1	13
O(12) - C(12)	1.13(1)	1.131(8)
O(13) - C(13)		1.143(7)
O(14) - C(14)		1.149(9)
O(15) - C(15)		1.159(7)
C(2) - C(3)	1.40(2)	1.454(8)
C(3) - C(4)	1.37(2)	1.379(9)
C(4) - C(5)	1.36(2)	1.427(8)
C(21) - C(22)	1.44(1)	1.36(1)
C(22) - C(23)	1.48(1)	1.44(1)
C(23) - C(24)	1.42(1)	1.44(1)
C(24) - C(25)	1.37(1)	1.39(1)
C(25) - C(21)	1.33(1)	1.35(1)
C(21) - C(31)	1.56(2)	1.55(1)
C(22) - C(32)	1.50(2)	1.58(1)
C(23) - C(33)	1.52(2)	1.53(1)
C(24) - C(34)	1.55(1)	1.48(1)
C(25) - C(35)	1.57(2)	1.53(1)

Table 5. Selected bond angles (deg)[a] for **1** and **13**

	1	**13**
C(2) - S - C(5)	92.8(7)	82.3(3)
C(13)-Fe-C(14)		99.0(3)
C(13)-Fe-C(15)		100.9(3)
C(14)-Fe-C(15)		91.4(3)
S - Re-C(11)	90.6(3)	93.0(2)
S - Re-C(12)	91.9(4)	93.4(2)
C(2)- C(3)-C(4)	115(1)	110.1(5)
C(3)- C(4)-C(5)	113(1)	110.4(5)
C(11)-Re-C(12)	90.9(5)	87.5(3)
S - C(2)-C(3)	108(1)	
S - C(5)-C(4)	111(1)	

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 6 Positional parameters and thermal parameters for Cp*(CO)$_2$Re(T) (1)

atom	x	y	z	B,^{a}(Å^2)
Re	0.13294(3)	0.76499(2)	0.98548(3)	4.140(7)
S	0.1175(3)	0.8348(2)	0.8142(2)	6.19(6)
O(11)	-0.1423(8)	0.8562(8)	1.0262(7)	9.7(3)
O(12)	-0.0264(1)	0.5900(5)	0.8988(9)	11.1(3)
C(2)	0.180(1)	0.9468(8)	0.8033(9)	8.7(3)
C(3)	0.264(1)	0.948(1)	0.721(1)	10.3(4)
C(4)	0.280(1)	0.863(1)	0.675(1)	10.6(4)
C(5)	0.216(1)	0.792(1)	0.7208(9)	8.4(3)
C(11)	-0.040(1)	0.8208(7)	1.0040(9)	6.4(3)
C(12)	0.033(1)	0.6572(7)	0.9257(9)	7.1(3)
C(21)	0.243(1)	0.7052(6)	1.1410(7)	5.4(2)
C(22)	0.334(1)	0.6855(6)	1.0621(9)	6.8(2)
C(23)	0.3813(9)	0.7782(8)	1.0293(7)	5.7(2)
C(24)	0.3167(9)	0.8433(6)	1.0913(7)	4.9(2)
C(25)	0.237(1)	0.7966(7)	1.1559(7)	5.3(2)
C(31)	0.183(1)	0.6272(9)	1.209(1)	11.6(4)
C(32)	0.380(2)	0.592(1)	1.027(1)	19.2(5)
C(33)	0.480(1)	0.800(1)	0.949(1)	13.0(5)
C(34)	0.346(1)	0.9497(7)	1.094(1)	9.1(4)
C(35)	0.159(1)	0.848(1)	1.240(1)	10.7(4)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 7. Positional parameters and thermal parameters for $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (**13**)

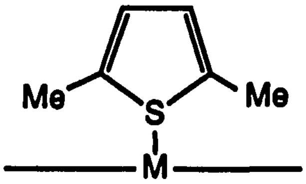
atom	x	y	z	B,[a](Å^2)
Re	0.65116(2)	0.07815(2)	0.29328(1)	3.147(4)
Fe	0.90291(7)	-0.09640(5)	0.11649(5)	3.23(2)
S	0.7671(1)	-0.0432(1)	0.24607(8)	3.39(3)
O(11)	0.7814(5)	0.2532(3)	0.2335(3)	6.4(1)
O(12)	0.4522(6)	0.4070(5)	0.5965(4)	8.2(2)
O(13)	0.9175(5)	-0.2837(3)	0.2264(4)	6.5(1)
O(14)	0.8441(5)	-0.1788(4)	-0.0782(3)	7.6(1)
O(15)	1.1624(5)	-0.0660(4)	0.1305(4)	7.0(1)
C(2)	0.9084(5)	0.0013(4)	0.2293(4)	3.6(1)
C(3)	0.8775(5)	0.0529(4)	0.1368(4)	3.8(1)
C(4)	0.7702(5)	0.0133(4)	0.0726(3)	3.3(1)
C(5)	0.7229(5)	-0.0648(4)	0.1177(3)	3.4(1)
C(11)	0.7326(5)	0.1850(4)	0.2548(4)	4.1(1)
C(12)	0.5297(6)	0.0850(5)	0.1698(4)	4.9(2)
C(13)	0.9129(5)	-0.2111(4)	0.1836(4)	4.3(1)
C(14)	0.8650(6)	-0.1482(4)	-0.0025(4)	4.5(1)
C(15)	1.0598(6)	-0.0800(4)	0.1240(4)	4.4(1)
C(21)	0.2869(6)	0.6114(6)	0.0431(4)	5.5(2)
C(22)	0.2980(6)	0.5099(6)	0.0547(4)	5.7(1)
C(23)	0.4255(7)	0.4852(5)	0.1081(4)	7.1(2)
C(24)	0.4896(6)	0.5801(7)	0.1276(5)	7.7(3)
C(25)	0.3999(7)	0.6526(5)	0.0866(4)	6.4(2)
C(31)	0.167(1)	0.6687(9)	-0.0152(6)	11.6(3)
C(32)	0.187(1)	0.4349(8)	0.0082(7)	14.3(3)
C(33)	0.479(1)	0.3792(8)	0.1286(7)	18.7(3)
C(34)	0.6250(9)	0.591(2)	0.1762(7)	21(1)
C(35)	0.433(1)	0.7641(7)	0.0859(7)	16.9(3)

[a] See Table 6 for footnote.

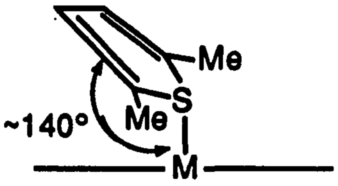
compared to that for C(3)-C(4) (1.379(9) Å) are often found in η^4-1,3-diene complexes[33]; this pattern of C-C bond distances is just the opposite of that in free thiophene, where C(2)-C(3) and C(4)-C(5) are shorter (1.37 Å) than C(3)-C(4) (1.42 Å).[31] The C(2)-S and C(5)-S distances (1.807(6), 1.802(5) Å) are substantially longer than the corresponding distances (1.72(1), 1.73(1) Å) in **1** and free thiophene (1.74(1) Å)[31] and somewhat shorter than those in $CpV(CO)_3(THT)$ (1.84(1) Å)[34] and $RhCl_3(THT)_3$ (1.823(1) Å).[35] The C(2)-S-C(5) angle (82.3 °) is more acute than in **1** (92.8(8)°) and in free thiophene (92.2(1)°).[31] In general, the geometry (the fold at the C(2)-C(5) line, the elongated C-S bonds, and the small C(2)-S-C(5) angle) of the thiophene in **13** is different from that of free thiophene and the S-coordinated thiophene in **1** but is very similar to that of the η^4-ligands in $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$[32], $Cp^*Rh(\eta^4\text{-}Me_4T)$,[36] $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-}2,5\text{-}Me_2T)Fe(CO)_4$,[27b] $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-}2,5\text{-}Me_2T)[Mo_2(CO)_4Cp_2]$,[36] $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-}2,5\text{-}Me_2T)[Fe_2(CO)_7]$,[27b] and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T{\cdot}BH_3)$[37] in which the BH_3 is coordinated to the sulfur.

Comments on the Mode of Thiophene Adsorption on HDS Catalysts

Of the various modes that have been proposed for thiophene adsorption on HDS catalysts, S-coordination is one of the earliest and most widely suggested. It had generally been assumed that S-bound thiophene would be perpendicularly bonded to the surface (**A** below) and α-methyl groups would sterically weaken S-thiophene coordination. However, it is now[3,8a,9,10] known that the metal does not lie in the thiophene plane and the sulfur is trigonal pyramidal (**B**), as shown in the crystal structure of **1**. This bent arrangement at the



A

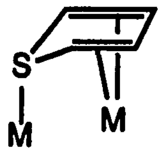


B

sulfur greatly reduces α-methyl steric interactions. Indeed there is evidence to suggest that α-methyl groups actually strengthen the thiophene coordination to a metal center.[23]

Several studies of thiophene adsorbed on single-crystal surfaces have been reported: on clean Ni(100),[38a] Pt(111),[38b] Cu(100),[38c] and Cu(111),[38d] and on clean and sulfided Mo(100),[38e,f] Mo(110),[38g] W(211),[38h] Ni(111),[38i] and Re(0001).[38j] The results indicate that, depending on the metal, thiophene surface coverage, and temperature, the thiophene may be S-bonded perpendicular to the surface, S-bonded but tilted at an angle of ~40° with respect to the surface, or η^5-bonded parallel to the surface.

Although there is much evidence to support $\eta5$-coordination and activation of thiophene in organometallic complexes and on catalysts,[5] there is no evidence to indicate that S-bound thiophene is activated to undergo reactions which results in C-S bond cleavage. Perhaps a major reason for this lack of reactivity is the generally weak and labile bonding of S-coordinated thiophene in its transition metal complexes, which has led to its ready displacement from metal centers by potential reactants. In the Cp'(CO)$_2$Re(Th) series of complexes, however, the thiophene (Th) ligands are not labile and react with Fe$_2$(CO)$_9$ according to eq 2. In fact, the S-coordination activates thiophene to react with "Fe(CO)$_3$", since thiophene itself does not react with Fe$_2$(CO)$_9$ under very similar conditions. Therefore, it seems possible that on an HDS catalyst, initial adsorption of thiophene through the sulfur atom to a single metal site would activate the diene system to coordinate to an adjacent metal as suggested in structure **C**.



C

As seen in structure **13**, a thiophene coordinated to two metal centers loses its aromatic character and the C-S bonds lengthen. These weakened C-S bonds are perhaps susceptible to cleavage and hydrogenation, although there is no précedent for such reactions at the present time.

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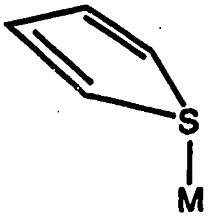
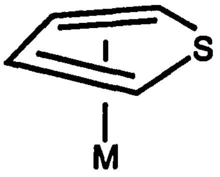
SECTION III. KINETIC STUDIES OF PPh_3 SUBSTITUTION OF S-COORDINATED THIOPHENES IN $Cp'(CO)_2Re(Th)$: A MODEL FOR THIOPHENE ADSORPTION ON HYDRODESULFURIZATION CATALYSTS[1]

INTRODUCTION

A point of central importance to the mechanism(s) of thiophene hydrodesulfurization (HDS) on heterogeneous catalysts is the mode of thiophene(T) adsorption and activation on a metal site.[2] Of the several known modes of thiophene coordination in transition metal complexes,[3] the S- and η^5-bound forms are most often suggested for thiophene adsorption to catalyst surfaces. While there is much evidence to support η^5-coordination and activation of thiophene in organometallic complexes and on catalysts,[4-6] there is little such evidence for the S-bonded form. This arises from the weak donor ability of the thiophene sulfur atom. Thus, in the only known S-bound thiophene complexes, $Ru(NH_3)_5(T)^{2+}$,[7] $CpFe(CO)_2(T)^+$,[8] $CpFe(NCMe)_2(2,5\text{-}Me_2T)^+$,[9] $W(CO)_3(PCy_3)_2(T)$,[10] and $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$ in which thiophene is part of a chelate ligand,[11] the thiophene is very weakly coordinated and easily displaced. This suggests that it would also be weakly coordinated to a metal site on a catalyst. However, recently we reported[12] a stable S-



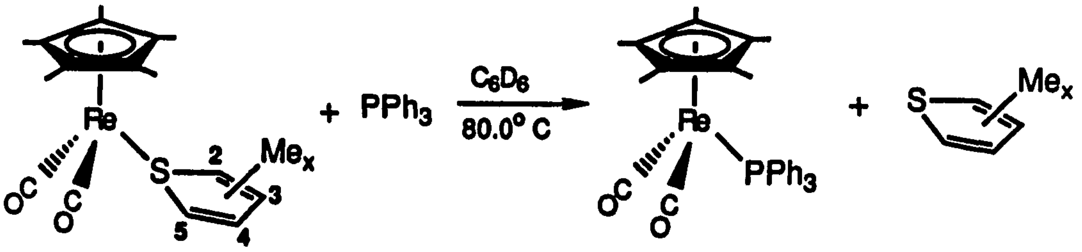
S-bound



η^5-bound

bound thiophene complex Cp*(CO)$_2$Re(T) and showed that the diene portion of the thiophene is activated to bind to Fe(CO)$_3$ giving a dinuclear complex Cp*(CO)$_2$Re(μ_2-η^4(S)-T)Fe(CO)$_3$, in which the thiophene is S-bound to the Re and η^4-bound through the four carbons to the Fe(CO)$_3$.

In addition to Cp*(CO)$_2$Re(T), we have prepared[13] a series of Cp*(CO)$_2$Re(Th) and Cp(CO)$_2$Re(Th) complexes, where Th is thiophene, a methyl-substituted thiophene, or dibenzothiophene. These complexes allow us to compare the reactivity of these different S-bound thiophenes. In this paper, we report studies of the mechanism and compare the rates of substitution of a series of methyl-substituted thiophenes by PPh$_3$ according to eq 1.



(1)

x = 0, 1, 2, 4 and the cyclopentadienyl ligand is C$_5$H$_5$ or C$_5$Me$_5$

Of particular interest is the effect of methyl groups in the 2- and 5-positions on the rates of thiophene dissociation from these complexes. It has generally been stated[14,15] that such methyl groups would sterically inhibit thiophene adsorption to an HDS catalyst. This statement, however, was based on the assumption that S-bound thiophene is perpendicular to the surface, with the coordinated metal atom lying in the plane of the thiophene. In this configuration, methyl groups in the 2- and 5-positions would be expected to sterically weaken S-bonding to the metal. However, it is now known[8b,11,13] that the metal does not lie in the thiophene plane (i.e., the sulfur is pyramidal), as shown for $Cp(CO)_2Re(Th)$ in eq 1. Thus, 2,5-methyl groups may pose less of a steric problem than previously suggested. Kinetic studies of the reaction in eq 1 offer one approach to assessing steric effects of 2,5-methyl groups on thiophene bonding to metals.

EXPERIMENTAL

General Procedures

The complexes, $Cp(CO)_2Re(Th)$ and $Cp^*(CO)_2Re(Th)$, where Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, and Th = T, 2-MeT, 3-MeT, 2,5-Me_2T, Me_4T, and dibenzothiophene (DBT), were prepared as described elsewhere.[12,13] The PPh_3 was purified by recrystallization from warm hexanes and cooling to -20 °C. The C_6D_6 was distilled under Ar from Na/benzophenone. The products, $Cp(CO)_2Re(PPh_3)$ and $Cp^*(CO)_2Re(PPh_3)$, were identified[16] by their ^1H NMR and IR spectra; they were the only products of the reactions studied.

Kinetic Measurements

The reaction solutions used in the kinetic studies were prepared as follows: The S-bound thiophene rhenium complex (0.005 mmol) and the desired amount (usually 0.05 mmol, 0.10 mmol, or 0.20 mmol) of PPh_3 were placed in an NMR tube; then 500 µL of d_6-benzene was added by microsyringe. The solution was frozen immediately at liquid nitrogen temperature, and the NMR tube was sealed with a flame under vacuum. For the slow reactions ($t_{1/2} > 20$ h; $Cp(CO)_2Re(2\text{-}MeT)$, $Cp(CO)_2Re(2,5\text{-}Me_2T)$, $Cp^*(CO)_2Re(2,5\text{-}Me_2T)$, $Cp(CO)_2Re(Me_4T)$, and $Cp(CO)_2Re(DBT)$), the samples were thermostatted in a constant temperature bath (80.0 ± 0.2 °C), and the reactions were followed by removing the NMR tubes from the bath at appropriate times, taking their ^{1}H NMR spectra on a Nicolet NT-300 spectrometer, and returning the tubes to the bath. Since the reactions are negligibly slow at room temperature, the times of reaction were considered to be only those periods when the NMR tubes were in the 80.0 °C bath. For the fast reactions ($t_{1/2} < 1.5$ h; $Cp(CO)_2Re(T)$, $Cp(CO)_2Re(3\text{-}MeT)$, and $Cp^*(CO)_2Re(2\text{-}MeT)$), the NMR tubes were thermostatted in the probe of a Bruker WM-200 NMR spectrometer at 80.0 ± 0.5 °C. After a few minutes of temperature equilibration, ^{1}H NMR spectra of the samples were recorded automatically at specific time intervals. Pseudo-first-order conditions were maintained in all runs by using at least a ten-fold excess of the PPh_3 ligand concentration over the Re complex concentration of 0.010 M.

The data were analyzed using the NMR1 program.[17] Pseudo-first-order rate constants, k_{obs}, were obtained from least-squares slopes of linear plots of $\ln(1+F)$ vs time, where $F = P/R$, and P is the integrated area of the proton of interest in the product and R is the area of a reactant proton. Generally, the areas of the reactant and product Cp and Cp* signals were integrated; however, for the 2,5-Me_2T and Me_4T complexes, the α-Me protons of the reactant and product were followed. Plots of $\ln(1+F)$ vs time were linear to 70-90% reaction completion with correlation coefficients greater than 0.984.

RESULTS AND DISCUSSION

The rates of PPh_3 substitution of various thiophenes in the $Cp'(CO)_2Re(Th)$ complexes according to eq 1 are independent of the PPh_3 concentration (Table 1) and follow a first-order rate law (eq 2). This rate expression suggests that the reaction

$$-\frac{d[Cp'(CO)_2Re(Th)]}{dt} = k_1[Cp'(CO)_2Re(Th)] \quad (2)$$

proceeds by a dissociative mechanism (eq 3) in which

$$Cp'(CO)_2Re(Th) \xrightarrow[\text{slow}]{} \underset{\displaystyle Th}{\underset{+}{\{Cp'(CO)_2Re\}}} \xrightarrow[\text{fast}]{PPh_3} Cp'(CO)_2Re(PPh_3) \quad (3)$$

the rate-determining step is dissociation of the thiophene from Re.

For the cyclopentadienyl complexes $Cp(CO)_2Re(Th)$, the rate constants(k_1) decrease (Table 2) with the thiophene in the order: T > 3-MeT > 2-MeT > 2,5-Me_2T > Me_4T. From this order, it is clear that adding methyl groups to the thiophene ring *decreases* the rate of thiophene dissociation. Moreover, a methyl group on an α-carbon (2- or 5-position) decreases the rate much more than a methyl on a β-carbon (3- or 4-position). Thus, the rate of 2-MeT dissociation is 13 times slower than that of 3-MeT. This can be rationalized in terms of the electron-donating ability of methyl groups in α-positions making the sulfur a better σ-donor than methyl groups in the more distant β-positions; this is consistent with theoretical calculations[18] of S-bound

Table 1. Rate constants (k_{obs}) for the reactions of $Cp'(CO)_2Re(Th)$ with PPh_3 in d_6-benzene at 80.0 °C according to Eq 1.

Complex	$[PPh_3]$, M	k_{obs}, s^{-1}
$Cp(CO)_2Re(T)$	0.10	2.9×10^{-4}
	0.20	3.1×10^{-4}
	0.30	3.0×10^{-4}
$Cp(CO)_2Re(3\text{-}MeT)$	0.10	1.3×10^{-4}
	0.20	1.2×10^{-4}
	0.40	1.2×10^{-4}
$Cp(CO)_2Re(2\text{-}MeT)$	0.10	9.0×10^{-6}
	0.20	8.9×10^{-6}
	0.40	9.5×10^{-6}
$Cp(CO)_2Re(2,5\text{-}Me_2T)$	0.10	1.4×10^{-6}
	0.20	1.3×10^{-6}
	0.40	1.3×10^{-6}
$Cp(CO)_2Re(Me_4T)$	0.10	2.8×10^{-7}
	0.20	2.6×10^{-7}
	0.40	2.6×10^{-7}
$Cp(CO)_2Re(DBT)$	0.10	1.6×10^{-7}
	0.20	1.5×10^{-7}
$Cp^*(CO)_2Re(3\text{-}MeT)$	0.10	4.1×10^{-4}
	0.20	4.3×10^{-4}
$Cp^*(CO)_2Re(2,5\text{-}Me_2T)$	0.10	4.9×10^{-6}
	0.20	5.2×10^{-6}

Table 2. Rate constants (k_1) for the reactions of $Cp'(CO)_2Re(Th)$ with PPh_3 in d_6-benzene at 80.0 °C according to Eq 1

Complex	10^7k_1, s^{-1}
$Cp(CO)_2Re(T)$	3,000
$Cp(CO)_2Re(3\text{-}MeT)$	1,200
$Cp(CO)_2Re(2\text{-}MeT)$	91
$Cp(CO)_2Re(2,5\text{-}Me_2T)$	13
$Cp(CO)_2Re(Me_4T)$	2.7
$Cp(CO)_2Re(DBT)$	1.6
$Cp^*(CO)_2Re(3\text{-}MeT)$	4,200
$Cp^*(CO)_2Re(2,5\text{-}Me_2T)$	51

thiophene complexes where the metal-sulfur interaction is primarily σ in character. In the 2,5-Me_2T complex, the rate of dissociation is 7 times slower than 2-MeT and 230 times slower than thiophene (T) itself. These large electronic effects suggest that the donor ability of the thiophene is greatly enhanced by methyl groups. It is important to note that the trends in rates are opposite what would be expected if steric effects of the α-methyl groups governed the rates of thiophene dissociation. Molecular models indicate that the bent arrangement (eq 1) at the sulfur in these complexes greatly reduces steric interactions between α-methyl groups and the other ligands bound to the rhenium.

Consistent with sulfur being primarily a donor to the Re are the somewhat faster rates (~ 3.7 times faster) of 3-MeT and 2,5-Me_2T dissociation from the pentamethylcyclopentadienyl (Cp*) derivatives as compared with the analogous Cp compounds. In the Cp* complex the Re is more electron-rich and therefore a poorer Lewis acid for the sulfur donor ligand. It is interesting to note that 2,5-Me_2T dissociation is 87±5 times slower than 3-MeT dissociation in both the $Cp(CO)_2Re(Th)$ and the $Cp^*(CO)_2Re(Th)$ complexes; this indicates that there is little, if any, steric acceleration of 2,5-Me_2T dissociation in the pentamethylcyclopentadienyl (Cp*) complex.

The rate of dibenzothiophene(DBT) substitution is 1.9×10^3 times slower than that of thiophene. This greater kinetic stability of the DBT complex is also consistent with the generally higher stability[8b] of $Cp(CO)_2Fe(DBT)^+$ as compared with $Cp(CO)_2Fe(T)^+$.

The only related kinetic study reported[19] in the literature is that of the thioether complexes $CpMn(CO)_2(SR_2)$ with phosphines and phosphites (L) to give $CpMn(CO)_2(L)$ at 85.0°C in methylcyclohexane solvent. As in the present study, the rates were independent of the L concentration. The rate of $(n\text{-}Pr)_2S$ dissociation was 2.4 times faster than that of Me_2S, presumably due to steric effects. A much larger increase in rate (203-fold) was observed for Ph_2S dissociation as compared with Me_2S; this probably results from the weaker electron-donor ability of the Ph group as compared with Me. Thus, electronic rather than steric factors also appear to dominate rates of thioether dissociation from $CpMn(CO)_2(SR_2)$.

Relevance to Thiophene Adsorption on HDS Catalysts

Relative adsorption coefficients (K_{rel}) for the adsorption of methyl-substituted thiophenes on a $Co\text{-}Mo/Al_2O_3$ catalyst at 350 °C increase in the order:[15] T(1.0) < 2-MeT(1.6) ~ 3-MeT(1.7) < 2,5-Me_2T(2.5). It should be noted that these adsorptions do not necessarily occur at HDS active sites. The relative HDS reactivities of methyl thiophenes also increase with the number of methyl groups: T(1.0) < 2-MeT(1.5) < 3-MeT(1.9) < 2,5-Me_2T(2.0).[20] Another HDS study[21] also over $Co\text{-}Mo/Al_2O_3$ shows a similar trend: T ~ 2-MeT < 3-MeT. Thus, methyl groups on the α-carbons do not reduce the reactivity of thiophenes but actually enhance it. These results were interpreted to mean that S-coordination of thiophene was unlikely to be important in HDS since α-methyl groups were thought to inhibit sterically the adsorption of thiophenes and should therefore reduce their HDS rates.

Steric inhibition would not be a problem for η^5-coordinated thiophenes. The η^5 binding mode accounts for the stronger adsorption of thiophenes with increasing methyl substitution;[5] it also explains relative rates of thiophene proton exchange with deuterium.[22] In addition, η^5 adsorption and reactivity provide a reasonable and useful mechanism for thiophene HDS.[4,23] Thus, η^5-coordination offers reasonable explanations for several types of thiophene behavior on HDS catalysts.

However, results of the studies presented in this paper indicate that S-coordination is not as unreasonable as previously assumed. Since 2,5-methyl groups do not sterically accelerate thiophene dissociation from $Cp'(CO)_2Re(Th)$ but inhibit it, this suggests that 2,5-methyl groups strengthen the Re-thiophene bond. A stronger metal-thiophene bond would presumably also increase equilibrium adsorption constants for methyl-substituted thiophenes on HDS catalysts, as observed.[15] Thus, one can account for the relative order of methyl thiophene binding to HDS catalysts by assuming either η^5- or S-thiophene coordination. However, at this time, there is no evidence to suggest that S-binding promotes thiophene C-S bond cleavage as there is in η^5-thiophene complexes. So, the η^5 adsorption mode still offers the more complete explanation of thiophene reactivity on HDS catalysts.

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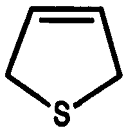
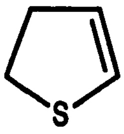
SECTION IV. SYNTHESIS AND DESULFURIZATION OF 2,5-DIHYDROTHIOPHENE TRANSITION METAL COMPLEXES: MODELS FOR HYDRODESULFURIZATION OF THIOPHENE[1]

INTRODUCTION

Hydrodesulfurization is an important catalytic process[2,3] in which sulfur is removed from sulfur-containing organic compounds in petroleum feedstocks by hydrogen treatment over Co- or Ni-promoted Mo or W catalysts supported on Al_2O_3. A mechanism (Scheme I) for thiophene HDS proposed and supported by results from these laboratories[2,4] involves initial partial hydrogenation of thiophene (Steps 1 and 2 in Scheme I) to the dihydrothiophene isomers, 2,5-DHT and



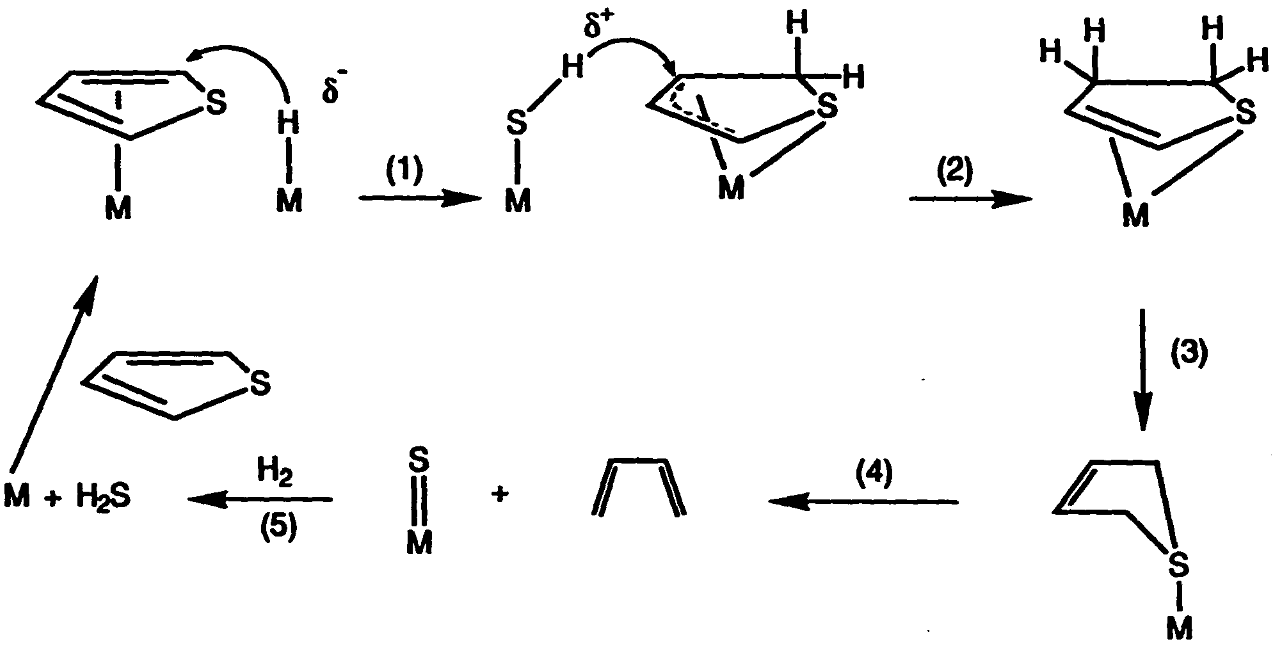
2,5-DHT



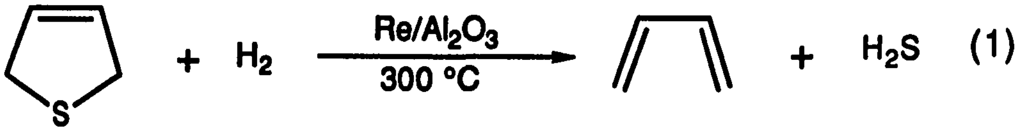
2,3-DHT

2,3-DHT. The participation of these isomers as intermediates is supported by HDS reactor studies[4c,d] of 2,5-DHT and 2,3-DHT over Mo/γ-Al_2O_3 and Re/γ-Al_2O_3 heterogeneous catalysts. Over both catalysts, both 2,5-DHT and 2,3-DHT are much more reactive than thiophene and at 400 °C give the same distribution of desulfurized C_4 products as thiophene. Over Re/γ-Al_2O_3, 2,3-DHT and 2,5-DHT interconvert and both are desulfurized to butadiene. The mechanism in Scheme I suggests that the actual desulfurization step in thiophene HDS is step 4 in which S-coordinated 2,5-DHT eliminates butadiene leaving an S-atom coordinated on the catalyst surface. That this is a

Scheme I. Mechanism for Thiophene HDS



reasonable step is supported by HDS reactor studies[4d] which show that the major product of 2,5-DHT hydrodesulfurization is butadiene (eq 1).



We had shown previously that butadiene is released when the unstable $Fe(CO)_4$(2,5-DHT) with an S-coordinated 2,5-DHT decomposes.[4c] In this paper, we describe the synthesis of several S-coordinated 2,5-DHT transition metal complexes and explore their tendencies to eliminate butadiene upon heating, thereby determining whether or not S-coordination of 2,5-DHT to various metal centers promotes butadiene liberation as proposed in the thiophene HDS mechanism in Scheme I. We also examine the reaction of 2,5-DHT with the trinuclear cluster $Ru_3(CO)_{12}$ which leads to quite a different type of product.

EXPERIMENTAL

General Procedures

All reactions were carried out under an atmosphere of prepurified N_2 at room temperature using standard Schlenk techniques[5] unless otherwise stated. All solvents were reagent grade and dried following standard methods.[6] Tetrahydrofuran (THF) and Et_2O were distilled from Na/benzophenone, CH_2Cl_2 and hexanes from CaH_2, and benzene from $LiAlH_4$. Acetone was dried with K_2CO_3.

The ^1H and ^{13}C NMR spectra were obtained on a Nicolet NT-300 spectrometer with deuteriated solvents used as internal locks. All ^1H NMR chemical shifts (δ) were referenced to $(CH_3)_4Si$. Electron-ionization mass spectra (EIMS) were runs on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were obtained by using a Kratos MS-50 mass spectrometer. Infrared spectra were obtained on either a Perkin-Elmer 681 or Digilab FTS-7 FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The following compounds were prepared by literature methods: 2,5-DHT,[7] 3,4-dimethyldihydrothiophene,[8] $Cp^*Re(CO)_3$,[9] $Re_2(CO)_9(CNCH_3)$,[10] $Ru_3(CO)_{12}$,[11] $CpRu(PMe_3)_2Cl$,[12] $[Ru(CO)_3Cl_2]_2$.[13] $PdCl_2(CH_3CN)_2$ was prepared from MeCN by the method used for the synthesis of $PdCl_2(PhCN)_2$.[14]

Preparation of $W(CO)_5$(2,5-DHT) (1)

Compound **1** was prepared by a modified literature method.[15] A solution of $W(CO)_6$ (0.15 g, 0.43 mmol) in freshly distilled THF (30 mL) in a quartz photolysis tube equipped with an N_2 bubbler was irradiated with a 450W mercury UV lamp for ~3 h. The progress of the reaction to give $W(CO)_5$(THF) was monitored by IR spectroscopy. To the yellow solution of $W(CO)_5$(THF) was added 2,5-DHT (50 μL, 0.62 mmol), and the resulting mixture was stirred for 0.5 h. After removing the solvent under vacuum, the yellow brown residue was extracted with pentane (2 x 20 mL). The pale yellow solution was filtered through Celite. Slow evaporation of the solvent gave pale yellow crystals (0.14 g, 81%) of **1**. IR and ^1H NMR spectra agree with those reported[15] for this compound. IR(hexanes): υ(CO) 2071(w), 1980(m), 1938(vs) cm^{-1}. ^1H NMR(d_6-acetone): δ 6.04 (s, 2H, H3,H4), 4.20 (s, 4H, H2,H5).

Preparation of $W(CO)_5$(3,4-Me_2DHT) (2)

Compound **2** was prepared by the same method as described above using $W(CO)_6$ (0.10 g, 0.28 mmol) and 3,4-Me_2DHT (35 μL, 0.31 mmol). The product **2** was obtained as pale yellow crystals (0.10 g, 82%). IR(hexanes): υ(CO) 2075(w), 1988(s), 1935(vs, br) cm^{-1}. ^1H NMR($CDCl_3$): δ 3.95 (s, 4H, H2,H5), 1.75 (s, 6H, CH_3). ^{13}C NMR($CDCl_3$): 201.1 (axial CO), 197.3 (equatorial CO), 128.6 (C_3,C_4), 55.6 (C_2,C_5), 14.0 (CH_3 of DHT). EIMS (16 eV) m/e 438 (M^+), 410 (M^+-CO), 382 (M^+-2CO), 354 (M^+-3CO), 326 (M^+-4CO), 298 (M^+-5CO), 114 (Me_2DHT^+), 99 (Me_2DHT^+-Me), 82 (Me_2DHT^+-S). Anal. Calcd for $C_{11}H_{10}O_5SW$: C, 30.16; H, 2.30. Found: C, 30.26; H, 2.28.

Preparation of $Re_2(CO)_9$(2,5-DHT) (3)

To a benzene solution (15 mL) of $Re_2(CO)_9(CH_3CN)$ (0.15 g, 0.23 mmol) was added 2,5-DHT (25 µL, 0.31 mmol). The solution was refluxed for 3 h, and the solvent was evaporated under vacuum to yield an oily yellow residue. The residue was extracted with hexanes. The extract was filtered through Celite. After removing the solvent under vacuum, the crude product was recrystallized from hexane at -70 °C to give pale yellow crystals of **3** (0.098 g, 61%). IR(hexanes): υ(CO) 2105(w), 2075(w), 2040(s), 2018(s), 1990(vs), 1975(s), 1930(s), 1900(w), 1835(s) cm^{-1}. ^1H NMR ($CDCl_3$): 5.97 (s, 2H, H3,H4), 4.08 (s, 4H, H2,H5). ^{13}C NMR ($CDCl_3$): 201.1, 199.9, 191.8, 187.8 (CO), 127.3 (C_3,C_4), 52.3 (C_2,C_5). EIMS (70 eV) m/e 710 (M^+), 682 (M^+-CO), 86 (DHT^+), 54 (DHT^+-S). Anal. Calcd for $C_{13}H_6O_9Re_2S$: C, 21.97; H, 0.85. Found: C, 21.97; H, 0.79.

Preparation of Cp*$(CO)_2$Re(2,5-DHT) (4)

A solution of Cp*$(CO)_2$Re(THF), prepared by UV irradiation[16] of a THF solution (30 mL) of Cp*$Re(CO)_3$ (0.10 g, 0.25 mmol) at -20 °C, was stirred with 2,5-DHT (50 µL, 0.61 mmol) at room temperature for 5 h. Following the removal of solvent in vacuo, the residue was chromatographed on a neutral alumina column (1 x 15 cm). First, unreacted Cp*$Re(CO)_3$ was eluted with hexanes, and then a yellow band containing the product was eluted with hexanes/CH_2Cl_2 (4:1). The yellow eluent was concentrated and cooled to -70 °C to give tan colored crystals (0.065 g, 57%) of **4**. IR(hexanes): υ(CO) 1919(s), 1858(s) cm^{-1}. ^1H NMR ($CDCl_3$): 5.85 (s, 2H, H3,H4), 3.93 (s, br, 4H, H2,H5), 2.04 (s, 15H, Cp*). ^{13}C NMR ($CDCl_3$): 207.1(CO), 127.4(C3,C4), 56.5(C2,C5), 95.1(C of Cp*), 10.7 (Me of Cp*). EIMS (70 eV) m/e 464 (M^+, based on ^{187}Re), 408 (M^+-2CO), 85 (DHT^+-H). Anal. Calcd for $C_{16}H_{21}O_2ReS$: C, 41.45; H, 4.57. Found: C, 41.72; H, 4.60.

Preparation of [CpRu(PMe_3)$_2$(2,5-DHT)](PF_6) (5)

To a MeOH (10 mL) solution of CpRu(PMe_3)$_2$Cl (0.10 g, 0.28 mmol) were added 2,5-DHT (100 µL, 1.2 mmol) and NH_4PF_6 (0.23 g, 1.4 mmol). The resulting reaction mixture was stirred for 12 h. After removing the solvent under vacuum, the yellow residue was extracted with CH_2Cl_2 (2 x 10 mL). The extract was filtered through Celite. The solution was reduced to about 5 mL and Et_2O (20 mL) was added; the solution was kept at -20 °C for 3 days to give yellow crystals (0.11 g, 71%) of **5**. ^1H NMR ($CDCl_3$): 5.95 (s, 2H, H3,H4), 3.87 (s, br, 4H, H2,H5), 4.79 (s, 5H, Cp), 1.55 (pseudo t, 18H, PMe_3). ^{13}C NMR(CD_2Cl_2): 127.7 (C3,C4), 55.6 (C2,C5), 82.5 (Cp), 22.5 (pseudo t, PMe_3). MS (FAB, 3-NBA) m/e 405(M^+), 319(M^+-DHT). Anal. Calcd for $C_{15}H_{29}F_6P_3RuS$: C, 32.79; H, 5.24. Found: C, 32.58; H, 5.32.

X-ray Structure Determination of [CpRu(PMe$_3$)$_2$(2,5-DHT)](PF$_6$) (5)

A yellow crystal of [CpRu(PMe$_3$)$_2$(2,5-DHT)](PF$_6$) (**5**), formed by vapor diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution at -20°C, was mounted on a glass fiber in a random orientation. A total of 8144 reflections were collected in the +h, ±k, ±l hemisphere, of which 3921 were unique. An absorption correction based on a series of psi-scans was applied, as were Lorentz and polarization corrections. Decay corrections were not applied, since the intensity standards indicated no change within the error of the measurements during data collection. The agreement factors for the averaging of 6994 observed reflections were 1.4% based on intensity and 1.2% based on F$_{obs}$.

The position of the Ru atom was taken from a Patterson map.[17a] Following refinement of the scale factor, the remainder of the non-hydrogen atoms were located in subsequent difference Fourier maps. In the final stages of refinement, all 26 non-hydrogen atoms were given anisotropic temperature factors. Although the fluorine atoms exhibited large amplitudes of thermal motion, the positions and temperature factors refined smoothly. Hydrogen atoms were not considered in the model.

Refinement of the structure was carried out using the SHELX76 package.[17b] Important crystallographic data are summarized in Table 1. Selected bond distances and angles of **5** are presented in Table 2. The final positional and thermal parameters are listed in Table 3 and an ORTEP drawing of **5** is given in Figure 1.

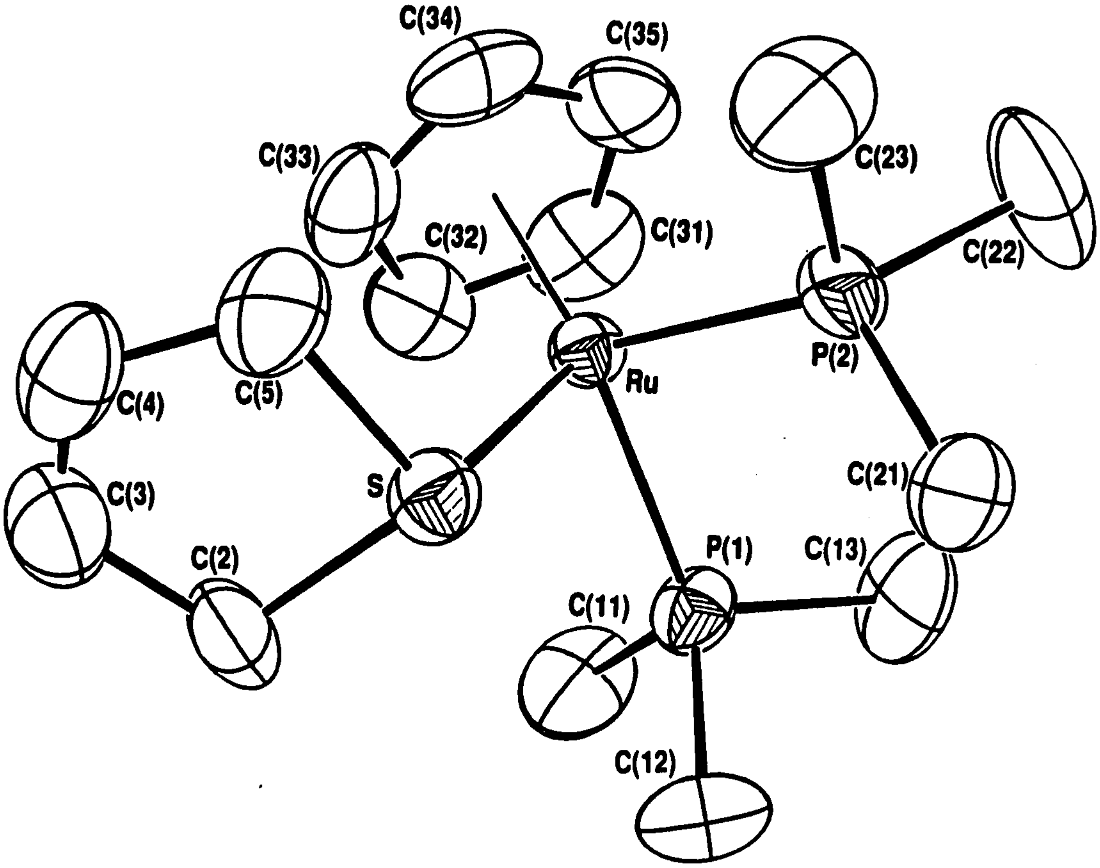


Figure 1. ORTEP drawing of $[Cp(PMe_3)_2Ru(2,5\text{-}DHT)]^+$ (5)

Table 1. Crystal and data collection parameters for $[CpRu(PMe_3)_2(2,5\text{-}DHT)](PF_6)$ (**5**) and $(\mu_2\text{-}H)Ru_3(CO)_9(\mu_3\text{-}S,2,3,4\text{-}\eta^4\text{-}DHT)$ (**7**)

	5	**7**
Formula	$C_{15}H_{29}F_6P_3RuS$	$C_{13}H_6O_9Ru_3S$
Formula weight	549.44	497.46
Space Group	$P2_1/c$	$P2_1$
a, Å	8.687(1)	8.703(1)
b, Å	10.428(1)	11.733(1)
c, Å	24.747(2)	8.919(1)
b, deg	95.092(8)	92.39(1)
V, Å^3	2232.8(7)	913.0(3)
Z	4	2
d_{calc}, g/cm^3	1.634	2.33
Crystal size, mm	0.30 x 0.42 x 0.44	0.22 x 0.14 x 0.10
$\mu(MoK_a)$, cm^{-1}	10.365	25.57
Data collection instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	$MoK_\alpha(\lambda=0.71073Å)$	$MoK_\alpha(\lambda=0.71073Å)$
Orientation reflections, number, range (2θ)	25, 23° <2θ < 32°	25, 18° < 2θ < 36°
Temperature, °C.	22(1)	22(1)
Scan method	θ-2θ	ω scan
Data col. range, 2θ, deg	4.0-50.0	4.0-50.0
No. unique data,total:	3921	2195
with $F_o^2 > 3\sigma(F_o^2)$:	3397	1766

Table 1. Continued

	5	**7**
Trans. factors, max., min. (psi-scans)	0.9999, 0.9391	0.998, 0.633
R[a]	0.0408	0.0505
R_w[b]	0.0644	0.0635
Quality-of-fit indicator[c]	2.90	1.44
Largest shift/esd, final cycle	0.01	0.02
Largest peak, e/Å^3	0.8(1)	1.49

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$; $\omega = 1/\sigma^2(|F_o|)$.

[c] Quality-of-fit $= [\Sigma\omega(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (deg) for $[CpRu(PMe_3)_2(2,5\text{-}DHT)](PF_6)$ (**5**).

Bond Distances (Å)

Ru-S	2.3295(7)[a]	S-C(5)	1.861(3)
Ru-P(1)	2.2933(7)	C(2)-C(3)	1.468(5)
Ru-P(2)	2.2891(7)	C(3)-C(4)	1.327(6)
S-C(2)	1.855(3)	C(4)-C(5)	1.493(5)

Bond Angles (deg)

S-Ru-P(1)	91.43(3)	C(2)-S-C(5)	93.8(2)
S-Ru-P(2)	88.00(3)	S-C(2)-C(3)	105.6(3)
P(1)-Ru-P(2)	93.47(3)	C(2)-C(3)-C(4)	117.8(3)
Ru-S-C(2)	111.0(1)	C(3)-C(4)-C(5)	118.0(3)
Ru-S-C(5)	109.4(1)	S-C(5)-C(4)	104.5(3)

[a] The numbers in parentheses are estimated standard deviations.

Table 3. Positional parameters and thermal parameters for $[CpRu(PMe_3)_2(2,5\text{-DHT})](PF_6)$ (**5**)

atom	x	y	z	B,^{a}(Å^2)
Ru	0.43172(3)	0.22049(3)	0.35246(1)	2.562(7)
S	0.4919(1)	0.1906(1)	0.44521(5)	3.49(2)
C(2)	0.6029(6)	0.3287(6)	0.4756(2)	5.4(1)
C(3)	0.7613(7)	0.2817(7)	0.4879(3)	6.1(2)
C(4)	0.7884(6)	0.1583(7)	0.4795(2)	5.7(1)
C(5)	0.6573(6)	0.0773(6)	0.4562(2)	5.2(1)
C(11)	0.3192(7)	0.5394(5)	0.3575(3)	6.7(2)
C(12)	0.1786(7)	0.3875(6)	0.4344(2)	5.6(1)
C(13)	0.0773(6)	0.3752(7)	0.3209(3)	6.8(2)
C(21)	0.1150(6)	0.0592(5)	0.4049(2)	4.7(1)
C(22)	0.1365(8)	0.0241(8)	0.2904(3)	8.2(2)
C(23)	0.3488(8)	-0.1019(5)	0.3695(4)	7.5(2)
C(31)	0.4802(7)	0.3021(6)	0.2734(2)	5.8(1)
C(32)	0.5967(6)	0.3488(6)	0.3139(2)	5.7(1)
C(33)	0.6781(8)	0.2380(7)	0.3349(2)	5.7(1)
C(34)	0.6181(6)	0.1289(6)	0.3085(2)	5.7(1)
C(35)	0.4930(7)	0.1667(6)	0.2700(2)	5.4(1)
P(1)	0.2525(1)	0.3746(1)	0.36798(5)	3.48(2)
P(2)	0.2577(1)	0.0562(1)	0.35487(5)	3.77(2)
P(3)	0.8103(2)	0.7148(1)	0.39025(7)	4.51(3)
F(1)	0.9793(6)	0.7222(6)	0.3771(4)	14.1(2)
F(2)	0.6496(6)	0.7107(7)	0.4094(4)	15.1(3)
F(3)	0.8544(8)	0.5935(5)	0.4248(2)	13.6(2)
F(4)	0.7707(9)	0.6266(6)	0.3421(2)	14.9(2)
F(5)	0.7761(7)	0.8428(5)	0.3590(3)	11.9(2)
F(6)	0.8561(7)	0.8057(5)	0.4414(2)	10.7(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Preparation of $RuCl_2(CO)_3(2,5\text{-}DHT)$ (6)

To a solution of $[Ru(CO)_3Cl_2]_2$ (0.15 g, 0.29 mmol) in CH_2Cl_2 (30 mL) was added 2,5-DHT (80 μL, 0.98 mmol) by micro syringe, and the mixture was stirred for 12 h. Removal of the solvent in vacuo gave a creamy-white powder, which was recrystallized from CH_2Cl_2 and hexanes at -20°C. White needle-shaped crystals of **6** were obtained (0.14 g, 70%). IR(hexanes): υ(CO) 2130(s), 2070(s), 2041(s) cm^{-1}. ^1H NMR($CDCl_3$): 5.99 (s, 2H, H3,H4), 4.51 and 4.00 (s, br, 4H, H2,H5). EIMS(16 eV) m/e 306 (M^+-HCl), 270 (M^+-2HCl), 242 (M^+-(2HCl+CO)), 85 (DHT^+-H). Anal. Calcd for $C_7H_6Cl_2O_3RuS$: C, 24.57; H, 1.77. Found: C, 24.65; H, 1.73.

Preparation of $(\mu_2\text{-}H)Ru_3(CO)_9(\mu_3\text{-}S,2,3,4\text{-}\eta^4\text{-}DHT)$ (7)

To a stirred solution of $Ru_3(CO)_{12}$ (0.20 g, 0.31 mmol) in THF (30 mL) was added 2,5-DHT (100 μl, 1.22 mmol). (The 2,5-DHT must be very pure; otherwise, the yield of **7** decreases dramatically.) After 3 h of refluxing, the orange solution changed to dark brown. The solvent was evaporated under vacuum; the residue was extracted with hexanes (2 x 15 mL). The extract was chromatographed on neutral alumina eluting with hexanes. The first orange-yellow band was unreacted $Ru_3(CO)_{12}$ (0.036 mg). The second yellow-orange band was eluted with Et_2O/hexanes (1:4 mixture) and collected. After removal of the solvent under vacuum, the crude product was recrystallized from hexanes at -20 °C to give yellow-orange crystals (0.031 g, 24% yield based on consumed $Ru_3(CO)_{12}$) of **7**. IR(hexanes): υ(CO) 2082 (m), 2058 (s), 2036 (s), 2018 (s), 2000 (m), 1922 (w), 1975 (w), 1964 (w). ^{1}H NMR(CDCl$_3$): 4.46 (d, 1H, H2), 4.28 (m, 1H, H5endo), 3.89 (m, 1H, H3), 3.41 (d of d, 1H, H4), 2.61 (m, 1H, H5exo), -18.56 (d, 1H, Ru-H), ($J_{RuH,H5endo}$ = 2.9 Hz, $J_{H2,H3}$ = 3.2 Hz, $J_{H4,H5endo}$ = 2.8 Hz, $J_{H5endo,H5exo}$ = 12.3 Hz, $J_{H3,H4}$ = 5.1 Hz, $J_{H2,H5endo}$ = 0.9 Hz, $J_{H3,H5}$ = 0.7 Hz). ^{13}C NMR(CDCl$_3$) 199.8 (CO), 15.5 (C2), 36.5 (C3), 79.7 (C4), 59.8 (C5). EIMS (17 eV): m/e 644 (M$^+$ based on ^{102}Ru), 616 (M$^+$-CO), 588 (M$^+$-2CO), 560 (M$^+$-3CO), 532 (M$^+$-4CO), 504 (M$^+$-5CO), 86 (DHT$^+$), 84 (DHT$^+$-2H), 54 (DHT$^+$-S). Anal. Calcd for $C_{13}H_6O_9Ru_3S$: C,24.34; H, 0.97. Found: C, 24.39; H, 1.01.

X-ray Structure Determination of (μ_2-H)Ru$_3$(CO)$_9$(μ_3-S,2,3,4-η^4-DHT) (7)

A yellow-orange crystal of (μ_2-H)Ru$_3$(CO)$_9$(μ_3-S,2,3,4-η^4-DHT) (7), formed by slow cooling from hexanes at -20 °C, was mounted on a glass fiber in a random orientation. The cell constants were determined from a list of reflections found by an automated search routine. A total of 3901 reflections were collected in the ±h, +k, ±l hemisphere, of which 2195 were unique. Intensity standards indicated no change within error of the measurements over the duration of the data collection. An absorption correction based on a series of psi-scans was applied, as were Lorentz and polarization corrections. The agreement factors for averaging of 3032 observed reflections were 3.6% based on intensity and 2.4% based on F_{obs}.

The positions of the three Ru atoms were located by direct methods.[17a] Examination of a difference map produced after full-matrix least-squares refinement of the three metal atoms revealed most of the remainder of the non-hydrogen atoms, including the atoms of the major orientation of the capping ligand. Following further least-squares refinement and a subsequent difference map, the existence of a minor orientation of the capping ligand became evident. Two orientations of the five non-hydrogen atoms of the SC_4H_5 ligand were thus modeled so that the sum of the occupancies of the two groups equaled one. Due to a large amount of correlation between the two overlapping moieties, a loose restraint was applied to keep the S-C bond distances close to 1.8 Å. In the final refinement stages, the major orientation converged to an occupancy of 62% (indicated by the non-primed atom labels). Only the Ru and S atoms were refined with anisotropic thermal parameters. The final cycle of refinement included 150 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.0505$ and $R_w = 0.0635$.

The refinement calculations were carried out using the SHELX76 package.[17b] Important crystallographic data are given in Table 1. Selected bond lengths and angles of **7** are presented in Table 4. The final positional and thermal parameters are listed in Table 5. An ORTEP drawing of **7**, showing the major orientation of the capping ligand is given in Figure 2.

Preparation of $PdCl_2(2,5\text{-}DHT)_2$ (8)

To a solution of $PdCl_2(CH_3CN)_2$ (0.20 g, 0.77 mmol) in CH_2Cl_2 (15 mL) was added 2,5-DHT (133 μL, 1.62 mmol). The reaction mixture was stirred for 2 h, and then the solvent was removed under vacuum to give a golden powder. This crude product was redissolved in a minimum amount of hot acetone and the solution was slowly cooled at -20 °C to give tan colored needle crystals (0.19 g, 71%) of **8**. ^1H NMR ($CDCl_3$): 5.90 (s, 2H, H3,H4), 4.43 and 3.84 (s, br, 4H, H2,H5). Anal. Calcd for $C_8H_{12}Cl_2PdS_2$: C, 27.48; H, 3.46. Found: C, 26.89; H, 3.54.

Preparation of $PtCl_2(2,5\text{-}DHT)_2$ (9)

To solution of K_2PtCl_4 (0.25 g, 0.60 mmol) in 10 mL of water was added 2,5-DHT (84 μL, 0.95 mmol) in small portions. The mixture was stirred vigorously after each addition to ensure complete reaction. The bright yellow precipitate was immediately separated by suction filtration, washed with ice-cold ethanol (2 x 5 mL), and then washed with water (3 x 5 mL) to remove the potassium chloride. The product was dried in vacuo (0.19 g, 72 %). ^1H NMR ($CDCl_3$): 5.92 (s, 2H, H3,H4), 4.55 and 3.68(2 br m, 4H, H2,H5). Anal. Calcd for $C_8H_{12}Cl_2PtS_2$: C, 21.92; H, 2.76. Found: C, 22.01; H, 2.51.

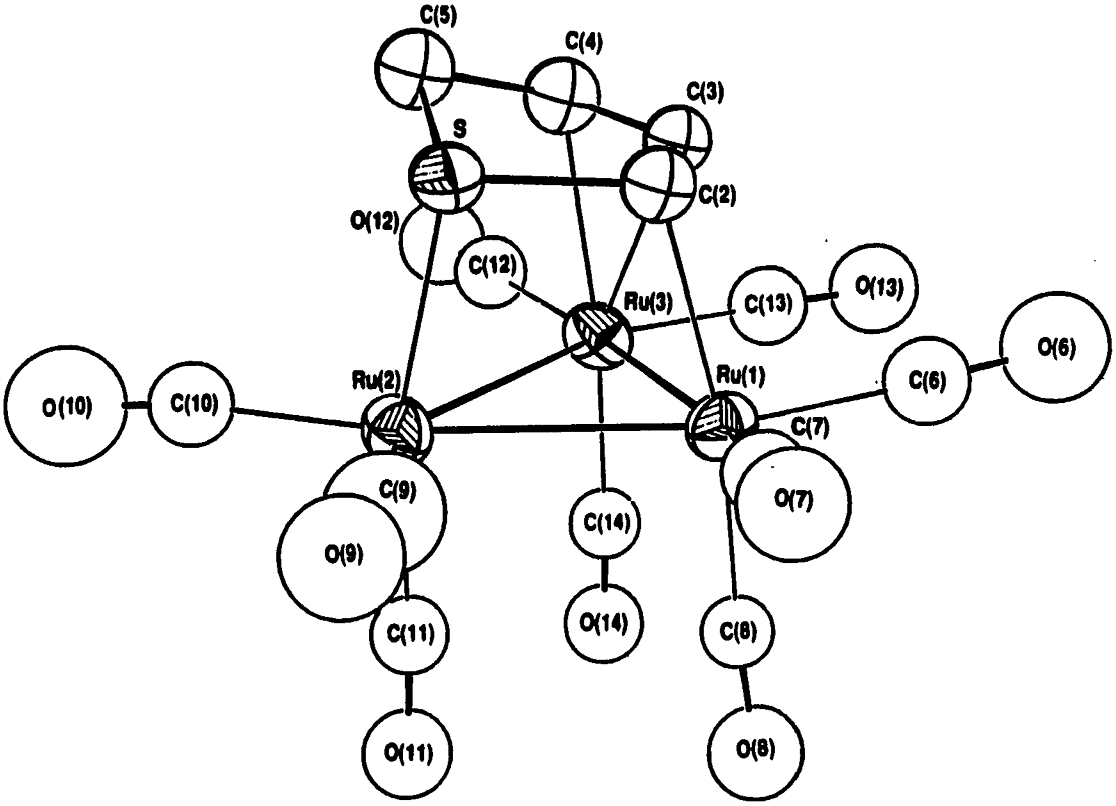


Figure 2. ORTEP drawing of (μ_2-H)$Ru_3(CO)_9$(S,2,3,4,5-η^4-DHT) (7)

Table 4. Selected bond distances (Å) and angles (deg) for $(\mu_2\text{-H})Ru_3(CO)_9(\mu_3\text{-S},2,3,4\text{-}\eta^4\text{-DHT})$ (7)

Bond Distances (Å)

Ru(1)-Ru(2)	2.803(2)[a]	S-C(2)	1.77(3)
Ru(1)-Ru(3)	2.821(2)	S-C(5)	1.72(3)
Ru(2)-Ru(3)	3.032(2)	S'-C(2')	1.80(4)
Ru(1)-C(2)	2.18(3)	S'-C(5')	1.83(4)
Ru(1)-C(2')	2.18(4)	C(2)-C(3)	1.50(5)
Ru(2)-S	2.331(6)	C(3)-C(4)	1.33(5)
Ru(2)-C(3')	2.52(3)	C(4)-C(5)	1.62(5)
Ru(2)-C(4')	2.40(6)	C(2')-C(3')	1.45(6)
Ru(3)-S'	2.26(1)	C(3')-C(4')	1.40(9)
Ru(3)-C(3)	2.44(3)	C(4')-C(5')	1.53(9)
Ru(3)-C(4)	2.39(3)		

Bond Angles (deg)

Ru(2)-Ru(1)-Ru(3)	65.25(5)	C(2)-C(3)-C(4)	119(3)
Ru(1)-Ru(2)-Ru(3)	57.65(3)	Ru(3)-C(4)-C(3)	76(2)
C(3')-Ru(2)-C(4')	33(2)	Ru(3)-C(4)-C(5)	115(2)
Ru(1)-Ru(3)-Ru(2)	57.10(5)	C(3)-C(4)-C(5)	109(3)
C(3)-Ru(3)-C(4)	32(1)	S-C(5)-C(4)	105(2)
Ru(2)-S-C(2)	97.3(9)	Ru(1)-C(2')-S'	110(2)
Ru(2)-S-C(5)	103(1)	Ru(1)-C(2')-C(3')	97(2)
C(2)-S-C(5)	97(2)	S'-C(2')-C(3')	101(3)
Ru(3)-S'-C(2')	96(1)	Ru(2)-C(3')-C(2')	107(3)
Ru(3)-S'-C(5')	101(1)	Ru(2)-C(3')-C(4')	69(3)
C(2')-S'-C(5')	95(2)	C(2')-C(3')-C(4')	127(4)
Ru(1)-C(2)-S	108(1)	Ru(2)-C(4')-C(3')	78(3)
Ru(1)-C(2)-C(3)	94(2)	Ru(2)-C(4')-C(5')	115(4)
S-C(2)-C(3)	104(2)	C(3')-C(4')-C(5')	104(4)
Ru(3)-C(3)-C(2)	109(2)	S'-C(5')-C(4')	108(4)
Ru(3)-C(3)-C(4)	72(2)		

[a] See Table 2 for footnote.

Table 5. Positional and thermal parameters for $(\mu_2\text{-H})Ru_3(CO)_9(\mu_3\text{-S},2,3,4\text{-}\eta^4\text{-DHT})$ (7)^a

atom	x	y	z	B,^{b}(Å^2)
Ru(1)	0.2417(1)	0.000	0.6575(1)	3.70(2)
Ru(2)	0.3408(1)	-0.0699(2)	0.9460(1)	4.05(2)
Ru(3)	0.2549(1)	-0.2374(1)	0.6983(1)	3.89(2)
S	0.0766(6)	-0.0463(7)	0.9670(9)	4.3(2)
S'	0.006(1)	-0.203(1)	0.746(2)	3.9(3)
O(6)	0.084(2)	0.008(2)	0.341(2)	9.6(5)*
O(7)	0.209(2)	0.252(2)	0.710(2)	7.6(3)*
O(8)	0.566(2)	0.023(2)	0.539(2)	7.2(3)*
O(9)	0.365(2)	0.179(2)	1.053(2)	9.3(5)*
O(10)	0.426(3)	-0.173(2)	1.242(3)	11.0(6)*
O(11)	0.675(1)	-0.061(1)	0.858(2)	6.4(3)*
O(12)	0.262(2)	-0.484(2)	0.803(2)	7.6(4)*
O(13)	0.144(2)	-0.286(2)	0.375(2)	7.9(4)*
O(14)	0.583(1)	-0.241(1)	0.603(1)	6.0(3)*
C(2)	0.029(3)	-0.026(3)	0.773(3)	4.1(6)*
C(3)	0.006(3)	-0.144(3)	0.713(3)	3.7(4)*
C(4)	0.009(3)	-0.231(4)	0.807(4)	4.8(7)*
C(5)	0.011(4)	-0.183(3)	0.978(4)	4.8(6)*
C(6)	0.148(2)	0.011(2)	0.468(2)	6.0(4)*

[a] Parameters with an asterisk were refined isotropically.

[b] See Table 3 for footnote.

Table 5. Continued

atom	x	y	z	B,[b](Å^2)
C(7)	0.222(2)	0.159(2)	0.690(2)	4.8(3)*
C(8)	0.446(2)	0.010(2)	0.588(2)	4.0(2)*
C(9)	0.356(4)	0.095(4)	0.997(4)	9.9(8)
C(10)	0.384(2)	-0.139(2)	1.130(2)	5.4(3)*
C(11)	0.547(2)	-0.064(2)	0.886(2)	4.8(3)*
C(12)	0.258(2)	-0.392(2)	0.772(2)	5.1(3)*
C(13)	0.187(2)	-0.267(2)	0.503(2)	5.8(4)
C(14)	0.463(2)	-0.232(2)	0.637(2)	4.7(3)
C(2')	0.021(4)	-0.050(3)	0.744(5)	3.0(7)*
C(3')	0.059(4)	-0.027(3)	0.901(6)	2.8(6)*
C(4')	0.082(6)	-0.106(7)	1.1016(7)	6.(1)*
C(5')	0.012(4)	-0.215(4)	0.950(4)	3.3(7)*

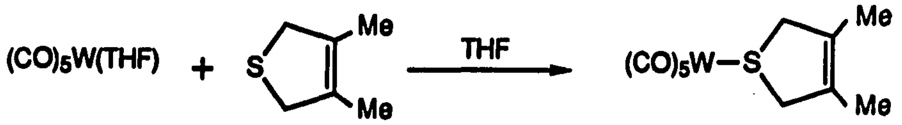
RESULTS AND DISCUSSION

Preparation of Transition-Metal Complexes with Sulfur-Bound 2,5-DHT Ligands

Dihydrothiophene exists in two isomeric forms, 2,3-DHT and 2,5-DHT. While 2,3-DHT is not very stable,[19] polymerizing upon heating and slowly decomposing on exposure to air, 2,5-DHT is relatively stable.[20] In principle, 2,5-DHT may coordinate to metals via either the S atom or the olefinic bond.

In all of the mononuclear complexes described in this paper the 2,5-DHT coordinates through the sulfur atom, as is typical of simple thioethers[21] and also occurred in 2,3-DHT complexes.[4a,b,e] The complexes containing the S-bound 2,5-DHT described in this paper are air-stable.

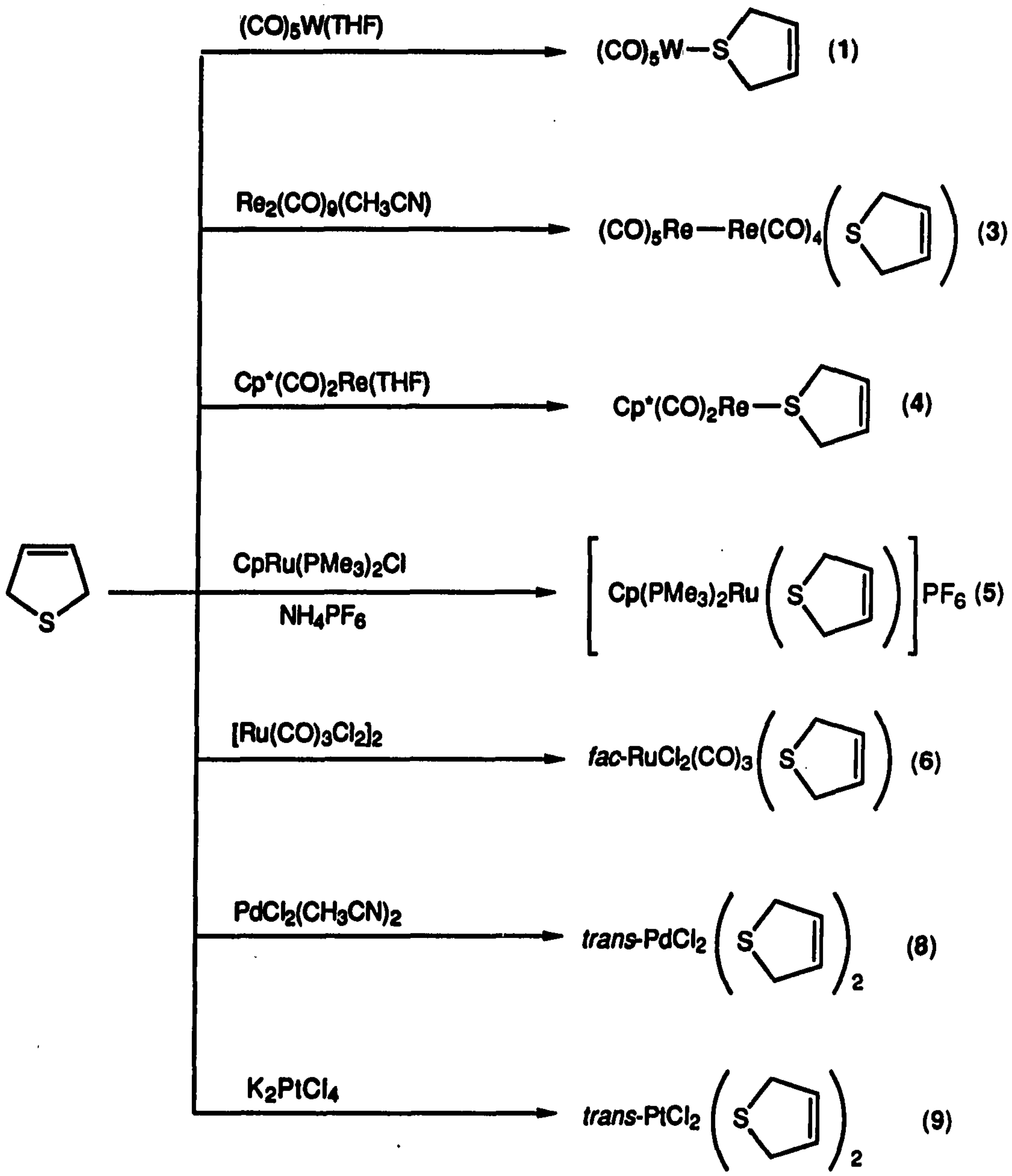
Reactions leading to S-bound 2,5-DHT complexes are summarized in Scheme II. Substitution of the labile THF ligand in $W(CO)_5(THF)$ with 2,5-DHT leads to the S-coordinated DHT complex $(CO)_5W(2,5\text{-DHT})$ (**1**). The analogous reaction with $3,4\text{-Me}_2DHT$ gives $(CO)_5W(3,4\text{-Me}_2DHT)$ (**2**) (eq 1). The reaction of $Re_2(CO)_9(CH_3CN)$ and 2,5-DHT in



2

(1)

Scheme II


(CO)5W(THF)
(CO)5W—S
(1)
Re2(CO)9(CH3CN)
(CO)5Re—Re(CO)4
(3)
Cp*(CO)2Re(THF)
Cp*(CO)2Re—S
(4)
S
CpRu(PMe3)2Cl
NH4PF6
Cp(PMe3)2Ru
PF6
(5)
[Ru(CO)3Cl2]2
fac-RuCl2(CO)3
(6)
PdCl2(CH3CN)2
trans-PdCl2
2
(8)
K2PtCl4
trans-PtCl2
2
(9)

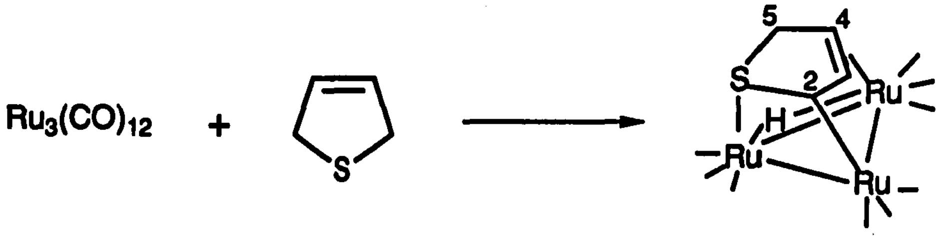
refluxing benzene leads to the formation of the S-coordinated complex **3**. Complex **3** presumably has a structure in which the 2,5-DHT is in an equatorial position since its υ(CO) pattern is very similar to that of $Re_2(CO)_9(CH_3CN)$[10] for which a structure with an equatorial CH_3CN has been assigned. Compound **4** was prepared by the substitution of the THF ligand in $Cp^*(CO)_2Re(THF)$ with 2,5-DHT. The reaction of $CpRu(PMe_3)_2Cl$ with excess 2,5-DHT and NH_4PF_6 in CH_3OH yields $[Cp(PMe_3)_2Ru(2,5\text{-DHT})]PF_6$. Cleavage of the chloride bridges in $[Ru(CO)_3Cl_2]_2$ by 2,5-DHT gives *cis*-$RuCl_2(CO)_3(2,5\text{-DHT})$ (**6**). The IR spectrum of **6** shows three CO bands (2130, 2070, and 2041 cm^{-1}) of the same intensity. Its υ(CO) pattern is a very similar to *fac*-$RuCl_2(CO)_3(L)$ (L = pyridine, EtCN, and PhCN).[22] Displacement of CH_3CN from $PdCl_2(CH_3CN)_2$ by 2,5-DHT gives *trans*-$PdCl_2(2,5\text{-DHT})_2$ (**8**). When K_2PtCl_4 is reacted with 2,5-DHT, it forms *trans*-$PtCl_2(2,5\text{-DHT})_2$ (**9**). The products of **8** and **9** are presumed to have the *trans* structures as are typical of other bis(thioether)palladium[4e,23] and platinum complexes.[18,23]

All of these S-coordinated 2,5-DHT complexes are characterized by their IR, ^1H and ^{13}C NMR, mass spectra as well as elemental analyses (see Experimental Section). In the ^1H NMR spectra of the 2,5-DHT complexes both the H2, H5 and H3, H4 sets of resonances are downfield compared to those (δ 5.85, 3.76, $CDCl_3$) in free 2,5-DHT; since they are closer to the coordinated sulfur, H2, H5 move further downfield than H3, H4. Similar small downfield shifts also have been observed in previously reported S-coordinated 2,3-DHT complexes: $W(CO)_5(2,3\text{-DHT})$,[4c] $[Re(CO)_5(2,3\text{-DHT})]^+$,[4c] *trans*-$PdCl_2(2,3\text{-DHT})_2$,[4c] $Ru(CO)_3Cl_2(2,3\text{-DHT})$,[4c] $Cr(CO)_5(2,3\text{-DHT})$,[15] and $[HPt(PEt_3)_2(2,3\text{-DHT})]^+$.[4a] If olefin coordination had occurred, H3 and H4 would be expected to shift upfield. In the ^{13}C NMR spectra, large upfield shifts of the olefinic carbons would also be expected upon coordination of the double bond. Such upfield shifts are observed in η^2-bound olefins[24] and arenes[25] in both the ^1H and ^{13}C NMR spectra. However, the C3 and C4 resonances for the complexes in Scheme II lie in the region typical of uncoordinated olefins. Therefore, both the ^1H and ^{13}C NMR spectra support S-coordination of 2,5-DHT in these complexes.

An x-ray diffraction study of $[Cp(PMe_3)_2Ru(2,5\text{-DHT})]PF_6$ (**5**) confirms (Figure 1) the S-coordination of 2,5-DHT. The Ru-S distance (2.330(1) Å) is similar to that (2.355(1) Å) between Ru and the tetrahydrothiophene (THT) in *mer*-(BEPS)-*cis*-$Br_2(THT)Ru$ (BEPS = bis(3-(ethyl-sulfinyl)propyl)sulfide)[26] and to the Ru-S distance (2.367(3) Å)[27] in $(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)^+$. The C3-C4 distance (1.327(6) Å) of DHT ring is very similar to that (1.32 Å)[28] of normal $C(sp^2) = C(sp^2)$ bonds. The C-S distances (1.855(3), 1.861(3) Å) in **5** appear to be slightly longer than normal $C(sp^3)$-S distances (1.82 Å)[28] in thioethers. The dihedral angle between the planes defined by C(2), C(3), C(4), C(5) and C(2), S, C(5) is 26.2(3)°.

Reaction of $Ru_3(CO)_{12}$ with 2,5-DHT

The reaction of $Ru_3(CO)_{12}$ with 2,5-DHT in refluxing THF forms the cluster compound, $(\mu_2\text{-H})Ru_3(CO)_9(\mu_3\text{-S},2,3,4\text{-}\eta^4\text{-DHT})$ (7) (eq 4).



7

(4)

Compound **7** was obtained as a yellow-orange crystalline solid and characterized by its IR, MS, ^1H and ^{13}C NMR spectra, elemental analysis and x-ray determined structure. The ^1H NMR spectrum shows six different chemical resonances, compared to the simple spectra of S-coordinated 2,5-DHT complexes. The hydride of **7** is observed at -18.56 ppm as a doublet with a coupling constant of $J_{RuH,H5endo} = 2.9$ Hz; coupling of the hydride to H5 endo was established by a COSY 2-D NMR experiment. This experiment together with a computer simulation of the spectrum using observed coupling constants provide assignments of the other protons. The signals at 4.46 (d, $J_{H2,3} = 3.2$ Hz), 4.28 (m, $J_{H4,H5endo} = 2.8$ Hz, $J_{H5\ exo,endo} = 12.3$ Hz), and 2.61 (m, $J_{H3,H5exo} = 0.7$ Hz) are assigned to H2, H5endo and H5exo, respectively. The H3 and H4 protons of the coordinated olefin are observed at 3.89 (m, $J_{H3,4} = 5.1$ Hz) and 3.41 (d of d, $J_{H3,4} = 5.1$ Hz, $J_{H4,6} = 2.8$ Hz), which is 2~2.5 ppm upfield of the olefinic protons in free 2,5-DHT (5.85 ppm, $CDCl_3$) as expected for a coordinated olefin. In the ^{13}C NMR spectrum, the coordinated carbon resonances (C3, 79.9 and C4, 36.5) are also upfield by 40-80 ppm compared to free 2,5-DHT (C3, C4; 128.9 ppm).[29] The other two carbon resonances are at 59.8 ppm (C5) and 15.5 ppm (C2). These chemical shifts are unequivocally assigned based on the selective ^1H-coupled ^{13}C NMR experiments. The structural assignment based on spectroscopic data was established by an x-ray diffraction study of complex **7**. The structure shown in Figure 2 shows that the sulfur and the olefin coordinate to two different ruthenium atoms and C-H activation occurs at C2 of the 2,5-DHT forming a C-Ru bond at the third ruthenium atom of the cluster. Thus, the C_4H_5S ligand sits on the triangle of ruthenium atoms. Since there are two orientations of the 2,5-DHT ring in the crystal, the bond distances and angles of the 2,5-DHT ligand have relatively large errors. The longest Ru-Ru distance (3.032(2)Å) is assigned to the hydride-bridged Ru(2)-Ru(3) bond, as it is known that metal-metal bonds are lengthened by a hydride bridge.[30] This hydride location is also supported by ^1H NMR spectroscopic data which show that the metal-hydride is coupled with the proximate $H5_{endo}$ proton.

Relevance to Thiophene HDS

As noted in the Introduction, 2,5-DHT undergoes HDS over Re/γ-Al_2O_3 at 300 °C to give butadiene as the major desulfurized product (eq 1).[4d] Under the same conditions but using D_2 instead of H_2, 65% of the butadiene product contained no deuterium.[4d] This suggests that

2,5-DHT adsorbs to the catalyst in a manner which does not promote C-H cleavage and/or exchange with deuterium on the catalyst surface prior to or during butadiene formation. Since sulfur is the strongest donor in 2,5-DHT, as observed in its coordination to metal complexes in this paper, this mode coordination may also be involved on the catalyst. If such coordination were to also promote the liberation of butadiene from 2,5-DHT, it would reasonably account for the large amount of butadiene formed and the relatively low amount of deuterium incorporation into the butadiene product. Thus, we examined the decomposition of our S-coordinated 2,5-DHT complexes to determine whether or not this coordination promotes butadiene liberation. The solid complexes $W(CO)_5(2,5\text{-}DHT)$ and $Re_2(CO)_9(2,5\text{-}DHT)$ start to decompose at 110 °C. The volatile products were collected after 15-20 min at 110 °C in a liquid nitrogen bath. The ^1H NMR spectra of these volatile materials from both complexes show the presence of butadiene (~20%) and free 2,5-DHT (~80%). The analogous $W(CO)_5(3,4\text{-}Me_2DHT)$ also decomposes at 110-120 °C to give off 2,3-dimethyl-1,3-butadiene (~15%) and free $3,4\text{-}Me_2DHT$ (~85%) under the same conditions.

Uncoordinated 2,5-DHT itself does not decompose at all at 120 °C after 3 days. Therefore, S-coordination of 2,5-DHT to metal centers does promote the liberation of butadiene. Butadiene elimination is also a major decomposition pathway 2,5-DHT adsorbed on Mo(110).[31]

Other S-coordinated 2,5-DHT complexes, $Cp^*(CO)_2Re(2,5\text{-}DHT)$ and $RuCl_2(CO)_3(2,5\text{-}DHT)$, give only free 2,5-DHT upon heating at

110 °C. The S-coordinated 2,5-DHT palladium and platinum complexes $MCl_2(2,5\text{-DHT})_2$, **8** and **9**, are more stable and require higher temperatures (180 °C) for decomposition. Upon heating at 180 °C for 15-20 min, complexes **8** and **9** give off mainly thiophene and free 2,5-DHT (1:1) with only small amounts of butadiene. The formation of thiophene was not observed from the other 2,5-DHT complexes. Presumably, this occurs by elimination of two HCl molecules to give very a unstable intermediate, M(2,5-DHT)(thiophene) (M = Pd, Pt), which decomposes to 2,5-DHT, thiophene and the metals. This dehydrogenation of 2,5-DHT to give thiophene accompanies the formation of butadiene in the reactor studies[4d] as well. Thus, butadiene and thiophene formation are competing reactions on $Re/\gamma\text{-}Al_2O_3$. In the Pd and Pt complexes, **8** and **9**, thiophene is the primary product. However, $W(CO)_5(2,5\text{-DHT})$, $Re_2(CO)_9(2,5\text{-DHT})$ and $Fe(CO)_4(2,5\text{-DHT})$[4c] give butadiene but no thiophene. At this point, it is not clear what properties of the metal complex determine whether or not butadiene is formed. Although it is tempting to suggest that butadiene formation occurs by a concerted process, further studies are required before any mechanistic conclusions can be drawn. However, it is clear that S-coordination does promote butadiene release in certain complexes. Thus, it is possible, or perhaps even probable, that the formation of butadiene from 2,5-DHT over $Re/\gamma\text{-}Al_2O_3$ (eq 1) occurs by such a reaction. These results also support step 4 in Scheme I as a viable desulfurization reaction in the HDS of thiophene.

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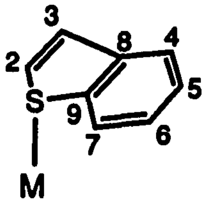
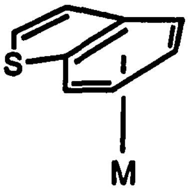
SECTION V. S- VERSUS 2,3-η^2-BENZO[b]THIOPHENE COORDINATION IN Cp'(CO)$_2$Re(BENZO[b]THIOPHENE)[1]

COMMUNICATION

Recent studies of thiophene coordination and reaction in transition metal complexes have suggested new modes of thiophene adsorption and activation on hydrodesulfurization (HDS) catalysts.[2,3] Much less is known about benzo[b]thiophene (BT) coordination in transition metal complexes. Although there is one example of an S-bound BT complex, $Cp(CO)_2Fe(S\text{-}\eta^1\text{-}BT)^+$,[4] all other characterized complexes contain an η^6-BT ligand which is coordinated via the π-system of the benzene ring: $CpRu(\eta^6\text{-}BT)^+$,[5] $Cp^*Rh(\eta^6\text{-}BT)^{+2}$,[5] $Cp^*Ir(\eta^6\text{-}BT)^{+2}$,[5] and $Cr(CO)_3(\eta^6\text{-}BT)$.[6] However, η^6-binding to a catalyst does not account for deuterium exchange of BT on HDS catalysts since the sites of deuterium exchange in BT are different over the catalyst and in $CpRu(\eta^6\text{-}BT)^+$.[7] Likewise, the reactions of $CpRu(\eta^6\text{-}BT)^+$ do not lead to products in which sulfur is fully or even partially cleaved from the BT.[8] Thus, η^6-adsorption to a metal site on an HDS catalyst appears to be an unlikely mode of activating BT toward



$S\text{-}\eta^1\text{-}BT$

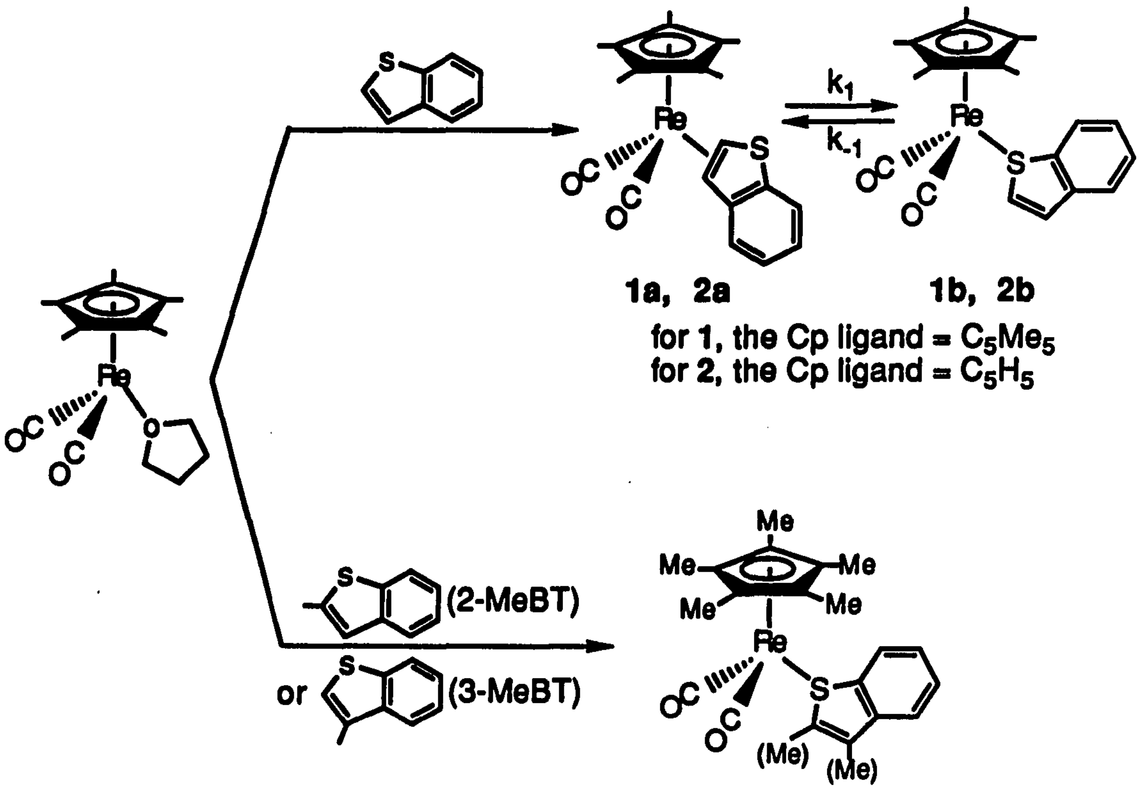


$\eta^6\text{-}BT$

desulfurization. In the present communication, we describe the complexes Cp'(CO)$_2$Re(BT), where Cp' = η^5-C$_5$H$_5$(Cp) or -C$_5$Me$_5$(Cp*), which exist as S- and 2,3-η^2-bound BT isomers in rapid equilibrium with each other. A structural determination of Cp*(CO)$_2$Re(2,3-η^2-BT) confirms the new 2,3-η^2-BT bonding mode.

A solution of Cp*(CO)$_2$Re(THF), generated by UV irradiation of a THF (30 mL) solution of Cp*Re(CO)$_3$ (0.20 g, 0.49 mmol) at -20 °C,[9] was stirred with BT (0.30 g, 2.24 mmol) at room temperature for 10 h. After removing the solvent under vacuum, the residue was chromatographed on neutral alumina using CH$_2$Cl$_2$/hexanes (1:4) eluent. The yellow band was concentrated under vacuum and slowly cooled to -20 °C to give pale yellow, moderately air-stable crystals of **1** (0.053 g, 21%). Although elemental analyses and the mass spectrum establish the composition of **1** as Cp*(CO)$_2$Re(BT),[10] it is evident from the number of bands in the solution IR and ^{1}H and ^{13}C NMR spectra that it consists of 2 isomers, the η^2- (**1a**) and S- (**1b**) isomers, which are present at equilibrium in a 1.6:1 ratio in CDCl$_3$ solution at room temperature (Scheme I). The H2 and H3 ^{1}H NMR signals (δ 7.5~7.1, 3 m; 4.25, d; 3.96 d) of the BT in the major isomer (**1a**) are substantially upfield of those in free BT (δ 7.33 (H2) and 7.22 (H3)).[11] Also, two of the ^{13}C NMR resonances (δ 47.9 and 46.6),[10] presumably those of C2 and C3, are substantially upfield of those in BT. Such upfield ^{1}H and ^{13}C NMR shifts were observed previously in Cp*(CO)$_2$Re(η^2-selenophene)[12] and are characteristic of η^2-olefin[13] and η^2-arene[14] bonding. Thus, the major isomer (**1a**, Scheme I) contains 2,3-η^2-BT.

Scheme I



for 1, the Cp ligand = C_5Me_5
for 2, the Cp ligand = C_5H_5

3 : with 2-MeBT
4 : with 3-MeBT

This was established by an X-ray diffraction study[15] of a crystal of **1a** selected from the product **1**. Although the structure (Fig. 1) did not refine well, it is clear that the BT is coordinated to the Re via C(2) and C(3) in each of the four crystallographically independent molecules, and the BT ring is planar (within experimental error). The average C(2)-C(3) distance (1.53(3) Å) is longer than corresponding bond distances in 5-bromo-2,3-dimethylbenzo[b]thiophene (1.36(1)Å)[16] and 3-formylbenzo[b]thiophene (1.37(1)Å).[17]

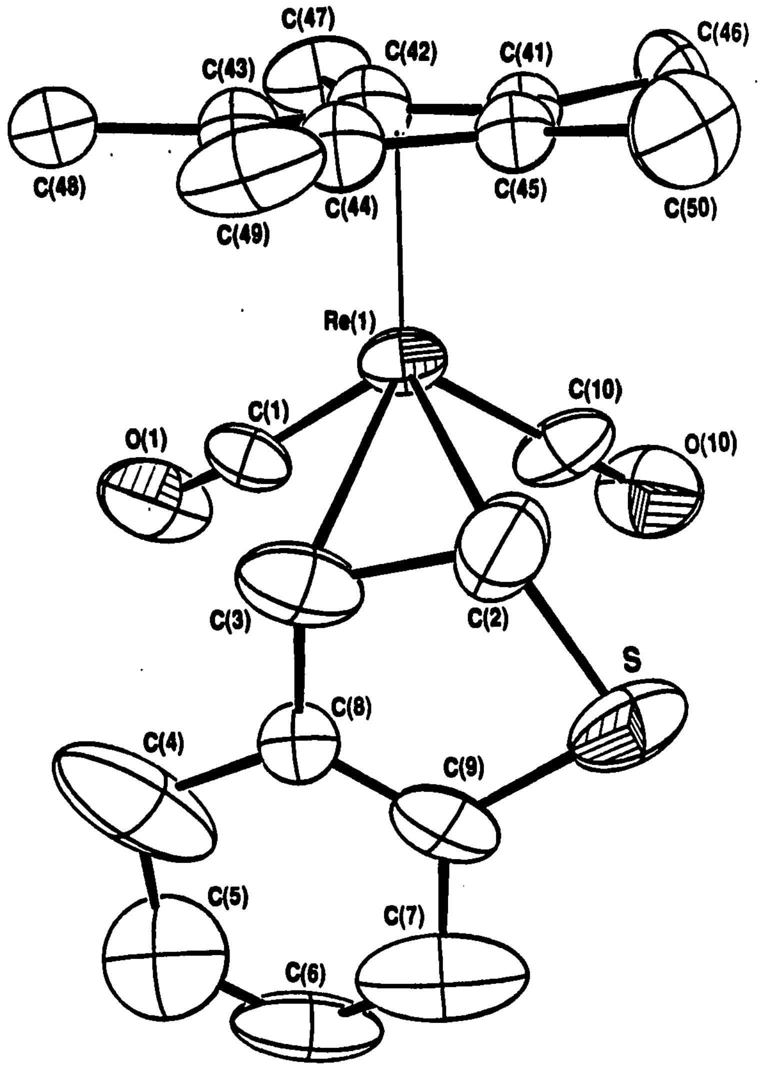
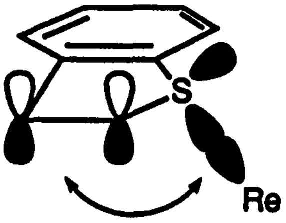


Figure 1. ORTEP drawing of Cp*(CO)$_2$Re(2,3-η^2-BT) (**1a**). Selected average bond distances (Å) and angles (deg) of the four crystallographically independent molecules: Re-C(2) = 2.26(2), Re-C(3) = 2.28(2), S-C(2) = 1.77(2), S-C(9) = 1.76(2), C(2)-C(3) = 1.53(3), C(3)-C(8) = 1.50(2), C(8)-C(9) = 1.34(2), C(2)-S-C(9) = 92(1). The average dihedral angle between the C(2)-Re-C(3) and S-C(2)-C(3)-C(8)-C(9) planes is 113(±4)°.

The ^{1}H and ^{13}C NMR chemical shifts of the BT ligand in the minor isomer (**1b**)[10] are similar to those in free BT[11] (^{1}H NMR CCl_4 δ 7.79, 7.72, 7.33, 7.24; ^{13}C NMR ($CDCl_3$) δ 139.7, 139.6, 126.2, 124.2, 124.1, 123.8, 123.6), which are also similar to those[4] of the S-coordinated BT in $Cp(CO)_2Fe(S\text{-}BT)^+$. These comparisons together with the similarity of the υ(CO) bands of **1b** and those of the S-bound thiophene complex $Cp^*(CO)_2Re(T)$[18] strongly suggest that **1b** contains an S-coordinated BT. Since all structures[3,19] of S-coordinated thiophene complexes contain pyramidal sulfur (approximately sp^3 hydridized), the sulfur in **1b** presumably has the same geometry.

The Cp analogue of **1** was prepared in the same manner as described for **1** from $CpRe(CO)_3$ (0.20 g, 0.60 mmol) and BT (0.40 g, 3.0 mmol). After chromatography, the product $Cp(CO)_2Re(BT)$ (**2**) was isolated as moderately air-stable pale yellow crystals in 27% yield. The spectroscopic data[20] indicate that **2**, like **1**, also exists in solution as an equilibrium mixture of η^2-(**2a**) and S-(**2b**) isomers in a 1:3 ratio in $CDCl_3$ solvent at room temperature. Thus, the S-bound isomer is the major form of **2**, but the η^2-isomer predominates in **1**. The additional electron-density provided by the Cp* ligand in **1** presumably reduces the Lewis acid character of the Re which weakens the bond with the electron-donating sulfur in the S-bonded isomer (**1b**); at the same time, the higher electron density on Re increases π back-bonding to the 2,3-η^2-olefinic bond of BT ligand which favors the η^2-isomer (**1a**).

The η^2-isomers (**1a** and **2a**) can be separated by hand from the S-isomers (**1b** and **2b**) based on the morphology of the crystals. After dissolving the η^2-isomers in CH_2Cl_2, approximate rates of isomerization to the S-isomers at room temperature were determined by following the changes in intensity of the reactant and product CO bands until they reached equilibrium. The isomerization of **1a** ($k_1 = 9.0 \times 10^{-4}$, $k_{-1} = 15 \times 10^{-4}$ s^{-1}; $t_{1/2}$ = 13 min for k_1) was approximately 8 times slower than that ($k_1 = 7.0 \times 10^{-3}$, $k_{-1} = 2.3 \times 10^{-3}$ s^{-1}; $t_{1/2}$ = 1.7 min for k_1) of **2a**. These isomerizations must occur intramolecularly, since BT does not dissociate from either the η^2- or S-isomer during the time of the isomerization. This was shown by observing that no Cp*(CO)2Re(2-MeBT) formed, when a $CDCl_3$ solution of Cp*$(CO)_2$Re(BT) (1) and 2-MeBT was stirred at room temperature for 26 h. Also there was no formation of Cp*$(CO)_2$Re(PPh_3) when 1 and PPh_3 were stirred in CD_2Cl_2 at room temperature for 24 h; at longer times Cp*$(CO)_2$Re(PPh_3) was observed. The intramolecular interconversion of the η^2- and S-isomers probably involves a migration of the Re between sulfur and carbon orbitals on the same side of the BT ring.



Reactions as described for 1 (Scheme I) of 2-methyl-benzo[b]-thiophene (2-MeBT; 0.50 g, 3.38 mmol) and 3-methyl-benzo[b]-thiophene (3-MeBT; 1.0 mL, 1.17 g, 7.91 mmol) with Cp*$(CO)_2$Re(THF) generated from Cp*Re(CO)$_3$ (0.20 g, 0.49 mmol) gave after chromatography the S-coordinated BT complexes Cp*(CO)$_2$Re(2-MeBT) (**3**)[21] (23%) and Cp*(CO)$_2$Re(3-MeBT) (**4**)[22] (39%) as moderately air stable, light yellow crystals. The IR, ^{1}H and ^{13}C NMR spectra of **3**[21] and **4**[22] indicate that only the S-coordinated BT complex is present in each case. The preference for S-bonding by 2-MeBT and 3-MeBT is probably caused by two factors: (1) a methyl group on C(2) or C(3) reduces the π-acceptor character of the olefin and also sterically hinders such coordination; (2) the electron-donating Me groups enhance the donor ability of the sulfur thereby favoring S-coordination.

Summarizing the above results, we find that BT coordinates in Cp'(CO)$_2$Re(BT) as an equilibrium mixture of S- and η^2-isomers. When the electron density on the Re is increased by replacing Cp with Cp* the η^2-isomer is favored; when methyl groups are added to the BT, the S-isomer is favored. These shifts in equilibrium can be readily explained by assuming that the sulfur in BT is an electron donor toward Re while bonding of the C(2)-C(3) olefinic bond to Re involves an important component of π back-bonding.

These studies suggest that BT may coordinate to metal sites either via the sulfur or the C(2)-C(3) olefin, and these S- and η^2-isomers may be in rapid equilibrium with each other. It is reasonable to assume that on a catalyst, hydrogenation of BT would occur by insertion of the η^2-form into a metal hydride to give an alkyl intermediate which would with another hydride reductively eliminate to give 2,3-dihydrobenzo[b]thiophene (DHBT). In fact, the homogeneous hydrogenation catalysts

$Ru(H)(Cl)(PPh_3)_3$,[23] $Rh(Cl)(PPh_3)_3$,[24] $RuCl_2(PPh_3)_3$,[25] $Ru(H)(Cl)(CO)(PPh_3)_3$,[25] $Os(H)(Cl)(CO)(PPh_3)_3$,[25] $Rh(COD)(PPh_3)_2^+$,[25] and $Ir(COD)(PPh_3)_2^+$[25] hydrogenate BT to DHBT under mild conditions. A similar process is also likely to occur on an HDS catalyst. Much evidence[25-29] indicates that hydrogenation of BT to 2,3-dihydrobenzo[b]thiophene (DHBT) is the first step in an important pathway to the HDS of BT. It is especially interesting to note that on a $Co\text{-}Mo/Al_2O_3$ catalyst the rates of hydrogenation and HDS of benzo[b]thiophenes decrease with increasing methyl substitution in the order: BT > 2-MeBT > 3-MeBT > 2,3-Me_2BT.[28,29] This can be readily explained by the results of our rhenium studies which show that 2,3-methyl substitution decreases the amount of η^2-coordinated BT, which is therefore likely to reduce the overall rate of hydrogenation.

Finally, the preferential exchange of H2 and H3 in BT when it is passed with D_2 over several HDS catalysts ($PbMo_{6.2}S_8$, $Co_{0.25}MoS$ and $Re/\gamma\text{-}Al_2O_3$)[7] can be explained by reversible β-deuteride transfer to an η^2-coordinated BT. Thus, the observed η^2-BT ligand in **1a** and **2a** provides for the first time a basis for understanding BT hydrogenation and deuterium exchange on HDS catalysts.

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(10) **1**: EIMS (15 eV) m/e 512 (M^+ based on ^{187}Re), 456 (M^+-2CO), 378 (M^+-BT), 350 (M^+-(BT+CO)), 134 (BT). Anal. Calcd for $C_{20}H_{21}O_2ReS$: C, 46.95; H, 4.14. Found: C, 46.95; H, 4.13. **1a**: IR(hexanes) υ(CO) 1970(w), 1908(w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5~7.1 (3 m, 4H, BT), 4.25 (d, 1H, BT), 3.96 (d, 1H, BT), 2.02 (s, 15H, Cp*); ^{13}C NMR ($CDCl_3$) δ 204.4 and 204.3 (CO), 125.5,

123.7, 123.2, 122.6, 47.9 and 46.6 (BT), 97.8 (C of Cp*), 10.2 (Me of Cp*).

1b: IR(hexanes) υ(CO) 1932(s), 1871(s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.8~7.3 (4 m, 6H, BT), 1.81 (s, 15H, Cp*); ^{13}C NMR ($CDCl_3$) δ 205.5 (CO), 145.6, 137.8, 128.1, 126.7, 124.6 and 123.4 (BT), 95.9 (C of Cp*), 10.4 (Me of Cp*).

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(15) Crystallographic data for **1a**: pale yellow crystal, triclinic, space group $P\bar{1}$ (No. 2), a = 12.068(7) (Å), b = 28.25(1) (Å), C = 10.986(3) (Å), α = 94.81(3), β = 101.36(2), γ = 81.40(3), V =

3624(3) Å^3, d_{calcd} = 1.881 g/cm^3, Z = 8, $\mu(MoK_\alpha)$ = 69.35 cm^{-1}. Diffraction data were collected at -40±1 °C by using an Enraf-Nonius CAD4 diffractometer. Of the 8695 unique data, 7039 reflections having $I>3\sigma(I)$ were used to solve the structure. The positions of the four Re and four S atoms were taken from a direct methods E-map. The remainder of the non-hydrogen atoms were located via subsequent cycles of least-squares refinement and difference Fourier maps. R = 9.3% and Rw = 11.6% (w = $1/\sigma^2(|Fo|)$.

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(20) **2a**: IR(hexanes) υ(CO) 1977(w), 1909(w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.3~7.1 (3m, 4H, BT), 5.31 (d, 1H, BT), 5.11 (d, 1H, BT), 4.95 (s, 5H, Cp); ^{13}C NMR($CDCl_3$) δ 202.5 and 201.9 (CO), 126.2, 124.4, 124.0, 122.5, 45.5 and 44.1 (BT), 88.6 (C of Cp).
2b: IR(hexanes) υ(CO) 1947(s), 1885(s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9~7.4 (3m, 4H, BT), 7.20 (d, 1H, BT), 7.14 (d, 1H, BT), 4.81 (s, 5H, Cp); ^{13}C NMR ($CDCl_3$) δ 201.6 (CO) 151.8, 140.7, 138.5, 127.2, 125.0 and 123.9 (BT), 83.0 (C of Cp).

2: EIMS (15 eV) m/e 442 (M^+ based on ^{187}Re), 386 (M^+-2CO), 308 (M^+-BT), 280 (M^+-(BT+CO)), 252 (M^+-(BT+2CO)), 134 (BT). Anal. Calcd for $C_{15}H_{11}ReO_2S$: C, 40.81; H, 2.51. Found: 40.63; H, 2.30.

(21) **3**: IR(hexanes) ν(CO) 1929(s), 1870(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6~7.0 (4m, 5H, BT), 2.34 (s, 3H, Me on BT), 1.81 (s, 15H, Cp*); ^{13}C NMR ($CDCl_3$) δ 205.4 (CO), 148.9, 146.8, 140.7, 126.7, 124.7, 124.6, 123.4, and 123.3 (BT), 95.6 (C of Cp*), 14.0 (CH_3 on BT), 10.2 (CH_3 of Cp*); EIMS (70 eV) m/e 512 (M^+ based on ^{187}Re), 470 (M^+-2CO), 378 (M^+-MeBT), 148 ($MeBT^+$).

(22) **4**: IR(hexanes) ν(CO) 1929(s), 1868(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8~6.7 (4m, 5H, BT), 2.40 (s, 3H, Me on BT), 1.81 (s, 15H, Cp*); ^{13}C NMR ($CDCl_3$) δ 205.8 (CO), 148.3, 141.1, 136.6, 132.1, 126.6, 125.5, 123.7, and 122.4 (BT), 95.9 (C of Cp*), 14.1 (CH_3 on BT), 10.4 (CH_3 of Cp*); EIMS (70 eV) m/e 526 (M^+ based on ^{187}Re), 470 (M^+-2CO), 378 (M^+-MeBT), 148 ($MeBT^+$). Anal. Calcd for $C_{21}H_{23}ReO_2S$: C, 47.98; H, 4.41. Found: C, 47.92; H, 4.24.

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SUPPLEMENTARY MATERIAL

Data Collection and Structure Refinement

Data were collected on two pale-yellow crystals to obtain one hemisphere of data (+h, ±k, ±l). The complete h = 0 layer was collected on both crystals for merging purposes. The orientation matrix for each crystal was determined from a set of reflections found by an automatic search routine. Broad peaks and difficulty in obtaining a good orientation matrix on each crystal indicated marginal crystal quality. More accurate cell parameters were determined after data collection using a set of 25 carefully centered high-angle reflections. Each data set was corrected for Lorentz and polarization effects. The data for crystal No. 1 were corrected for a 5.1% intensity loss during the collection of 8739 reflections. No decay was observed for crystal No. 2, on which 3231 reflections were collected. An absorption correction based on a series of ψ-scans for each crystal was applied.

A total of 11970 measurements were merged (using the method of Rae and Blake[1]) to give 8695 unique reflections (R_{int} = 0.086). Further data collection and reduction information is given in Table 1.

The initial choice of the centric group $P\bar{1}$ was suggested by intensity statistics, and was confirmed by the successful solution and refinement of the structure. The positions of the four Re and four S atoms were taken from a direct methods E-map.[2] The remainder of the non-hydrogen atoms were located via subsequent cycles of least-squares refinement and difference Fourier maps.

In the final cycle of refinement, a majority of the atoms of the complex were refined anisotropically. The 5 ring atoms of each pentamethylcyclopentadienyl group were left isotropic. Also, atoms C(5), C(8), C(31), and C(34) could not be refined anisotropically. The temperature factors and the electron density residuals indicated a significant amount of unaccounted absorption. Hydrogen atoms were not considered in the model. Neutral-atom scattering factors and anomalous scattering corrections were taken from reference[3].

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP programs.[4]

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Table 1. Crystal and data collection parameters for $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}BT)$ (**1a**)

Formula	$C_{20}H_{21}O_2ReS$
Formula weight	511.65
Space Group	$P\bar{1}$
a, Å	12.068(7)
b, Å	28.25(1)
c, Å	10.986(3)
α, deg	94.81(3)
β, deg	101.36(2)
γ, deg	81.40(3)
V, $Å^3$	3624(3)
Z	8
d_{calc}, g/cm^3	1.881
Crystal size, mm(No. 1)	0.59 x 0.42 x 0.13
(No. 2)	0.38 x 0.22 x 0.09
$\mu(MoK_\alpha)$, cm^{-1}	69.353
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	$MoK_\alpha(\lambda = 0.71073Å)$
Orientation reflections, (No. 1)	24, 25-34°
number, range (2θ) (No. 2)	25, 20-34°
Temperature, °C.	-40(1)

Table 1. Continued

Scan method	ω-scans
Data col. range, 2θ, deg	4.0-45.0
Number of parameters refined	745
Trans. factors, max., min. (No. 1)	0.999, 0.468
(psi-scans) (No. 2)	0.997, 0.488
R^a	0.093
$R_w{}^b$	0.116
Quality-of-fit indicator[c]	2.50
Largest shift/esd, final cycle	0.13
Largest peak, e/Å^3	3.9(4)

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$; $\omega = 1/\sigma^2(|F_o|)$.

[c] Quality-of-fit = $[\Sigma\omega(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (deg)[a] for $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}BT)$ (**1a**)

Bond Distances (Å)			
Re(1)-C(1)	1.88(2)	C(4)-C(5)	1.51(4)
Re(1)-C(2)	2.25(2)	C(4)-C(8)	1.45(3)
Re(1)-C(3)	2.32(2)	C(5)-C(6)	1.31(3)
Re(1)-C(10)	1.90(2)	C(6)-C(7)	1.27(3)
Re(1)-C(41)	2.30(1)	C(8)-C(9)	1.33(2)
Re(1)-C(42)	2.21(2)	C(41)-C(42)	1.35(2)
Re(1)-C(43)	2.33(2)	C(41)-C(45)	1.43(2)
Re(1)-C(44)	2.31(2)	C(41)-C(46)	1.51(2)
Re(1)-C(45)	2.34(2)	C(42)-C(43)	1.43(2)
S(1)-C(2)	1.75(2)	C(42)-C(47)	1.64(2)
S(1)-C(9)	1.74(2)	C(43)-C(44)	1.43(2)
O(1)-C(1)	1.18(2)	C(43)-C(48)	1.49(2)
O(10)-C(10)	1.13(2)	C(44)-C(45)	1.36(2)
C(2)-C(3)	1.56(3)	C(44)-C(49)	1.55(2)
C(3)-C(8)	1.47(2)	C(45)-C(50)	1.54(2)

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2 Continued

Bond Angles (deg)

C(1) - Re(1) - C(2)	111.1(7)	C(2) - C(3) - C(8)	105(2)
C(1) - Re(1) - C(3)	77.6(6)	C(5) - C(4)- C(8)	107(3)
C(1) - Re(1) - C(10)	89.5(8)	C(4) - C(5) - C(6)	127(3)
C(2) - Re(1) - C(3)	39.8(6)	C(5) - C(6) - C(7)	120(3)
C(2) - Re(1) - C(10)	85.7(7)	C(6) - C(7) - C(9)	120(2)
C(3) - Re(1) - C(10)	106.6(7)	C(3) - C(8) - C(4)	117(2)
C(2) - S(1) - C(9)	92(1)	C(3)- C(8) - C(9)	117(2)
Re(1)-C(1) - O(1)	174(1)	C(4) - C(8) - C(9)	125(2)
Re(1)-C(2) - S(1)	124(1)	S(1) - C(9) - C(7)	127(2)
Re(1)-C(2) - C(3)	72.8(9)	S(1) - C(9) - C(8)	115(1)
S(1) - C(2) - C(3)	111(1)	C(7) - C(9) - C(8)	118(2)
Re(1)-C(3) - C(2)	67(1)	Re(1)-C(10)-O(10)	176(2)
Re(1)-C(3) - C(8)	114(1)		

Table 3 Positional and thermal parameters for Cp*(CO)$_2$Re(2,3-η^2-BT) (**1a**)[a]

atom	x	y	z	B,[b] (Å^2)
Re(1)	0.21970(7)	0.13514(4)	0.42800(9)	2.71(2)
Re(2)	0.85151(7)	0.39385(4)	0.97189(9)	2.71(2)
Re(3)	0.43946(8)	0.36339(3)	0.43914(9)	2.71(2)
Re(4)	-0.20342(7)	0.12621(4)	0.89568(9)	2.71(2)
S(1)	0.4668(6)	0.1919(3)	0.4574(9)	6.0(2)
S(2)	1.1009(6)	0.4413(3)	0.9497(9)	4.8(2)
S(3)	0.1961(6)	0.3032(3)	0.3929(8)	5.3(2)
S(4)	-0.4743(7)	0.1990(3)	0.889(1)	6.6(2)
O(1)	0.269(2)	0.0450(8)	0.263(2)	6.0(6)
O(10)	0.226(2)	0.1961(7)	0.216(2)	5.5(5)
O(11)	0.822(2)	0.4716(7)	0.789(2)	5.1(5)
O(20)	0.913(2)	0.3178(7)	0.770(2)	5.2(5)
O(21)	0.374(1)	0.4400(7)	0.634(2)	5.1(5)
O(30)	0.447(2)	0.2931(8)	0.633(2)	7.2(6)
O(31)	-0.218(2)	0.0419(7)	1.040(2)	5.5(5)
O(40)	-0.238(2)	0.1925(7)	1.118(2)	5.5(5)
C(1)	0.256(2)	0.0804(9)	0.327(3)	3.8(6)
C(2)	0.378(3)	0.1643(9)	0.529(3)	4.9(7)
C(3)	0.407(2)	0.109(1)	0.518(3)	4.5(7)
C(4)	0.526(3)	0.050(1)	0.398(4)	9(1)
C(5)	0.613(3)	0.049(1)	0.317(4)	8(1)*
C(6)	0.642(2)	0.087(1)	0.273(3)	6.0(9)
C(7)	0.609(2)	0.129(1)	0.313(3)	7(1)
C(8)	0.485(2)	0.0994(8)	0.429(2)	3.0(5)*
C(9)	0.524(2)	0.1371(9)	0.396(2)	3.6(6)

[a] Parameters with an asterisk were refined isotropically.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. Continued

atom	x	y	z	B,^{b}(Å^{2})
C(10)	0.226(2)	0.1742(9)	0.298(2)	3.6(6)
C(11)	0.837(2)	0.4409(8)	0.864(3)	4.0(6)
C(12)	1.012(2)	0.4280(9)	1.048(2)	3.4(6)
C(13)	1.031(2)	0.3765(9)	1.068(2)	2.6(5)
C(14)	1.162(2)	0.3027(9)	1.013(3)	4.5(7)
C(15)	1.246(2)	0.286(1)	0.938(3)	5.8(7)
C(16)	1.276(2)	0.313(1)	0.860(3)	5.2(7)
C(17)	1.239(2)	0.361(1)	0.855(2)	4.5(7)
C(18)	1.120(2)	0.3523(8)	1.002(2)	3.2(5)
C(19)	1.158(2)	0.3811(9)	0.935(2)	3.9(6)
C(20)	0.897(2)	0.3471(9)	0.849(3)	3.8(6)
C(21)	0.394(2)	0.4112(8)	0.558(2)	3.1(6)
C(22)	0.286(2)	0.3336(9)	0.330(3)	4.1(6)
C(23)	0.252(2)	0.3871(8)	0.355(2)	3.3(6)
C(24)	0.126(2)	0.4406(9)	0.485(3)	4.4(7)
C(25)	0.052(2)	0.442(1)	0.570(3)	4.2(7)
C(26)	0.016(2)	0.399(1)	0.599(3)	4.5(7)
C(27)	0.059(2)	0.357(1)	0.549(2)	3.8(6)
C(28)	0.172(2)	0.3965(9)	0.439(2)	3.5(6)
C(29)	0.136(2)	0.3553(8)	0.468(2)	2.8(5)
C(30)	0.439(2)	0.3202(9)	0.554(3)	4.7(7)
C(31)	-0.215(2)	0.0752(9)	0.980(3)	3.4(5)*
C(32)	-0.374(3)	0.164(1)	0.800(3)	5.8(8)
C(33)	-0.378(2)	0.110(1)	0.794(3)	5.7(7)
C(34)	-0.495(3)	0.060(1)	0.888(3)	7.1(9)*
C(35)	-0.572(3)	0.064(1)	0.979(3)	8.2(9)
C(36)	-0.620(3)	0.105(1)	1.049(4)	9(1)
C(37)	-0.585(2)	0.147(2)	1.026(2)	7(1)

Table 3. Continued

atom	x	y	z	B,[b](Å^2)
C(38)	-0.466(2)	0.106(1)	0.882(3)	6.2(7)
C(39)	-0.508(3)	0.146(1)	0.939(3)	5.9(8)
C(40)	-0.231(2)	0.166(1)	1.034(2)	4.4(6)
C(41)	0.047(2)	0.1767(8)	0.456(2)	2.6(4)*
C(42)	0.039(2)	0.1295(9)	0.430(2)	3.8(5)*
C(43)	0.102(2)	0.0979(8)	0.522(2)	3.2(5)*
C(44)	0.152(2)	0.1324(9)	0.610(2)	3.4(5)*
C(45)	0.121(2)	0.1781(8)	0.574(2)	2.8(5)*
C(46)	-0.017(2)	0.2186(9)	0.384(3)	4.3(7)
C(47)	-0.044(2)	0.107(1)	0.311(2)	4.0(6)
C(48)	0.109(2)	0.0451(9)	0.528(3)	4.2(7)
C(49)	0.230(2)	0.118(1)	0.735(2)	4.6(7)
C(50)	0.150(3)	0.225(1)	0.649(3)	5.1(7)
C(51)	0.781(2)	0.4087(9)	1.156(2)	3.9(6)*
C(52)	0.789(2)	0.359(1)	1.125(3)	4.3(6)*
C(53)	0.711(2)	0.3503(9)	1.007(2)	3.5(5)*
C(54)	0.665(2)	0.3978(9)	0.978(2)	3.5(5)*
C(55)	0.702(2)	0.4341(8)	1.061(2)	2.8(4)*
C(56)	0.841(2)	0.433(1)	1.273(3)	5.7(8)
C(57)	0.853(3)	0.320(1)	1.207(3)	5.2(7)
C(58)	0.686(2)	0.303(1)	0.945(3)	5.8(8)
C(59)	0.566(2)	0.409(1)	0.859(2)	4.6(7)
C(60)	0.665(2)	0.4863(8)	1.057(3)	3.7(6)
C(61)	0.539(2)	0.4065(8)	0.348(2)	3.0(5)*
C(62)	0.491(2)	0.3704(8)	0.253(2)	2.9(5)*
C(63)	0.549(2)	0.3270(9)	0.298(3)	4.2(6)*
C(64)	0.619(2)	0.333(1)	0.416(3)	4.5(6)*
C(65)	0.617(2)	0.379(1)	0.439(3)	4.8(6)*

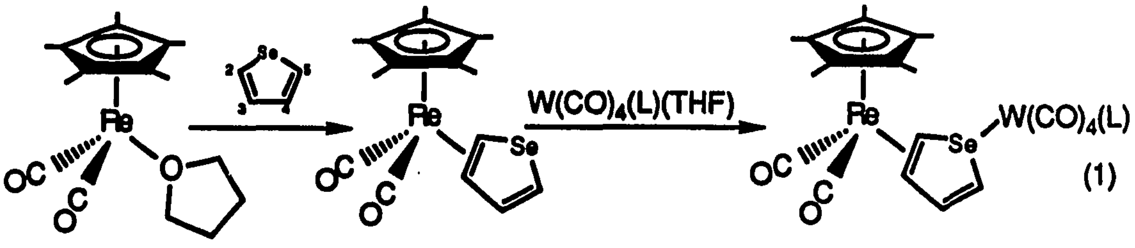
Table 3. Continued

atom	x	y	z	B,^{b}(Å^{2})
C(66)	0.517(3)	0.461(1)	0.334(4)	7(1)
C(67)	0.462(2)	0.382(1)	0.136(3)	5.9(8)
C(68)	0.532(3)	0.279(1)	0.222(3)	8(1)
C(69)	0.694(3)	0.292(1)	0.489(4)	9(1)
C(70)	0.690(3)	0.404(1)	0.553(3)	8(1)
C(71)	-0.059(2)	0.0810(8)	0.814(2)	2.6(4)*
C(72)	-0.137(2)	0.1098(8)	0.715(2)	3.1(5)*
C(73)	-0.125(2)	0.1547(9)	0.749(2)	3.7(5)*
C(74)	-0.049(2)	0.1599(9)	0.870(2)	3.6(5)*
C(75)	-0.017(2)	0.1112(8)	0.902(2)	2.8(5)*
C(76)	-0.036(2)	0.0263(9)	0.813(3)	4.7(7)
C(77)	-0.202(2)	0.091(1)	0.595(2)	6.0(8)
C(78)	-0.175(2)	0.200(1)	0.668(3)	4.9(7)
C(79)	-0.009(2)	0.2056(9)	0.939(3)	4.5(7)
C(80)	0.080(2)	0.096(1)	1.014(2)	4.1(7)

SECTION VI. η^2- AND μ_2-η^2(*Se*)-SELENOPHENE(Sel) COORDINATION IN Cp*(CO)$_2$Re(2,3-η^2-Sel) AND Cp*(CO)$_2$Re(μ_2-η^2(*Se*)-Sel)[W(CO)$_4$(PPh$_3$)][1]

COMMUNICATION

In connection with our interest in the mechanism(s) of the hydrodesulfurization (HDS) of thiophenes on heterogeneous catalysts,[2] we have explored various modes of thiophene(T) coordination in transition metal complexes. Those which are known are shown in Chart I. Complexes with η^5-,[3] S-,[4] η^4-,[5] μ_2-η^4,S-,[6] μ_3-η^4,S-,[7] and ring-opened[8] thiophene coordination have been characterized by X-ray crystallography. The complex $(NH_3)_5Os(2,3\text{-}\eta^2\text{-}T)^{2+}$ was proposed[9] to contain a 2,3-η^2-thiophene ligand based on ^1H NMR spectroscopic evidence. In a previous report,[6] we described the synthesis of the complex $Cp^*(CO)_2Re(T)$ in which the thiophene(T) was S-coordinated to the rhenium. In this Communication, we report the analogous selenophene (Sel) complex $Cp^*(CO)_2Re(Sel)$ in which the selenophene is 2,3-η^2-coordinated to the metal (eq 1).

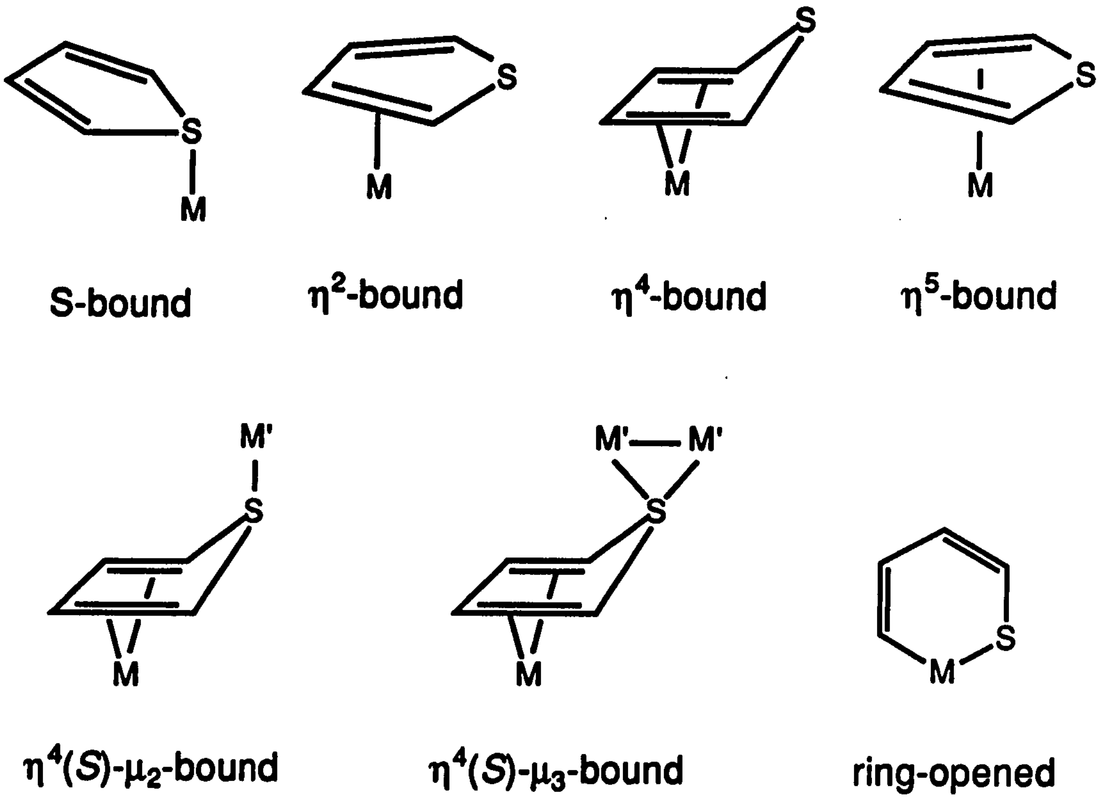


(1)

1

2 : L=CO
3 : L=PPh$_3$

Chart I



S-bound

η^2-bound

η^4-bound

η^5-bound

$\eta^4(S)$-μ_2-bound

$\eta^4(S)$-μ_3-bound

ring-opened

Moreover, Cp*(CO)$_2$Re(2,3-η^2-Sel)(**1**) reacts with W(CO)$_4$(L)(THF), where L = CO or PPh$_3$ and THF = tetrahydrofuran, to give Cp*(CO)$_2$Re(μ$_2$-η^2(*Se*)-Sel)[W(CO)$_4$(L)](**2**, L = CO; **3**, L = PPh$_3$) in which the selenophene is η^2-bonded to the Re and Se-bonded to the W, a bonding mode not previously observed for either thiophene or selenophene.

A solution of Cp*(CO)$_2$Re(THF), prepared by UV irradiation[10] of a THF solution (30 mL) of Cp*Re(CO)$_3$ (0.20 g, 0.49 mmol) at -20 °C, was stirred with selenophene[11] (2.0 mL, 24.5 mmol) at room temperature for 7 h. After removal of the solvent in vacuo, the residue was chromatographed in CH$_2$Cl$_2$/hexane (1:4) on neutral alumina. Slow evaporation of the solvent from the yellow band gave moderately air-stable light yellow crystals of Cp*(CO)$_2$Re(2,3-η^2-Sel)(**1**)[12] (45% yield). As compared with the ^{1}H NMR spectrum of free selenophene (δ 8.05 m, H2,5; 7.37 m, H3,4 in CDCl$_3$),[13] two of the selenophene protons in **1** move substantially upfield (δ 4.52 d, H2; 3.64 m br, H3; 7.02 m br, H4; 6.72 d, H5) characteristic of η^2-olefin ligands.[14] In addition, the expected splitting patterns of the four individual protons for 2,3-η^2-Sel coordination are observed. In the ^{13}C NMR spectrum of **1**, two of the four carbon resonances (δ 46.4, 52.4, 119.8, 134.3) lie considerably upfield of those in free selenophene (δ 129.3, 130.3 in CDCl$_3$) also indicating η^2-coordination[14] via two carbon atoms.

The uncoordinated selenophene Se atom in **1** is capable of binding to a W(CO)$_5$ group to give **2** (eq 1). Thus, Cp*(CO)$_2$Re(η^2-Sel) (**1**; 50 mg, 0.098 mmol) reacts with a solution of W(CO)$_5$(THF),[15] prepared by

UV irradiation of a THF solution (25 mL) of $W(CO)_6$ (60 mg, 0.17 mmol), at room temperature for 7 h. After evaporation of the solution to dryness in vacuo, the residue was chromatographed on neutral alumina with hexanes/CH_2Cl_2 (2:1) as the eluent. The yellow band was collected and reduced in volume under vacuum. Cooling the concentrated solution to -70 °C gave air-stable, pale yellow crystals (70% yield) of **1**.[16] As in **1**, the ^1H and ^{13}C NMR spectra of **2** show two upfield protons (δ 4.16 d, H2; 3.18 d of d, H3; 7.01 d of d, H4; 6.29 d, H5) and two upfield carbons (δ 44.0, 51.1, 119.1, 140.9) which indicate the presence of the η^2-selenophene.

The PPh_3 derivative of **2** was prepared in the same manner from $Cp^*(CO)_2Re(\eta^2\text{-Sel})$ (60 mg, 0.012 mmol) and $W(CO)_4(PPh_3)(THF)$, generated by UV photolysis of $W(CO)_5(PPh_3)$ (90 mg, 0.015 mmol) in THF. Crystals of air-stable, pale yellow **3**[17] (73% yield) were obtained from hexanes/CH_2Cl_2 (2:1) at -70 °C. An X-ray diffraction study[18] of **3** shows (Figure 1) the selenophene ring to be planar. The Re-coordinated C(2)-C(3) distance (1.44(2)Å) is substantially longer than that (1.369(1) Å) in free Sel,[19] while the uncoordinated C(3)-C(4) and C(4)-C(5) distances (1.44(2) and 1.34(2) Å, respectively) are nearly the same as those (1.433(3) and 1.369(1) Å, respectively) in free Sel. Although the C(2)-Se-C(5) angle (86.3(5)°) is essentially the same as that (87.46(4)°) in free Sel,[19] the C(2)-Se and C(5)-Se distances (1.95(1) and 1.92(1)Å) are considerably longer than in Sel(1.855(1)Å).[19] As in S-coordinated thiophene complexes, the Se in **3** is pyramidal as indicated by the angle (112.1(6)°) between the W-Se vector and the vector from Se to the

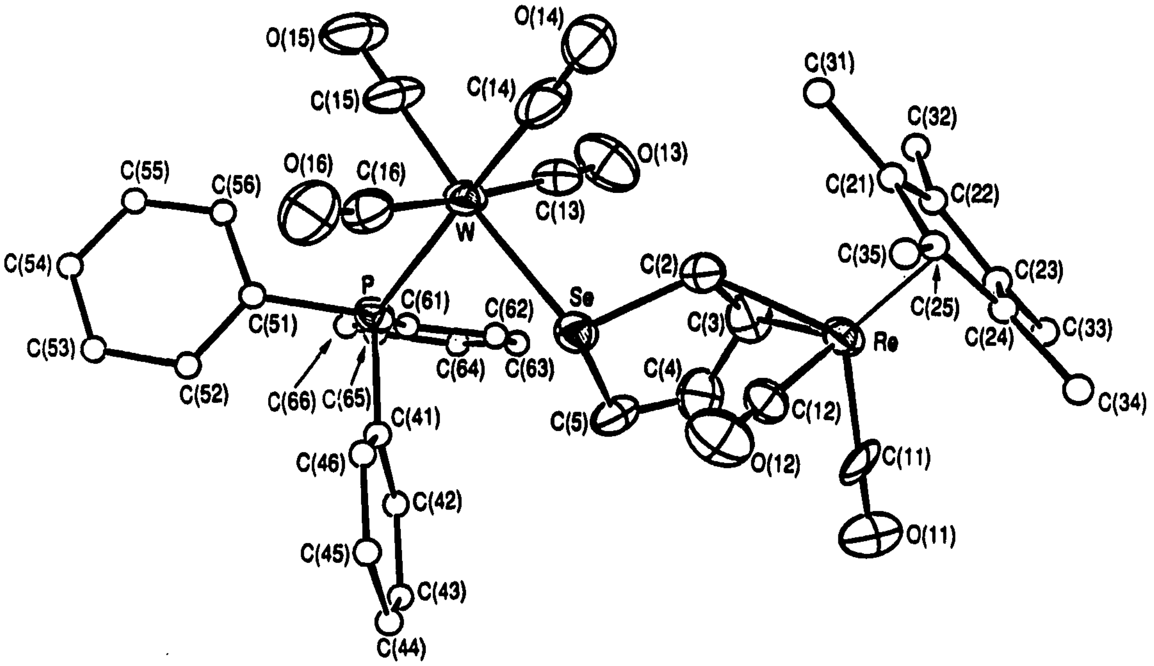


Figure 1. ORTEP drawing of $Cp^*(CO)_2Re(\eta^2,Se\text{-}\mu_2\text{-}Sel)[W(CO)_4(PPh_3)]$ (3). Selected bond distances (Å) and angles (deg) are Re-C(2) = 2.23(1), Re-C(3) = 2.28(2), W-Se = 2.681(2), Se-C(2) = 1.95(1), Se-C(5) = 1.92(1), C(2)-C(3) = 1.44(2), C(3)-C(4) = 1.44(2), C(4)-C(5) = 1.34(2), C(2)-Se-C(5) = 86.3(5). Dihedral angle between the C(2)-Re-C(3) and Se-C(2)-C(3)-C(4)-C(5) planes is 117(1)°.

midpoint of the line from C(2) to C(5). The corresponding angle in Cp*$(CO)_2$Re(T) is 140°.[20] From the above data, it is clear that the structure of the selenophene has been changed significantly as a result of its coordination to the two metals. The lengthening of the C-Se bonds is especially interesting because it is the analogous C-S bonds in thiophenes which must be cleaved on HDS catalysts.

A question which arises in this work is why selenophene is 2,3-η^2-bonded to Cp*$(CO)_2$Re and thiophene is S-bonded. A possible explanation is that the π-system of selenophene, which has been suggested to be more electron-rich than that of thiophene,[21] would form a stronger π-donor bond to the Re than would thiophene. On the other hand, the relative π-accepting properties of Sel and T, as well as the coordinating ablilities of the Se and S atoms, are also involved; thus it is not clear at this time what factors determine the coordination modes of these ligands.

Acknowledgment

I am grateful to Dr. Lee M. Daniels of the Iowa State University Molecular Structure Lab for determining the structure of **3**.

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(12) **1**: IR(hexanes) υ(CO) 1962(s), 1898(s) cm^{-1}; ^{1}H NMR($CDCl_3$) δ 7.02 (br, m, 1H, Sel), 6.72 (d, 1H, Sel), 4.52 (d, 1H, Sel), 3.64 (br, m, 1H, Sel), 1.98 (s, 15H, Cp*); ^{13}C NMR($CDCl_3$) δ 205.4 and 205.0 (CO), 134.3, 119.8, 52.4 and 46.4 (Sel), 97.4 (C of Cp*), 10.3 (Me of Cp*); EIMS (70 eV) m/e 510 (M^+, based on ^{187}Re and ^{80}Se), 454 (M^+-2CO), 378 (M^+-Sel), 350 (M^+-(Sel + CO)). Anal. Calcd for $C_{16}H_{19}O_2ReSe$: C, 37.79; H, 3.77. Found: C, 37.96; H, 3.75. An X-ray study of **1** clearly shows 2,3-η^2-coordination of Sel, but final refinement was not successful due to disorder of the Sel ring.

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(16) **2**: IR(hexanes) υ(CO) 2076(w), 1980(m), 1940(s), 1932(s), 1924(s), 1912(m) cm^{-1}; ^{1}H NMR($CDCl_3$) δ 7.01 (d of d, 1H, Sel), 6.29 (d, 1H, Sel), 4.16 (d, 1H, Sel), 3.18 (d of d, 1H, Sel), 2.01 (s, 15H, Cp*); ^{13}C NMR($CDCl_3$) δ 204.9, 200.9, 198.1 (CO); 140.9, 119.1, 51.1, and 44.0 (Sel), 99.0 (C of Cp*), 10.1 (Me of Cp*);

EIMS (70 eV) m/e 778 (M^+-2CO, based on ^{187}Re and ^{80}Se), 750 (M^+-3CO), 722 (M^+-4CO), 694 (M^+-5CO), 510 (M^+-W(CO)$_5$). Anal. Calcd for $C_{21}H_{19}O_7ReSeW$: C, 30.30; H, 2.30. Found: C, 30.58; H, 2.34.

(17) **3**: IR(hexanes) υ(CO) 2014(m), 1955(m), 1908(m), 1873(s), 1852(s) cm^{-1}; ^{1}H NMR($CDCl_3$) δ 7.53-7.38 (m, 15H, PPh_3), 6.82 (d of d, 1H, SeI), 5.29 (d, 1H, SeI), 4.32 (d, 1H, SeI), 3.19 (d of d, 1H, SeI), 1.97 (s, 15H, Cp*).

(18) Crystallographic data for **3**: Pale yellow crystals of **3**•1.5CH_2Cl_2 were grown from CH_2Cl_2/hexanes at -70 °C. Triclinic, space group $P\bar{1}$ (No. 2) ; a = 13.390 (5) Å, b = 13.812 (6) Å, c = 12.559 (3) Å; α = 116.89 (2)°, β = 95.89 (2)°, γ = 86.66 (2)°; V = 2060 (1) $Å^3$; d_{calcd} = 1.915 g/cm^3; Z = 2; μ = 69.77 cm^{-1} (Mo Kα). Diffraction data were collected at -75 ±1 °C by using an Enraf-Nonius CAD4 automated diffractometer. A total 6723 reflections were collected. Of the 4980 unique data, 4085 reflections having $I > 3\sigma(I)$ were used to solve the structure. The positions of the Re, W, Se, and P atoms were given by direct methods. The remainder of the non-hydrogen atoms were located in difference Fourier maps following least-squares refinement of the known atoms. R = 4.8% and R_w = 6.4% ($w = 1/(\sigma^2/(|F_o|)$. Details of data collection and refinement are given in the supplementary material.

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SUPPLEMENTARY MATERIAL

Data Collection and Structure Refinement

Data were collected on two pale-yellow crystals having approximate dimension 0.19 x 0.13 x 0.10 and 0.24 x 0.18 x 0.11 mm. The orientation matrix for each crystal was determined from a set of automatically centered reflections (crystal 1: 24 reflections, 22° < 2θ < 27°; crystal 2: 22 reflections, 17° < 2θ < 33°). Accurate cell parameters were determined after data collection using a set of 25 carefully centered high-angle reflections. Each data set was corrected for Lorentz and polarization effects. An absorption correction based on a series of ψ-scans for each crystal was applied (min. and max. transmission factors: crystal 1, 0.8075-0.9988; crystal 2, 0.7898-0.9990). No decay was detected in etheir crystal. A total of 6723 measurements were merged (using the method of Rae and Blake[1]) to give 4980 unique reflections (R_{int} = 0.047). Further data collection and reduction information is given in Table1.

The initial choice of the centric space group $P\bar{1}$ was confirmed by the successful solution and refinement of the structure. The positions of the Re, W, Se, and P atoms were taken from a direct methods E-map.[2] The remainder of the non-hydrogen atoms were located via subsequent cycles of least-squares refinement and difference Fourier maps.

Attempts to refine a single pentamethylcyclopentadienyl group were unsuccessful; a second orientation was included in the model, in which the 10-atom group was rotated approximately 18° about its centroid. Each of the two groups were then refined as flat, rigid groups[3] with C-C(ring) distances of 1.417 Å and C-CH_3 distances of 1.512 Å. The relative occupancy of the rings was then included as a variable in the refinement, which converged to a value of 0.53(2) for the major orientation. Each group of five ring carbon atoms and each group of five methyl carbon atoms was refined with a common isotropic temparature factor.

Two sites containing CH_2Cl_2 were located in the lattice, one of which was disorded about the crystallographic center of inversion. The atoms at the disorded site do not give rise to chemically reasonable bond distances.

In the final cycles of refinement, the atoms of the disordered Cp* group were left with isotropic temperature factors, while the rest of the atoms of the complex were refined anisotropically. The Cl atoms of the solvent species were also given anisotropic temperature factors. A secondary extinction coefficient was included and refined to a value of 3.5×10^{-8}. Hydrogen atoms were not considered in the model. Neutral-atom scattering factors and anomalous scattering corrections were taken from reference.[4]

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the SHELX-76 programs.[5]

References

(1) Rae, A. D; Blake, A. B. *Acta Crystallogr.* **1966**, *20*, 586.

(2) SHELXS-86, G. M. Sheldrick, Institut fur Anorganische Chemie der Universitat, Gottingen, F. R. G.

(3) Bond lengths for the rigid pentamethylcyclopentadienyl groups were taken from: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc. Dalton Trans.* **1989**, S1.

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Table 1. Crystal data for Cp*(CO)$_2$Re(μ_2-η^2(*Se*)-Sel)[W(CO)$_4$(PPh$_3$)], (3)

Formula	$C_{38}H_{34}$O6PReSeW 1.5CH2Cl2
Formula weight	1194.08
Space Group	$P\bar{1}$
a, Å	13.390(5)
b, Å	13.812(6)
c, Å	12.559(3)
α, deg	116.89(2)
β, deg	95.89(2)
γ, deg	86.66(2)
V, Å3	2060(1)
Z	2
d_{calc}, g/cm^3	1.915
μ(MoK$_a$), cm^{-1}	69.77
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	MoK$_\alpha$ (λ= 0.71073Å)
Temperature, °C.	-75(1)
Scan method	ω scans
Data col. range, 2θ, deg	4-45
Total No. data measured	6723
No. unique data, total:	4980
with $F_o^2 > 3\sigma(F_o^2)$:	4085

Table 1 Continued

Number of parameters refined	405
R[a]	0.048
R_w[b]	0.064
Quality-of-fit indicator[c]	1.6
Largest shift/esd, final cycle	0.16
Largest peak, e/Å^3	1.8(2)

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(|F_o|) + 0.001|F_o|^2]$.

[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

Table 2. Bond Distances (Å) for $Cp^{*}(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-}Sel)$ $[W(CO)_4(PPh_3)]$ (3)

Re - C(2)	2.23(1)[a]	C(41) - C(46)	1.42(3)
Re - C(3)	2.28(2)	C(42) - C(43)	1.43(2)
Re - C(11)	1.91(1)	C(43) - C(44)	1.41(3)
Re - C(12)	1.89(2)	C(44) - C(45)	1.38(2)
W - Se	2.681(2)	C(45) - C(46)	1.42(3)
W - P	2.546(3)	C(51) - C(52)	1.41(2)
W - C(13)	2.01(2)	C(51) - C(56)	1.39(2)
W - C(14)	1.98(2)	C(52) - C(53)	1.43(2)
W - C(15)	1.96(2)	C(53) - C(54)	1.37(2)
W - C(16)	2.01(2)	C(54) - C(55)	1.37(2)
Se - C(2)	1.95(1)	C(55) - C(56)	1.36(2)
Se - C(5)	1.92(1)	C(61) - C(62)	1.41(2)
P - C(41)	1.83(1)	C(61) - C(66)	1.40(2)
P - C(51)	1.82(1)	C(62) - C(63)	1.41(2)
P - C(61)	1.83(2)	C(63) - C(64)	1.38(3)
C(2) - C(3)	1.44(2)	C(64) - C(65)	1.38(2)
C(3) - C(4)	1.44(2)	C(65) - C(66)	1.39(2)
C(4) - C(5)	1.34(2)	Re - C(21)	2.33(1)

[a] Numbers in parentheses are estimated standard deviations in the least siginificant digits.

Table 2 Continued

C(11)	-	O(11)	1.14(2)	Re	-	C(22)	2.32(1)
C(12)	-	O(12)	1.14(2)	Re	-	C(23)	2.25(1)
C(13)	-	O(13)	1.14(2)	Re	-	C(24)	2.28(1)
C(14)	-	O(14)	1.15(2)	Re	-	C(25)	2.29(1)
C(15)	-	O(15)	1.15(2)	Re	-	C(21')	2.33(1)
C(16)	-	O(16)	1.14(2)	Re	-	C(22')	2.34(1)
C(41)	-	C(42)	1.39(2)	Re	-	C(23')	2.25(1)
Re	-	C(24')	2.33(1)	C(S1)	-	Cl(2)	1.57(4)
Re	-	C(25')	2.30(1)	C(S2)	-	Cl(3)	1.9(1)
C(S1)	-	Cl(1)	1.78(3)	C(S2)	-	Cl(4)	1.1(1)

Table 3. Bond Angles (deg) for $Cp^*(CO)_2Re(\mu_2\text{-}\eta^2(Se)\text{-}Sel)$ $[W(CO)_4(PPh_3)]$, **3**

C(2) - Re - C(3)	37.1(5)[a]	C(14) - W - C(16)	91.9(7)
C(2) - Re - C(11)	110.1(5)	C(15) - W - C(16)	87.5(8)
C(2) - Re - C(12)	87.8(6)	W - Se - C(2)	100.8(5)
C(3) - Re - C(11)	81.7(6)	W - Se - C(5)	111.3(5)
C(3) - Re - C(12)	110.1(5)	C(2) - Se - C(5)	86.3(5)
C(11) - Re - C(12)	87.0(6)	W - P - C(41)	115.2(5)
Se - W - P	91.52(9)	W - P - C(51)	116.0(4)
Se - W - C(13)	90.9(5)	W - P - C(61)	116.9(4)
Se - W - C(14)	87.3(5)	C(41) - P - C(51)	102.7(6)
Se - W - C(15)	173.9(5)	C(41) - P - C(61)	102.7(7)
Se - W - C(16)	91.3(4)	C(51) - P - C(61)	101.1(7)
P - W - C(13)	94.9(4)	Re - C(2)- Se	122.0(8)
P - W - C(14)	178.7(5)	Re - C(2)- C(3)	73.3(8)
P - W - C(15)	94.4(5)	Se - C(2)- C(3)	109.0(9)
P - W - C(16)	88.5(5)	Re - C(3)- C(2)	69.6(9)
C(13) - W - C(14)	84.8(8)	Re - C(3)- C(4)	120(1)
C(13) - W - C(15)	90.0(8)	C(2) - C(3)- C(4)	115(1)
C(13) - W - C(16)	176.0(5)	C(3) - C(4)- C(5)	117(1)
C(14) - W - C(15)	86.8(7)	Se - C(5)- C(4)	113(1)

[a] Numbers in parentheses are estimated standard deviations in the least siginificant digits.

Table 3 Contined

Re - C(11)- O(11)	179(1)	C(52) - C(51) C(56)	119(1)
Re - C(12)- O(12)	175(1)	C(51) - C(52) - C(53)	119(1)
W - C(13)- O(13)	177(1)	C(52) - C(53) - C(54)	120(1)
W - C(14)- O(14)	178(2)	C(53) - C(54) - C(55)	119(1)
W - C(15)- O(15)	178(1)	C(54) - C(55) - C(56)	123(2)
W - C(16)- O(16)	176(1)	C(51) - C(56) - C(55)	120(1)
P - C(41)- C(42)	122(1)	P - C(61) - C(62)	118(1)
P - C(41)- C(46)	117(1)	P - C(61) - C(66)	122.1(9)
C(42) - C(41) - C(46)	121(1)	C(62) - C(61) - C(66)	120(2)
C(41) - C(42) - C(43)	119(2)	C(61) - C(62) - C(63)	118(1)
C(42) - C(43) - C(44)	121(1)	C(62) - C(63) - C(64)	122(1)
C(43) - C(44) - C(45)	119(2)	C(63) - C(64) - C(65)	119(2)
C(44) - C(45) - C(46)	121(2)	C(64) - C(65) - C(66)	122(2)
C(41) - C(46) - C(45)	119(1)	C(61) - C(66) - C(65)	119(1)
P - C(51) - C(52)	121(1)	Cl(1) - C(S1) - Cl(2)	110(1)
P - C(51) - C(56)	120.4(8)	Cl(3) - C(S2) - Cl(4)	147(1)

Table 3. Positional parameters and thermal parameters for Cp*(CO)$_2$Re(μ_2-η^2(*Se*)-Sel)[W(CO)4(PPh3)^a, (3)

atom	x	y	z	B,^{b}(Å^2)
Re	0.73149(4)	0.37755(4)	0.79941(4)	2.35(2)
W	0.63871(4)	0.17382(4)	0.28476(5)	2.58(2)
Se	0.7415(1)	0.1829(1)	0.4837(1)	2.75(4)
P	0.7924(3)	0.1022(3)	0.1665(3)	2.3(1)
C(2)	0.696(1)	0.323(1)	0.604(1)	3.0(4)
C(3)	0.776(1)	0.399(1)	0.641(1)	3.3(4)
C(4)	0.870(1)	0.354(1)	0.592(1)	3.7(5)
C(5)	0.8697(9)	0.250(1)	0.511(1)	2.9(4)
C(11)	0.873(1)	0.384(1)	0.837(1)	2.8(4)
C(12)	0.7423(9)	0.229(1)	0.765(1)	2.6(4)
C(13)	0.667(1)	0.331(1)	0.337(1)	3.7(5)
C(14)	0.521(1)	0.231(1)	0.380(1)	4.6(6)
C(15)	0.551(1)	0.169(1)	0.148(1)	4.0(5)
C(16)	0.600(1)	0.019(1)	0.232(1)	3.3(5)
O(11)	0.9582(8)	0.3905(9)	0.8602(9)	4.2(4)
O(12)	0.7425(8)	0.1407(9)	0.748(1)	4.4(4)
O(13)	0.678(1)	0.421(1)	0.366(1)	5.9(5)
O(14)	0.4520(9)	0.265(1)	0.433(1)	6.1(4)
O(15)	0.4962(9)	0.168(1)	0.070(1)	6.1(5)
O(16)	0.5724(9)	-0.066(1)	0.204(1)	5.8(4)

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[a] Parameters with an asterisk were refined isotropically.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined 4/3[a^2B(1,1)+ b^2B(2,2) + c^2B(3,3) + ab(cos γ)B(1,2) + ac(cos β)B(1,3) + bc(cos α) B(2,3)].

Table 3. Continued

atom	x	y	z	B,[b](Å^2)
C(21)	0.5649(9)	0.437(1)	0.823(1)	2.9(3)*
C(22)	0.6247(9)	0.527(1)	0.848(1)	2.9(3)*
C(23)	0.6956(9)	0.542(1)	0.946(1)	2.9(3)*
C(24)	0.6761(9)	0.465(1)	0.986(1)	2.9(3)*
C(25)	0.5976(9)	0.397(1)	0.907(1)	2.9(3)*
C(31)	0.4790(9)	0.393(1)	0.727(1)	8.0(6)*
C(32)	0.6115(9)	0.599(1)	0.785(1)	8.0(6)*
C(33)	0.7808(9)	0.622(1)	0.994(1)	8.0(6)*
C(34)	0.7254(9)	0.459(1)	1.097(1)	8.0(6)*
C(35)	0.5584(9)	0.298(1)	0.910(1)	8.0(6)*
C(21')	0.591(1)	0.491(1)	0.832(1)	2.3(3)*
C(22')	0.672(1)	0.554(1)	0.912(1)	2.3(3)*
C(23')	0.706(1)	0.503(1)	0.986(1)	2.3(3)*
C(24')	0.639(1)	0.418(1)	0.962(1)	2.3(3)*
C(25')	0.572(1)	0.407(1)	0.862(2)	2.3(3)*
C(31')	0.536(1)	0.511(1)	0.733(1)	7.1(6)*
C(32')	0.707(1)	0.661(1)	0.926(1)	7.1(6)*
C(33')	0.804(1)	0.526(1)	1.065(1)	7.1(6)*
C(34')	0.632(1)	0.360(1)	1.038(1)	7.1(6)*
C(35')	0.499(1)	0.315(1)	0.792(1)	7.1(6)*
C(41)	0.8896(9)	0.039(1)	0.229(1)	2.4(4)
C(42)	0.990(1)	0.064(1)	0.242(1)	3.2(4)
C(43)	1.062(1)	0.014(1)	0.295(1)	3.7(5)
C(44)	1.030(1)	-0.057(10	0.337(1)	4.4(5)
C(45)	0.930(1)	-0.084(1)	0.320(2)	4.8(6)
C(46)	0.857(1)	-0.035(1)	0.268(1)	3.6(5)

Table 3. Continued

atom	x	y	z	B,^{b}(Å^{2})
C(51)	0.7693(9)	-0.002(1)	0.012(1)	2.3(4)
C(52)	0.827(1)	-0.098(1)	-0.032(1)	3.3(4)
C(53)	0.811(1)	-0.175(1)	-0.155(1)	4.0(5)
C(54)	0.737(1)	-0.155(1)	-0.228(1)	3.7(5)
C(55)	0.681(1)	-0.062(1)	-0.181(1)	3.9(5)
C(56)	0.693(1)	0.012(1)	-0.064(1)	3.4(4)
C(61)	0.8635(9)	0.201(1)	0.146(1)	2.9(4)
C(62)	0.890(1)	0.298(1)	0.248(1)	3.2(4)
C(63)	0.945(1)	0.375(1)	0.233(1)	3.8(5)
C(64)	0.975(1)	0.355(1)	0.123(1)	3.9(5)
C(65)	0.947(1)	0.259(1)	0.024(1)	3.4(5)
C(66)	0.8931(9)	0.180(1)	0.033(1)	3.2(5)
C(S1)	0.219(2)	0.364(2)	0.565(2)	7.6(5)*
Cl(1)	0.1264(6)	0.3828(7)	0.4629(6)	12.1(3)
Cl(2)	0.189(2)	0.267(1)	0.588(1)	31(1)
C(S2)	0.52(1)	0.946(8)	0.50(1)	14(3)
Cl(3)	0.661(1)	0.908(1)	0.467(1)	10.1(6)
Cl(4)	0.450(1)	0.963(1)	0.454(1)	12.5(9)

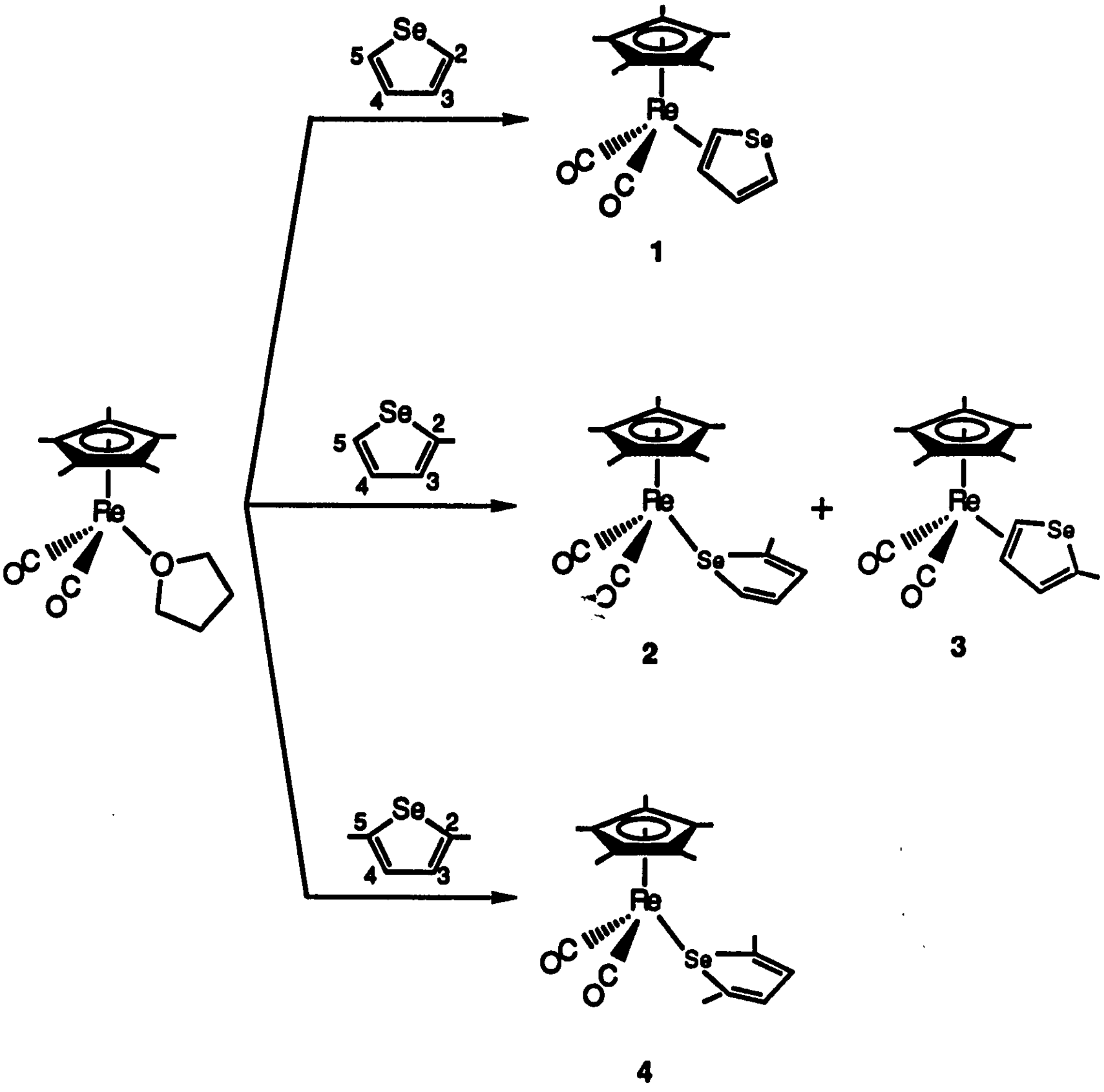
SECTION VII. Se- VERSUS η^2-SELENOPHENE COORDINATION IN $Cp^*(CO)_2Re(SELENOPHENE)^1$

COMMUNICATION

One aspect of our studies of the mechanism(s) of thiophene hydrodesulfurization on heterogeneous catalysts[2] involves examining various modes of thiophene (T) coordination in transition metal complexes. Although T is a weak S-donor ligand,[2] we recently reported[3] the stable S-bound complex $Cp^*(CO)_2Re(T)$. Rather surprisingly the analogous selenophene (Sel) compound $Cp^*(CO)_2Re(\eta^2\text{-Sel})$ (**1**) (Scheme I) contains Sel η^2-coordinated through the 2- and 3-carbons.[4] This η^2 preference was attributed to a higher electron density in the π-system of the Sel as compared to that in T. In this communication, we report a delicate balance between Se- and η^2-coordination depending on the number of methyl substituents in the selenophene. Thus, while $Cp^*(CO)_2Re(Sel)$ is η^2-bound, the analogous 2,5-dimethyl selenophene (2,5-Me_2Sel) complex is Se-coordinated, and the complex of 2-methyl selenophene (2-MeSel) exists as an equilibrium mixture of the Se- and η^2-isomers, which are in rapid equilibrium with each other.

The synthesis of $Cp^*(CO)_2Re(2,5\text{-}Me_2Sel)$ (**4**) follows the same procedure as that used for $Cp^*(CO)_2Re(\eta^2\text{-Sel})$ (**1**).[4] Photolysis (UV) of $Cp^*(CO)_3Re$ (0.20 g, 0.49 mmol) in THF (30mL) at -20 °C to give $Cp^*(CO)_2Re(THF)$ was followed by addition of 2,5-Me_2Sel (0.40 mL, 4.0 mmol).[5] After stirring at room temperature for 7 h, **4** was separated by chromatography on neutral alumina using CH_2Cl_2/hexane (1:4) eluent; **4** was obtained as yellow, moderately air-stable yellow crystals (0.12 g,

Scheme I


Se
5
2
4
3
Re
OC
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Se
1
Re
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3
Re
OC
OC
Se
4

46%).[6] Equivalent H3 and H4 protons (δ 6.59) and CH_3 groups (δ 2.26) slightly upfield of those (δ 6.65 and 2.50) in free 2,5-Me_2Sel establish the ligand as being Se-coordinated. There is no evidence for another isomer either in the IR nor NMR spectra. Although no Se-coordinated selenophenes have been reported previously, the Se atom in **4** is presumably pyramidal and the Re therefore would not lie in the 2,5-Me_2Sel plane; this structural type is characteristic of S-bound thiophene complexes.[2,3,7]

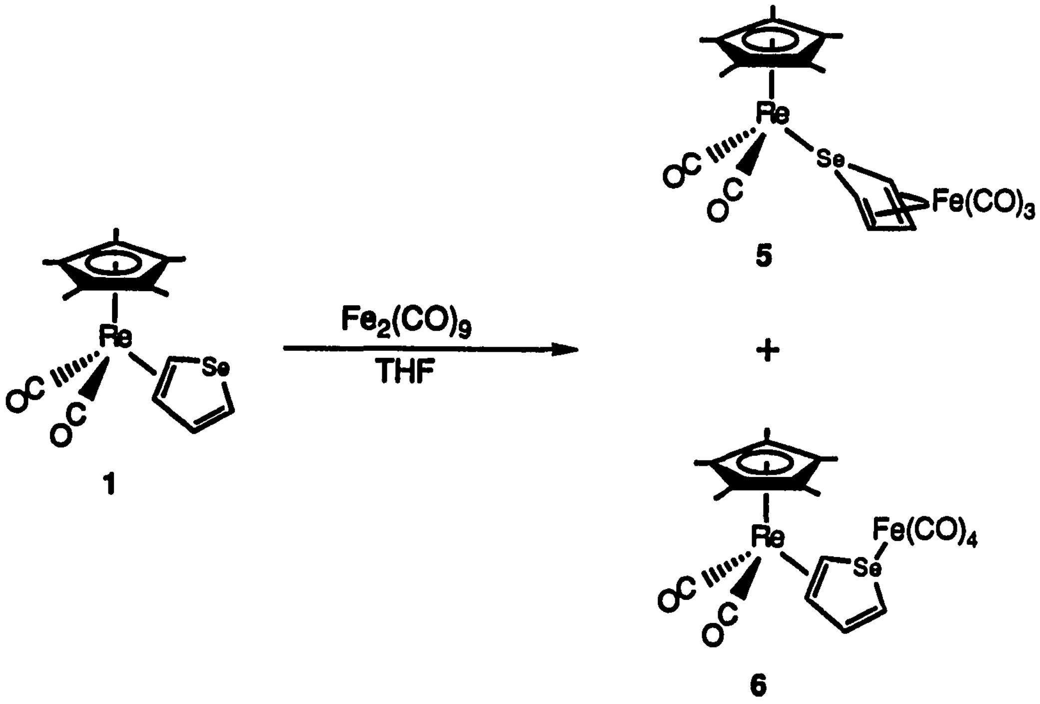
The preference for Se-binding by 2,5-Me_2Sel and η^2-binding by Sel is probably caused by the electron-donating 2,5-methyl groups which make the Se a better donor atom (the methyls may also sterically inhibit η^2-bonding). We previously showed[8] that the rate of dissociation of the analogous S-coordinated thiophenes from $Cp(CO)_2Re(2,5\text{-}Me_2T)$ and $Cp(CO)_2Re(T)$ is much slower for 2,5-Me_2T, which suggests that 2,5-Me_2T is more strongly bonded than T. The methyl groups in 2,5-Me_2Sel should also make it a stronger Se-coordinating ligand than Sel. Clearly there is a delicate balance between Se- and η^2-binding of selenophenes in this system; the addition of electron donating methyl groups is sufficient to shift the balance from η^2- to Se-bonding.

The reaction of 2-Me-Sel (0.60 g, 4.1 mmol)[9] with $Cp^*(CO)_2Re(THF)$, generated from 0.20 g (0.49 mmol) of $Cp^*(CO)_3Re$, was performed as described for **4** (Scheme I). After chromatography, the product $Cp^*(CO)_2Re(2\text{-}MeSel)$ was isolated as moderately air-stable light yellow crystals in 48% yield. Although elemental analyses confirm the composition of the compound,[10] it is evident from the number of absorptions in the solution IR and ^{1}H and ^{13}C NMR spectra that it consists of 2 isomers, the Se-(**2**) and η^2-coordinated (**3**) isomers, which are present in a 1:1.1 ratio in $CDCl_3$ solution. ^{1}H NMR signals assignable to the 2-MeSel ligand in the minor isomer **2** (δ 7.64 d, H5; 7.03 m, H4; 6.82 m, H3; 2.35 s, CH_3) are slightly upfield of those (δ 7.77 m, H5; 7.11 m, H4; 6.92 m, H3; 2.59 s, CH_3) in free 2-MeSel in $CDCl_3$; a similar small upfield shift was observed for the Se-bound 2,5-Me_2Sel in **4**. In contrast, the major isomer **3** shows (δ 4.45 d H5; 3.58 m, H4; 6.57 m, H3; 2.29 s, CH_3) two resonances (H4 and H5) which are substantially upfield from those in free 2-MeSel; this indicates that η^2-coordination occurs at C4 and C5. Such an upfield shift was observed previously[4] in $Cp^*(CO)_2Re(\eta^2$-Sel) (**1**) and is well-known[11] in η^2-bound olefins and arenes. Two high-field resonances (δ 53.5 and 47.3) in the ^{13}C NMR spectrum[10] of the mixture of **2** and **3** also support 4,5-η^2-coordination of 2-MeSel in **3**. Such upfield ^{13}C signals are characteristic[4,11] of η^2-olefin and η^2-arene bonding.

It is not possible to separate isomers **2** and **3** because they are in rapid equilibrium, as indicated by the coalescence at 42 °C of their methyl peaks in the ^{1}H NMR spectrum of the mixture in $CDCl_3$. The mechanism of **2** $\leftrightarrows$ **3** isomerization is intramolecular since 2-MeSel does not dissociate on the isomerization time scale. This is shown by the slower rate ($t_{1/2}$ ~20 min) of 2-MeSel substitution in **2**, **3** by PPh_3 to form $Cp^*(CO)_2Re(PPh_3)$ in $CDCl_3$ at 45 °C; this reaction presumably occurs by rate-determining 2-MeSel dissociation, as was established[8] for thiophene substitution by PPh_3 in the $Cp(CO)_2Re$(thiophene) complexes. The intramolecular interconversion of **2** and **3** presumably involves simple Re migration from its position on the Se out of the plane of the selenophene ring to the C4-C5 π-bond above the ring plane.

Although only one isomer of **1** and **4** is detected spectroscopically in solution, these compounds are, in principle, in rapid equilibrium with the other isomer. Thus, reactions of any of these $Cp^*(CO)_2Re$(selenophene) complexes could occur through either the Se- or the η^2-isomer. The Se-bound isomer might be expected to react with metal complexes which coordinate to the diene portion of the selenophene, as has been observed in the reaction of $Cp^*(CO)_2Re(T)$ with $Fe_2(CO)_9$,[3] while the η^2-isomer would react with complexes that coordinate to the selenium. This latter type of reaction occurs between $Cp^*(CO)_2Re(\eta^2$-Sel) (**1**) and $W(CO)_4(L)(THF)$ (L=CO or PPh_3),[4] but we now observe that **1** reacts with $Fe_2(CO)_9$ to give both types of products (Scheme II). After stirring a solution of **1** (70 mg, 0.14 mmol) with $Fe_2(CO)_9$ (100 mg, 0.27 mmol) in THF (20 mL) for 24 h at room temperature, the product mixture was chromatographed on neutral Al_2O_3 in hexanes to elute a red material. Elution with CH_2Cl_2/hexane (1:4) gave two yellow product solutions which were concentrated and cooled at -20 °C to give yellow crystals of **6** (25%) and **5** (28%). Compound **5** is formulated[12] as $Cp^*(CO)_2Re(\mu_2$-η^4(*Se*)-Sel)$Fe(CO)_3$, in which selenophene is Se-bound to the Re and η^4-bound through the diene to the Fe. This structure is based on the very similar spectroscopic properties of **5** and the thiophene analog $Cp^*(CO)_2Re(\mu_2$-η^4(S)-T)$Fe(CO)_3$, whose structure was established by X-ray diffraction studies.[3] Based on ^{1}H and ^{13}C NMR spectra,[13] compound **6** is assigned the same basic structure as that of Cp*(CO)$_2$Re(μ_2-η^2(*Se*)-Sel) [W(CO)$_4$(L)] (L=CO or PPh$_3$), whose structure was determined[4] by crystallography to have a bridging selenophene which is η^2-bonded to the Re and bound through the Se to the W. The isolation of both **5** and **6** from the reaction of Cp*(CO)$_2$Re(η^2-Sel) (**1**) suggests that the η^2-Sel ligand is in rapid equilibrium with a small amount of the Se-bound isomer which leads to the formation of **5** in the reaction with Fe$_2$(CO)$_9$.

Scheme II



In conclusion, selenophenes may bond to a metal either through the Se or η^2 through two carbons. Coordination through the Se is favored by electron-donating methyl groups in the selenophene. In the case of 2-MeSel, both isomers, **2** and **3**, are present and are in rapid equilibrium. There is evidence to suggest that the η^2-Sel complex **1** also is in equilibrium with small amounts of the Se-bonded isomer which leads, upon reaction with $Fe_2(CO)_9$, to the complex $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(\mathit{Se})\text{-}Sel)Fe(CO)_3$ (**5**). Other factors, such as the metal and its other ligands, will presumably also affect the tendency of selenophenes to coordinate through either the Se or the two carbons. With recent evidence[14] for η^2-bonding of thiophene in $(NH_3)_5Os(\eta^2\text{-}T)^{2+}$, it is also reasonable to consider rapidly interconverting S- and η^2-adsorbed forms of thiophene on HDS catalysts, and such species may be important intermediates in the overall HDS process.

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(6) **4**: IR(hexanes) υ(CO) 1925 (s), 1866 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.59 (s, 2H, H3, H4), 2.26 (s, 6H, CH_3 on Sel), 1.97 (s, 15H, CH_3 of Cp*); ^{13}C NMR ($CDCl_3$) δ 129.4 and 128.2 (Sel), 94.5 (C of Cp*), 16.2 (CH_3 on Sel), 10.5 (CH_3 of Cp*); EIMS (70 eV) m/e 538 (M^+, based on ^{187}Re and ^{80}Se), 482 (M^+-2CO), 378 (M^+-Me_2Sel), 350 (M^+-(Me_2Sel+CO)). Anal. Calcd for $C_{18}H_{23}O_2ReSe$: C, 40.29; H, 4.32. Found: C, 40.20; H, 4.35.

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(10) The mixture of **2** and **3**: ^{13}C NMR ($CDCl_3$) δ 206.1, 206.0 and 205.3 (CO), 140.6, 132.4, 130.1, 128.3, 53.5 and 47.3 (SeI), 97.3 and 94.8 (C of Cp*) 18.1 and 15.8 (CH_3 on SeI), 10.6 and 10.2 (CH_3 of Cp*); EIMS (16 eV) m/e 524 (M^+ based on ^{187}Re and ^{80}Se), 468 (M^+-2CO), 378 (M^+-MeSeI), 350 (M^+-(MeSeI+CO)). Anal. Calcd for $C_{17}H_{21}O_2ReSe$: C, 39.08; H, 4.05. Found: C, 39.09; H, 4.05.

2: IR(hexanes) υ(CO) 1927 (s), 1865 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.64 (d, 1H, H5), 7.03 (m, 1H, H4), 6.82 (m, 1H, H3), 2.35 (s, 3H, CH_3 on SeI), 1.97 (s, 15H, CH_3 of Cp*).

3: IR(hexanes) υ(CO) 1962 (s), 1898 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.57 (m, 1H, H3), 4.45 (d, 1H, H5), 3.58 (m, 1H, H4), 2.29 (s, 3H, CH_3 on SeI), 1.97 (s, 15H, CH_3 of Cp*);

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(12) **5**: IR(hexanes) υ(CO) 2062 (s), 2002 (s), 1990 (s), 1900 (s), 1862 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.85 (m, 2H, SeI), 3.54 (m, 2H, SeI), 1.99 (s, 15H, Cp*); ^{13}C NMR ($CDCl_3$) δ 94.9 (C of Cp*), 77.0 and 46.2 (SeI), 10.7 (CH_3 of Cp*); CIMS(Ammonia) m/e

651 (M^++H, based on ^{187}Re and ^{80}Se). Anal. Calcd for $C_{19}H_{19}O_5$FeReSe: C, 35.20; H, 2.95. Found: C, 35.28; H, 2.97.

(13) **6**: IR(hexanes) υ(CO) 2060 (s), 2000 (s), 1989 (s), 1920 (s), 1900(s), 1862 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.09 (d of d, 1H, Sel), 6.12 (d, 1H, Sel), 4.02 (d, 1H, Sel), 3.20 (d of d, 1H, Sel), 2.01 (s, 15H, Cp*); ^{13}C NMR ($CDCl_3$) δ 214.7, 204.8 203.0 (CO), 143.2, 118.6, 51.1 and 43.7 (Sel) 99.2 (C of Cp*) 10.1 (Me of Cp*); CIMS(Ammonia) m/e 679 (M^++H, based on ^{187}Re and ^{80}Se). Anal. Calcd for $C_{20}H_{19}O_6$FeReSe: C, 35.52; H, 2.83. Found: C, 34.87; H, 2.54.

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SUMMARY

The synthesis of stable S-coordinated thiophene complexes Cp'(CO)2Re(Th) has provided an opportunity to determine the detailed structure of an S-coordinated thiophene ligand and to assess the effect of methyl groups on thiophene bonding to a metal atom. Adding methyl groups to the thiophene ring decreases the rate of thiophene dissociation. Since 2,5-methyl groups do not sterically accelerate thiophene dissociation from $Cp'(CO)_2Re(Th)$ but inhibit it, the 2,5-methyl groups appear to strengthen the metal-sulfur bond. It is demonstrated that S-coordination activates thiophene to react with $Fe(CO)_3$ to give thiophene bridged complexes $Cp'(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}Th)Fe(CO)_3$. The discovery of several novel bonding modes (η^2, μ_2-η^4(*S*)-, and μ_2-η^2(*Se*)) for thiophene, benzo[b]thiophene and selenophene in their $Cp'(CO)_2Re$ complexes suggests new modes of thiophene adsorption and activation on hydrodesulfurization catalysts. The existence of an equilibrium between S- and 2,3-η^2-bound isomers of BT in $Cp'(CO)_2Re(BT)$ suggests that a similar equilibrium may occur on an HDS catalyst. Such an equilibrium provides a reasonable explanation for BT hydrogenation and deuteration on HDS catalysts.

ACKNOWLEDGMENTS

I am deeply indebted to Professor Robert J. Angelici for his guidance, encouragement, and support during the course of this work. It has been a great pleasure working with the past and present members of Angelici research group. Special thanks to John Sowa, Jr. for his friendship and help. I would also like to express my gratitude to Professor Robert A. Jacobson and Dr. Lee M. Daniels for their assistance on X-ray structural studies.

I am very grateful for the constant love and support provided by my entire family, especially my wife Ok-Joo and my mother who raised six sons and provided them all with a university education.

This work was performed at Ames Laboratory under contract no. W-7405-eng-82 with the U. S. Department of Energy. The United States goverment has assigned the DOE Report number IS-T 1499 to this thesis.