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$Re_2(CO)_{10}$-Promoted S-Binding, C−S Bond Cleavage, and Hydrogenation of Benzothiophenes: Organometallic Models for the Hydrodesulfurization of Thiophenes

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Abstract: In hydrodesulfurization model reactions of dinuclear metal complexes with thiophenes, we observe that ultraviolet photolysis of $Re_2(CO)_{10}$ and benzothiophenes (BT*) in hexanes solution produces the ring-opened BT* complexes $Re_2(CO)_7(\mu\text{-BT*})$ (**1a**−**d**) (BT* = benzothiophene (BT) **1a**, 2-methylbenzothiophene (2-MeBT) **1b**, 3-methylbenzothiophene (3-MeBT) **1c**, and 3,5-dimethylbenzothiophene (3,5-Me_2BT) **1d**). The η^1(S)-bound BT* complexes $Re_2(CO)_9(\eta^1\text{(S)-BT*})$ (**2a**−**d**), prepared from $Re_2(CO)_9$(THF) and BT*, are readily converted into **1a**−**d** in good yields (40−60%) during UV photolysis in hexanes solution, which suggests that the η^1(S)-bound complexes **2a**−**d** are precursors to **1a**−**d** in the reactions of $Re_2(CO)_{10}$ with BT*. Irradiation of $Re_2(CO)_{10}$ and 3,5-Me_2BT with UV light in decane solution under an atmosphere of H_2 produces complex **1d** and the partially hydrogenated BT* complex $Re_2(CO)_7(\mu\text{-3,5-Me}_2\text{BT-H})(\mu\text{-H})$ (**3d**). Reactions of **1a** with phosphines yield further ring-opened BT−Re complexes of the types $Re_2(CO)_7(PMe_3)_3$-(μ-BT) (**4**) and $Re_2(CO)_7(PR_3)_2(\mu\text{-BT})$ (R = Me (**5**), ^{i}Pr (**6**), Cy (**7**), and bis(diethylphosphino)ethane (**8**)). Structures of **1d**, **2c**, **3d**, and **6**, which demonstrate various bonding modes of benzothiophene and its C−S cleaved derivatives to two metal centers, were determined by X-ray crystallographic studies.

Introduction

Hydrodesulfurization (HDS) is the transition-metal-catalyzed process used for removing sulfur from organosulfur compounds in petroleum feedstocks.[1,2] This large-scale process is typically performed at high H_2 pressures (<200 atm) and temperatures (300−450 °C) in the presence of sulfided metal-based catalysts such as Ni- and Co-promoted MoS_2 and WS_2 supported on alumina.[1,2] The sulfur content in crude petroleum is typically in the range of 0.1−5 wt % and is present in the form of thiols, thioethers, disulfides, and thiophenes (T*). However, it is the alkyl-substituted benzothiophenes (BT*)[3] and dibenzothiophenes (DBT*) that are among the most difficult to desulfurize during the HDS process due to their greater molecular size and aromatic character.[1,2]

One approach to studying the catalytic HDS of thiophenes and benzothiophenes at transition metal centers is to use organometallic complexes as models. Thiophene coordination to metal centers of organometallic complexes has been studied by several groups as models of thiophene adsorption on HDS catalysts and has been the subject of reviews.[4−6] Several reports[6−9] also describe reactions of thiophenes in mononuclear metal complexes that lead to cleavage of C−S bonds. However, there are relatively few examples of C−S bond cleavage in complexes that contain multiple metal centers.[10−13] The com-

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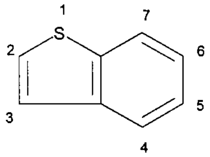
(3) The numbering scheme for benzothiophenes (BT*) is shown below:



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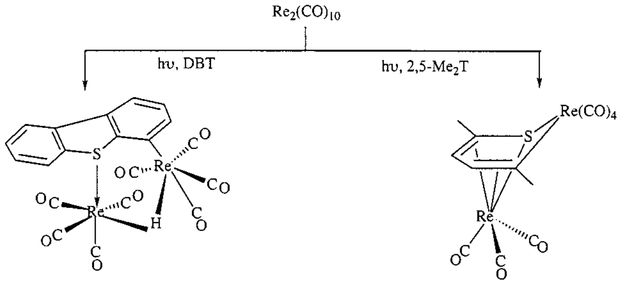
Scheme 1



plexes $Mn_2(CO)_7(\mu\text{-}T^*)$,[14−17] $[Cp^*Co]_2(\mu\text{-}T^*)$,[18] $[(dippe)Ni]_2(\mu\text{-}T^*)$,[19] and $Fe_2(CO)_6(\mu\text{-}T^*)$[20] ($T^* = T$ and BT) represent some of the bimetallic complexes that contain bridging, ring-opened thiophenes. Recently, we found that $Re_2(CO)_{10}$ promotes C−H cleavage of DBT to produce $Re_2(CO)_8(\mu\text{-}C_{12}H_7S)(\mu\text{-}H)$ and C−S cleavage of 2,5-dimethylthiophene (2,5-Me_2T) to afford $Re_2(CO)_7(\mu\text{-}2,5\text{-}Me_2T)$ during UV photolysis (Scheme 1).[21] We also communicated our preparation of $Re_2(CO)_7(\mu\text{-BT})$ and its reactions with PMe_3.[22]

Herein we report detailed studies of the $Re_2(CO)_{10}$-promoted cleavage of C_{vinyl}−S bonds in alkyl-substituted benzothiophenes (BT*) during UV photolysis to afford BT* complexes of the type $Re_2(CO)_7(\mu\text{-BT}^*)$. These new investigations also include reactions of the $Re_2(CO)_7(\mu\text{-BT}^*)$ complexes with phosphines and H_2 to produce unexpected dinuclear ring-opened and partially hydrogenated BT* complexes.

Results and Discussion

Synthesis of $Re_2(CO)_7(\mu\text{-BT}^*)$ Complexes (1a−d). Ultraviolet irradiation of a $Re_2(CO)_{10}$ and 2−3 equiv of BT* (BT* = BT, 2-MeBT, 3-MeBT, or 3,5-Me_2BT) in hexanes solution for 24 h produces the ring-opened BT* complexes $Re_2(CO)_7(\mu\text{-BT}^*)$ (**1a**−**d**) in moderate yields (20−50%) (pathway a in Scheme 2). Complexes **1a**−**d** are air-stable, orange solids that are soluble in most organic solvents including CH_2Cl_2, benzene, and hexanes. In solution, **1a**−**d** are stable for days at room temperature if stored under an inert atmosphere. The molecular structure for **1d** (Figure 1) contains a ring-opened 3,5-Me_2BT ligand that has been cleaved regioselectively at the C_{vinyl}−S bond and bridges the $Re_2(CO)_7$ backbone through the S atom and the η^1,η^2-bonded vinyl group. Cleavage of the vinyl C−S bond in the BT* ligands of **1a**−**d** was unaffected even by a methyl substituent at the 2-position of the BT* ligand. This is in contrast to results reported for other systems[6b] including those by Jones et al.[8c] for the reaction of 2-MeBT with $Cp^*Rh(PMe_3)(Ar)(H)$ ($Cp^* = \eta^5\text{-}C_5Me_5$; Ar = Ph or 3,5-xylyl). In this system, Rh metal insertion into the C_{vinyl}−S bond of 2-MeBT gave, as the kinetic product, $Cp^*Rh(PMe_3)(C_{vinyl},S\text{-}2\text{-MeBT})$ which readily converted into the C_{aryl}−S cleaved isomer $Cp^*Rh(PMe_3)(C_{aryl},S\text{-}2\text{-MeBT})$ upon heating (74 °C, 38 h) in C_6D_{12} solution. Complex **1a** was not converted into a C_{aryl}−S metal-inserted isomer even after heating in refluxing toluene for 2 d. Complexes **1a**−**d** do not react with the electrophiles methyl iodide, methyl trifluoromethane sulfonate (TfOMe), or TfOH.

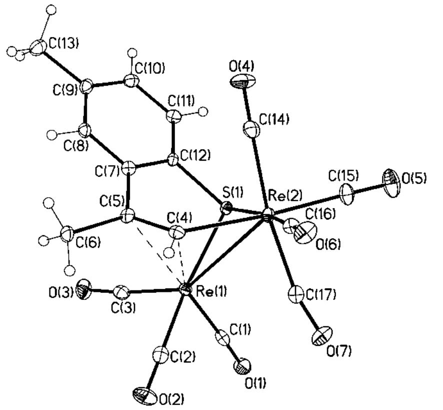
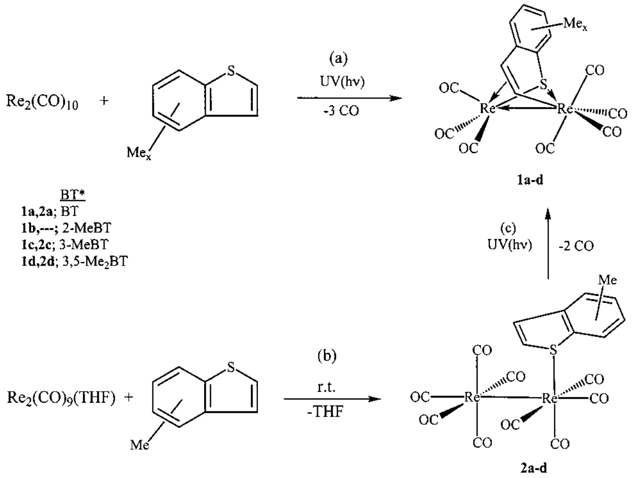


Figure 1. Molecular structure of $Re_2(CO)_7(\mu\text{-}3,5\text{-}Me_2BT)$ (**1d**). Thermal ellipsoids were drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Re(1)−Re(2), 2.9245(3); Re(1)−S(1), 2.4320(13); Re(2)−S(1), 2.4995(13); C(4)−C(5), 1.403(7); S(1)−C(12), 1.787(5); C(5)−C(7), 1.503(7); Re(1)−S(1)−Re(2), 72.73(3); C(4)−C(5)−C(7), 122.9(5); Re(1)−S(1)−C(12), 101.38(18); Re(2)−S(1)−C(12), 102.31(17).

Scheme 2. Preparations of $Re_2(CO)_7(\mu\text{-BT}^*)$ (**1a**−**d**)



In the ^1H NMR spectra of **1a**−**d** (in CD_2Cl_2), the chemical shift for the terminal vinyl proton of **1a** (δ 8.63, d, $J = 11.4$), **1c** (δ 8.22, s), and **1d** (δ 8.20, s) is shifted to low field as compared to that in the free BT* molecules (δ 7.95−7.00). This significant downfield shift of the vinyl protons is consistent with C_{vinyl}−S cleavage of the BT* ligands and η^1-binding of the terminal vinyl carbon to a Re metal center. In the iron complex $Fe_2(CO)_6(\mu\text{-BT})$,[20] which contains a bridging ring-opened BT ligand similar to that in **1a**, a significant downfield shift for the terminal BT vinyl proton (δ 8.99 in $CDCl_3$) was also observed. The chemical shift for the methyl protons of the 2-MeBT ligand (CD_2Cl_2) in **1b** (δ 3.16, s) is also downfield of that in free 2-MeBT (δ 2.60).

Proposed Mechanism for the Formation of 1a−d. A possible mechanism (Scheme 3) for the formation of complexes **1a**−**d** by pathway a in Scheme 2 is similar to that proposed by Brown and co-workers for the formation of alkenyl complexes

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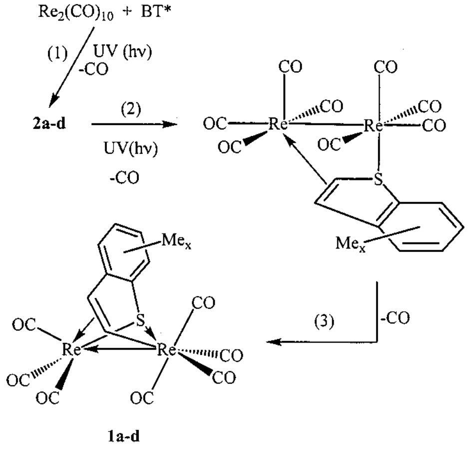
Scheme 3. Mechanism for the Formation of Complexes **1a**−**d**



of the type $Re_2(CO)_8$(μ-alkenyl)(μ-H).[23] The first step (1), which involves the formation of the $Re_2(CO)_9$(η^1(S)-BT*) (**2a**−**d**) complexes, is similar to that for the photochemical reaction of $Re_2(CO)_{10}$ with donor ligands (L = phosphines)[24] to form complexes of the type $Re_2(CO)_9$(L) and $Re_2(CO)_8(L)_2$, which can occur by two mechanisms: [1] CO dissociation from $Re_2(CO)_{10}$ to afford $Re_2(CO)_9$ species (eq 1) and [2] cleavage of the Re−Re bond in $Re_2(CO)_{10}$ to generate •$Re(CO)_5$ radicals (eq 3). In the CO dissociation pathway, the $Re_2(CO)_9$ species would react with BT* molecules to give the $Re_2(CO)_9$(η^1(S)-BT*) (**2a**−**d**) complexes (eq 2).[24] In the Re−Re bond cleavage pathway, •$Re(CO)_5$ radicals would undergo thermal CO substitution by BT* to produce •$Re(CO)_4$(η^1(S)-BT*) radicals (eq 4). Coupling of these radicals with •$Re(CO)_5$ (eq 5) or another •$Re(CO)_4$(η^1(S)-BT*) (eq 6) would produce complexes **2a**−**d** or $Re_2(CO)_8$(η^1(S)-BT*)$_2$.

$$\mathrm{Re_2(CO)_{10}} \overset{h\nu}{\rightleftharpoons} \mathrm{Re_2(CO)_9} + \mathrm{CO} \qquad (1)$$

$$\mathrm{Re_2(CO)_9} + \mathrm{BT^*} \rightleftharpoons \mathrm{Re_2(CO)_9(BT^*)} \qquad (2)$$

$$\mathrm{Re_2(CO)_{10}} \overset{h\nu}{\rightleftharpoons} \mathrm{2Re(CO)_5} \qquad (3)$$

$$\mathrm{Re(CO)_5} + \mathrm{BT^*} \rightleftharpoons \mathrm{Re(CO)_4(BT^*)} + \mathrm{CO} \qquad (4)$$

$$\mathrm{Re(CO)_4(BT^*)} + \mathrm{Re(CO)_5} \rightleftharpoons \mathrm{Re_2(CO)_9(BT^*)} \qquad (5)$$

$$\mathrm{2Re(CO)_4(BT^*)} \rightleftharpoons \mathrm{Re_2(CO)_8(BT^*)_2} \qquad (6)$$

The following experiments were conducted to provide supporting evidence for either the CO dissociation or the Re−Re homolytic bond cleavage pathways. When $Re_2(CO)_{10}$ (0.377 mmol) and excess BT (1.00 mmol) were irradiated with UV light under CO (1 atm) for 42 h (15 °C) in hexanes solution (35 mL), the $Re_2(CO)_{10}$ and BT remained unreacted. In this experiment, the CO could inhibit both pathways by suppressing eqs 1 and 4. If a $Re(CO)_5$ radical pathway is involved, a radical scavenger such as TEMPO (2,2,6,6-tetramethyl-piperidinyl-1-oxy radical) should inhibit the formation of the **2a**−**d** complexes. TEMPO has been used to trap $M(CO)_5$ (M = Mn or Re) radicals during UV photolysis of $M_2(CO)_{10}$ to produce the neutral M−N−O metallacycles of the type (TEMPO)$M(CO)_3$.[25] When a hexanes solution (35 mL) containing $Re_2(CO)_{10}$ (0.238 mmol) and BT (0.714 mmol) was irradiated with UV light (−5 °C) in the presence of TEMPO (0.474 mmol), unreacted $Re_2(CO)_{10}$ and a trace of $Re_2(CO)_7$(μ-BT) (**1a**) was detected by IR spectroscopy after 2 h. After 23 h, all of the $Re_2(CO)_{10}$ had reacted, and the intensity of the ν(CO) bands corresponding to **1a** had not increased. Although other Re products were not identified, an IR spectroscopic analysis of the oily precipitate resulting from the reaction did not reveal any ν(CO) bands that corresponded to **1a** or **2a**. The inhibitory effect of TEMPO is consistent with Re−Re bond homolysis as the major pathway in the formation of **1a**. The small amount of **1a** detected in the TEMPO experiment could likely result from the CO dissociation pathway (eqs 1 and 2) which would not have been inhibited by the TEMPO. However, since the ν(CO) bands corresponding to **1a** were very weak during the TEMPO reaction, this cannot be a dominant pathway.

The formation of **1a**−**d** from **2a**−**d** in steps 1 and 3 of Scheme 3 must also be promoted photolytically as this conversion does not occur thermally under the conditions of the reactions. Photolytic loss of a CO from the adjacent $Re(CO)_5$ moiety in **2a**−**d** with subsequent η^2-binding of the BT vinyl group would yield (step 2) a bridging BT* species $Re_2(CO)_8$(μ_2-η^1(S),η^2-BT*). Subsequent CO loss and oxidative addition of the vinyl C−S bond of BT* would produce the **1a**−**d** products. None of the proposed intermediates, including $Re_2(CO)_9$(η^1(S)-BT*) (**2a**−**d**) and $Re_2(CO)_8$(η^1(S)-BT*)$_2$, were observed during the formation of **1a**−**d**; however, irradiation of $Re_2(CO)_9$(η^1(S)-3-MeBT) (**2c**) in hexanes solvent for 1−5 h did produce **1c** in good yield (>50%) as illustrated in reaction c of Scheme 2. This conversion of **2c** to **1c** supports the proposal that **2a**−**d** are precursors to **1a**−**d**.

Synthesis of $Re_2(CO)_9$(η^1(S)-BT*) (2a−d). The S-bound complexes $Re_2(CO)_9$(η^1(S)-BT*) (**2a**−**d**) were prepared by two different routes. In method A, BT* was added to a THF solution of $Re_2(CO)_9$(THF) prepared by UV photolysis of $Re_2(CO)_{10}$ in THF (path b, Scheme 2). In method B, the $Re_2(CO)_9$(THF) precursor was prepared by reaction of $Re_2(CO)_{10}$ with Me_3NO,[26,27] in a procedure similar to that used for the preparation of $Re_2(CO)_9(CH_3CN)$. Both methods produced **2a**−**d** in low to moderate yields (10−40%). Complexes **2a**−**d** are moderately air-stable in the solid state and are soluble in CH_2Cl_2, benzene, and hexanes solvents. The BT* ligands of **2a**−**d** are labile as demonstrated by the reaction of **2d** with CO (1 atm) which resulted in displacement of the 3,5-Me_2BT ligand to give $Re_2(CO)_{10}$ in less than 2 min; this is the time required to record the IR spectrum.

The ^{1}H NMR spectra of **2a**−**d** indicate S-binding of the BT* ligands; chemical shifts of the BT* protons are within ±0.05−0.30 ppm of those of free BT* (δ 7.95−7.00 in CD_2Cl_2). Similar small chemical shifts were observed in ^{1}H NMR spectra of the S-bound BT complexes $CpRe(CO)_2$(η^1(S)-BT),[28,29] $M(CO)_5$(η^1-

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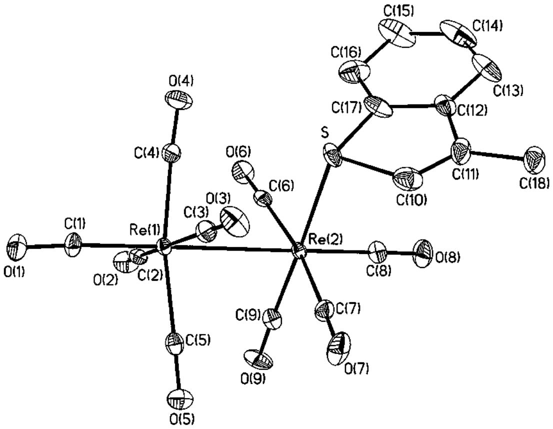


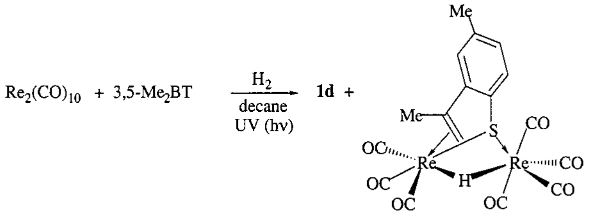
Figure 2. Molecular structure of *eq*-$Re_2(CO)_9(\eta^1(S)\text{-3-MeBT})$ (**2c**). Thermal ellipsoids drawn at the 30% probability level. Selected distances (Å) and angles (deg): Re(1)−Re(2), 3.0343(4); Re(2)−S, 2.5220(18); Re(2)−C(9), 1.927(7); S−C(10), 1.806(9); S−C(17), 1.685(9); C(10)−C(11), 1.268(12); Re(1)−Re(2)−S, 89.21(4); Re(2)−S−C(10), 106.3(3); Re(2)−S−C(17), 111.5(3); C(10)−S−C(17), 90.5(4); tilt angle (θ) = 116.9°.

(S)-BT) (M = Cr or W),[30] and $[CpFe(CO)_2(\eta^1(S)\text{-BT})^+]$.[31] If the BT* ligands were η^2-bonded through the olefin moiety, then the olefinic protons would be expected to shift to higher field as observed in the ^1H NMR spectrum of $Cp^*Re(CO)_2(2,3\text{-}\eta^2\text{-BT})$[29] ($\delta$ 4.25 and 3.96 ppm in $CDCl_3$). Complexes of the type $Re_2(CO)_8(\eta^1(S)\text{-BT*})_2$ were not observed during the synthesis of $Re_2(CO)_9(\eta^1(S)\text{-BT})$ by either method.

In the structure of **2c** (Figure 2), the Re−S bond distance (2.5220(18) Å) is similar to those in the analogous DBT complex $Re_2(CO)_9(\eta^1(S)\text{-DBT})$[21] (2.5375(8) Å) and the thietane complex $Re_2(CO)_9(\overline{SCH_2C(CH_3)_2CH_2})$ (2.485(4) Å).[32] However, as compared to Re complexes which have more electron density on the Re center such as $Cp^*Re(CO)_2(\eta^1(S)\text{-T})$ (2.360(3) Å)[33] and $Cp^*Re(CO)_2(\eta^1(S)\text{-3-MeBT})$[29] (2.349(2) Å), the Re−S distance for **2c** is significantly longer. The tilt angle (θ) for **2c**, which is defined as the angle between the Re−S bond and the vector from the sulfur to the midpoint between the C(11) and C(12) carbons of the 3-MeBT ligand, is used to describe the geometry around the thiophene sulfur atom. In complex **2c**, the value of θ is 116.9°, which indicates that the 3-MeBT sulfur is pseudo-sp^3 hybridized, in contrast to a value of 180° which would indicate a sp^2 sulfur. The tilt angle for **2c** is similar to that in the analogous DBT complex $Re_2(CO)_9(\eta^1(S)\text{-DBT})$ (θ = 113.6°)[21] and comparable to that in other complexes which contain electron-deficient metal centers such as $(CO)_5W(\eta^1(S)\text{-DBT})$[30] (118.8°), $(CO)_5Cr(\eta^1(S)\text{-DBT})$ (121.8°),[30] and $[CpFe(CO)_2(\eta^1(S)\text{-DBT})^+]$ (119.4°).[31] However, the tilt angle in **2c** is much smaller as compared to that in the electron-rich complexes $Cp^*Re(CO)_2(\eta^1(S)\text{-3-MeBT})$ (θ = 131.0°)[29] and $Cp^*Re(CO)_2(\eta^1(S)\text{-T})$ (θ = 140.4°).[33] Harris[34] has proposed that the tilt angle in S-bound metal−thiophene complexes can be used as an indicator of π-back-donation from the metal to the thiophene ligand. More electron density on the metal center increases π-back-bonding, which results in a larger tilt angle and also a shorter M−S bond distance. Therefore, the relatively electron-deficient Re center in **2c** exhibits a smaller tilt angle and longer Re−S bond distance as compared to these parameters in the $Cp^*Re(CO)_2(\eta^1(S)\text{-T*})$ (T* = T or 3-MeBT)[29,33] complexes. The sulfur geometry in **2c** is also described by the sum of the angles around the sulfur (308.3°) which would equal 360° if the S atom were planar (sp^2-hybridized).

The C−S bonds in **2c** (C(10)−S, 1.746(14) Å; C(17)−S, 1.737(7) Å) are significantly shorter than those in $Cp^*Re(CO)_2(\eta^1(S)\text{-3-MeBT})$ (1.92(2) Å and 1.74(3) Å, respectively),[29] but similar to those (1.75(1) and 1.741(9) Å) in free 2,3-dimethylbenzothiophene.[35a] The Re−Re bond distance (3.0343(4) Å) compares well with that in both $Re_2(CO)_9(\eta^1(S)\text{-DBT})$ (3.0389(2) Å)[21] and $Re_2(CO)_{10}$ (3.0413(11) Å).[35b]

Photolysis Reaction of $Re_2(CO)_{10}$ and 3,5-Me_2BT with H_2. When $Re_2(CO)_{10}$ and 3−5 equiv of 3,5-Me_2BT are irradiated with UV light in a H_2-saturated decane solution (24−36 h, 10 °C), the complexes $H_2Re_2(CO)_8$, $Re_2(CO)_7(\mu\text{-3,5-}Me_2BT)$ (**1d**), and the partially hydrogenated BT* complex $Re_2(CO)_7(\mu\text{-3,5-}Me_2BT\text{-H})(\mu\text{-H})$ (**3d**) are produced (eq 7).



3d (7)

Complex **3d**, obtained in low yield (6−18%), contains a bridging ring-opened 3,5-Me_2BT ligand that formally results from the addition of H_2 across the Re−C vinyl bond of **1d** to give an η^2-bound vinyl group and bridging hydride. To determine whether complex **3d** was indeed formed from **1d**, a decane solution of **1d** was irradiated with UV light (1 atm H_2, 10 °C, 15−18 h) to give $Re_2(CO)_7(\mu\text{-3,5-}Me_2BT\text{-H})(\mu\text{-H})$ (**3d**). Under the same reaction conditions, complex **1c** also converted into $Re_2(CO)_7(\mu\text{-3-MeBT-H})(\mu\text{-H})$ (**3c**) in a similar fashion. Complexes **3c** and **3d** are colorless solids that are soluble in CH_2Cl_2, toluene, and THF, but only moderately soluble in hexanes and decane. Both complexes are air-stable in the solid state but in solution must be stored under an inert atmosphere. The ^1H NMR spectra of **3c** and **3d** are significantly different from those of **1c** and **1d**. The chemical shift of the protons on the η^2-vinyl group of **3c** (in CD_2Cl_2) are observed at δ 4.31 and 4.06 ppm which are upfield as compared to the terminal proton on the vinyl carbon of **1c** (δ 8.22 ppm). Similar differences in chemical shifts were observed between the vinyl protons of the partially hydrogenated 3,5-Me_2BT ligand in **3d** (in $CDCl_3$, δ 4.28 and 4.03 ppm) when compared to the shift of the vinyl proton in **1d** (δ 8.14 ppm). The hydride ligand signals were observed in the spectra of **3c** and **3d** at δ −12.60 and δ −12.62, respectively.

In the molecular structure of **3d** (Figure 3), the Re−Re bond distance (3.1083(3) Å) is similar to that in other dirhenium complexes that contain a bridging hydride ligand such as Re_2-

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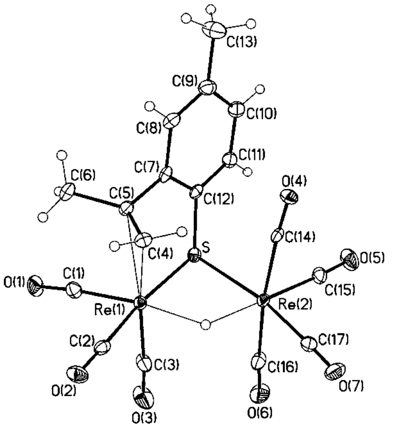
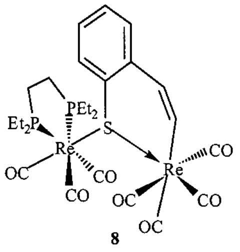


Figure 3. Molecular structure of $Re_2(CO)_7(\mu\text{-}3,5\text{-}Me_2BT\text{-}H)(\mu\text{-}H)$ (**3d**). Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Re(1)−Re(2), 3.1083(3); Re(1)−S, 2.4444(14); Re(2)−S, 2.4883(14); Re(1)−C(4), 2.417(6); Re(1)−C(5), 2.532(6); S−C(12), 1.783(6); C(4)−C(5), 1.379(8); Re(1)−S−Re(2), 78.11(4); Re(1)−S−C(12), 104.6(2); Re(2)−S−C(12), 103.21(18); C(4)−C(5)−C(7), 120.3(5).

$(CO)_8(\mu\text{-}H)(SC_6H_{11})$ (3.0934(10) Å)[36] and $Re_2(CO)_8(\mu\text{-}H)$(2-S-naphthyl) (3.0909(8) Å).[36] However, this distance is significantly shorter than that in the C−H cleaved DBT complex $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}SC_{12}H_7)$ (3.345 Å)[21] (Scheme 1). The vinyl group in **3d** is bound in a η^2-fashion to the $Re(CO)_3$ moiety as evidenced by the Re(1)−C(4) (2.417(6) Å) and Re(1)−C(5) (2.532(6) Å) bond distances.

The reaction of $Re_2(CO)_{10}$ with 3-MeBT or 3,5-Me_2BT and H_2 (eq 7) to form **3c** and **3d** likely involves $Re_2(CO)_7(\mu\text{-}BT^*)$ intermediates (**1c** and **1d**) as noted above. Both the formation of these intermediates and their subsequent conversion to the products (**3c** and **3d**) must be promoted by UV light as neither of these steps occurs without light. The mechanism of formation of **1c** and **1d** was discussed above. The mechanism for converting **1c** and **1d** to **3c** and **3d** could involve photopromoted dissociation of the olefin or cleavage of the Re−Re bond. Either process would allow coordination of η^2-H_2 which could lead to the product.

Reactions of 1a with Phosphines. In a recent communication,[22] we reported the reaction of $Re_2(CO)_7(\mu\text{-}BT)$ (**1a**) with an excess of PMe_3 in toluene solution at room temperature to produce the further ring-opened BT complexes $Re_2(CO)_7(PMe_3)_3(\mu\text{-}BT)$ (**4**) and $Re_2(CO)_7(PMe_3)_2(\mu\text{-}BT)$ (**5**) whose structures were established by X-ray diffraction studies (Scheme 4). Complex **1a** also reacts with P^iPr_3 (5 equiv) and PCy_3 (2 equiv) to produce the $Re_2(CO)_7(PR_3)_2(\mu\text{-}BT)$ complexes **6** (R = ^{i}Pr) and **7** (R = Cy) which are structural analogues of **5**, but no evidence for complexes analogous to **4** was observed in these reactions. Also, **1a** reacts with the bidentate phosphine bis(diethylphosphino)ethane (depe) to give $Re_2(CO)_7(depe)(\mu\text{-}BT)$ (**8**) with the proposed structure below. The colorless complex **4** and the pale yellow complexes **5**−**8** are soluble in CH_2Cl_2, toluene, and benzene but sparingly soluble in hexanes. Each complex can be handled in air for short times (<1 h) and is moderately stable in solution.



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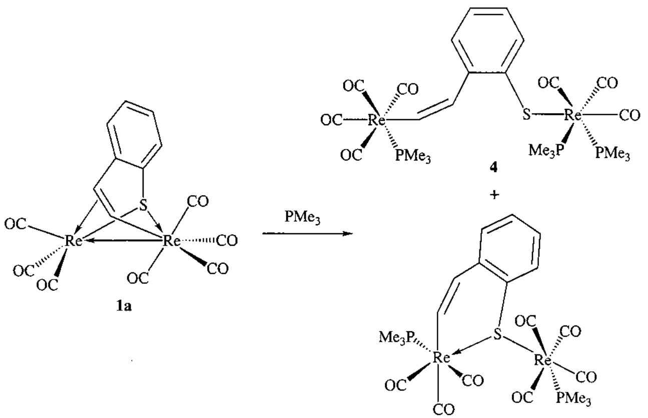
Scheme 4



In the ^1H NMR spectrum of **4** (in CD_2Cl_2), the chemical shift for the vinyl proton in the 2-position of the BT ligand (δ 7.89, dd, J = 13.5, 3.9 Hz) is shifted upfield of that in the spectrum of **1a** (δ 8.63, d, J = 11.4 Hz). However, the proton in the 3-position (δ 7.43, dd, J = 7.8, 1.2 Hz) is shifted downfield as compared to that of **1a** (δ 7.00, d, J = 11.4 Hz). The dd pattern for the vinyl proton signals for **4** is due to coupling (J_{HP} = 3.9 Hz) to the PMe_3 phosphorus. In the ^1H NMR spectra of **5**−**7**, the proton in the 2-position of the BT ligand of **5** (8.06, dd, J = 14.1, 2.4 Hz), **6** (δ 8.30, dd, J = 14.4, 2.1 Hz), and **7** (δ 8.33, dd, J = 14.0, 2.0 Hz) is upfield of that observed in the spectrum of **1a** (δ 8.63 d, J = 11.4 Hz). The vinyl proton in the 3-position of the BT ligand in **5** (δ 7.44, dd, J = 14.1, 3.6 Hz), **6** (δ 7.43, dd, J = 14.4, 3.0 Hz), and **7** (δ 7.46, dd, J = 14.4, 2.4 Hz) is downfield of that of **1a** (δ 7.00, d, J = 11.4 Hz). Again, the vinyl protons in the spectra of **5**−**7** are split by coupling to each other and to the phosphine ligand on the same Re.

In the structure of **6** (Figure 4), a BT ligand that is cleaved at the C_{vinyl}−S position bridges the two Re metal centers through the sulfur atom, and the η^1-vinyl group is bonded to the $Re(CO)_3(P^iPr_3)$ moiety. Each Re in **6** also contains one coordinated P^iPr_3 group similar to that reported for the structurally analogous **5** which contains PMe_3 ligands. The sulfur in **6** bridges the two Re centers nearly symmetrically with distances of 2.5296(15) Å for Re(1)−S and 2.5499(15) Å for Re(2)−S. These distances are slightly longer than those observed in the structure of **1a** (Re(1)−S, 2.506(2) Å; Re(2)−S, 2.431(3) Å) in which there is a Re−Re bond. The C═C distance of the vinyl group in **6** is 1.343(10) Å which is the same as that in **5** (1.343(5) Å) and slightly shorter than that in **1a** (1.370(14) Å). The Re(1)−C(13) distance of 2.173(6) Å is also similar to that observed in **5** (2.169(3) Å) but shorter than that in complex **1a** (2.208(10) Å) in which the vinyl group is bridging.

In the ^1H NMR spectrum of complex **8** (in CD_2Cl_2), the vinyl BT protons (δ 7.71 and 7.43 ppm) are observed as doublets due to coupling between these protons. The absence of phosphorus coupling to the vinyl protons in **8** indicates that the

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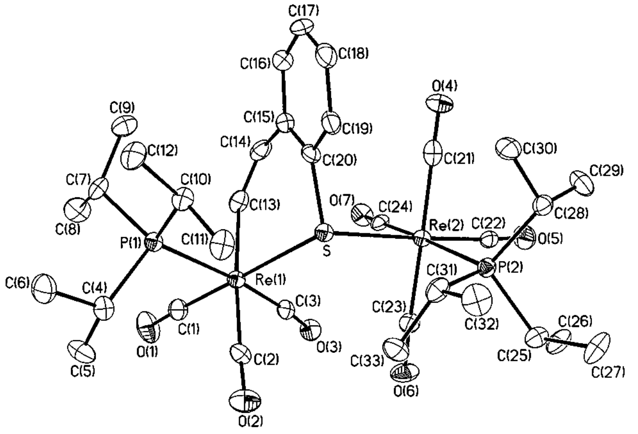
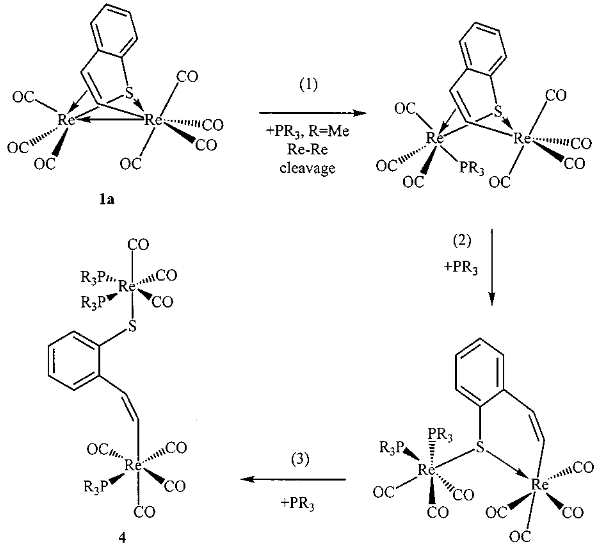


Figure 4. Molecular structure of $Re_2(CO)_7(P^iPr_3)_2(\mu\text{-BT})$ (**6**). Thermal ellipsoids are drawn at the 40% probability level. Selected bond distances (Å) and angles (deg): Re(1)−S, 2.5296(15); Re(2)−S, 2.5499(15); Re(1)−C(13), 2.173(6); C(13)−C(14), 1.343(10); C(14)−C(15), 1.492(9); Re(1)−P(1), 2.5467(14), Re(2)−P(2), 2.5316(14); Re(1)−S−Re(2), 116.69(5); Re(1)−S−C(20), 108.8(2); Re(2)−S−C(20), 102.7(2).

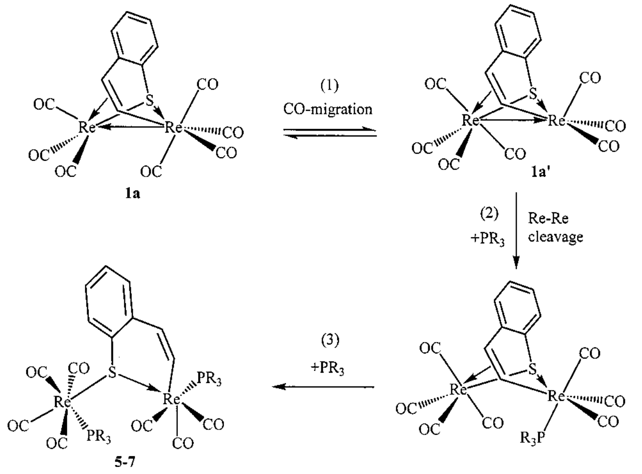
Scheme 5. Proposed Mechanism for the Formation of $Re_2(CO)_7(PMe_3)_3(\mu\text{-Bt})$ (**4**) According to Scheme 4



coordinated vinyl group is bound to the Re center that is not coordinated to the phosphine ligand. Additional evidence that the structure of **8** is different from that of **5**−**7** is found in the different pattern and intensities of the CO stretching frequencies in **8** (in CH_2Cl_2: 2079 w, 2029 s, br, 1974 s, 1964 s, br, and 1907 s, br, cm^{-1}) as compared with those for **5** (in CH_2Cl_2: 2100 w, 2018 m, 2003 s, 1953 m, 1896 m, and 1873 m cm^{-1}).

Scheme 5 shows a possible mechanism that accounts for the formation of **4** from the reaction of complex **1a** with PMe_3. The first step (1) of this mechanism involves cleavage of the Re−Re bond upon reaction with PMe_3 to give the intermediate $Re_2(CO)_7(PMe_3)(\mu\text{-BT})$. Addition of a second PMe_3 ligand to the $Re(CO)_3(PMe_3)$ unit results (step 2) in displacement of the η^2-bound vinyl group by PMe_3 to produce the intermediate $Re_2(CO)_7(PMe_3)_2(\mu\text{-BT})$. We propose that this intermediate, although not observed directly, has a structure that is analogous to $Re_2(CO)_7(depe)(\mu\text{-BT})$ (**8**). In the final step, an additional PMe_3 displaces the sulfur ligand to produce **4**. The order of steps 1 and 2 could be interchanged since there is no spectroscopic evidence (^{1}H NMR) to support the existence of either intermediate. Steps 1 and 2 also reasonably account for the formation of **8** in the reaction of **1a** with depe. Displacement of the BT sulfur in the final step in Scheme 5 is proposed because the bridging sulfur in **5** is stable and is not displaced by PMe_3 under the conditions of the reaction.

Scheme 6. Proposed Mechanism for the Formation of $Re_2(CO)_7(PR_3)_2(\mu\text{-Bt})$ (**5**−**7**) According to Scheme 4



A possible mechanism for the formation of the $Re_2(CO)_7(PR_3)_2(\mu\text{-BT})$ complexes **5**−**7** from **1a**−**d** is shown in Scheme 6. A distinguishing structural feature in these complexes is that the terminal BT vinyl carbon is η^1-bound to the $Re(CO)_3$ unit and not to the $Re(CO)_4$ unit as observed in **1a** and also in **4**. A reasonable mechanism for the formation of **5**−**7** must account for the η^1-vinyl bond to the $Re(CO)_3$ moiety in the structures of the products. The first step in the proposed mechanism (Scheme 6) is the migration of a CO ligand from the $Re(CO)_4$ group in **1a** to the $Re(CO)_3$ moiety to afford the isomer **1a′**. Although **1a′** has not been observed in the ^{1}H NMR spectrum of **1a** in solution, as shown by the absence of any change in the ^{1}H NMR spectrum of **1a** in CD_2Cl_2 over the temperature range from +20 to −50 °C, a variable temperature ^{13}C NMR study of **1a** (in CD_2Cl_2 solution) did show evidence for rapid CO migration between the Re metal centers. The ^{13}C NMR spectrum of **1a** at −50.1 °C exhibits a signal for each of the seven carbonyl ligands at δ 193.4, 192.6, 189.9, 185.6, 184.7, 184.3, and 177.6 ppm. This spectrum is consistent with the static structure of **1a** in the solid state which was established by an X-ray diffraction study.[22] However, at +20.1 °C, the seven signals observed at −50.1 °C coalesce into three signals (at δ 189.1 br, 187.4 br, and 185.9 sh ppm), which suggests that the carbonyl ligands of the $Re(CO)_3$ unit and the $Re(CO)_4$ unit of **1a** are rapidly exchanging between the Re centers.

Although presumably formed in only low concentration, isomer **1a′** is proposed to react with a PR_3 ligand at either the η^2-vinyl group or the Re−Re bond (Scheme 6). Cleavage of the Re−Re bond (step 2) seems more likely as the relatively unhindered $Re(CO)_3$ unit would be susceptible to attack by PR_3. Phosphine displacement of the η^2-bound vinyl group on the $Re(CO)_4$ unit in step 3 would give observed products $Re_2(CO)_7(PR_3)_2(\mu\text{-BT})$ (**5**−**7**). Although this proposed mechanism reasonably accounts for the formation of **5**−**7**, neither of the intermediates could be observed spectroscopically.

The phosphines used in the preparations of complexes **6** and **7** were chosen for their larger cone angles (P^iPr_3, 160°; PCy_3, 170°)[37] and similar basicities as compared to PMe_3 (118°).[37] All three phosphines produce similar disubstituted phosphine complexes of the type $Re_2(CO)_7(PR_3)_2(\mu\text{-BT})$ (**5**−**7**). However, complex **1a** reacts with PMe_3 to also yield the trisubstituted phosphine complex **4**. Since the relative amounts of **4** and **5** formed are the same whether 1 or 5 equiv of PMe_3 is used (Scheme 4), the tris(phosphine) product **4** cannot be formed from the bis(phosphine) product **5**. Therefore, **4** and **5** must be formed by independent pathways, as suggested in Schemes 5 and 6. The observation that only complexes of type **5** are formed in reactions of **1a** with the bulky phosphines suggests that these phosphines react faster with **1a′** (Scheme 6) than with **1a** (Scheme 5). Perhaps the less crowded $Re(CO)_3$ unit in **1a′** is more susceptible to attack by bulky phosphines than either Re in **1a**.

Conclusion

Although the HDS of thiophenes and benzothiophenes is often considered to occur by similar pathways, it is clear in the present studies that each of these thiophenes reacts with $Re_2(CO)_{10}$ to give different types of products. With 2,5-dimethylthiophene under UV photolysis, $Re_2(CO)_{10}$ gives $Re_2(CO)_7(\mu\text{-2,5-}Me_2T)$ (Scheme 1) in which a C−S bond is cleaved but there is no Re−Re bond.[21] However, the reaction of $Re_2(CO)_{10}$ with benzothiophene under the same conditions gives $Re_2(CO)_7(\mu\text{-BT})$ (**1a**) (Scheme 2) in which the C−S bond is cleaved but there is a Re−Re bond. The presence or absence of a Re−Re bond appears to be related to the availability of π-coordinating olefinic groups in the bridging thiophene ligand. In $Re_2(CO)_7(\mu\text{-BT})$ (**1a**), there is only one coordinating olefinic group which allows the formation of the Re−Re bond in order to achieve an 18-electron count at both metal centers. In $Re_2(CO)_7(\mu\text{-2,5-}Me_2T)$, two olefins are capable of coordinating which obviates the need for a Re−Re bond. The reaction of $Re_2(CO)_{10}$ with DBT under UV photolysis gives quite different products.[21] One is the S-coordinated $Re_2(CO)_9(\eta^1(S)\text{-DBT})$, while the other is the C−H cleaved $Re_2(CO)_8(\mu\text{-}C_{12}H_7S)(\mu\text{-H})$ (Scheme 1). Moreover, DBT gives no products resulting from C−S cleavage. Thus, $Re_2(CO)_{10}$ demonstrates unique reactivities with 2,5-Me_2T, BT, and DBT, which contrasts with reactions of these thiophenes with other dinuclear complexes.[18−20]

In $Re_2(CO)_7(\mu\text{-BT})$ (**1a**), the Re atoms can be partially removed from the bridging C−S-cleaved BT ligand by reaction with phosphines (Scheme 4). The resulting products arise from the replacement of Re−Re, Re−olefin, and Re−S bonds in **1a** with Re−PR_3 bonds. Complexes **1**, **4**, and **5**−**8** illustrate three different ways in which C−S-cleaved BT can bridge two metal centers, as may occur on an HDS catalyst surface.

When the $Re_2(CO)_7(\mu\text{-BT*})$ complexes, where BT* = 3-MeBT or 3,5-Me_2BT, are photolyzed under an atmosphere of H_2, 1 equiv of H_2 is added to give $Re_2(CO)_7(\mu\text{-BT*}\bullet\text{H})(\mu\text{-H})$ with a bridging 2-vinylthiophenolate ligand resulting from the cleavage of a Re−C bond and partial hydrogenation of the bridging BT (eq 7). This addition of H_2 to a C−S-cleaved BT ligand in a dinuclear complex may also be involved in the hydrogenation[37a] of benzothiophene in the presence of $[Cp^*Ir(Cl)(\mu\text{-H})]_2$ under an atmosphere of H_2 at 90° to give $(Cp^*IrCl)_2(\mu\text{-H})[(\mu\text{-S}(C_6H_4)(CH_2CH_3)]$, a complex in which a 2-ethylthiophenolate ligand bridges the Ir atoms through the sulfur.

Experimental Section

General Considerations. All reactions were performed under a nitrogen or argon atmosphere in reagent grade solvents using standard Schlenk techniques. The solvents, hexanes, methylene chloride, toluene, and tetrahydrofuran (THF), were dried using the Grubbs solvent purification system[38] (Solv-Tek, Inc.). Benzene and decane were dried and distilled over CaH_2 prior to use. Deutero-methylene chloride (Cambridge) and $CDCl_3$ (Cambridge) were stored over 4 Å molecular sieves. Rhenium carbonyl was purchased from Strem Chemicals Inc. Benzothiophene (Aldrich Chemical Co.), 3-methylbenzothiophene (Maybridge Chemical Co.), and 3,5-dimethylbenzothiophene (Maybridge Chemical Co.) were used as received without further purification. 2-Methylbenzothiophene was prepared according to a literature procedure.[8c] The preparation of $Re_2(CO)_9(THF)$ was previously described.[21] Trimethylamine *N*-oxide (Me_3NO) (Aldrich) was dried by azeotropic distillation of water in dry benzene. Silica gel (40−140 mesh, J. T. Baker) was dried and degassed under vacuum for 14 h at ambient temperature and stored under argon. TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) was purchased from Aldrich.

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

Preparation of $Re_2(CO)_7(\mu\text{-BT*})$ (1a−d). $Re_2(CO)_7(\mu\text{-BT})$ (1a). In a typical experiment, a hexanes (40 mL) solution of $Re_2(CO)_{10}$ (224 mg, 0.343 mmol) and BT (97.0 mg, 0.723 mmol) was prepared in a quartz Schlenk photolysis tube containing a Teflon-coated magnetic stir bar. A coldfinger (10 °C) was inserted into the solution, and the tube was fitted with an oil bubbler. The solution was then irradiated for 24 h with stirring under a slow, but constant, flow of N_2 during which time the solution gradually became orange and an orange precipitate formed. The orange solution was transferred to a silica gel column (1 × 9 cm) packed in hexanes, and an orange band was eluted using a mixture of hexanes and CH_2Cl_2 (10:1). The orange band was collected, and the solvent was removed in vacuo to afford **1a** as an orange microcrystalline solid (61.0 mg, 24% yield). ^1H NMR (CD_2Cl_2, 300 MHz): δ 8.63 (d, 1H, J = 11.4 Hz), 7.11 (m, 2H), 7.05 (dt, 1H, J = 7.5, 1.5 Hz), 7.00 (d, 1H, J = 11.4 Hz), 6.93 (dt, 1H, J = 7.2, 1.5 Hz). ^{13}C NMR (300 MHz, −50.1 °C, CD_2Cl_2): δ 193.4, 192.6, 189.9, 185.6, 184.7, 184.3, 177.6 (CO); 150.0, 144.7, 135.6, 129.7, 129.5, 128.0, 127.7, 115.8 (BT). IR (hexanes) ν_{CO}: 2099 (m), 2043 (s), 2027 (s), 1981 (s), 1977 (s), 1957 (m), and 1947 (s) cm^{-1}. Anal. Calcd for $C_{15}H_6O_7Re_2S$: C, 25.64; H, 0.86. Found: C, 25.54; H, 0.69.

$Re_2(CO)_7(\mu\text{-2-MeBT})$ (1b). Complex **1b** was prepared in a similar fashion as **1a** from a hexanes (30 mL) solution containing $Re_2(CO)_{10}$ (122 mg, 0.187 mmol) and 2-MeBT (61.0 mg, 0.412 mmol) (29.5 h, 15 °C). After purification and isolation as described for **1a**, an orange solid was obtained and characterized as **1b** (50.1 mg, 37% yield based on $Re_2(CO)_{10}$). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.09 (m, 2H), 7.01 (dt, 1H, J_1 = 7.5 Hz, J_2 = 1.2 Hz), 6.89 (dt, 1H, J_1= 7.5 Hz, J_2 = 1.5 Hz), 6.36 (s, 1H), 3.16 (s, 3H, Me). IR (hexanes): 2096 (m), 2041 (vs), 2026 (s), 1980 (s), 1974 (vs), 1956 (m), 1944 (s) cm^{-1}. Anal. Calcd for $C_{16}H_8O_7Re_2S$: C, 26.81; H, 1.13. Found: C, 26.94; H, 1.20.

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$Re_2(CO)_7$(*μ*-3-MeBT) (1c). Complex **1c** was prepared in a fashion analogous to that for **1a** from a hexanes solution (35 mL) containing $Re_2(CO)_{10}$ (298 mg, 0.457 mmol) and 3-MeBT (282 mg, 1.90 mmol) (24 h, 10 °C). Orange microcrystals of **1c** (159 mg, 49% yield based on $Re_2(CO)_{10}$) were isolated and purified as described for **1a**. ^1H NMR (200 MHz, CD_2Cl_2): δ 8.22 (s, 1H), 7.37 (d, 1H, $J = 7.6$ Hz), 7.00 (m, 3H), 2.58 (s, 3H, Me). IR (hexanes): ν(CO) cm^{-1} 2097 (m), 2040 (vs), 2024 (s), 1979 (vs), 1973 (s), 1954 (w), 1941 (m). Anal. Calcd for $C_{16}H_8O_7Re_2S$: C, 26.81; H, 1.13. Found: C, 26.71; H, 1.17.

$Re_2(CO)_7$(3,5-Me_2BT) (1d). Complex **1d** was prepared and isolated from the reaction of $Re_2(CO)_{10}$ (238 mg, 0.365 mmol) and 3,5-Me_2BT (200 mg, 1.23 mmol) in a hexanes (36 mL) solution, as in the procedure for the synthesis of **1a**. The yield (112 mg) was 42% based on $Re_2(CO)_{10}$. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.20 (s, 1H), 7.20 (s, 1H), 6.97 (d, 1H, $J = 7.8$ Hz), 6.79 (d, 1H, $J = 7.8$ Hz), 2.58 (s, 3H, Me), 2.27 (s, 3H, Me). IR (hexanes): ν(CO) cm^{-1} 2097 (m), 2040 (vs), 2023 (s), 1978 (vs), 1972 (s), 1953 (m), 1940 (s). Anal. Calcd for $C_{17}H_{10}O_7Re_2S$: C, 27.94; H, 1.38. Found: C, 27.85; H, 1.16.

Preparation of $Re_2(CO)_9$(η^1(S)-BT*) (2a−d). $Re_2(CO)_9$(η^1(S)-BT) (2a): Method A. Benzothiophene (79.0 mg, 0.589 mmol) was added to $Re_2(CO)_9$(THF) prepared by UV photolysis of a solution of $Re_2(CO)_{10}$ (0.313 mmol) in 30 mL of THF. While being stirred, the yellow-orange solution gradually became lemon yellow (1−2 h); it was stirred for an additional 12 h at which time the solvent was removed in vacuo to produce a yellow-brown oily residue. The residue was dissolved in CH_2Cl_2 (1 mL) and layered with hexanes (5 mL) followed by cooling overnight (−20 °C) to give pale yellow crystals of **2a** (45 mg, 19% yield based on $Re_2(CO)_{10}$) which were filtered and dried under vacuum. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.89 (m, 2H), 7.57 (m, 2H), 7.44 (d, 1H, $J = 5.7$ Hz), 7.32 (d, 1H, $J = 5.7$ Hz). IR (CH_2Cl_2): 2101 (w), 2045 (m), 1990 (s, br), 1967 (m), and 1931 (m) cm^{-1}.

Method B. A THF (15 mL) solution of $Re_2(CO)_{10}$ (327 mg, 0.501 mmol) was prepared under an inert atmosphere in a 50 mL Schlenk flask containing a stir bar. Anhydrous Me_3NO (40 mg, 0.523 mmol) was then added with stirring to produce a yellow-orange solution that was stirred for an additional 1 h. The volatiles (THF and NMe_3) were removed in vacuo, and the resulting yellow residue was again dissolved in THF (10 mL). BT (258 mg, 1.92 mmol) was added, and the resulting yellow-orange solution was stirred for 15−18 h. During this time, the solution lightened to a pale yellow. The solvent was removed under vacuum, and the yellow oily residue was dried under reduced pressure. The crude residue was dissolved in toluene (1 mL) and layered with hexanes (6−7 mL) followed by cooling (−20 °C) until **2a** precipitated as a yellow solid. The precipitate of **2a** was then filtered and dried in vacuo (42 mg, 11% yield based on $Re_2(CO)_{10}$). Complex **2a** was characterized as described in Method A.

$Re_2(CO)_9$(η^1(S)-3-MeBT) (2c): Method A. A THF (30 mL) solution of $Re_2(CO)_9$(THF) (0.342 mmol based on $Re_2(CO)_{10}$) and 3-MeBT (112 mg, 0.756 mmol) was stirred for 20 h. The yield of **2c** was 72 mg (27% yield based on $Re_2(CO)_{10}$).

Method B. A THF solution (25 mL) of $Re_2(CO)_{10}$ (310 mg, 0.475 mmol) and Me_3NO (35 mg, 0.460 mmol) was stirred for 1 h, followed by addition of 3-MeBT (215 mg, 1.45 mmol) with further stirring for 15 h. Complex **2c** (93 mg, 25% yield) was isolated following the procedure used for **2a**. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.90 (m, 1H), 7.80 (m, 1H), 7.61 (m, 2H), 6.96 (s, 1H), 2.53 (s, 3H, Me). IR (CH_2Cl_2): 2102 (w), 2043 (m), 1989 (s, br), 1967 (m), 1931 (m) cm^{-1}. Anal. Calcd for $C_{18}H_8O_9Re_2S$: C, 27.98; H, 1.04. Found: C, 27.76; H, 1.00.

$Re_2(CO)_9$(η^1(S)-3,5-Me_2BT) (2d): Method A. A THF (30 mL) solution containing 3,5-Me_2BT (505 mg, 3.08 mmol) and $Re_2(CO)_9$(THF) (0.314 mmol based on $Re_2(CO)_{10}$) was stirred for 18 h. Yellow crystals of **2d** (106 mg, 43% yield) were afforded after recrystallization from CH_2Cl_2/hexanes (−20 °C). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.74 (d, 1H, $J = 8.1$ Hz), 7.58 (s, 1H), 7.38 (d, 1H, $J = 8.1$ Hz), 6.91 (s, 1H), 2.53 (s, 3H, Me), 2.47 (s, 3H, Me). IR (CH_2Cl_2): 2102 (w), 2042 (m), 1989 (s, br), 1963 (m), and 1931 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{10}O_9Re_2S$: C, 29.01; H, 1.28. Found: C, 28.53; H, 1.13.

Method B. A THF solution (20 mL) of $Re_2(CO)_{10}$ (147 mg, 0.225 mmol) and Me_3NO (27.0 mg, 0.360 mmol) was stirred for 1.5 h. The volatiles were then removed in vacuo, and both THF (10−15 mL) and 3,5-Me_2BT (112 mg, 0.691 mmol) were added with stirring (10 h). Complex **2d** (62.4 mg, 35% based on $Re_2(CO)_{10}$) was isolated and recrystallized as described for **2a**.

Photolysis of $Re_2(CO)_{10}$ and 3,5-Me_2BT in the Presence of H_2. A decane (30 mL) solution containing $Re_2(CO)_{10}$ (288 mg, 0.441 mmol) and 3,5-Me_2BT (226 mg, 1.39 mmol) was irradiated in a quartz reaction tube at 10−15 °C for 24 h under a steady flow of H_2 which was bubbled through the solution. During the reaction, the solution became yellow, and an insoluble light-brown residue formed. The solution was then transferred to a silica gel column (1 × 10 cm) packed in hexanes. A yellow band corresponding to $H_2Re_2(CO)_8$ (12% based on $Re_2(CO)_{10}$)[39] was eluted with hexanes. An orange band that was eluted with CH_2Cl_2/hexanes (1:10) was then evaporated to leave an orange solid that contained **1d** (based on IR and ^1H NMR spectroscopies) and a second product. The orange solid was recrystallized from a toluene (1 mL) solution layered with hexanes (5 mL) (−20 °C). After 1 d, orange crystals of **1d** and colorless crystals of the new product $Re_2(CO)_7$(*μ*-3,5-Me_2BT•H)(*μ*-H) (**3d**) were formed; crystals of these products were separated by hand. The hand-picked crystals of **3d** were then dissolved in toluene (1 mL) and layered with hexanes followed by recrystallization at −20 °C to afford pure crystals of **3d** (1−2 d) which were dried in vacuo (20−30 mg, 6−18% based on $Re_2(CO)_{10}$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.20 (d, 1H, $J = 8.1$ Hz), 7.00 (m, 1H), 6.84 (s, 1H), 4.24 (s, 1H), 4.03 (d, 1H, $J = 2.1$ Hz), 2.81 (s, 3H, Me), 2.30 (s, 3H, Me), −12.62 (s, hydride). IR (hexanes): ν_{CO} 2100 (w), 2039 (vs), 2003 (s), 1992 (vs), 1964 (vs), 1955 (w), 1943 (m) cm^{-1}.

Photolysis of 1c with H_2. A decane solution (30 mL) of **1c** (125 mg, 0.174 mmol) was prepared in a quartz photolysis tube equipped with a magnetic stir bar. Hydrogen was bubbled through the orange solution while it was UV-irradiated for 15−18 h at 10 °C. During this time the solution became dark, and a dark brown precipitate formed. The solution was filtered and chromatographed on silica gel (1 × 10 cm) using hexanes to remove the decane solvent. A solvent combination of CH_2Cl_2 and hexanes (1:10) was then used to elute the complex $Re_2(CO)_7$(*μ*-3-MeBT•H)(*μ*-H) (**3c**) with careful monitoring of the eluents by IR spectroscopy. The volatiles were removed under vacuum to give **3c** as a white solid (15 mg, 12%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.34 (td, 1H, $J_1 = 7.8$ Hz, $J_2 = 0.9$ Hz), 7.19 (m, 1H), 7.09 (m, 2H), 4.32 (s, 1H), 4.06 (d, 1H, $J = 2.1$ Hz), 2.81 (s, 3H, Me), −12.60 (s, hydride). IR (hexanes): 2102 (w), 2041 (vs), 2005 (s), 1994 (vs), 1966 (vs), 1958 (m), and 1946 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{10}O_7Re_2S$: C, 26.74; H, 1.40. Found: C, 26.69; H, 1.31.

Reaction of 1a with PMe_3. To a toluene solution (3−5 mL) of **1a** (41.0 mg, 0.058 mmol) was added a toluene solution of PMe_3 (0.31 mL, 0.31 mmol, in 1 M toluene solution). The solution color changed immediately from orange to light yellow. After 35 min, the volatiles were removed in vacuo, and the resulting yellow oil was dissolved in CH_2Cl_2 (1 mL) and layered with hexanes (4−6 mL). Colorless crystals of $Re_2(CO)_7(PMe_3)_3$(*μ*-BT) (**4**) and yellow crystals of $Re_2(CO)_7(PMe_3)_2$(*μ*-BT) (**5**) precipitated as a mixture from the solution overnight at −20 °C. After filtering and drying under vacuum, crystals of **4** and **5** were partially separated by hand-picking the crystals of each complex from the 30−40 mg mixture. For **4**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.89 (dd, 1H, $J = 13.5$, 3.9 Hz), 7.43 (dd, 1H, $J = 7.8$, 1.2 Hz), 7.21 (d, 1H, $J = 7.2$ Hz), 6.99 (dt, 1H, $J = 7.5$, 1.5 Hz), 6.92 (m, 2H), 1.62 (m, 27H, 3PMe_3). IR (CH_2Cl_2) ν_{CO}: 2079 (w), 2018 (s), 1978 (s, sh), 1972 (s), 1933 (s), and 1893 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{33}O_7P_3Re_2S$: C, 30.97; H, 3.57. Found: C, 30.72; H, 3.47. For **5**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 8.06 (dd, 1H, $J = 14.1$, 2.4 Hz), 7.44 (dd, 1H,

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[39] Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 1556.

J = 14.1, 3.6 Hz), 7.26 (d, 1H, J = 7.8 Hz), 7.00 (m, 2H), 6.87 (m, 1H), 1.87 (d, 9H, PMe_3, J = 9.3 Hz), 1.19 (d, 9H, PMe_3, J = 8.4 Hz). IR (CH_2Cl_2) ν_{CO}: 2100 (w), 2018 (m, sh), 2003 (s), 1953 (m, br), 1896 (m, br), and 1873 (m, br) cm^{-1}. Anal. Calcd for $C_{21}H_{24}O_7P_2Re_2S$: C, 29.51; H, 2.83. Found: C, 29.24; H, 2.78.

Reaction of 1a with P^{i}Pr$_3$. To a stirred CH_2Cl_2 solution (6 mL) of complex **1a** (50 mg, 0.071 mmol) was added P^iPr_3 (0.069 mL, 0.36 mmol). The solution lightened within 5 min and was stirred for an additional 2 h, followed by removal of the solvent in vacuo to produce a pale yellow solid. The solid was then dissolved in benzene (1 mL) and layered with hexanes (3−4 mL) (5 °C) to afford crystals of $Re_2(CO)_7(P^iPr_3)_2(\mu\text{-BT})$ (**6**) after 1 d. After filtering, washing with cold hexanes (0 °C), and drying in vacuo, crystals of **6** (21−36 mg) were isolated in 28−50% yield. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.30 (dd, 1H, J_{HH} = 14.4 Hz, J_{HP} = 2.1 Hz), 7.43 (dd, 1H, J_{HH} = 14.4 Hz, J_{HP} = 3.0 Hz), 7.19 (d, 1H, J = 6.9), 6.94 (m, 2H), 6.79 (m, 1H), 2.77 (m, 3H, CH), 2.08 (m, 3H, CH), 1.42−0.86 (m, 36H, Me). IR (hexanes): 2100 (w), 2026 (m), 2007 (vs), 1949 (m), 1905 (m), and 1884 (m) cm^{-1}.

Reaction of 1a with PCy$_3$. A toluene solution (5 mL) of **1a** (40.2 mg, 0.057 mmol) and PCy_3 (36.0 mg, 0.128 mmol) was prepared in a 25 mL Schlenk flask. The color of the solution changed from orange to pale yellow within 1 h, and the solution was stirred for an additional 7 h. The solvent was then removed in vacuo, and the yellow solid residue was dissolved in toluene (1 mL); the solution was layered with hexanes (6 mL), followed by cooling (−20 °C) overnight which produced a yellow crystalline solid of $Re_2(CO)_7(PCy_3)_2(\mu\text{-BT})$ (**7**). Crystals of complex **7** (33.8 mg, 0.026 mmol, 46%) were filtered, washed with hexanes (2 × 4 mL), and dried under vacuum. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.33 (dd, 1H, J_{HH} = 14.0 Hz, J_{HP} = 2.0 Hz), 7.46 (dd, 1H, J_{HH} = 14.4 Hz, J_{HP} = 2.4 Hz), 7.24 (m, 1H), 6.98 (m, 2H), 6.80 (m, 1H), 2.41−0.88 (m, 66H, Cy). IR (CH_2Cl_2): 2096 (w), 2016 (m, sh), 1999 (vs), 1944 (m, br), 1888 (m, br), and 1868 (m, br) cm^{-1}. Anal. Calcd for $C_{51}H_{72}O_7P_2Re_2S$: C, 48.48; H, 5.74. Found: C, 48.94; H, 6.01.

Reaction of 1a with Bis(diethylphosphino)ethane. Complex **1a** (49.0 mg, 0.070 mmol) and bis(diethylphosphino)ethane (depe) (0.017 mL, 0.073 mmol) were dissolved in toluene (6 mL) in a 50 mL Schlenk flask. The solution was stirred for 1 h, followed by removal of the volatiles in vacuo, yielding a pale yellow oil. Solid pale yellow $Re_2(CO)_7(\text{depe})(\mu\text{-BT})$ (**8**) was precipitated from a benzene/hexanes (1:6) solution (−5 °C) and isolated by filtration and dried in vacuo (32−40 mg). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.71 (d, 1H, J = 13 Hz), 7.43 (d, 1H, J = 13 Hz), 7.21 (d, 1H, J = 7.8 Hz), 7.04 (m, 2H), 6.78 (m, 1H), 1.94−1.53 (m, 12H, 6CH_2), 1.10 (m, 12H, 4Me). IR (CH_2Cl_2): ν_{CO} 2079 (w), 2029 (s), 1974 (s, br), 1964 (s, br), and 1907 (s, br). Anal. Calcd for $C_{25}H_{30}O_7P_2Re_2S$: C, 33.04; H, 3.33. Found: C, 32.77; H, 3.22.

Crystallographic Structural Determinations for Complexes 2c, 1d, 3d, and 6. Systematic absences in the diffraction data were uniquely consistent for space group *Pbca* for **1d** and also for the space groups $P1$ and $P\bar{1}$ for **2c**, **3d**, and **6**. In the latter three cases, the *E* statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement.[40] In all cases, the absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[41] The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions.

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

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Supporting Information Available: Crystallographic data including atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **1c**, **1d**, **2c**, **3d**, and **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (Sheldrick, G. Bruker Analytical X-ray Systems, Madison, Wisconsin, 1997).