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$Re_2(CO)_{10}$-Mediated Carbon−Hydrogen and Carbon−Sulfur Bond Cleavage of Dibenzothiophene and 2,5-Dimethylthiophene†

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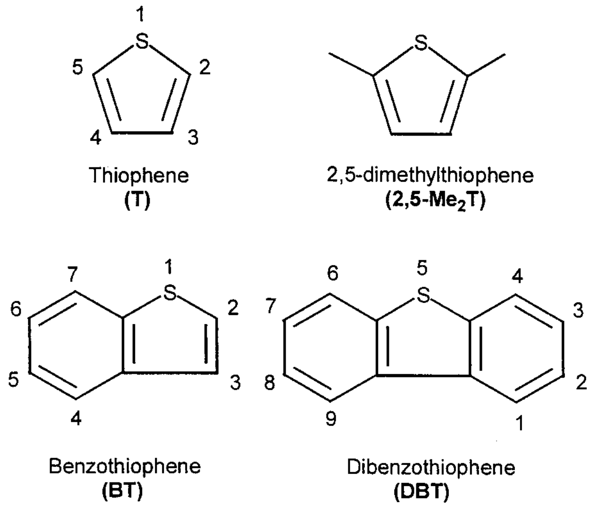
Ultraviolet photolysis of $Re_2(CO)_{10}$ and excess dibenzothiophene (DBT) in the noncoordinating solvent hexanes produces the S-bound eq-$Re_2(CO)_9(\eta^1(S)$-DBT) (**1**) and the novel C−H-cleaved DBT complex $Re_2(CO)_8(\mu$-$C_{12}H_7S)(\mu$-H) (**2**). Under similar conditions, $Re_2(CO)_{10}$ reacts with excess 2,5-dimethylthiophene (2,5-Me_2T) to give the interesting C−S-cleaved 2,5-Me_2T complex $Re_2(CO)_7(\mu$-2,5-$Me_2T)$ (**3**). The photolysis reactions of $Re_2(CO)_{10}$ with DBT and 2,5-Me_2T were inhibited by CO (1 atm) and also by the radical scavenger TEMPO, which suggests that both CO dissociation and homolytic Re−Re bond cleavage are involved. The η^1(S)-bound thiophene complexes **1** and $Re_2(CO)_9(\eta^1(S)$-2,5-$Me_2T)$ (**5**) were prepared from $Re_2(CO)_9$(THF) (**4**). The DBT ligand in **1** is labile and rapidly (<2 min) reacts with CO (1 atm) to form $Re_2(CO)_{10}$ in 1,2-DCE. On the basis of its X-ray structure, complex **1** has one of the smallest tilt angles ($\theta = 113°$) observed for a metal−thiophene complex, which may be understood in terms of π-back-bonding arguments. Complexes **1**−**3** were characterized by spectroscopic (IR, NMR) methods and by their structures that were determined by X-ray crystallography. Mechanisms for the formation of **1**−**3** are presented and discussed.

Introduction

Hydrodesulfurization (HDS), the catalytic hydrotreating process used for removing sulfur from organosulfur compounds present in petroleum feedstocks, is important for two primary reasons.[1−3] First, current U.S. federal regulations require refineries to cap gasoline sulfur levels at 300 ppm (by the year 2004[3]) in order to decrease the amount of sulfur oxides (SO_x, $x = 2, 3$) produced during the combustion of petroleum fuels. These sulfur oxides are known precursors to acid rain and present a significant threat to the environment. Second, sulfur poisons precious metal-based re-forming catalysts, which consequently increases the cost of petroleum re-forming. The sulfur in crude petroleum, whose amount ranges from 0.2 to 4%,[2,4] is present in the form of thiols (RSH), thioethers (RSR), disulfides (RSSR), and thiophenes (T*) such as thiophene (T), benzothiophene (BT), and dibenzothiophene (DBT) (Chart 1). It is the thiophenic compounds, however, that are the most difficult to desulfurize under current commercial hydrotreating conditions due to aromatic stabilization of the thiophene and benzothiophene rings.[5]

Chart 1



The common commercial HDS catalysts are typically MoS_2 and WS_2 promoted by Co or Ni on an alumina support, but several other metal sulfides, MS_x (M = Ru, Re, Os, Rh, and Ir), have demonstrated higher catalytic activities for the desulfurization of thiophenes and benzothiophenes under various hydrotreating conditions.[6,7] The most active catalysts are those of the second-row (such as Ru and Rh) and third-row elements (such as Re, Os, and Ir), but their high costs prevent them from being used commercially.[2]

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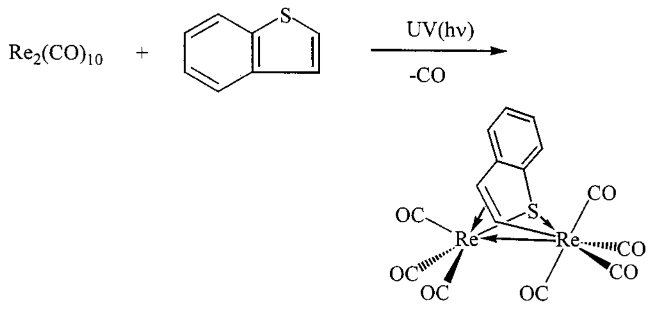
Organometallic modeling of thiophene binding modes and ring-opened intermediates formed at transition-metal centers is one approach to better understanding how desulfurization might occur in the commercial HDS catalytic process. Examples of organometallic complexes that contain thiophenes and benzothiophenes bound to transition-metal centers through many different binding modes (i.e.; η^1(S), η^2, η^4, η^5, and η^6)[8-10] are known. Several organometallic complexes of ring-opened thiophenes and benzothiophenes at single metal centers have also been reported;[11-13] however, there are few reports of such complexes with two or more metals.

Sweigart et al.[14-17] described the synthesis of the C–S-cleaved thiophene complexes $Mn_2(CO)_7(\mu\text{-T*})$ by reduction of the complexes $[(\eta^5\text{-T})Mn(CO)_3]^+$ and $[(\eta^6\text{-BT})Mn(CO)_3]^+$. Jones and Vicic[18] recently reported that the bimetallic Ni complex $[(dippe)Ni(H)]_2$ reacts with T or BT under mild conditions (22 °C) in hexanes solvent, with loss of H_2, to produce the metal-inserted thiophene-based metallacycles (dippe)Ni(η^2(*C,S*)-T) and (dippe)Ni(η^2(*C,S*)-BT). Both of these Ni–thiophene complexes reacted further in solution to give the bimetallic species $[(dippe)Ni]_2(\mu\text{-T})$ and $[(dippe)Ni]_2(\mu\text{-BT})$, respectively, which contain bridging, ring-opened thiophenes.

Building on previous studies,[19] Rauchfuss[20] reported both C–S cleavage and desulfurization of thiophenes and benzothiophene during thermolysis with $Fe_3(CO)_{12}$ to obtain the thiaferroles $Fe_2(CO)_6(\mu\text{-T*})$[19,20] (T* = T, BT). In the case of thiophene, ferroles such as $Fe_2(CO)_6(C_4H_4)$ resulted from metal insertion and desulfurization of the parent thiophene ligand.

Recently, we reported the preparation of the C–S-cleaved BT complex $Re_2(CO)_7(\mu\text{-BT})$,[21] by UV irradiation of $Re_2(CO)_{10}$ and benzothiophene in hexanes solvent (Scheme 1). In this novel bimetallic Re complex, the BT ligand is opened at the C_{vinyl}–S bond and bridges the two Re centers of a $Re_2(CO)_7$ moiety through both the S atom and the vinyl group, which behaves as an η^1 and η^2 ligand to the two Re centers. Our recent success in preparing $Re_2(CO)_7(\mu\text{-BT})$ prompted us to investigate the reactivity of DBT and thiophenes such as 2,5-Me_2T under similar conditions. Here we report our results of UV-light-promoted reactions of dibenzothiophene (DBT) and 2,5-dimethylthiophene (2,5,-Me_2T) with $Re_2(CO)_{10}$ to afford dinuclear Re complexes with S-bound, C–H-cleaved, and C–S-cleaved thiophene ligands.

Scheme 1



Experimental Section

General Considerations. All reactions were performed under a nitrogen or argon atmosphere in reagent grade solvents, using standard Schlenk techniques. Hexanes, THF, ethyl ether, and methylene chloride were dried and purified using the Grubbs solvent purification process[22] purchased from Solv-Tek, Inc. Benzene was dried over CaH_2 and then distilled prior to use. Deuteriomethylene chloride (Cambridge) was stored over 4 Å molecular sieves. Rhenium carbonyl was purchased from Strem Chemicals Inc. TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical), dibenzothiophene, and 2,5-dimethylthiophene were purchased from Aldrich Chemical Co. and used without further purification. Trimethylamine oxide hydrate (Aldrich) was dried by azeotropic distillation of the water from benzene. Silica gel (J. T. Baker, 40–140 mesh) was dried under vacuum at ambient temperature for 14 h and stored under argon prior to use. Neutral alumina (Aldrich, Brockmann I) was dried under vacuum at ambient temperature for 14 h and treated with 10% (by weight) water under argon with vigorous shaking.

The ^{1}H NMR spectra for all complexes were recorded on either a Varian VXR-300 MHz or an in-house 400 MHz NMR spectrometer using the deuterated solvent as both internal lock and internal reference. Solution infrared spectra were recorded on a Nicolet-560 spectrophotometer using NaCl cells with 0.1 mm spacers. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O analyzer. All photochemical reactions were carried out in a 40–60 mL capacity quartz Schlenk photolysis tube fitted with a coldfinger, which was immersed into the reaction solution. Irradiation was performed using a Hanovia 450 W Hg medium-pressure lamp as the light source (inserted into either a quartz or Pyrex water-cooled jacket). The reaction temperature was controlled using an Isotemp 1013P refrigerated circulating bath (Fisher Scientific) with circulation hoses connected to the coldfinger.

Preparation of *eq*-$Re_2(CO)_9(\eta^1(S)\text{-DBT})$ (1) and $Re_2(CO)_8(\mu\text{-}C_{12}H_7S)(\mu\text{-H})$ (2). A hexanes solution (30 mL) of $Re_2(CO)_{10}$ (150 mg, 0.230 mmol) and DBT (82.6 mg, 0.448 mmol) was prepared in a quartz photolysis tube, containing a

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magnetic stir bar. A coldfinger (15 °C) was immersed into the reaction solution, and an oil bubbler was then connected to the tube. The solution was irradiated under nitrogen for 18−24 h with stirring, during which time a light yellow solution containing a brown precipitate was produced. More yellow precipitate was also present above the solution on the sides of the tube. The solution was filtered into a Schlenk flask, and the solvent was removed in vacuo to produce a crude lemon yellow solid residue containing complexes **1** and **2**, unreacted $Re_2(CO)_{10}$, DBT, and the Re cluster $HRe_3(CO)_{14}$[23] (<10% based on $Re_2(CO)_{10}$). The yellow residue on the photolysis tube wall was washed with hexanes (2 × 5 mL), dried in vacuo, and dissolved in CH_2Cl_2. This solution was then filtered and the filtrate combined with the lemon yellow solid residue from the previous filtration. More CH_2Cl_2 was added to the now yellow-brown solution until all solids were dissolved (3−6 mL). The resulting solution was layered with hexanes and cooled (−20 °C) overnight. After 1 day, yellow crystals of complex **2** formed and complex **1** also precipitated from solution as a yellow powder. The crystals and yellow solid were filtered and dried in vacuo. Complexes **1** (9.2−28 mg, 5−15%) and **2** (18−36 mg, 10−20%) were separated by hand-picking crystals of **2** from the mixture. Attempts to purify the crude mixture of products by chromatography on silica gel or alumina were unsuccessful due to decomposition. However, $HRe_3(CO)_{14}$ was recovered during chromatography of the crude mixture on silica gel. Complex **1** was characterized by IR and ^1H NMR spectroscopy of the mixture of **1** and **2** and compared to an authentic sample that was prepared as described below from $Re_2(CO)_9(THF)$ and DBT. Data for **2**: ^1H NMR (CD_2Cl_2, 300 MHz) δ 8.06 (m, 1 H), 7.87 (d, 1 H, $J = 7.2$ Hz), 7.80 (d, 1 H, $J = 7.2$ Hz), 7.69 (m, 1 H), 7.56 (m, 2 H), 7.21 (t, 1 H, $J = 7.2$ Hz), −14.8 (s, 1 H); IR (hexanes) ν_{CO} 2114 (w), 2087 (w), 2023 (vs), 2013 (s), 1995 (m), 1985 (s), 1958 (m). Anal. Calcd for $C_{20}H_8O_8Re_2S$: C, 30.77; H, 1.03. Found: C, 30.74; H, 1.03.

Preparation of $Re_2(CO)_7(2,5\text{-}Me_2T)$ (3). A hexanes solution (30 mL) of $Re_2(CO)_{10}$ (204 mg, 0.313 mmol) and 2,5-Me_2T (0.20 mL, 1.76 mmol) was prepared in a quartz reaction tube containing a magnetic stir bar. The solution was irradiated with stirring for 15−20 h, at 10 °C under a constant flow of nitrogen. During this time, the solution turned yellow-orange and a brown precipitate formed. The solution was then transferred to a column of silica gel (1 × 8 cm) packed in hexanes. A yellow band eluted, using a combination of CH_2Cl_2 and hexanes (1:5), and was collected. The volatiles were removed in vacuo, leaving a yellow-orange oily residue which was then dissolved in CH_2Cl_2 (1 mL) and layered with hexanes (5 mL) followed by slow cooling (−20 °C) until yellow crystals of **3** formed (1 day). The solution was then filtered, and the yellow crystals of **3** (20−30 mg, 10−15% yield based on $Re_2(CO)_{10}$) were dried under vacuum. ^1H NMR (CD_2Cl_2, 400 MHz): δ 6.49 (d, 1 H, $J = 6.0$ Hz), 5.05 (d, 1 H, $J = 5.6$ Hz), 2.71 (s, 3 H, Me), 2.31 (s, 3 H, Me). IR (hexanes): ν_{CO} 2093 (w), 2039 (s), 1993 (s), 1990 (s), 1963 (m), 1950 (vs) cm^{-1}. Anal. Calcd for $C_{13}H_8O_7Re_2S$: C, 22.94; H, 1.18; S, 4.71. Found: C, 22.80; H, 1.20; S, 4.08.

Preparation of $Re_2(CO)_9(THF)$ (4). Complex **4** was prepared using the following preparation (method A) and a previously described procedure (method B).[24] In method A, a THF solution (30 mL) of $Re_2(CO)_{10}$ (200 mg, 0.307 mmol) was added to a quartz photolysis tube containing a magnetic stir bar. A coldfinger was then inserted into the solution (10 °C), and an oil bubbler was connected to the tube. The solution was then irradiated with stirring under N_2 until the ν_{CO} bands for **4** reached a maximum (1−1.5 h). The orange-yellow solution of **4**, which contains some residual $Re_2(CO)_{10}$, was then ready for use in further experiments (see below). Complex **4** was isolated as an impure orange-yellow oil by removing the solvent under vacuum. The oil also contained unreacted $Re_2(CO)_{10}$ (on the basis of IR spectroscopy) and other unidentified impurities (on the basis of ^1H NMR spectroscopy). Attempts to purify **4** on silica gel or alumina using THF as the solvent produced an orange band that did not elute in THF, CH_2Cl_2, or benzene solvents. However, crude **4** was sufficiently stable for spectroscopic analysis. ^1H NMR (CD_2Cl_2, 300 MHz): δ 3.86 (m, 4 H), 1.89 (m, 4 H). IR (THF): 2101 (w), 2038 (m), 1987 (vs), 1980 (sh), 1952 (m), 1912 (m) cm^{-1}.

Preparation of the $Re_2(CO)_9(\eta^1(S)\text{-}T^*)$ Complexes 1 and 5 from 4. Complex 1. A solution of $Re_2(CO)_9(THF)$ (**4**) was prepared as described above (using method A) from a THF (30 mL) solution of $Re_2(CO)_{10}$ (206 mg, 0.316 mmol). The solution of complex **4** was warmed to room temperature, followed by the addition of DBT (114 mg, 0.619 mmol) with stirring. The orange-yellow solution lightened in color after 1−2 h, and stirring was continued for an additional 18 h. The solvent was then removed in vacuo, and the remaining yellow residue was extracted with CH_2Cl_2 (1 mL) and layered with hexanes (5 mL) followed by cooling to −20 °C until crystals of **1** were produced (1−2 days). The crystals were then filtered, washed with hexanes (2 × 10 mL), and dried to produce pure **1** (70 mg, 27% based on $Re_2(CO)_{10}$). ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.17 (m, 2 H), 7.84 (m, 2 H), 7.61 (m, 4 H). IR (CH_2Cl_2): ν_{CO} 2102 (w), 2042 (m), 1988 (vs), 1963 (m), 1933 (m) cm^{-1}. Anal. Calcd for $C_{21}H_8O_9Re_2S$: C, 31.19; H, 1.00. Found: C, 31.09; H, 0.83.

Complex 1 (from Method B).[24] A THF solution (20 mL) of $Re_2(CO)_{10}$ (306 mg, 0.469 mmol) was prepared in a 100 mL Schlenk flask containing a magnetic stir bar. Anhydrous Me_3NO (35.6 mg, 0.475 mmol) was then added, and the yellow solution was stirred for an additional 50 min. At this time, an IR spectrum of the solution showed ν_{CO} bands corresponding to complex **4**. The volatiles (THF and NMe_3) were then removed under vacuum, followed by the addition of more THF (20 mL) and DBT (94.7 mg, 0.514 mmol) with stirring for an additional 15 h. The solvent was then removed in vacuo, and the yellow residue was dissolved in CH_2Cl_2 (1 mL) and layered with hexanes (6 mL). Yellow crystals of **1** (128 mg, 34% based on $Re_2(CO)_{10}$) were grown after 1 day (−20 °C) and isolated after filtration, washing with hexanes (1 × 5 mL), and drying in vacuo.

$Re_2(CO)_9(\eta^1(S)\text{-}2,5\text{-}Me_2T)$ (5). Complex **5** was prepared in a similar manner as for **1** (method A) from a solution of $Re_2(CO)_9(THF)$ (0.222 mmol based on $Re_2(CO)_{10}$). The freshly prepared solution of $Re_2(CO)_9(THF)$ and 2,5-Me_2T (0.150 mL, 1.32 mmol) was stirred at room temperature for 23 h, during which time the solution lightened in color. The solvent and residual 2,5-Me_2T were then removed in vacuo, leaving a yellow-brown oil. Attempts to purify the crude product by column chromatography on silica gel or neutral alumina were unsuccessful due to complete decomposition of **5**. ^1H NMR spectroscopic analyses of crude **5** indicated free 2,5-Me_2T. ^1H NMR (CD_2Cl_2, 300 MHz): δ 6.71 (s, 2 H), 2.42 (s, 6 H, Me's). IR (hexanes): 2101 (w), 2047 (m), 1991 (s), 1987 (s), 1961 (m), 1928 (m) cm^{-1}.

Crystallographic Structural Determinations of 1−3. The single-crystal X-ray diffraction experiments were performed on a Bruker CCD-1000 diffractometer for **1** and **3** and on a CAD4 diffractometer for **2**. The systematic absences in the diffraction data were consistent for space groups $P1$ and $P\bar{1}$ for **1** and **3** and for space groups Cc and $C2/c$ for **2**. In all cases the latter centrosymmetric space groups were chosen, on the basis of the chemically reasonable and computationally stable results of refinement.[25] The structures were solved using direct methods, completed by subsequent difference Fourier

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Table 1. Crystallographic Data for 1−3

	1	**2**	**3**
formula	$C_{21}H_8O_9Re_2S\cdot{}^1/_2CH_2Cl_2$	$C_{20}H_8O_8Re_2S$	$C_{13}H_8O_7Re_2S$
fw	851.20	780.72	680.65
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a, Å	9.4152(4)	18.231(2)	8.5886(6)
b, Å	11.2600(5)	17.490(1)	9.2722(6)
c, Å	11.9289(6)	15.677(2)	12.4626(8)
α, deg	95.972(1)		69.566(1)
β, deg	109.303(1)	122.64(1)	87.392(1)
γ, deg	93.279(1)		62.591(1)
V, Å^3	1181.41(9)	4214.2(7)	817.65(9)
Z	2	8	2
cryst color, habit	yellow block	yellow block	yellow block
D(calcd), g cm^{-3}	2.393	2.461	2.765
μ(Mo Kα), mm $^{-1}$	10.49	11.62	14.95
temp, K	163(2)	293(2)	163(2)
diffractometer	Bruker CCD-1000	Enraf-Nonius CAD4	Bruker CCD-1000
abs cor	empirical	empirical	empirical
T(max)/T(min)	0.32/0.16	1.00/0.53	1.00/0.52
no. of rflns collected	10 433	4321	9606
no. of indep rflns	4795 (R(int) = 0.020)	3475 (R(int) = 0.064)	3338 (R(int) = 0.031)
$R(F)$ ($I \geq 2\sigma(I)$), %[a]	1.66	3.19	2.32
$R_w(F^2)$, %[a]	4.24	7.77	5.99

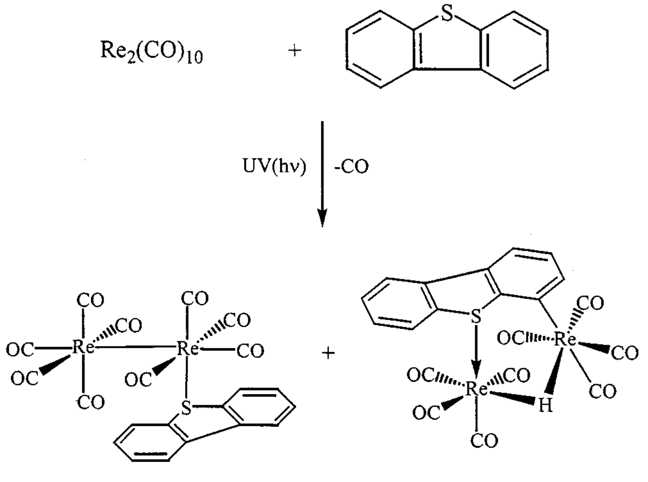
[a] Quantity minimized = $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

synthesis, and refined by full-matrix least-squares procedures. The empirical absorption corrections for **1** and **3** were applied by using the program SADABS[26] and by using the program DIFABS[27] for **2**. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. In the case of **1**, there was a severely disordered solvent molecule also present in the asymmetric unit. Attempts to identify and refine this molecule gave models that suggested the molecule was mobile. In addition, the refinement was computationally unstable. The option SQUEEZE of the program PLATON[28] was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecules. PLATON calculated the upper limit of volume that can be occupied by the solvent to be 110.6 Å^3, or 9.4% of the unit cell volume. The program calculated 40 electrons in the unit cell for the diffuse species. This approximately corresponds to one dichloromethane molecule in the unit cell (42 electrons). All data in Table 1 reflect the presence of a half-molecule of dichloromethane per molecule of complex in the lattice of **1**. In the case of **2**, the hydride ligand was restrained to be equidistant from the Re atoms.

Results and Discussion

Reaction of $Re_2(CO)_{10}$ with DBT. Ultraviolet irradiation of a stirred hexanes solution (10 °C) containing $Re_2(CO)_{10}$ and 2 equiv of DBT produced the bi- and trimetallic Re complexes *eq*-$Re_2(CO)_9(\eta^1(S)\text{-DBT})$ (**1**), $Re_2(CO)_8(\mu\text{-}C_{12}H_7S)(\mu\text{-H})$ (**2**), and $HRe_3(CO)_{14}$ after 18−24 h (Scheme 2). Hexanes was chosen as the reaction solvent because it is noncoordinating, inert during UV photolysis, and easy to remove under reduced pressure. No reaction occurred between $Re_2(CO)_{10}$ and DBT under similar photolytic conditions in either benzene or diethyl ether solvents. The photolysis reaction of DBT (2−4-fold excess) and $Re_2(CO)_{10}$ in CH_2Cl_2 produced only $(CO)_5ReCl$[29a] (<10%) and $Re_2(CO)_8(\mu\text{-}Cl)_2$[29b] (>90%) within 1 h, and no evidence for complexes **1** and **2** was observed. THF reacts with $Re_2(CO)_{10}$ during photolysis to give $Re_2(CO)_9$(THF); however, no Re−DBT-containing complexes were observed when $Re_2(CO)_{10}$ and DBT were irradiated in THF (20 h, 10 °C).

Scheme 2



1 **2**

Complex **1** is a moderately air-stable solid that is soluble in CH_2Cl_2 and benzene but sparingly soluble in hydrocarbons such as hexanes. The DBT ligand in **1** is labile and is completely replaced at room temperature by CO (1 atm) to give $Re_2(CO)_{10}$ in 1,2-DCE solvent in less than 2 min.

The ^{1}H NMR spectrum of **1** indicates S-binding of DBT, because the benzo-ring proton signals are shifted only 0.05−0.12 ppm downfield in comparison to those of free DBT (δ 8.21−7.47). This small chemical shift is common for η^1(S)-bound DBT complexes such as $CpRe(CO)_2(\eta^1(S)\text{-DBT})$,[30] $[CpFe(CO)_2(\eta^1(S)\text{-DBT})^+]$,[31] $Cp^*Ir(Cl)_2(\eta^1(S)\text{-DBT})$,[32] $CpMn(CO)_2(\eta^1(S)\text{-DBT})$,[33] $(CO)_5W(\eta^1(S)\text{-DBT}),)$[33] and $(CpSiMe_2Cp)Mo(\eta^1(S)\text{-DBT})$[34] (Cp = η^5-C_5H_5, Cp* = C_5Me_5).

The X-ray structure of **1** (Figure 1) shows an S-bound DBT ligand coordinated in the equatorial position to the $Re_2(CO)_9$ unit. The Re(2)−S distance (2.5375(8) Å) is similar to those observed in the structures of $Re_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ (2.485(4) Å)[35] and $Re_2(CO)_9[(SCH_2CH_2CH_2)_3]$ (2.498(3) Å)[36] but longer than those in $Cp^*Re(CO)_2(\eta^1(S)\text{-T})$[30] (2.360(3) Å) and $Cp^*Re(CO)_2(\eta^1(S)\text{-3-MeBT})$[37] (2.356(4) Å) (3-MeBT = 3-methylbenzothiophene), both of which contain the strongly electron-donating Cp* ligand. The geometry about the bound DBT sulfur is trigonal pyramidal, as suggested by the

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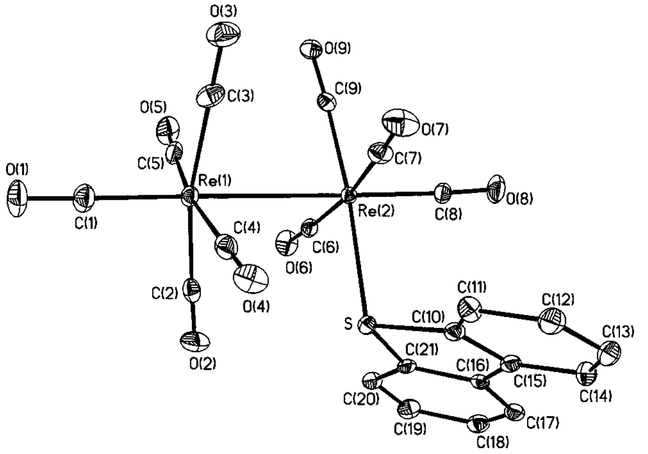

Figure 1. Molecular structure of $Re_2(CO)_9(\eta^1(S)\text{-DBT})$ (**1**) with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Re(1)−Re(2), 3.0389(2); Re(2)−S, 2.5375(8); S−C(10), 1.781(3); S−C(21), 1.782(3); Re(1)−C(1), 1.933(4); Re(2)−C(9), 1.926(3); C(9)−Re(2)−S, 174.69(10); Re(2)−S−C(10), 107.08(11); Re(2)−S−C(21), 106.60(11); C(10)−S−C(21), 90.98(16); Re(2)−S−Midpt, 113.6.

sum of the angles around the sulfur atom (304.7°). A second parameter used for determining the sulfur geometry in metal−thiophene complexes is the tilt angle (θ). In complex **1**, θ is defined as the angle between the Re−S bond and the vector from the sulfur to the midpoint of the C(15) and C(16) ring carbon atoms of the DBT ligand. The tilt angle for **1** ($\theta = 113.6°$) is similar to that reported for other η^1(S)-bound DBT complexes which contain relatively electron-deficient metal centers, including $(CO)_5W(\eta^1(S)\text{-DBT})$[33] (118.8°), $[CpFe(CO)_2(\eta^1(S)\text{-DBT})^+]$[31] (119.4°), and $(CO)_5Cr(\eta^1(S)\text{-DBT})$[33] (121.8°). Notably, θ is much larger in the Re−thiophene complexes $Cp^*Re(CO)_2(\eta^1(S)\text{-T})$ (140.4°)[33] and $Cp^*Re(CO)_2(\eta^1(S)\text{-3-MeBT})$[37] (131.0°), which contain Re centers that are more electron rich than in **1**.

The smaller θ and longer Re−S distance in **1** compared to those parameters in the $Cp^*Re(CO)_2(\eta^1(S)\text{-T}^*)$[33,37] complexes are in agreement with Harris' proposal,[38] which suggests that the more electron-rich the metal center, the more π-back-donation from the metal to the thiophene ligand and, hence, the larger the tilt angle. Related to this proposal is the trend in the Re−S distances in $Cp^*Re(CO)_2(\eta^1(S)\text{-T})$[33] (2.360(3) Å) and $Cp^*Re(CO)_2(\eta^1(S)\text{-3-MeBT})$[37] (2.356(4) Å), which are shorter than in **1** (2.5375(8) Å). We previously used Harris' argument to explain the smaller tilt angle and longer metal−sulfur distance observed in $[CpFe(CO)_2(\eta^1(S)\text{-DBT})^+]$ (119.4°, 2.289(1) Å) compared with those parameters for the more electron-rich $CpMn(CO)_2(\eta^1(S)\text{-DBT})$ (125.6°, 2.255(1) Å).[33]

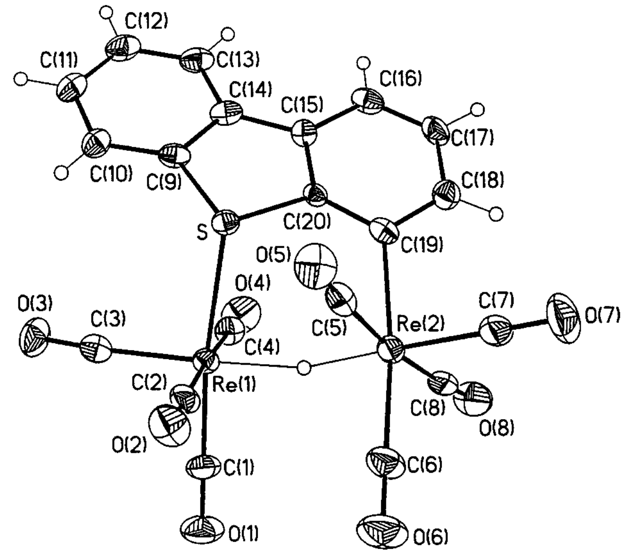

Figure 2. Molecular structure of $Re_2(CO)_8(\mu\text{-}C_{12}H_7S)(\mu\text{-}H)$ (**2**) with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Re(1)−S, 2.475(2); Re(2)−C(19), 2.230(9); Re(1)- - -Re(2), 3.345; S−C(9), 1.765(8); S−C(20), 1.768(7); Re(1)−C(2), 1.996(10); Re(1)−C(3), 1.961(10); Re(1)−C(4), 2.002(10); Re(2)−C(5), 1.981(11); Re(2)−C(6), 1.962(10); Re(2)−C(7), 1.897(11); Re(2)−C(8), 2.009(12); C(1)−Re(1)−S, 173.5(3); C(3)−Re(1)−S, 94.5(3); C(6)−Re(2)−C(19), 172.6(4); C(7)−Re(2)−C(19), 87.8(4); Re(1)−S−C(9), 116.0(3); C(9)−S−C(20), 92.7(4); Re(1)−S−C(20), 107.4(3); Re(1)−S−Midpt, 124.8.

Complex **2** is a moderately air-stable yellow solid that is soluble in benzene and CH_2Cl_2 but sparingly soluble in hexanes. Crystals of **2**, hand-picked from the mixture of **1** and **2**, were characterized by spectroscopy (^1H NMR and IR) and by an X-ray diffraction study. The ^1H NMR spectrum for **2** shows six signals in the aromatic region with chemical shifts in the range δ 8.06−7.21 for the ring protons of the C−H-cleaved DBT ligand. This spectrum differs from that of the DBT ligand in complex **1** (δ 8.20−7.55) and free DBT (8.21−7.47 ppm), both of which show only three signals (multiplets) for the DBT ring protons in the aromatic region due to the two equivalent DBT benzo-rings. A signal for the hydride ligand was also observed in the spectrum of **2** (δ −14.8) in a region which is characteristic of a hydride residing between two Re metal centers, as reported for other Re−H−Re-containing complexes.[39,40]

In the molecular structure of **2** (Figure 2) the DBT ligand is bridging the two $Re(CO)_4$ units through both the sulfur and the C(19) carbon. Although the hydride ligand was not observed in this structure, it was observed in the ^1H NMR spectrum. The Re(1)−S distance (2.475(2) Å) is shorter than that in **1** (2.5375(8) Å), while the Re−Re distance (3.345 Å) is longer compared to that in both **1** (3.0389(7) Å) and $Re_2(CO)_{10}$ (3.0413(11) Å),[41] possibly due to the bridging nature of the DBT and hydride ligands. The DBT sulfur is trigonal pyramidal, on the basis of both the tilt angle ($\theta = 124.8°$) and the sum of the angles around the sulfur (316.1°).

Complex **2** is a rare structural example of selective C−H bond cleavage in DBT at a transition-metal center. In related studies, Jones et al.[42] reported that $Cp^*Rh(PMe_3)$ reacts with alkyl-substituted dibenzothiophenes to afford complexes such as $Cp^*Rh(PMe_3)(C_{12}H_7S)(H)$, which exist as several isomers resulting from the cleavage of a DBT C−H bond. More recently,[43] $Os_3(CO)_{10}$-

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[38] (a) Harris, S. *Polyhedron* **1997**, *16*, 3219. (b) Harris, S. *Organometallics* **1994**, *13*, 2628.

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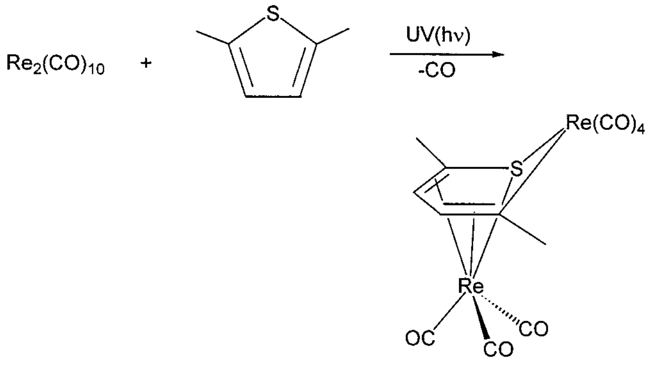
Scheme 3



3

$(CH_3CN)_2$ was reported to react with DBT to give the triosmium benzyne cluster $Os_3(CO)_9(\mu\text{-}C_{12}H_6S)(\mu\text{-}H)_2$, in which the C−H bonds of the DBT ligand were cleaved in both the 2- and 3-positions. This complex was proposed to form by initial DBT C−H bond cleavage in the 2-position to give the triosmium intermediate $Os_3(CO)_{10}(\mu\text{-}C_{12}H_7S)(\mu\text{-}H)$. Although this intermediate was not detected, its formation is supported by the isolation and characterization of complex **2** described here.

Reactions of $Re_2(CO)_{10}$ with Thiophenes. UV photolysis of a hexanes solution (10 °C) containing $Re_2(CO)_{10}$ and 3−5 equiv of 2,5-Me_2T in a quartz photolysis tube produced the ring-cleaved thiophene complex $Re_2(CO)_7(\mu\text{-}2,5\text{-}Me_2T)$ (**3**) in 15−20% yield after 24 h (Scheme 3). Complex **3**, which is soluble in most organic solvents such as benzene, CH_2Cl_2, and hexanes, is stable for months in air in the solid state but will decompose in solution unless kept under an inert atmosphere. Complex **3** has been characterized by IR and ^1H NMR spectroscopy and elemental analysis and also by an X-ray diffraction study. Its IR spectrum (in hexanes) shows six ν_{CO} bands at 2093 (w), 2039 (s), 1993 (s), 1990 (s), 1963 (m), and 1950 (vs) cm^{-1}. This spectrum is similar to that of its Mn analogue $Mn_2(CO)_7(\mu\text{-}2,5\text{-}Me_2T)$[14] (in hexanes: 2079 (m), 2033 (vs), 1995 (s), 1991 (vs), 1969 (m) and 1958 (vs) cm^{-1}), which was prepared using a very different synthetic method. The ^1H NMR spectrum of **3** (in CD_2Cl_2) consists of two doublets at δ 6.49 and 5.05 which correspond to the two inequivalent protons H(3) and H(4) and two singlets for the inequivalent methyl groups at δ 2.71 and 2.31; these chemical shifts are similar to those observed in the Mn analogue $Mn_2(CO)_9(\mu\text{-}2,5\text{-}Me_2T)$.[14]

In the structure of **3** (Figure 3), a $Re(CO)_4$ fragment is inserted into a C−S bond of the 2,5-Me_2T ring and bent out of the thiophene plane; the resulting ring-opened thiophene is also η^5-coordinated to the $Re(CO)_3$ unit. The structure of **3** is similar to that reported by Sweigart[14] and co-workers for the 2-MeT derivative $Mn_2(CO)_7(\mu\text{-}2\text{-}MeT)$. The distance between Re atoms (3.749 Å) is out of bonding range compared to those reported for both $Re_2(CO)_{10}$ (3.0413(11) Å)[41] and complex **1** (3.0389(2) Å). The Re(1)−S distance of 2.5048(13) Å and the Re(2)−S distance of 2.4722(14) Å are nearly the same.

In addition to the Mn analogue of **3**, $Mn_2(CO)_7(\mu\text{-}2,5\text{-}Me_2T)$, similar complexes with bridging thiophene (T), 2-methylthiophene (2-MeT), and 3-methylthiophene (3-MeT) ligands are also known.[14b] We have not, however, been successful in preparing the analogous Re complexes by photolysis of T, 2-MeT, and 3-MeT with $Re_2(CO)_{10}$ in hexanes solvent and under conditions similar to those used in the preparation of **3**. This lack of reactivity may be attributed to the fact that T, 2-MeT, and 3-MeT are weaker S-donor ligands[44] than 2,5-Me_2T and may not form the S-bonded $Re_2(CO)_9(\eta^1(S)\text{-}T^*)$ (T^* = T, 2-MeT, or 3-MeT) complex which are possible precursors to the C−S-cleaved products. Complex **3** does not react with electrophiles such as triflic acid and methyl triflate ($MeOSO_2CF_3$). The sulfur in the Mn analogue is similarly unreactive with these same electrophiles.[14a]

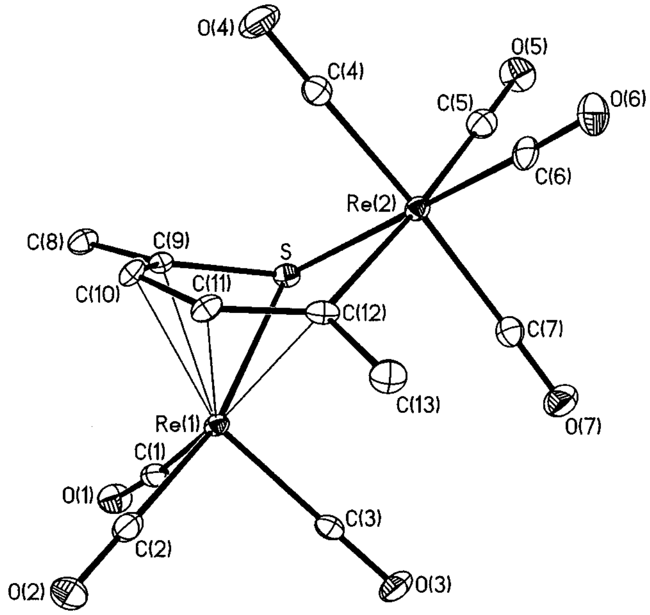


Figure 3. Molecular structure of $Re_2(CO)_7(2,5\text{-}Me_2T)$ (**3**) with 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Re(1)−S, 2.5048(13); Re(2)−S, 2.4722(14); Re(1)−C(12), 2.554(5); Re(2)−C(12), 2.206(6); S−C(9), 1.773(5); C(9)−C(10), 1.382(8); C(10)−C(11), 1.473(7); C(11)−C(12), 1.370(8); Re(1)−S−Re(2), 97.74(5); Re(1)−C(12)−Re(2), 103.7(2); S−Re(2)−C(12), 80.73(14); C(9)−S−Re(1) 62.77(18); C(9)−S−Re(2), 108.40(18).

Preparation and Characterization of $Re_2(CO)_9(THF)$ (4). Complex **4** was prepared using two separate methods (A and B). The first, method A, involves irradiation of a dry THF solution containing $Re_2(CO)_{10}$ at 10 °C with UV light (1−1.5 h), which produces a yellow-orange solution characterized as predominately **4** (>50%). The second method (B) was previously reported[24] and involves the chemically induced removal of a CO ligand from $Re_2(CO)_{10}$ using anhydrous Me_3NO. The IR spectrum for samples taken from solutions produced by both methods A and B exhibited ν_{CO} bands at 2101 (w), 2038 (m), 1987 (vs), 1980 (sh), 1952 (m) and 1912 (m) cm^{-1}, which correspond well with those previously reported for **4**.[24] Solvent removal under reduced pressure from solutions of **4** generated by either method A or B gave an oily yellow-orange residue that was characterized by ^1H NMR spectroscopy. The ^1H

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(44) (a) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922. (b) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *12*, 680.

NMR spectrum of this solution revealed two multiplets (δ 3.86 and 1.89) that were integrated in a 1:1 ratio and were assigned as the THF adduct complex **4**. Addition of a 5−10-fold excess of THF to the NMR sample, followed by collection of another ^{1}H NMR spectrum, revealed a second set of two signals (δ 3.69 and 1.86) corresponding to free THF adjacent to those observed for the proposed complex **4**. This result indicates that the signals at δ 3.86 and 1.89 are due to the complexed THF and not free or rapidly exchanging THF. Further evidence for the existence of species **4** is given by its reactivity with thiophenes to produce the S-bound complexes of type $Re_2(CO)_9(\eta^1(S)\text{-}T^*)$ (**1** and **5**, see below). The ^{1}H NMR spectrum (in CD_2Cl_2) of crude **4**, prepared using method B, also exhibits signals for **4** as well as other signals which could be attributed to the previously reported $Re_2(CO)_9(NMe_3)$[24] (δ 2.89) and unreacted Me_3NO (δ 3.04).

Synthesis and Characterization of $Re_2(CO)_9(\eta^1\text{-}(S)\text{-}T^*)$ Complexes (1 and 5). The S-bound thiophene complexes $Re_2(CO)_9(\eta^1(S)\text{-}T^*)$ (T* = DBT (**1**), 2,5-Me_2T (**5**)) were prepared in low to moderate yields (20−35%) by addition of DBT (2 equiv) or 2,5-Me_2T (3−5 equiv) to a THF solution of **4** with stirring for 15−20 h. Unreacted $Re_2(CO)_{10}$, $Re_2(CO)_9(NMe_3)$ (method B only), and other unidentified species were observed in the reaction mixtures when the crude products were analyzed spectroscopically (^{1}H NMR and IR). No reaction was observed under similar conditions when a 3−5-fold excess of T, 2-MeT, or 4,6-Me_2DBT was added to **4** in THF solution. These results suggest, as mentioned earlier, that these thiophenes are poor donor ligands[44] and cannot compete with other σ-donors such as NMe_3 and THF that are also present in the reaction solutions. The yields of **1** were similar (27−34%) using both methods A and B, which implies that DBT is a better σ-donor ligand under these reaction conditions than THF and NMe_3.

Complex **5** was prepared using method A, from a stirred THF solution of **4** and 3−5 equiv of 2,5-Me_2T. The ^{1}H NMR spectrum of **5** in CD_2Cl_2 shows a singlet (δ 6.71) for the equivalent H(3) and H(4) protons of the 2,5-Me_2T ligand; this signal is shifted 0.19 ppm downfield compared to that in the free ligand (δ 6.52 in CD_2Cl_2). The methyl signal for the two chemically equivalent Me groups in **5** is also a singlet (δ 2.42), which is shifted only 0.01 ppm from that in the free ligand (δ 2.41 ppm). Chemical shifts in the range of ±0.02−0.20 ppm are common for the methyl groups in η^1(S)-bound 2,5-Me_2T ligands such as those observed in $CpRe(CO)_2(\eta^1(S)\text{-}2,5\text{-}Me_2T)$[30] and $(CO)_5M(\eta^1(S)\text{-}2,5\text{-}Me_2T)$ (M = Cr, W).[33] The S-bound thiophene ligand in **5** is labile and partially dissociates in solution (CD_2Cl_2, 20 °C) at room temperature, on the basis of ^{1}H NMR studies.

Mechanisms for the Reactions in Schemes 2 and 3. It has been established that $Re_2(CO)_{10}$ is activated by UV light (1) to lose a CO ligand to generate $Re_2(CO)_9$ species (eq 1) or (2) to undergo metal−metal bond homolysis to produce 17-electron $^\bullet Re(CO)_5$ radical species[45] (eq 3). Such processes have been proposed for the formation of $Re_2(CO)_9(L)$ and $Re_2(CO)_8(L)_2$ complexes (L = phosphines, pyridine)[46,47] during UV photolysis of $M_2(CO)_{10}$ (M = Mn, Re) with L donor ligands (eqs 1−5). Complex **1** is also a $Re_2(CO)_9(L)$-type complex (L = DBT) and could be formed by either pathway 1 (eqs 1 and 2) or pathway 2 (eqs 3−5) during UV photolysis of $Re_2(CO)_{10}$ and DBT.

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

$$Re_2(CO)_9 + L \rightleftharpoons Re_2(CO)_9(L) \qquad (2)$$

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

$$Re(CO)_5 + L \rightleftharpoons Re(CO)_4(L) + CO \qquad (4)$$

$$Re(CO)_4(L) + Re(CO)_5 \rightleftharpoons Re_2(CO)_9(L) \qquad (5)$$

In an effort to understand the mechanism of the photolysis reaction between $Re_2(CO)_{10}$ and DBT (Scheme 2), a series of experiments were undertaken. When the UV-light-promoted reaction of $Re_2(CO)_{10}$ and 2−3 equiv of DBT was carried out (in hexanes, 24 h, 15 °C) under a CO atmosphere instead of N_2, the formation of complexes **1** and **2** did not not occur and the $Re_2(CO)_{10}$ remained unreacted. This result is consistent with the CO dissociation mechanism (eqs 1 and 2). It is known[48] that the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) reacts with $^\bullet M(CO)_5$ (M = Mn, Re) radicals to form neutral M−N−O cyclic complexes of the type $(TEMPO)M(CO)_3$. Therefore, if $Re(CO)_5$ radicals are intermediates in the photolytic reaction of $Re_2(CO)_{10}$ and DBT, the formation of complex **1** should be inhibited by TEMPO. When a hexanes solution of $Re_2(CO)_{10}$ and 3 equiv of DBT was photolyzed under N_2 in the presence of TEMPO (1 equiv based on $Re_2(CO)_{10}$), complex **2** was afforded after 8 h, as detected by IR spectroscopy, with no indication for the formation of **1**. However, when the ratio of $Re_2(CO)_{10}$ to TEMPO was changed to 1:2, which is stoichiometric with respect to the formation of $Re(CO)_5$ radicals, neither complex **1** nor **2** was observed after 10 h (10−15 °C). On the basis of the results of these two experiments, it is likely that Re radical species are also involved in the formation of **1**. Thus, a mechanism for the formation of **1** is probably best represented by pathway 2 (eqs 3−5) in which eq 4 is the step that is inhibited by CO.

If **1** were an intermediate in the formation of **2**, then the formation of **2** would be inhibited as well because of the inhibiting effect of CO and TEMPO on the formation of **1**. Unfortunately, it was not possible to determine whether **1** converts into **2** under the photolytic conditions of the reaction (Scheme 2) because **1** was too insoluble in hexanes to perform the experiment. However, it seems reasonable that **1** is the precursor to **2** and that this conversion is promoted by UV light, as **1** does not transform to **2** under thermal conditions (in refluxing toluene). A possible mechanism for the photolytic conversion of **1** to **2** is shown in Scheme 4. It involves photolytic loss of CO from the $Re(CO)_5$ unit in

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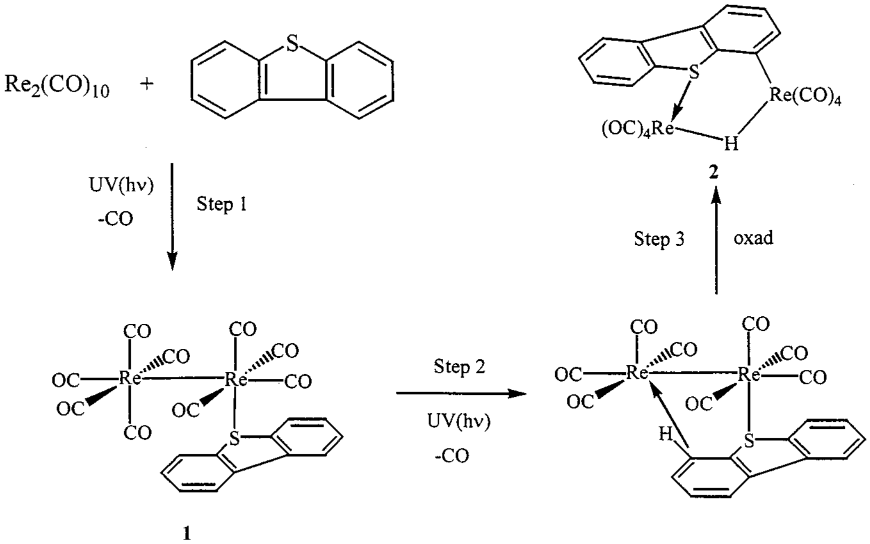
Scheme 4



1 to give an intermediate in which there is an agostic interaction between the C−H bond in the 4-position of the DBT ligand with the $Re(CO)_4$ unit (step 2). In step 3, oxidative addition of the DBT C−H bond leads to the product **2**. Although the mechanism proposed in Scheme 4 does account for the products (**1** and **2**) observed during the photolytic reaction, it is not possible to exclude mechanisms in which $Re_2(CO)_{10}$ is converted to **2** without involving **1** as an intermediate.

The formation (Scheme 3) of $Re_2(CO)_7(\mu$-2,5-$Me_2T)$ (**3**) could occur in a fashion similar to that proposed for **2**, from the S-bound complex $Re_2(CO)_9(\eta^1(S)$-2,5-$Me_2T)$ (**5**). In this mechanism, complex **5** undergoes photolytic loss of CO from the $Re(CO)_5$ unit, followed by η^2-binding of a C=C double bond of the 2,5-Me_2T ligand to give an intermediate of the type $(CO)_4Re(\mu$-$\eta^1(S),\eta^2$-2,5-$Me_2T)$-$Re(CO)_4$ (**A**). This intermediate (**A**) then undergoes scission of the Re−Re bond, oxidative addition of a C−S bond, and loss of a CO to give product **3**. Attempts to observe the photolytic conversion of **5** to **3** were unsuccessful due to the instability of **5**.

Because of the very different route used for the synthesis of the Mn analogue of **3**, $Mn_2(CO)_7(\mu$-2,5-$Me_2T)$, it is not surprising that the proposed mechanism for the formation of **3** differs significantly from that proposed[14,15] by Sweigart for the formation of $Mn_2(CO)_7$-$(\mu$-2,5-$Me_2T)$. This complex was prepared by the chemical reduction of $[(\eta^5$-2,5-$Me_2T)Mn(CO)_3]^+$ with cobaltocene. The proposed mechanism involves electron transfer to $[(\eta^5$-2,5-$Me_2T)Mn(CO)_3]^+$ to generate a $(\eta^4$-2,5-$Me_2T)Mn(CO)_3^-$ species which then attacks the thiophene of a second molecule of $[(\eta^5$-2,5-$Me_2T)Mn$-$(CO)_3]^+$ with subsequent formation of a bimetallic species which then converts into $Mn_2(CO)_7(\mu$-2,5-$Me_2T)$.

Conclusion

In summary, UV photolysis is a useful method for cleaving C−H or C−S bonds in thiophenes in the presence of $Re_2(CO)_{10}$. UV photolysis of $Re_2(CO)_{10}$ with excess DBT in hexanes solvent produces both the S-bound DBT complex $Re_2(CO)_9(\eta^1(S)$-DBT) (**1**) and the C−H-cleaved DBT complex $Re_2(CO)_8(\mu$-$C_{12}H_7S)(\mu$-H) (**2**). These products were not expected, since under similar conditions the reaction of $Re_2(CO)_{10}$ with benzothiophene (BT) did not produce S-bound or C−H-cleaved complexes but, rather, $Re_2(CO)_7(\mu$-BT) in which the C_{vinyl}−S bond was cleaved (Scheme 1).[21] This difference in reactivity between BT and DBT suggests that C_{vinyl}−S cleavage is more facile than C_{aryl}−S cleavage; moreover, the DBT reaction indicates that C−H cleavage is more favorable than C_{aryl}−S cleavage. Irradiation of $Re_2(CO)_{10}$ and excess 2,5-Me_2T with UV light produces $Re_2(CO)_7(\mu$-2,5-$Me_2T)$ (**3**), in which the C−S bond of the 2,5-Me_2T ligand is cleaved. However, unlike $Re_2(CO)_7(\mu$-BT), there is no Re−Re bond in **3**. It is apparently the coordination of the additional olefin in 2,5-Me_2T, as compared with BT, that prevents the formation of a Re−Re bond in **3**. Although mechanistic pathways for the photolytic reactions between $Re_2(CO)_{10}$ and the thiophenes are not clear, the formation of the C−H-cleaved DBT product **2** and the C−S-cleaved 2,5-Me_2T product **3** represents a new type of reactivity not previously reported for dinuclear metal complexes. The S-bound complexes Re_2-$(CO)_9(\eta^1(S)$-T*) were prepared for T* = DBT (**1**), 2,5-Me_2T (**5**) by substituting the THF ligand in the reactive species $Re_2(CO)_9$(THF) (**4**). On the basis of the smaller tilt angle (θ) and longer Re−S distance in **1** (113.6°; 2.5375(8) Å) compared to those parameters in Cp*Re-$(CO)_2(\eta^1(S)$-T) (140.4°; 2.360(3) Å)[30] and Cp*Re$(CO)_2$-$(\eta^1$(S)-3-MeBT)[37] (131.0°; 2.356(4) Å), we conclude that π-back-bonding from Re to the DBT ligand in **1** is much less important than in the more electron rich Re complexes Cp*Re$(CO)_2(\eta^1(S)$-T)[30] and Cp*Re$(CO)_2(\eta^1(S)$-3-MeBT).[37]

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Supporting Information Available: Tables giving crystallographic data for **1**−**3**, including atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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