Transition Metal Complexes of Chromium, Molybdenum, Tungsten, and Manganese Containing η^1(*S*)-2,5-Dimethylthiophene, Benzothiophene, and Dibenzothiophene Ligands

Michael A. Reynolds, Ilia A. Guzei,[†] Bradley C. Logsdon, Leonard M. Thomas,[†]
Robert A. Jacobson, and Robert J. Angelici*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011

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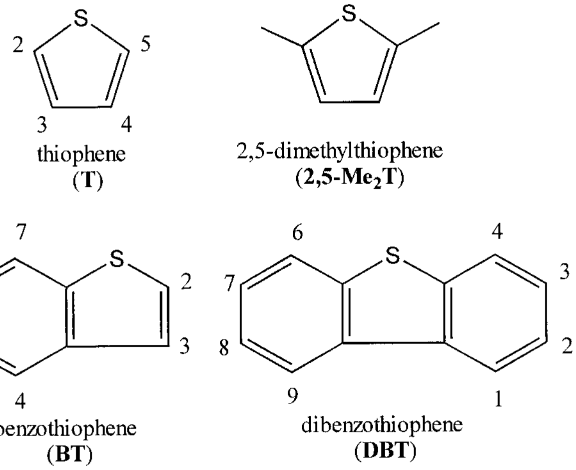
Ultraviolet photolysis of hexanes solutions containing the complexes $M(CO)_6$ (M = Cr, Mo, W) or $CpMn(CO)_3$ (Cp = η^5-C_5H_5) and excess thiophene (T*) (T* = 2,5-dimethylthiophene (2,5-Me_2T), benzothiophene (BT), or dibenzothiophene (DBT)) produces the η^1(*S*)-T* complexes $(CO)_5M(\eta^1(S)\text{-T*})$ **1**−**8** or $Cp(CO)_2Mn(\eta^1(S)\text{-T*})$ **9**−**11,** respectively. However, when T* = DBT and M = Mo, a mixture of two products results, which includes $(CO)_5Mo(\eta^1(S)\text{-DBT})$, **4a**, and the π-complex $(CO)_3Mo(\eta^6\text{-DBT})$, **4b**, as detected by ^{1}H NMR spectroscopy. Only the complexes $(CO)_5W(\eta^1(S)\text{-DBT})$ (**1**), $(CO)_5Cr(\eta^1(S)\text{-DBT})$ (**5**), and $Cp(CO)_2Mn(\eta^1(S)\text{-DBT})$ (**9**) were sufficiently stable (several days) to be isolated and characterized by elemental analyses. Rates of DBT ligand displacement by CO (1 atm) at room temperature decreased in the order **5** > **1** > **9**. Single-crystal, X-ray structural determinations are reported for **1**, **5**, and **9**. The tilt angle (θ) of the DBT ligand in these and related complexes is discussed in terms of π-back-bonding to the DBT ligand.

Introduction

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

A necessary first step in the commercial HDS reaction is the adsorption of the thiophenes to a sulfided metal catalyst surface such as Co- or Ni-promoted MoS_2 or WS_2 on alumina.[6,7] Organometallic modeling of this thiophene adsorption to metal centers has become a topic of interest in recent years. In fact, the literature is rich with transition metal−thiophene complexes containing thiophene ligands bound in many ways (i.e., η^1(*S*), η^2, η^4, η^5, η^6) to a variety of metal centers.[8−13] However, despite the central role of Mo and W in the commercial HDS process, organometallic complexes of group 6 metals containing thiophene ligands are still relatively rare. The complexes $(CO)_5Mo(\eta^1(S)\text{-T})$ and $(CO)_3Mo(\eta^5\text{-T})$ have been proposed to be theoretically possible on the basis of MO calculations, but neither complex has been prepared.[14] In fact, only two Mo

Scheme 1



[†] Iowa State University Molecular Structure Laboratory.

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complexes containing coordinated thiophene ligands have been reported. The first reported stable Mo–thiophene complex, $(CO)_3Mo[2,5\text{-}(Ph_2PCH_2CH_2)_2C_4H_2S]$,[15] exists as a pair of isomers (*mer* and *fac*) in which the thiophene is part of a chelating ligand that is bound to the Mo center through the phosphine groups and the sulfur. The second, $Mo(\eta^6\text{-}2\text{-}MeBT)_2$,[16] is a sandwich complex consisting of a Mo coordinated to two 2-methylbenzothiophene (2-MeBT) ligands through the arene rings in an η^6 fashion. Tungsten–thiophene complexes previously reported include $W(PCy_3)_2(CO)_3(\eta^1(S)\text{-}T)$[17] and $(CO)_5W(\eta^1(S)\text{-}T)$.[18] Both presumably have $\eta^1(S)$-coordinated thiophene ligands which are largely dissociated in solution. The former was fully characterized spectroscopically, while the latter was identified only by IR spectroscopy. One rare example of a bimetallic complex containing a BT ligand and a group 6 metal is $Cp^*(CO)_2Re(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)W(CO)_5$[19] ($Cp^* = \eta^5\text{-}C_5Me_5$) in which the $W(CO)_5$ moiety is coordinated to the BT ligand through the sulfur. S-binding to the $W(CO)_5^-$ fragment results from the enhanced donor ability of the BT sulfur, which is caused by η^2-coordination of the electron-rich $Cp^*Re(CO)_2^-$ fragment to the 2,3-double bond of BT. The η^5- and η^6-π-thiophene complexes of group 6 metals have been mostly limited to those of chromium, which include $(\eta^5\text{-}T)Cr(CO)_3$,[20] $(\eta^6\text{-}BT)Cr(CO)_3$,[21] and $(\eta^6\text{-}DBT)Cr(CO)_3$.[21]

Group 7 metals also form complexes containing coordinated thiophene ligands. Recent examples include $Cp^*(CO)_2Re(\eta^1(S)\text{-}T^*)$,[19,22] $[Cp(NO)(PPh_3)Re(\eta^1(S)\text{-}T^*)^+]$,[23] $[(\eta^5\text{-}T)Mn(CO)_3{}^+]$,[24] $[(\eta^6\text{-}DBT)Mn(CO)_3{}^+]$,[25] and $[(\eta^6\text{-}BT)Mn(CO)_3{}^+]$,[26] as well as several C,S-cleaved products.[27,28]

We now report the preparation of group 6 and 7 metal complexes of $2,5\text{-}Me_2T$, BT, and DBT obtained by UV irradiation of hexanes solutions containing $M(CO)_6$ or $CpMn(CO)_3$ and excess T* ligands. X-ray-determined molecular structures are reported for three complexes. Stabilities and labilities of the complexes are also described.

Experimental Section

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

^1H NMR spectra for all complexes were recorded on a Varian VXR-300 spectrometer using CD_2Cl_2 as the solvent, internal lock, and internal reference (δ 5.32 ppm for ^1H). Solution infrared spectra were recorded on a Nicolet-560 spectrometer using NaCl cells with 0.1 mm spacers and hexanes, CH_2Cl_2, or 1,2-DCE as the solvent. Electron–ionization mass spectra (EIMS) were recorded on a Finnigan TSQ700 instrument. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. All photochemical reactions were carried out in a 60 mL quartz, Schlenk photolysis tube fitted with a coldfinger condenser (which is immersed in the reaction solution) and using a Hanovia 450 W medium-pressure Hg lamp with a quartz jacket as the light source. The temperature of each reaction was controlled using an Isotemp 1013P refrigerated circulating bath (Fisher Scientific) with the circulation hoses connected to the coldfinger.

$(CO)_5W(\eta^1(S)\text{-}DBT)$ (1). The photolysis tube, equipped with a Teflon-coated magnetic stir bar, was charged with $W(CO)_6$ (262 mg, 0.745 mmol) and DBT (276 mg, 1.50 mmol). Hexanes (40 mL) were added, and the reaction tube was then fitted with the coldfinger (10 °C) and an oil bubbler. The actual solution temperature varied by ±5 °C. A slow, yet continuous flow of nitrogen was maintained over the solution while it was irradiated with stirring for 8 h. During this time the solution turned light yellow, and a yellow solid precipitated. After filtering by cannula, the remaining yellow solid residue was washed with cold hexanes (2 × 5 mL) to remove excess DBT and $W(CO)_6$ and then dried in vacuo. It was then extracted with methylene chloride to give a solution which was layered with hexanes (1:6). Slow cooling overnight (−20 °C) yielded yellow, air-stable, X-ray quality crystals of **1** (110 mg, 0.217 mmol, 29% based on $W(CO)_6$). Mp: 114–116 °C (dec). ^1H NMR (CD_2Cl_2): δ 8.17 (m, 2 H), 7.91 (m, 2 H), 7.62 (m, 4 H). IR (hexanes): ν(CO), 2078 w, 1951 s, 1946 sh, 1935 m, cm^{-1}. EIMS (70 eV): *m/e* 508 (M^+ for ^{184}W), 452 ($M^+ - 2CO$), 424 ($M^+ - 3CO$), 368 ($M^+ - 5CO$), 184 (DBT). Anal. Calcd for $C_{17}H_8O_5SW$: C, 40.18; H, 1.58; Found: C, 40.12; H, 1.71.

$(CO)_5W(\eta^1(S)\text{-}BT)$ (2). Complex **2** was prepared in a fashion similar to **1** by irradiation of a hexanes (40 mL) solution of $W(CO)_6$ (254 mg, 0.722 mmol) and BT (190 mg, 1.42 mmol) for 9 h at 0 °C. After filtration and solvent evaporation, a yellow-brown, air-sensitive oil characterized as impure **2** remained. Due to its instability, **2** was not purified. ^1H NMR (CD_2Cl_2): δ 7.92–7.83 (m, 2 H), 7.53 (m, 3 H), 7.47 (d, 1 H, *J* = 6 Hz). IR (hexanes): ν(CO), 2079 w, 1952 s, 1947 sh, 1935 m, cm^{-1}.

$(CO)_5W(\eta^1(S)\text{-}2,5\text{-}Me_2T)$ (3). Complex **3** was prepared in a manner similar to **1** by irradiating a hexanes (40 mL) solution of $W(CO)_6$ (204 mg, 0.580 mmol) and 2,5-dimethylthiophene (0.41 mL, 3.6 mmol) for 13 h at 10 °C with stirring. Removal of solvent and excess ligand in vacuo resulted in a yellow-brown, air-sensitive, oily residue characterized as **3**. ^1H NMR (CD_2Cl_2): δ 6.65 (s, 2 H), 2.47 (s, 6 H, Me). IR (hexanes): ν(CO), 2079 w, 1949 s, 1934 m, cm^{-1}.

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Table 1. Crystallographic Data for 1, 5, and 9

	1	**5**	**9**
formula	$C_{17}H_8O_5SW$	$C_{17}H_8CrO_5S$	$C_{19}H_{13}MnO_2S$
fw	508.14	376.29	360.31
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	9.576(2)	9.4074(6)	13.076(3)
b, Å	10.143(2)	10.0551(6)	10.309(2)
c, Å	10.420(2)	10.2053(6)	23.484(5)
α, deg	71.24(3)	70.398(1)	
β, deg	63.03(3)	62.901(1)	92.92(3)
γ, deg	67.58(3)	68.203(1)	
V, Å^3	820.2(3)	781.61(8)	3161.5(11)
Z	2	2	8
crystal color, habit	yellow block	yellow block	brown block
D(calcd), g cm^{-1}	2.058	1.599	1.514
μ (Mo Kα), mm^{-1}	7.193	0.889	0.973
temperature, K	293(2)	163(2)	295(2)
diffractometer	Enraf-Nonius CAD4	Bruker CCD-1000	Siemens P4
no. of reflns colld	4452	9291	12361
no. of indep refln	3773 (R(int) = 0.049)	3195 (R(int) = 0.020)	5268 (R(int) = 0.026)
$R(F)$,[a] ($I \geq 2\sigma(I)$)	0.0393	0.0249	0.0363
$R(wF^2)$[a]	0.0853	0.0671	0.0943

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

$(CO)_5Mo(\eta^1(S)$-DBT) (4a) and $(CO)_3Mo(\eta^6$-DBT) (4b). Compounds **4a** and **4b** were prepared following the same procedure as for **1** from $Mo(CO)_6$ (321 mg, 1.22 mmol) and DBT (454 mg, 2.46 mmol) dissolved in hexanes (40 mL). The solution was irradiated for 8 h at 10 °C under an N_2 atmosphere. Filtration and washing with hexanes yielded 83 mg of an air-sensitive, yellow-green mixture of solids **4a** and **4b**. The two complexes were unstable and could not be separated, but were identified spectroscopically. For **4a**, ^1H NMR (CD_2Cl_2): δ 8.18 (m, 2 H), 7.88 (m, 2 H), 7.62 (m, 4 H). IR (hexanes): ν(CO), 2080 w, 1958 s, 1937 m, cm^{-1}. For **4b**, ^1H NMR (CD_2Cl_2): δ 8.03 (m, 1 H), 7.79 (m, 1 H), 7.53 (m, 2 H), 6.83 (d, 1 H, J = 6.9 Hz), 6.54 (d, 1 H, J = 6.9 Hz), 5.93 (t, 1 H, J = 6.0 Hz), 5.67 (t, 1 H, J = 6.0 Hz).

$(CO)_5Cr(\eta^1(S)$-DBT) (5). Compound **5** was prepared in the same manner as **1** by irradiation of a hexanes (40 mL) solution of $Cr(CO)_6$ (246 mg, 1.12 mmol) and DBT (408 mg, 2.21 mmol) for 12 h at 10 °C. Golden brown, air-sensitive crystals of **5** were grown from a CH_2Cl_2/hexanes solution (1:6) of the crude mixture at −20 °C (120 mg, 0.319 mmol, 28.5% yield). Mp: 110−112 °C dec. ^1H NMR (CD_2Cl_2): δ 8.16 (m, 2 H), 7.91 (m, 2 H), 7.61 (m, 4 H). IR (hexanes): ν(CO), 2073 w, 1948 s, 1937 m, cm^{-1}. EIMS (70 eV): *m/e* 376 (M^+), 320 ($M^+ - 2CO$), 264 ($M^+ - 4CO$), 236 ($M^+ - 5CO$), 184 (DBT). Anal. Calcd for $C_{17}H_8CrO_5S$: C, 54.26; H, 2.14. Found: C, 54.01; H, 2.21.

$(CO)_5Cr(\eta^1(S)$-3-MeBT) (6). Compound **6** was prepared in a manner similar to **1** by irradiation of a hexanes (35 mL) solution of $Cr(CO)_6$ (250 mg, 1.14 mmol) and 3-MeBT (236 mg, 1.59 mmol) for 8 h at 10 °C. Filtration and solvent evaporation in vacuo yielded a dark yellow, air-sensitive, oily residue containing **6**, which was characterized spectroscopically. ^1H NMR (CD_2Cl_2): δ 8.01 (d, 1 H), 7.78 (d, 1 H), 7.59 (m, 2 H), 6.99 (s, 1 H), 2.47 (s, 3 H, Me). IR (hexanes): ν(CO), 2073 w, 1947 s, 1936 m, cm^{-1}.

$(CO)_5Cr(\eta^1(S)$-BT) (7). Complex **7** was prepared in a fashion similar to **1** by irradiation of $Cr(CO)_6$ (250 mg, 1.14 mmol) and BT (307 mg, 2.29 mmol) in hexanes (30 mL) for 9 h at 10 °C. The removal of solvent in vacuo produced **7** as a yellow, air-sensitive, oily residue. Attempts at further purification by both chromatography and crystallization were not successful. IR (hexanes): ν(CO), 2073 w, 1947 s, 1934 m, cm^{-1}.

$(CO)_5Cr(\eta^1(S)$-2,5-Me_2T) (8). Complex **8** was prepared in a manner similar to **1** by irradiation of a hexanes (38 mL) solution of $Cr(CO)_6$ (197 mg, 0.895 mmol) and 2,5-Me_2T (0.61 mL, 5.36 mmol) for 12 h at 10 °C. The solvent and excess ligand were removed in vacuo, affording an unstable, yellow oil containing **8**. ^1H NMR (CD_2Cl_2): δ 6.64 (s, 2 H), 2.45 (s, 6 H, Me). IR (hexanes): ν(CO), 2073 w, 1951 s, 1936 m, cm^{-1}.

Preparation of $Cp(CO)_2Mn(\eta^1(S)$-T*) Complexes 9−11 (T* = DBT, BT, 2,5-Me_2T). $Cp(CO)_2Mn(\eta^1(S)$-DBT) (9). The quartz reaction tube equipped with a magnetic stir bar was charged with $CpMn(CO)_3$ (300 mg, 1.47 mmol) and DBT (547 mg, 2.97 mmol) followed by the addition of hexanes (45 mL) under a nitrogen atmosphere. The solution was irradiated for 5 h at 10 °C, during which time the solution became orange and a precipitate formed. The solution was filtered, and the orange precipitate was washed with hexanes (3 × 10 mL) to remove residual DBT and $CpMn(CO)_3$. Orange-brown, air-stable, X-ray quality crystals of **9** were grown overnight at −20 °C in a CH_2Cl_2/hexanes solution (1:5) (207 mg, 0.574 mmol, 39% based on $CpMn(CO)_3$). Mp: 118−120 dec. ^1H NMR (CD_2Cl_2): δ 8.07 (m, 2 H), 7.97 (m, 2 H), 7.55 (m, 4 H), 4.09 (s, 5 H, Cp). IR (hexanes): ν(CO), 1952 s, 1890 s, cm^{-1}. EIMS (70 eV): 360 (M^+), 304 ($M^+ - 2CO$), 184 (DBT), 120 (CpMn). Anal. Calcd for $C_{19}H_{13}MnO_2S$: C, 63.34; H, 3.64. Found: C, 63.19; H, 3.61.

$Cp(CO)_2Mn(\eta^1(S)$-BT) (10). Complex **10** was made in the same manner as **9** by irradiation of a hexanes (35 mL) solution of $CpMn(CO)_3$ (201 mg, 0.986 mmol) and BT (398 mg, 2.97 mmol) for 10 h at 0 °C. The dark orange solution was then filtered, and the solvent was removed in vacuo, giving an oily residue characterized as **10**. ^1H NMR (CD_2Cl_2): δ 8.2−7.6 (m, 2 H), 7.5−7.2 (m, 4 H, br), 4.22 (s, 5 H, Cp). IR (hexanes): ν(CO), 1953 s, 1893 s, cm^{-1}.

Preparation of $Cp(CO)_2Mn(\eta^1(S)$-2,5-Me_2T) (11). Complex **11** was also prepared in a fashion similar to **9** by irradiation of a hexanes solution (40 mL) of $CpMn(CO)_3$ (278 mg, 1.36 mmol) and 2,5-Me_2T (0.60 mL, 5.27 mmol) for 6.5 h at 5 °C. Complex **11** was obtained as an orange oil after removal of solvent and excess 2,5-Me_2T in vacuo. ^1H NMR (CD_2Cl_2): δ 6.54 (s, 2 H), 4.23 (s, 5 H, Cp), 2.39 (s, 6 H, $2CH_3$). IR (hexanes): ν(CO) 1954 s, 1892 s, cm^{-1}.

X-ray Structural Determinations of 1, 5, and 9. Single crystals of both yellow **1** and **5** and brown **9** suitable for X-ray diffraction studies were obtained by recrystallization from CH_2Cl_2/hexanes solutions and slow cooling overnight (−20 °C). Crystal, data collection, and refinement parameters for **1**, **5**, and **9** are given in Table 1.

The systematic absences in the diffraction data were consistent for space groups $P1$ or $P\bar{1}$ for **1** and **5** and uniquely consistent for space group $P2_1/n$ for **9.** In the two former cases, the E-statistics strongly suggested the centrosymmetric choice $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares proce-

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(CO)_5W(\eta^1(S)\text{-DBT})$ (1)[a]

Distances			
W−S	2.580(2)	S−C(1)	1.762(7)
W−C(13)	2.006(8)	S−C(12)	1.764(7)
W−C(14)	2.039(8)	C(1)−C(2)	1.381(10)
W−C(15)	2.060(8)	C(1)−C(6)	1.387(10)
W−C(16)	2.020(8)	C(2)−C(3)	1.394(11)
W−C(17)	1.962(8)		
Angles			
C(1)−S−W	110.8(2)	C(13)−W−C(16)	90.9(3)
C(12)−S−W	108.2(2)	C(17)−W−C(15)	90.9(3)
C(17)−W−S	177.1(2)	C(16)−W−C(15)	88.0(3)
C(13)−W−C(15)	178.9(3)	C(14)−W−C(15)	90.4(3)
C(16)−W−C(14)	175.1(3)	C(13)−W−S	88.6(2)
C(17)−W−C(13)	89.3(3)	C(16)−W−S	92.3(2)
C(17)−W−C(16)	89.7(3)	C(14)−W−S	92.4(2)
C(17)−W−C(14)	85.7(3)	C(15)−W−S	91.2(2)
		C(1)−S−C(12)	90.7(3)

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(CO)_5Cr(\eta^1(S)\text{-DBT})$ (5)[a]

Distances			
Cr−S	2.4512(5)	Cr−C(4)	1.9030(18)
Cr−C(1)	1.9090(19)	Cr−C(5)	1.8550(19)
Cr−C(2)	1.8984(18)	S−C(6)	1.7727(16)
Cr−C(3)	1.9218(18)	S−C(17)	1.7692(16)
Angles			
C(6)−S−Cr	109.40(5)	C(1)−Cr−C(3)	90.77(7)
C(17)−S−Cr	112.78(5)	C(5)−Cr−C(2)	89.17(7)
C(1)−Cr−S	92.81(5)	C(5)−Cr−C(4)	89.27(7)
C(2)−Cr−S	88.06(5)	C(2)−Cr−C(4)	90.72(7)
C(3)−Cr−S	91.12(5)	C(5)−Cr−C(1)	86.19(8)
C(4)−Cr−S	91.78(5)	C(4)−Cr−C(1)	175.28(7)
C(5)−Cr−S	177.05(6)	C(5)−Cr−C(3)	91.67(7)
C(17)−S−C(6)	91.05(8)	C(2)−Cr−C(3)	178.49(7)
C(2)−Cr−C(1)	90.54(7)	C(4)−Cr−C(3)	88.03(7)

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

Table 4. Selected Bond Distances (Å) and Angles (deg) for $Cp(CO)_2Mn(\eta^1(S)\text{-DBT})$ (9)[a]

Distances			
Mn(1)−S(1)	2.2553(8)	Mn(1)−C(7)	1.767(3)
Mn(1)−C(6)	1.767(3)	S(1)−C(8)	1.771(3)
S(1)−C(19)	1.772(3)		
Angles			
S(1)−Mn(1)−C(1)	147.71(9)	S(1)−Mn(1)−C(6)	92.41(9)
S(1)−Mn(1)−C(2)	145.56(9)	S(1)−Mn(1)−C(7)	93.34(9)
S(1)−Mn(1)−C(3)	107.02(8)	C(6)−Mn(1)−C(7)	92.88(13)
S(1)−Mn(1)−C(4)	89.48(8)	Mn(1)−S(1)−C(8)	112.70(8)
S(1)−Mn(1)−C(5)	108.75(9)	Mn(1)−S(1)−C(19)	113.52(8)
		C(8)−S(1)−C(19)	90.80(12)

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

dures.[29,30] All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions.

Selected bond distances and angles for **1** and **5** are given in Tables 2 and 3, respectively. In the case of **9**, the asymmetric unit contains two independent molecules of the complex. Therefore, the bond distances and angles for **9** in Table 4 refer only to one of the two molecules. The geometry found for the second molecule is essentially identical to that found for the first, within standard deviations, and selected bond distances and angles for the second molecule can be found in the Supporting Information.

Results and Discussion

Synthesis and Characterization of $(CO)_5M(\eta^1(S)\text{-T*})$ Complexes (1−8). Ultraviolet irradiation of $M(CO)_6$ (M = Cr, Mo, W) complexes and excess T* (2−5 equiv) in hexanes solutions affords $\eta^1(S)$-T* complexes in low yields (<30%). Higher yields (40−50%) may be obtained for the DBT-containing complexes (**1**, **5**, and **9**) if the filtrates and washings are saved, reduced in volume, and cooled to −20 °C, but they usually still contain some thiophene impurity (<5%). IR spectroscopy serves as a useful tool for monitoring the progress of the reactions since none of the ν_{CO} bands of the $M(CO)_6$ starting materials overlap with those of the S-bound T* complexes. The complexes $(CO)_5W(\eta^1(S)\text{-DBT})$ and $(CO)_5Cr(\eta^1(S)\text{-DBT})$ are isolated as analytically pure solids, while the analogous $(CO)_5M(\eta^1(S)\text{-T*})$ complexes of BT, 3-MeBT, or 2,5-Me_2T, **2**−**4** and **6**−**8**, are only moderately stable in solution and could not be purified due to rapid dissociation of the thiophene ligand. Attempted isolations of complexes **2**−**4** and **6**−**8** by solvent removal led to complete decomposition of the oily complexes within 50−60 min under inert atmosphere. Column chromatography (silica, Celite, or alumina) was also unsuccessful. Complexes **1**−**8** are all soluble in hexanes, CH_2Cl_2, and DCE; however dissociation of the T* ligand occurs in the $\eta^1(S)$-BT and 2,5-Me_2T complexes (15−20 min) at room temperature with complete decomposition. The lability of the DBT ligand in complex **1** was evidenced by the substitution of DBT by CO in a CO-saturated hexanes solution of complex **1** under 1 atm of CO at room temperature ($t_{1/2}$ = 40 min) to give $W(CO)_6$. For the analogous $(CO)_5Cr(\eta^1(S)\text{-DBT})$, under the same conditions, displacement of DBT by CO occurs over the period of a few minutes and is complete in less than 5 min. When $(CO)_5W(\eta^1(S)\text{-DBT})$ was dissolved in THF, the DBT ligand was completely displaced to give $(CO)_5W(THF)$. The reaction of $(CO)_5W(THF)$ with 2 equiv of DBT gave a ∼10% yield of **1**.

The ^1H NMR chemical shifts for the protons of the S-bound thiophene ligands in complexes **1**−**8** are similar to those of the free thiophene ligands (±0.15 ppm). These chemical shifts are also similar to those of other known $\eta^1(S)$-DBT and $\eta^1(S)$-BT complexes: $Cp(CO)_2Re(\eta^1(S)\text{-BT})$,[19] $Cp(CO)_2Re(\eta^1(S)\text{-DBT})$,[22] and $[Cp(CO)_2Fe(\eta^1(S)\text{-DBT})^+]$.[31] The IR spectra in the ν_{CO} region for all the S-bound complexes, of the series **1**−**8**, are similar. Each complex has a weak a_1 band in the 2070 cm^{-1} region, a strong e band (1947−1958 cm^{-1}), and a medium a_1 band (1934−1937 cm^{-1}) in hexanes solution, which are typical for group 6 $(CO)_5M(L)$ complexes such as $(CO)_5Cr(THF)$[32] and $(CO)_5W(NC_5H_5)$.[33]

Synthesis of $(CO)_5Mo(\eta^1(S)\text{-DBT})$ (4a) and $(CO)_3Mo(\eta^6\text{-DBT})$ (4b). The complexes **4a** and **4b** were prepared

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(30) A package of locally developed crystallographic programs were used for data reduction for complex **9**. SHELX93 was used for refinement. The molecular drawing was produced using ORTEP (see Johnson, C. K. *ORTEPII, Report*. ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976).

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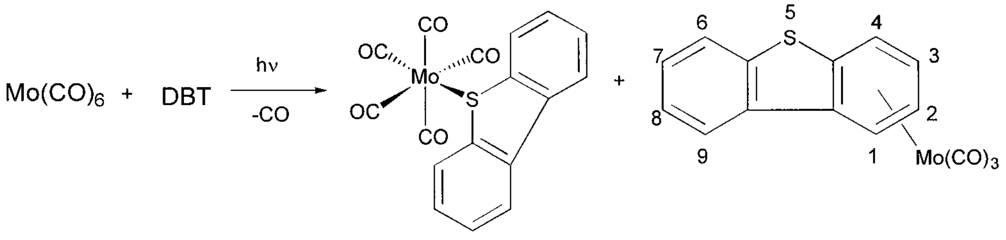
Scheme 2



4a **4b**

in the same way as **1**−**8** by UV irradiation of a hexanes solution of Mo(CO)$_6$ with excess DBT under an inert atmosphere (Scheme 2). The two complexes (**4a** and **4b**) are soluble in hexanes but decompose rapidly upon exposure to air in both the solid state and in solution. Although they could not be isolated as pure compounds, the ^{1}H NMR spectra of the mixture strongly support their formation. ^{1}H NMR spectra were obtained for **4a** and **4b** at 20 °C in CD$_2$Cl$_2$, but slow yet complete decomposition of both complexes occurs within 1−2 h in solution under inert atmosphere. Isolation of either **4a** or **4b** by column chromatography (alumina, silica gel, or Celite) was unsuccessful, as was attempted fractional crystallization at low temperature (−20 °C) in CH$_2$Cl$_2$/hexanes (1:4). Attempts to determine the ratio of the two complexes using ^{1}H NMR spectroscopy were unsuccessful due to their instability. Chemical shifts in the ^{1}H NMR spectra of the DBT proton signals assigned to **4a** are similar to those observed in **1** and **5** (±0.03 ppm). The proton resonances assigned to complex **4b** were based on those of the analogous Cr complex (η^6-DBT)-Cr(CO)$_3$.[21] The coordinated benzo-ring of **4b** has well-resolved splittings of the ring protons, which consist of a pair of doublets (δ 6.83 and 6.54) from the 1,4 protons and a pair of triplets (δ 5.93 and 5.67) corresponding to the 2,3 protons of the DBT ligand (Scheme 2). The uncoordinated ring of DBT has chemical shifts between 8.2 and 7.4 ppm that are similar to those in free DBT. The IR bands in the ν_{CO} region are assigned to **4a** on the basis of similar assignments for complexes **1** and **5**. However, the e and a$_1$(1) bands corresponding to **4a** are broad, indicating that the two bands expected for **4b** could be overlapping with those for **4a**. The EIMS of the mixture of **4a** and **4b** shows a Mo isotope pattern (*m*/*e* 366 for ^{98}Mo) corresponding to either an M$^+$ ion for the (η^6-DBT)Mo(CO)$_3$ complex or a fragment corresponding to **4a** with a loss of two CO ligands such as those observed in the spectra of (CO)$_5$Cr(η^1(*S*)-DBT) and (CO)$_5$W(η^1(*S*)-DBT). No M$^+$ was observed for complex **4a**.

Synthesis and Characterization of Cp(CO)$_2$Mn-(η^1(*S*)-T*) (9−11). Irradiation of a hexanes solution of CpMn(CO)$_3$ with excess T* (2−4 equiv) leads to the formation of Cp(CO)$_2$Mn(η^1(*S*)-T*) complexes. Complex **9** is stable for months in the solid state, while **10** and **11** are stable in hexanes solution for only several hours under an inert atmosphere and could not be isolated. Complexes **9**−**11** are soluble in most hydrocarbons and chlorinated solvents. Only **9** is stable in chlorinated solvents such as DCE. The DBT ligand in complex **9** was replaced to give CpMn(CO)$_3$ as determined by IR spectroscopy when 1 atm of CO was bubbled through a DCE solution of **9** at room temperature. The half-life of this reaction was 92 min. The rate of DBT substitution in CpRe(CO)$_2$(η^1(*S*)-DBT) by a dissociative mechanism was several orders of magnitude slower ($t_{1/2} = 7.2 \times 10^4$ min at 80 °C.)[34]

The ^{1}H NMR chemical shifts of the T* protons for **9**−**11** are similar to those of the analogous Cp(CO)$_2$Re-(η^1(*S*)-T*)[19,22] (T* = DBT, BT, 2,5-Me$_2$T) complexes (±0.4 ppm) and the cationic complex Cp(CO)$_2$Fe(η^1(*S*)-DBT)$^+$.[31] In the IR spectra for **9**−**11**, two bands with similar intensities are observed in the ν_{CO} region. The positions of these signals are essentially the same for all complexes of the series **9**−**11** (±3.0 cm^{-1}). The ν_{CO} bands of the analogous Cp(CO)$_2$Re(η^1(*S*)-T*)[19] complexes also differ from each other only by ±4.0 cm^{-1}. For complex **10**, sulfur rather than 2,3-η^2 coordination of the BT ligand is indicated by the IR bands (ν_{CO} 1953, 1893 cm^{-1}), which are much closer to those of Cp(CO)$_2$Re(η^1-(*S*)-BT)[19] (ν_{CO} 1947, 1885 cm^{-1}) than to those of Cp(CO)$_2$-Re(2,3-η^2-BT)[19] (ν_{CO} 1977, 1907 cm^{-1}).

Comparison of the Structures of (CO)$_5$W(η^1(*S*)-DBT) (1), (CO)$_5$Cr(η^1(*S*)-DBT (5), and Cp(CO)$_2$Mn-(η^1(*S*)-DBT) (9). In the structures of **1** (Figure 1), **5** (Figure 2) and **9** (Figure 3) the coordinated DBT ligand is S-bound to the metal center with trigonal-pyramidal geometry about the sulfur (pseudo-sp^3 hybridization). This geometry is indicated by the sum of the angles around the S atom in complexes **1** (309.7°), **5** (313.2°), and **9** (317.0°), which are considerably smaller in each complex than the 360° expected for an sp^2-hybridized sulfur. These angles are also similar to those found in Cp(CO)$_2$Fe(η^1(*S*)-DBT)$^+$ (309.8°)[31] and Cp*IrCl$_2$(η^1(*S*)-DBT)[35] (317.9°). The metal centers of complexes **1**, **5**, and **9** all have octahedral or pseudo-octahedral geometry, with angles of nearly 90° formed between adjacent carbonyls and the central metal atom (Tables 2−4). The C−M−C angles in **1** and **5**, defined by trans carbonyl ligands and the central metal atom, are nearly 180°. The M−C distances for the CO carbon trans to the DBT ligand in both **1** (1.962(8) Å) and **5** (1.8550(19) Å) are significantly shorter than those for the cis-CO carbons. The structure of **9** is very similar to that of Cp*IrCl$_2$-(η^1(*S*)-DBT)[35] with the DBT ligand oriented syn to the Cp ring. This is contrary to the observed ligand orientation in the structure of Cp(CO)$_2$Fe(η^1(*S*)-DBT)$^+$, in which the DBT ligand is anti to the Cp ring.[31] The W−S bond distance in **1** is 2.580(2) Å, which is slightly longer than for other complexes containing two-electron donor sulfur ligands as in (CO)$_5$W[η^1(*S*)-(CH$_3$S)$_2$C=PPh$_2$(CH$_3$)] (2.555-(2) Å)[36] and (CO)$_5$W($\overline{\text{SCH}_2\text{CH}_2\text{NHC}(=\text{O})\text{CH}_2}$) (2.551(14) Å).[37] The Cr−S bond distance in **5** is 2.4512(5) Å, which

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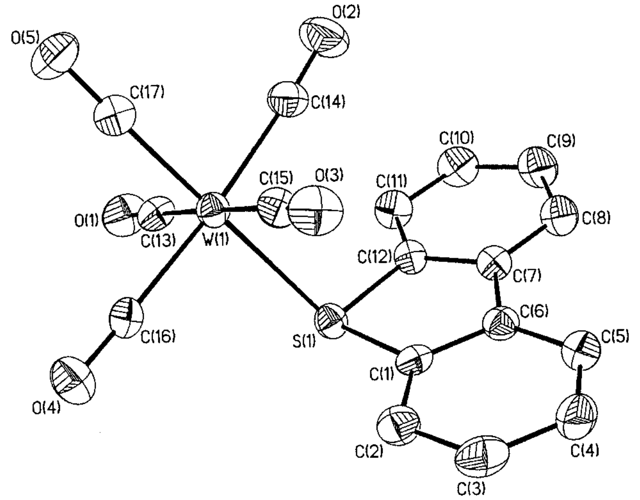

Figure 1. Thermal ellipsoid drawing of $(CO)_5W(\eta^1(S)$-DBT) (**1**).

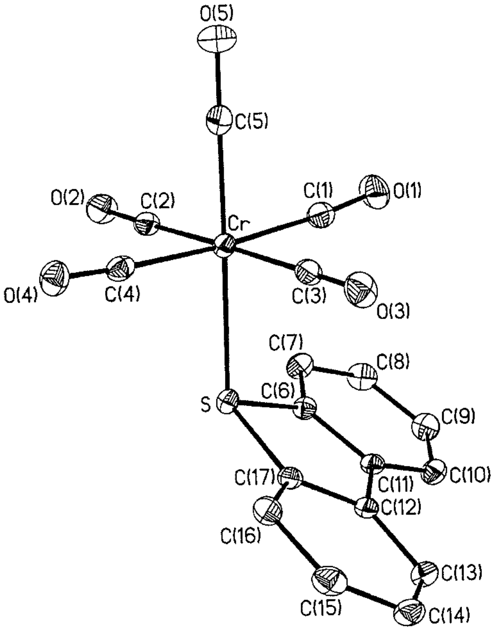

Figure 2. Thermal ellipsoid drawing of $(CO)_5Cr(\eta^1(S)$-DBT) (**5**).

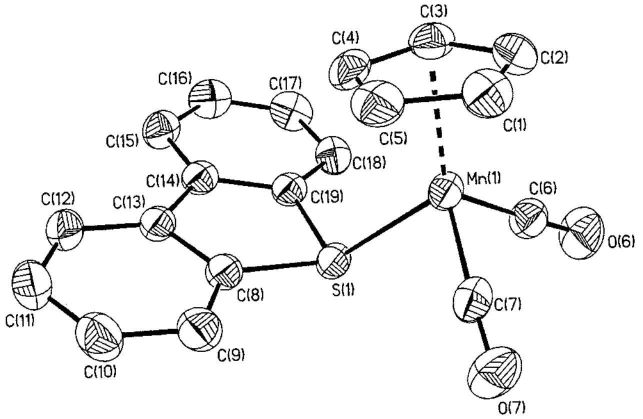

Figure 3. Thermal ellipsoid drawing of $CpMn(CO)_2(\eta^1(S)$-DBT) (**9**).

is similar to that for the sulfide complex $(CO)_5Cr[S(C_2H_5)(CH_2Ph)]$ (2.458(2) Å).[38] The Mn−S distance in **9** (2.255(1) Å) is shorter than both the Fe−S distance in $Cp(CO)_2Fe(\eta^1(S)\text{-DBT})^+$ (2.289(1) Å)[31] and the Ir−S distance in $Cp^*IrCl_2(\eta^1(S)$-DBT)[35] (2.375(2) Å). The mean C−S bond distance in the DBT ligand of **1**, **5**, and **9** is 1.763, 1.771, and 1.770 Å, respectively; all of these distances are slightly longer than that in free DBT (1.740 Å).[39] The C−S−C angle of the DBT ligand in each complex is 90.7(3)° for **1**, 91.05(8)° for **5**, and 90.8(12)° for **9**. These angles are similar to that observed in free DBT (91.5(4)°).[39] The DBT ligand is essentially planar, with the sulfur deviating 0.02 Å (for **1**) out of the least-squares plane which is defined by the C1, C6, C7, and C12 carbon atoms and 0.03 Å (for **5**) out of the plane defined by C6, C11, C12, and C17 atoms. The DBT ligand is also quite planar for **9**, with the sulfur 0.07 Å out of the least-squares plane as defined by the C8, C13, C14, and C19 atoms in the direction opposite the Mn atom.

The W lies out of the DBT ring plane, as shown by the angle between the W−S bond and the vector from the S to the midpoint of the C6 and C7 ring carbons (θ = 118.8°). The analogous θ angle for complexes **5** (121.8°) and **9** (125.6°) is slightly larger than that in **1**. Both of the θ angles for **1** and **5** are similar to those reported for $Cp(CO)_2Fe(\eta^1(S)\text{-DBT})^+$ (119.4°)[31] and $Cp^*IrCl_2(\eta^1(S)$-DBT)[35] (128.0°). Harris[40,41] proposed, on the basis of MO calculations, that the magnitude of the θ angle in metal−thiophene complexes depends on the metal's ability to π-back-donate to the thiophene ligand. The more electron-rich the metal, the more π-back-bonding to the thiophene and, thus, the larger the θ angle. Consistent with the proposal is the larger θ angle for $Cp(CO)_2Mn(\eta^1(S)$-DBT) (**9**) ($\theta = 125.6°$) as compared with that for the isoelectronic and isostructural $Cp(CO)_2Fe(\eta^1(S)\text{-DBT})^+$ ($\theta = 119.4°$). The greater π-back-bonding in the Mn complex might also be expected to lead to a stronger metal−sulfur bond than in the Fe complex. Indeed, the Mn−S bond (2.255(1) Å) in **9** is shorter than the Fe−S bond (2.289(1) Å) in $Cp(CO)_2Fe(\eta^1(S)\text{-DBT})^+$. In the absence of π-back-bonding, one would have expected the Mn−S bond to be longer than the Fe−S bond.

If the θ angle depends on the electron density on the metal and the C−O force constant (k_{CO}) of an analogous metal carbonyl complex depends on metal electron density, one might expect a correlation between θ and k_{CO}. Using Timney's method[42] for estimating k_{CO} values, we observe that k_{CO} for the metal carbonyl analogues of the following $\eta^1(S)$-DBT complexes increases in the following order (the θ angle is also given): $CpMn(CO)_2(\eta^1(S)$-DBT), 1561 N m^{-1}, 125.6° < $(CO)_5W(\eta^1(S)$-DBT), 1641 N m^{-1}, 118.9° < $(CO)_5Cr(\eta^1(S)$-DBT), 1647 N m^{-1}, 121.8° < $Cp^*IrCl_2(\eta^1(S)$-DBT), 1757 N m^{-1}, 128.0° ≈ $Cp(CO)_2Fe(\eta^1(S)\text{-DBT})^+$, 1758 N m^{-1}, 119.4°. As is evident from this trend, there is no general correlation between small θ and large k_{CO} values. Of course, these complexes exhibit a variety of geometries and ligands, which may contribute to the absence of a correlation.

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However, the expected trend in θ for the neutral Cp(CO)$_2$Mn(η^1(S)-DBT) and cationic Cp(CO)$_2$Fe(η^1(S)-DBT)$^+$ is consistent with Harris' bonding proposals.

Conclusion

UV photolysis of metal carbonyls in the noncoordinating solvent hexanes is a useful method for preparing (CO)$_5$M(η^1(S)-T*) [M = Cr, Mo, W] and Cp(CO)$_2$Mn(η^1-(S)-T*) complexes. The complex (CO)$_5$W(η^1(S)-DBT) is the first example of a fully characterized thiophene complex of the HDS-active metal tungsten. The stabilities of the complexes suggest that DBT binds more strongly than BT or 2,5-Me$_2$T. Earlier equilibrium studies[43,44] of the displacement of T* from Cp(CO)(PPh$_3$)Ru(η^1(S)-T*)$^+$ with a variety of thiophene ligands also showed that DBT binds more strongly than either BT or 2,5-Me$_2$T. Qualitative studies of Cp*IrCl$_2$(η^1(S)-T*)[35] followed the same trend. Semiquantitative studies of the rate of DBT substitution by CO show that the rates decrease in the following order: (CO)$_5$Cr(η^1(S)-DBT) (<5 min) > (CO)$_5$W(η^1(S)-DBT) ($t_{1/2}$ = 40 min) > Cp(CO)$_2$Mn(η^1(S)-DBT) ($t_{1/2}$ = 92 min). Structures of the DBT complexes **1**, **5**, and **9** determined by X-ray diffraction studies show that the coordinated sulfur has a trigonal pyramidal (sp^3-hybridized) geometry characteristic of S-coordinated thiophene ligands. The larger θ angle observed in CpMn(CO)$_2$(η^1(S)-DBT) as compared with that in the isoelectronic CpFe(CO)$_2$(η^1(S)-DBT)$^+$ is consistent with results of MO calculations that suggest the higher electron density on Mn favors π-back-bonding to the DBT ligand and thus a larger angle for θ.

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Supporting Information Available: Tables giving crystallographic data for **1**, **5**, and **9**, including atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, thermal ellipsoid drawings, unit cell and packing diagrams, and least-squares plane for the DBT ligand in **1**, **5**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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