(CDCl$_3$): δ 1.37 (t, 3 H, ^3J(H–H) = 14.14 Hz, Me), 2.09 (s, 3 H, Me), 2.96 (dd, 1 H, ^2J(H–H) = 17.19 Hz, ^2J(H–P) = 2.51 Hz, H$_6$), 3.6 (t, 1 H, ^2J(H–H) ~ ^2J(H–P) = 17.2 Hz, H$_6$′), 4.34 (m, 3 H, OCH$_2$ and OH), 6.04 (m, 1 H, H$_4$), 7.21 (dd, 1 H, ^3J(H–P) = 21.62 Hz, ^3J(H–H) = 7.45 Hz, H$_3$). Anal. Calcd for $C_{14}H_{13}PWO_8$: C, 32.08; H, 2.5. Found: C, 32.14; H, 2.52.

5-Methyl-2-[(diphenylphosphino)pentacarbonyltungsten]phosphinine (24). Phenyllithium (8 mmol, 2 mol/L in ether) was added to a solution of complex 14 (4 g, 7.6 mmol) in 75 mL of THF at −80 °C. Then, cyanodiphenylphosphine (1.6 g, 7.6 mmol) in 5 mL of THF was added and the reaction mixture was allowed to warm to room temperature. After evaporation of the solvent, benzene (30 mL) was added and the reaction mixture was heated at 70 °C for 10 h. After evaporation of the solvent, the final product was chromatographed with hexane/CH$_2$Cl$_2$ (4:1) as eluent. Yield: 2.84 g (60%), yellow solid. ^{31}P NMR (CH$_2$Cl$_2$), AB system: δ 227.03 (d, ^2J(P—P) = 107.42 Hz, –P═), 24.65 (d, ^1J(^{31}P—^{183}W) = 249.02 Hz, Ph$_2$P). ^{1}H NMR (CDCl$_3$): δ 2.56 (s, 3 H, Me), 7.41–7.65 (m, 11 H, C$_6$H$_5$ and H$_4$), 8.07 (ddd, 1 H, ^3J(H–P$_A$) = 16.02 Hz, ^3J(H–P$_B$) = 5.2 Hz, ^3J(H–H) = 8.68 Hz, H$_3$), 8.63 (dd, 1 H, ^2J(H–P$_A$) = 41.38 Hz, ^4J(H–P$_B$) = 4.92 Hz, H$_6$). ^{13}C NMR (CDCl$_3$): δ 24.66 (s, Me), 128.71 (d, J(C–P) = 9.66 Hz, CH of C$_6$H$_5$), 130.49 (s, CH of C$_6$H$_5$), 130.93 (d, ^1J(C–P) = 10.74 Hz, C of C$_6$H$_5$), 131.27 (d, ^1J(C–P) = 10.65 Hz, C of C$_6$H$_5$), 133.21 (d, J(C–P) = 11.75 Hz, CH of C$_6$H$_5$), 136.3 (dd, J(C–P$_A$) = 40.05 Hz, J(C–P$_B$) = 4.7 Hz, C$_3$), 140.56 (dd, J(C–P$_A$) = 12.44 Hz, J(C–P$_B$) = 8.96 Hz, C$_4$), 145.25 (d, ^2J(C–P) = 11.94 Hz, C$_5$), 153.92 (dd, ^2J(C–P$_A$) = 58.02 Hz, ^3J(C–P$_B$) = 13.1 Hz, C$_6$), 161.29 (dd, ^1J(C–P$_A$) = 68.32 Hz, ^1J(C–P$_B$) = 27.25 Hz, C$_2$), 197.67 (d, ^2J(C–P) = 5.94 Hz, CO cis), 199.54 (d, ^2J(C–P) = 21.76 Hz, CO trans). Mass spectrum, m/z (ion, relative intensity): 590 (M − CO, 32), 534 (M − 3CO, 62), 478 (M − 5CO, 100), 294 (M − W(CO)$_5$, 60). Anal. Calcd for $C_{23}H_{16}P_2WO_5$: C, 44.68; H, 2.60. Found: C, 44.08; H, 2.42.

Sulfur-Coordinated Thiophene and Dibenzothiophene in Cp′(CO)$_2$Re(thiophene) Complexes

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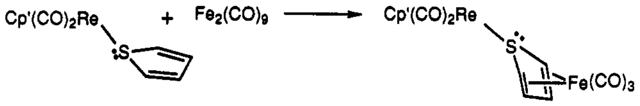
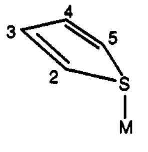
A series of stable S-bound thiophene complexes Cp′(CO)$_2$Re(Th), Cp′ = C$_5$H$_5$ or C$_5$Me$_5$, Th = thiophene (T), 2-MeT, 3-MeT, 2,5-Me$_2$T, Me$_4$T, and dibenzothiophene (DBT), are prepared by the reaction of Cp′(CO)$_2$Re(THF) with thiophenes. The first structural determination of a simple nonchelated S-coordinated thiophene complex Cp*(CO)$_2$Re(T) is reported. Reactions of several of the Cp′(CO)$_2$Re(Th) complexes



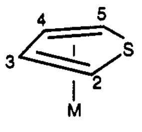
(Th = T, 2-MeT, and 3-MeT) with Fe$_2$(CO)$_9$ give thiophene-bridging dinuclear compounds Cp′(CO)$_2$Re-(μ_2-η^4(*S*)-Th)Fe(CO)$_3$ in which thiophene is coordinated to the Re via the sulfur and to the Fe through the four carbons of the diene system. This reaction is the first to demonstrate that S coordination activates thiophene to undergo further reactions.

Introduction

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



S-bound



η^5-bound

In a mechanism proposed in these laboratories[4c,5] for the catalytic hydrodesulfurization (HDS) of thiophenes, the thiophene is adsorbed via the entire π-ring in the η^5-mode.[6] Thiophenes coordinated in this manner in Mn and Ru complexes[7] are susceptible to attack by hydride sources,

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Table I. ^1H NMR Data (δ) for the Complexes in $CDCl_3$

complex	thiophene	Cp* or Cp	Me
$Cp^*(CO)_2Re(T)$ (1)	7.19 (br s, 2 H), 7.11 (br s, 2 H)	1.95 (s, 15 H)	
$Cp^*(CO)_2Re(2\text{-}MeT)$ (2)	6.98 (br m, 1 H), 6.91 (br m, 1 H) 6.86 (br m, 1 H)	1.95 (s, 15 H)	2.28 (s, 3 H)
$Cp^*(CO)_2Re(3\text{-}MeT)$ (3)	7.10 (br m, 1 H), 6.91 (br m, 1 H), 6.74 (br m, 1 H)	1.96 (s, 15 H)	2.25 (s, 3 H)
$Cp^*(CO)_2Re(2,5\text{-}Me_2T)$ (4)	6.63 (s, 2 H)	1.96 (s, 15 H)	2.22 (s, 6 H)
$Cp^*(CO)_2Re(Me_4T)$ (5)		1.95 (s, 15 H)	2.10 (s, 6 H), 1.99 (s, 6 H)
$Cp^*(CO)_2Re(DBT)$ (6)	8.01 (m, 2 H), 7.80 (m, 2 H), 7.50 (m, 4 H)	1.62 (s, 15 H)	
$Cp(CO)_2Re(T)$ (7)	7.28 (br s, 2 H), 7.03 (br s, 2 H)	4.92 (s, 5 H)	
$Cp(CO)_2Re(2\text{-}MeT)$ (8)	7.08 (br m, 1 H), 6.83 (br m, 1 H), 6.77 (br m, 1 H)	4.92 (s, 5 H)	2.35 (s, 3 H)
$Cp(CO)_2Re(3\text{-}MeT)$ (9)	7.19 (br m, 1 H), 6.83 (br m, 2 H)	4.92 (s, 5 H)	2.24 (s, 3 H)
$Cp(CO)_2Re(2,5\text{-}Me_2T)$ (10)	6.56 (s, 2 H)	4.89 (s, 5 H)	2.28 (s, 6 H)
$Cp(CO)_2Re(Me_4T)$ (11)		4.88 (s, 5 H)	2.17 (s, 6 H), 1.98 (s, 6 H)
$Cp(CO)_2Re(DBT)$ (12)	8.00 (m, 2 H), 7.89 (m, 2 H), 7.51 (m, 4 H)	4.71 (s, 5 H)	
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (13)	5.95 (m, 2 H), 3.56 (m, 2 H)	1.98 (s, 15 H)	
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}2\text{-}MeT)Fe(CO)_3$ (14)	5.78 (m, 1 H), 5.39 (m, 1 H), 3.53 (m, 1 H)	1.99 (s, 15 H)	1.64 (s, 3 H)
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}3\text{-}MeT)Fe(CO)_3$ (15)	5.98 (m, 1 H), 3.59 (m, 1 H), 3.41 (m, 1 H)	1.98 (s, 15 H)	2.16 (s, 3 H)
$Cp(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (16)	5.97 (m, 2 H), 3.55 (m, 2 H)	4.94 (s, 5 H)	
T[a,b]	7.48 (m, H2,5), 7.14 (m, H3,4)		
2-MeT[a,b]	7.18 (dd, H5), 6.88 (dd, H4), 6.78 (m, H3)		2.46 (s)
3-MeT[a,b]	7.34 (dd, H5), 7.02 (m, H2), 6.95 (d, H4)		2.25 (s)
$2,5\text{-}Me_2T$[a,b]	6.54 (s, H3,4)		2.37 (s)
Me_4T[c,d]			2.25 (s), 1.96 (s)
DBT[b,e]	8.30 (m, H1,9), 7.49 (m, H2,8), 7.50 (m, H3,7), 7.95 (m, H4,6)		

[a] Reference 6. [b] Acetone-d_6. [c] Reference 38. [d] $CDCl_3$. [e] Reference 39.

Table II. ^{13}C NMR Data (δ) for the Complexes in $CDCl_3$

complex	thiophene	Cp* or Cp	CO	Me
$Cp^*(CO)_2Re(T)$ (1)	138.9, 129.9	96.0,[a] 10.5[b]	205.2	
$Cp^*(CO)_2Re(2\text{-}MeT)$ (2)	150.8, 136.3, 129.3, 126.8	95.7, 10.3	205.2	13.3
$CP^*(CO)_2Re(3\text{-}MeT)$ (3)	140.6, 139.6, 133.3, 132.8	95.8, 10.5	205.4	16.1
$Cp^*(CO)_2Re(2,5\text{-}Me_2T)$ (4)	147.8, 126.6	95.4, 10.5	205.0	13.7
$Cp^*(CO)_2Re(Me_4T)$ (5)	138.6, 135.3	95.2, 10.5	205.5	13.6, 11.5
$Cp^*(CO)_2Re(DBT)$ (6)	145.4, 137.1, 127.6, 127.3, 124.4, 121.6	96.0, 10.2	205.7	
$Cp(CO)_2Re(T)$ (7)	143.9, 129.0	82.4	201.2	
$Cp(CO)_2Re(2\text{-}MeT)$ (8)	155.9, 141.0, 128.5, 125.6	82.5	201.4	13.8
$Cp(CO)_2Re(3\text{-}MeT)$ (9)	144.0, 139.7, 137.6, 132.0	82.4	201.5	16.2
$Cp(CO)_2Re(2,5\text{-}Me_2T)$ (10)	152.5, 125.2	82.7	201.4	14.3
$Cp(CO)_2Re(Me_4T)$ (11)	142.1, 134.7	82.7	201.9	13.6, 12.1
$Cp(CO)_2Re(DBT)$ (12)	149.3, 135.5, 128.0, 127.7, 124.9, 121.9	83.6	202.0	
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (13)	83.9, 57.1	95.5, 10.5	208.5, 207.0	
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}2\text{-}MeT)Fe(CO)_3$ (14)	85.9, 83.8, 75.1, 56.0	95.6, 10.6	209.5, 206.9, 206.4	16.1
$Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}3\text{-}MeT)Fe(CO)_3$ (15)	104.2, 85.0, 61.4, 54.5	95.5, 10.5	208.7, 207.2, 207.1	15.5
$Cp(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (16)	83.7, 57.3	82.7	208.0, 202.6	
T[c,d]	127.3 (C3,4), 125.6 (C2,5)			
2-MeT[c,d]	139.8 (C2), 125.9 (C3), 127.5 (C4), 123.7 (C5)			14.9
3-MeT[c,d]	121.3 (C2), 138.2 (C3), 130.1 (C4), 126.1 (C5)			15.5
$2,5\text{-}Me_2T$[e]	137.3 (C2,5), 124.7 (C3,4)			15.1
Me_4T[e,f]	133.0 (C2,5), 127.7 (C3,4)			13.0, 12.7
DBT[g,h]	121.9 (C1,9), 124.6 (C2,8), 127.0 (C3,7), 122.9 (C4,6), 138.5 (C4a,4b), 134.9 (C9a,9b)			

[a] Cp* ring carbon. [b] Cp* Me groups. [c] Reference 40. [d] Acetone-d_6. [e] Reference 38. [f] $CDCl_3$. [g] DMSO-d_6. [h] Reference 41.

and this reactivity is the basis for the proposed HDS mechanism.[4c,5] Another mechanism[4a] assumes initial coordination of the thiophene through only the sulfur atom, and this coordination is presumed to activate the thiophene so as to give the H_2S and C_4 hydrocarbon products. However, in the S-bound thiophene (T) complexes $CpFe(CO)_2(T)^+$,[8] $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$[2,9] $[RuClL_2]BF_4$[10a] (L = 6-(2-thienyl)-2,2′-bipyridine), $Pd(\eta^3\text{-allyl})(L')^+$,[10b] $[CuCl_2(L')]_2$,[10c] $PtBr_2(L')$[10d] (L′ = 2,5,8-trithia[9](2,5)thiophenophane), the thiophene is so weakly coordinated to the metal that all attempted reactions of the ligand have simply led to thiophene dissociation from the metal. Thus, there was no evidence that S-coordinated thiophene is activated to react until our preliminary report[11] of the reaction of $Cp^*(CO)_2Re(T)$ with $Fe_2(CO)_9$ to give the dinuclear thiophene-bridging complex, $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$. In this paper, we report the synthesis of a series of stable $Cp'(CO)_2Re(Th)$ ($Cp' = C_5H_5$ or C_5Me_5, Th = T, 2-MeT, 3-MeT, $2,5\text{-}Me_2T$, Me_4T, and dibenzothiophene (DBT)) and the X-ray structure determination of $Cp^*(CO)_2Re(T)$, which is the first structure of a simple nonchelated S-bound thiophene. Reactions of several of the $Cp'(CO)_2Re(Th)$ complexes with $Fe_2(CO)_9$ are also detailed.

Experimental Section

General Procedures. All reactions and reaction workups were carried out under an atmosphere of prepurified N_2 at room tem-

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

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

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

Preparation of $Cp^*(CO)_2Re(T)$ (1). A solution of $Cp^*(CO)_2Re(THF)$ was prepared by a modified literature method.[15] A solution of $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) in freshly distilled THF (30 mL) in a quartz photolysis tube equipped with a N_2 bubbler was irradiated with a mercury UV lamp (450 W Canrad-Hanovia) for 3 h at −20 °C. An IR spectrum of the solution (ν(CO) 1890, 1820 cm^{-1}) showed a maximum conversion to the THF complex without too much subsequent decomposition.

This solution of $Cp^*(CO)_2Re(THF)$ was stirred with thiophene (5.0 mL, 62 mmol) at room temperature for 6–8 h, the progress of the reaction being monitored by IR spectroscopy. After removal of the solvent in vacuo, the residue was extracted with hexanes/CH_2Cl_2 (20:1). The extract was chromatographed on neutral alumina column (1 × 15 cm). After the unreacted $Cp^*Re(CO)_3$ was eluted with hexanes, the yellow band containing the product was eluted with CH_2Cl_2/hexanes (1:4). The collected yellow band solution was concentrated under vacuum and slow cooling of the solution to −20 °C gave pale yellow crystals of 1 (0.098 g, 43%). IR (hexanes): ν(CO) 1934 (s), 1874 (s) cm^{-1}. EIMS (70 eV): *m/e* 462 (M^+), 404 ($M^+ - C_2H_2S$), 376 ($M^+ - (C_2H_2S + CO)$), 348 ($M^+ - (C_2H_2S + 2CO)$), 84 (T^+), 58 ($C_2H_2S^+$). Anal. Calcd for $C_{16}H_{19}O_2ReS$: C, 41.63; H, 4.15. Found: C, 41.70; H, 4.14.

Preparation of $Cp^*(CO)_2Re(2\text{-}MeT)$ (2). This compound was prepared from $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and 2-MeT (1.0 mL, 10.3 mmol) by using the same method as described for 1, giving pale yellow crystals (0.087 g, 37%). IR (hexanes): ν(CO) 1932 (s), 1872 (s) cm^{-1}. EIMS (70 eV) *m/e* 476 (M^+), 420 ($M^+ - 2CO$), 378 ($M^+ - MeT$), 350 ($M^+ - (MeT + 2CO)$), 97 ($MeT^+ - H$).

Preparation of $Cp^*(CO)_2Re(3\text{-}MeT)$ (3). Compound 3 was prepared in the same manner as 1 with use of $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and 3-MeT (1.0 mL, 10.3 mmol). Pale yellow crystals (0.082 g, 35%) of 3 were obtained. IR (hexanes): ν(CO) 1931 (s), 1870 (s) cm^{-1}. EIMS (70 eV) *m/e* 476 (M^+), 420 ($M^+ - 2CO$), 378 ($M^+ - MeT$), 350 ($M^+ - (MeT + CO)$), 97 ($MeT^+ - H$).

Preparation of $Cp^*(CO)_2Re(2,5\text{-}Me_2T)$ (4). This synthesis proceeds as for 1 by using $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and 2,5-Me_2T (3.0 mL, 26.3 mmol). Pale yellow crystals of 4 (0.085 g, 35%) were isolated. IR (hexanes): ν(CO) 1929 (s), 1868 (s) cm^{-1}. EIMS (70 eV) *m/e* 490 (M^+), 434 ($M^+ - 2CO$), 378 ($M^+ - Me_2T$), 350 ($M^+ - (Me_2T + CO)$), 111 ($Me_2T^+ - H$). Anal. Calcd for $C_{18}H_{23}O_2ReS$: C, 44.15; H, 4.73. Found: C, 44.29; H, 4.74.

Preparation of $Cp^*(CO)_2Re(Me_4T)$ (5). This complex was prepared analogously to 1 from $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and Me_4T (0.5 mL, 3.5 mmol). Pale yellow crystals of 5 (0.053 g, 21%) were obtained. IR (hexanes): ν(CO) 1926 (s), 1864 (s) cm^{-1}. EIMS (70 eV) *m/e* 518 (M^+), 462 ($M^+ - 2CO$), 378 ($M^+ - Me_4T$), 350 ($M^+ - (Me_4T + CO)$), 139 ($Me_4T^+ - H$).

Preparation of $Cp^*(CO)_2Re(DBT)$ (6). Compound 6 was synthesized in the same manner as that for 1 by using $Cp^*Re(CO)_3$ (0.25 g, 0.62 mmol) and DBT (0.85 g, 4.6 mmol). Pale yellow crystals of 6 (0.11 g, 32%) were obtained. IR (hexanes): ν(CO) 1930 (s), 1869 (s) cm^{-1}. EIMS (70 eV) *m/e* 562 (M^+), 506 ($M^+ - 2CO$), 378 ($M^+ - DBT$), 350 ($M^+ - (DBT + CO)$), 184 (DBT^+). Anal. Calcd for $C_{24}H_{23}ReO_2S$: C, 51.32; H, 4.13. Found: C, 50.84; H, 4.09.

Preparation of $Cp(CO)_2Re(T)$ (7). A THF solution (30 mL) of $CpRe(CO)_3$ (0.20 g, 0.60 mmol) was irradiated with the mercury UV lamp at −20 °C for 2 h until the concentration of $Cp(CO)_2Re(THF)$ was at a maximum as indicated by intensities of the ν(CO) bands at 1910 and 1837 cm^{-1}. Thiophene (4.0 mL, 50 mmol) was added and the solution was stirred at room temperature for 6–8 h. After chromatography and crystallization as described for 1, pale yellow crystals of 7 (0.094 g, 40%) were obtained. IR (hexanes): ν(CO) 1951 (s), 1888 (s) cm^{-1}. EIMS (15 eV) *m/e* 392 (M^+), 336 ($M^+ - 2CO$), 308 ($M^+ - T$), 208 ($M^+ - (T + CO)$), 84 (T^+). Anal. Calcd for $C_{11}H_9ReO_2S$: C, 33.75; H, 2.32. Found: C, 33.67; H, 2.31.

Preparation of $Cp(CO)_2Re(2\text{-}MeT)$ (8). This complex was prepared analogously to 7 from $CpRe(CO)_3$ (0.25 g, 0.75 mmol) and 2-MeT (1.0 mL, 10.3 mmol) to give pale yellow crystals (0.11 g, 36%) of 8. IR (hexanes): ν(CO) 1949 (s), 1885 (s) cm^{-1}. EIMS (16 eV): *m/e* 406 (M^+), 350 ($M^+ - 2CO$), 308 ($M^+ - MeT$), 280 ($M^+ - (MeT + CO)$), 97 ($MeT^+ - H$). Anal. Calcd for $C_{12}H_{11}ReO_2S$: C, 35.55; H, 2.73. Found: C, 35.69; H, 2.73.

Preparation of $Cp(CO)_2Re(3\text{-}MeT)$ (9). This synthesis proceeds as for 7 with use of $CpRe(CO)_3$ (0.20 g, 0.60 mmol) and 3-MeT (1.0 mL, 10.3 mmol). Pale yellow crystals of 9 (0.085 g, 35%) were isolated. IR (hexanes): ν(CO) 1948 (s), 1885 (s) cm^{-1}. EIMS (16 eV) *m/e* 406 (M^+), 350 ($M^+ - 2CO$), 308 ($M^+ - MeT$), 280 ($M^+ - (MeT + CO)$), 98 (MeT^+). Anal. Calcd for $C_{12}H_{11}ReO_2S$: C, 35.55; H, 2.73. Found: C, 35.54; H, 2.77.

Preparation of $Cp(CO)_2Re(2,5\text{-}Me_2T)$ (10). Complex 10 was synthesized in the same manner as 7 with use of $CpRe(CO)_3$ (0.25 g, 0.75 mmol) and 2,5-Me_2T (2.0 mL, 17.6 mmol) to give the product (0.14 g, 45%). IR (hexanes); ν(CO) 1948 (s), 1886 (s) cm^{-1}. EIMS (16 eV) *m/e* 420 (M^+), 364 ($M^+ - 2CO$), 308 ($M^+ - Me_2T$), 280 ($M^+ - (Me_2T + CO)$), 111 ($Me_2T^+ - H$).

Preparation of $Cp(CO)_2Re(Me_4T)$ (11). This complex was prepared analogously to 7 from $CpRe(CO)_3$ (0.20 g, 0.60 mmol) and Me_4T (0.5 mL, 3.5 mmol). After chromatography and recrystallization as described above, pale yellow crystals of 11 (0.041 g, 15%) were obtained. IR (hexanes): ν(CO) 1942 (s), 1879 (s) cm^{-1}. EIMS (16 eV) *m/e* 448 (M^+), 392 ($M^+ - 2CO$), 308 ($M^+ - Me_4T$), 139 ($Me_4T^+ - H$).

Preparation of $Cp(CO)_2Re(DBT)$ (12). The dibenzothiophene complex 12 was synthesized analogously to 7 from $CpRe(CO)_3$ (0.25 g, 0.75 mmol) and DBT (1.0 g, 5.4 mmol). The product 12 was isolated in 26% yield (0.095 g). IR (hexanes): ν(CO) 1945 (s), 1883 (s) cm^{-1}. EIMS (70 eV): *m/e* 492 (M^+), 436 ($M^+ - 2CO$), 308 ($M^+ - DBT$), 280 ($M^+ - DBT + CO)$), 184 (DBT^+). Anal. Calcd for $C_{19}H_{13}ReO_2S$: C, 46.42; H, 2.67. Found: C, 46.29; H, 2.80.

Reaction of 1 with $Fe_2(CO)_9$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4\text{-}(S)\text{-}T)Fe(CO)_3$ (13). To a solution of 1 (0.035 g, 0.076 mmol) in 15 mL of THF was added $Fe_2(CO)_9$ (0.10 g, 0.27 mmol). While the reaction mixture was stirred for 1.5 days, the solution color changed from orange-yellow to dark purple. After the solvent was evaporated in vacuo, the residue was extracted with 20 mL of a hexanes/CH_2Cl_2 mixture (10:1). The extract was chromatographed over neutral alumina (1 × 10 cm) in CH_2Cl_2/hexanes

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Table III. Crystal and Data Collection Parameters for $Cp^*(CO)_2Re(T)$ (1)

formula	$C_{16}H_{19}O_2ReS$
fw	461.60
space group	$P2_{1/m}$
a, Å	9.388 (2)
b, Å	14.346 (2)
c, Å	12.601 (3)
β, deg	99.63 (1)
V, Å^3	1673.1 (6)
Z	4
d_{calc}, g/cm^3	1.832
cryst size, mm	0.20 × 0.35 × 0.50
μ(Mo Kα), cm^{-1}	74.8
data collection instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo K$_\alpha$ (λ = 0.71073 Å)
orientation reflections: no.; range (2θ), deg	25; $20 < 2\theta < 32$
temp, °C	22 (1)
scan method	θ–2θ
data collection range, 2θ, deg	4.0–50.0
total unique rflns	3064
no. of unique rflns obsd ($F_o^2 > 3\sigma(F_o^2)$)	2099
no. of params refined	181
transmissn factors: max, min (ψ scans)	0.995, 0.557
R^a	0.0363
R_w^b	0.0461
quality-of-fit indicator^c	1.142
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	1.829

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

(1:3) to give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (13) as a yellow band. An intractable red-purple band remained at the top of the column. Slow cooling of the concentrated yellow band solution to −20 °C gave air-stable, yellow crystals of 13 (0.027 g, 59%). IR (hexanes): ν(CO) 2064 (s), 2002 (s), 1988 (s), 1922 (s), 1862 (s) cm^{-1}. CIMS (methane): m/e 603 (M^+ + H), 574 (M^+ − CO), 546 (M^+ − 2CO), 519 (M^+ + H − 3CO), 419 (M^+ + H − 4CO), 462 (M^+ − 5CO). Anal. Calcd for $C_{19}H_{19}FeO_5ReS$: C, 37.94; H, 3.18. Found: C, 38.08; H, 3.16.

Reaction of 2 with $Fe_2(CO)_9$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4\text{-}(S)\text{-}2\text{-}MeT)Fe(CO)_3$ (14). This reaction proceeds as described for 13 with use of 2 (0.045 g, 0.095 mmol) and $Fe_2(CO)_9$ (0.10 g, 0.27 mmol). The product 14 was isolated as air-stable yellow crystals (0.032 g, 55%). IR (hexanes): ν(CO) 2056 (s), 1996 (s), 1987 (s), 1922 (s), 1862 (s) cm^{-1}. CIMS (methane): m/e 617 (M^+ + H), 588 (M^+ − CO), 560 (M^+ − 2CO), 533 (M^+ + H − 3CO), 476 (M^+ + H − 4CO).

Reaction of 3 with $Fe_2(CO)_9$ To Give $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4\text{-}(S)\text{-}3\text{-}MeT)Fe(CO)_3$ (15). This reaction was performed as for 13 starting with 3 (0.050 g, 0.11 mmol) and $Fe_2(CO)_9$ (0.10 g, 0.27 mmol). Air-stable yellow crystals of 15 (0.036 g, 56%) were obtained. IR (hexanes): ν(CO) 2058 (s), 1990 (s), 1986 (s), 1921 (s), 1859 (s) cm^{-1}. CIMS (methane): m/e 617 (M^+ + H), 588 (M^+ − CO), 560 (M^+ − 2CO), 533 (M^+ + H − 3CO), 477 (M^+ + H − 5CO). Anal. Calcd for $C_{20}H_{21}FeO_5ReS$: C, 39.03; H, 3.44. Found: C, 39.29; H, 3.41.

Reaction of 7 with $Fe_2(CO)_9$ To Give $Cp(CO)_2Re(\mu_2\text{-}\eta^4\text{-}(S)\text{-}T)Fe(CO)_3$ (16). This reaction was performed in the same manner as for 13 with use of 7 (0.040 g, 0.10 mmol) and $Fe_2(CO)_9$ (0.10 g, 0.27 mmol). Air-stable yellow crystals of 16 (0.031 g, 57%) were obtained. IR (hexanes): ν(CO) 2064 (s), 2005 (s), 1995 (s), 1938 (s), 1877 (s) cm^{-1}. CIMS (methane): m/e 533 (M^+ + H), 504 (M^+ − CO), 476 (M^+ − 2CO), 449 (M^+ + H − 3CO). Anal. Calcd for $C_{14}H_9FeO_5ReS$: C, 31.65; H, 1.71. Found: C, 31.60; H, 1.63.

X-ray Structure Determination of $Cp^*(CO)_2Re(T)$ (1). A single crystal of complex 1 suitable for X-ray diffraction study was obtained by recrystallization from hexane solution at −80 °C. A single crystal of 1 was mounted on the end of a glass fiber. Pertinent data collection and reduction information for 1 are given in Table III. The cell constants were determined from a list of reflections found by an automated search routine. The empirical absorption corrections were made on the basis of a series of ψ scans. The positions of the Re and S atoms were given by direct methods.[16] The remainder of the non-hydrogen atoms were located in difference Fourier maps following least-squares refinement of the known atoms. Hydrogen atoms were not included in the model. In the final cycles of refinement, all of the atoms were given anisotropic temperature factors;[17] the refinement included 181 variable parameters and converged with unweighted

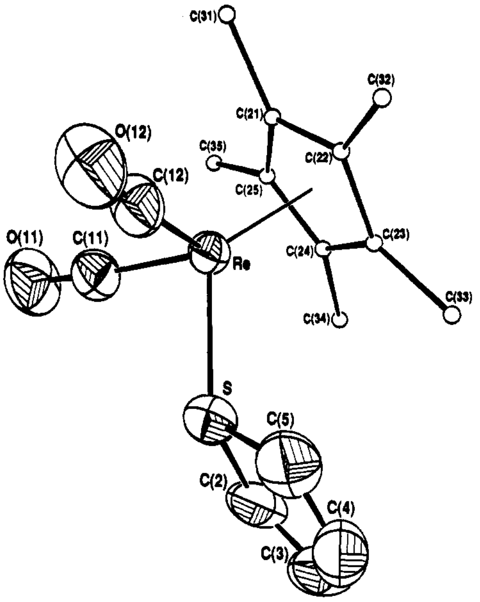

Figure 1. ORTEP drawing of $Cp^*(CO)_2Re(T)$ (1).

Table IV. Bond Distances (Å)^a for $Cp^*(CO)_2Re(T)$ (1) and $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (13)

	1	13
Re–S	2.360 (3)	2.330 (1)
Re–C(11)	1.86 (1)	1.883 (6)
Re–C(12)	1.90 (1)	1.884 (7)
Re–C(21)	2.227 (9)	2.307 (7)
Re–C(22)	2.275 (9)	2.296 (6)
Re–C(23)	2.313 (8)	2.281 (7)
Re–C(24)	2.290 (8)	2.266 (8)
Re–C(25)	2.249 (8)	2.255 (7)
Fe–C(2)		2.086 (6)
Fe–C(3)		2.044 (6)
Fe–C(4)		2.048 (6)
Fe–C(5)		2.099 (6)
S–C(2)	1.72 (1)	1.807 (6)
S–C(5)	1.73 (1)	1.802 (5)
O(11)–C(11)	1.16 (1)	1.157 (9)
O(12)–C(12)	1.13 (1)	1.131 (8)
C(2)–C(3)	1.40 (2)	1.454 (8)
C(3)–C(4)	1.37 (2)	1.379 (9)
C(4)–C(5)	1.36 (2)	1.427 (8)
C(21)–C(22)	1.44 (1)	1.36 (1)
C(22)–C(23)	1.48 (1)	1.44 (1)
C(23)–C(24)	1.42 (1)	1.44 (1)
C(24)–C(25)	1.37 (1)	1.39 (1)
C(25)–C(21)	1.33 (1)	1.35 (1)
C(21)–C(31)	1.56 (2)	1.55 (1)
C(22)–C(32)	1.50 (2)	1.58 (1)
C(23)–C(33)	1.52 (2)	1.53 (1)
C(24)–C(34)	1.55 (1)	1.48 (1)
C(25)–C(35)	1.57 (2)	1.53 (1)

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

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(16) Neutral-atom scattering factors and anomalous scattering corrections were taken from *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

(17) All crystallographic calculations were carried out on a Digital Equipment Corporation Micro VAX II computer with CAD4-SDP package; Enraf-Nonius: Delft, The Netherlands.

Table V. Selected Bond Angles (deg)[a] for $Cp^*(CO)_2Re(T)$ (1) and $Cp^*(CO)_2Re(\mu_2\text{-}\eta^4(S)\text{-}T)Fe(CO)_3$ (13)

	1	13
C(2)–S–C(5)	92.8 (7)	82.3 (3)
Re–S–C(2)	119.9 (4)	115.5 (2)
Re–S–C(5)	120.9 (4)	115.4 (2)
S–Re–C(11)	90.6 (3)	93.0 (2)
S–Re–C(12)	91.9 (4)	93.4 (2)
C(2)–C(3)–C(4)	115 (1)	110.1 (5)
C(3)–C(4)–C(5)	113 (1)	110.4 (5)
C(11)–Re–C(12)	90.9 (5)	87.5 (3)
S–C(2)–C(3)	108 (1)	109.1 (4)
S–C(5)–C(4)	111 (1)	110.3 (4)

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

Table VI. Positional and Thermal Parameters for $Cp^*(CO)_2Re(T)$ (1)

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

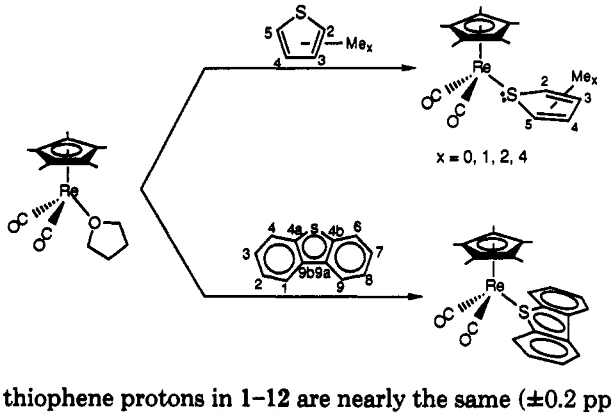
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

and weighted agreement factors of $R = 0.0363$ and $R_w = 0.0461$.

Selected bond distances and angles are presented in Tables IV and V, and an ORTEP drawing of 1 is given in Figure 1. The final positional and thermal parameters are listed in Table VI.

Results and Discussion

Preparation of the S-Coordinated Thiophene Complexes. Substitution reactions of the weakly coordinated THF ligand in $Cp'(CO)_2Re(THF)$ ($Cp' = C_5H_5$ or C_5Me_5) with excess thiophenes or dibenzothiophene give moderately air-stable S-bound thiophene complexes in 20–45% yield (eq 1). The ^1H NMR chemical shifts of the



(1)

thiophene protons in 1–12 are nearly the same (±0.2 ppm) as those of the free ligand (Table I). Similar small changes were also observed for other S-bound thiophene complexes: $Cp(CO)_2Fe(T)^+$,[8] $Cp(CO)_2Fe(2,5\text{-}Me_2T)^+$,[18] $Cp(CH_3CN)_2Fe(2,5\text{-}Me_2T)^+$,[19] and $Cp(CO)_2Fe(DBT)^+$.[8a] If, on the other hand, the thiophenes in 1–12 were η^2-coordinated as in $(NH_3)_5Os(2,3\text{-}\eta^2\text{-}T)^{+2}$,[2,20] and the selenophene in $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}Sel)$,[21] the coordinated olefinic proton resonances would be expected to move to substantially higher field. Such upfield shifts are also well-known in η^2-bound olefins and arenes.[22]

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

Comparisons of the IR spectra of the Cp and Cp* analogues show the ν(CO) bands in the Cp* analogues to be about 15 cm^{-1} lower than those of the Cp complexes. The methyl groups of the Cp* ligand provide more electron density to the metal, thereby increasing π back bonding from the metal to the CO π^* orbitals and weakening the C≡O bond thus accounting for the lower ν(CO) bands in the Cp* complexes. The electron-donating ability of methyl groups in the methyl-substituted thiophenes also adds more electron density to the Re by enhancing the donor character of the thiophene sulfur. For example, in the Me_4T complexes, the ν(CO) bands (1926, 1864 cm^{-1} for Cp*; 1942, 1879 cm^{-1} for Cp) are about 8 cm^{-1} lower than those in the thiophene complexes (1934, 1874 cm^{-1} for Cp*; 1951, 1888 cm^{-1} for Cp). Methyl substitution in the thiophene ring also appears to strengthen the Re–S bond as indicated by kinetic studies of thiophene substitution by PPh_3 in the reaction, $Cp'(CO)_2Re(Th) + PPh_3 \rightarrow Cp'(CO)_2Re(PPh_3) + Th$.[23] Rate constants ($10^7k_1$, s^{-1}) for thiophene dissociation from $Cp(CO)_2Re(Th)$ in this reaction decrease with increasing methyl substitution: T (3000) > 3-MeT (1200) > 2-MeT (91) > 2,5-Me_2T (13) > Me_4T (2.7). It has been generally assumed that methyl groups in the 2- and 5-positions (α to the S) sterically hinder S coordination to the metal. However, this assumption was based on a coordination geometry in which the metal atom lies in the plane of the thiophene. The crystal structure of 1 (discussed in detail later) shows that Re lies out of the thiophene plane and the sulfur has a trigonal-pyramidal geometry. Therefore, methyl groups in the 2,5-positions pose much less of a steric problem than supposed, but their electronic effect does enhance S coordination of methyl-substituted thiophenes to the metal.

Reactions of $Cp'(CO)_2Re(Th)$ with $Fe_2(CO)_9$. Reactions of S-bound thiophene complexes 1, 2, 3, and 7 with $Fe_2(CO)_9$ in THF at room temperature give the thiophene-bridged dinuclear complexes 13, 14, 15, and 16, respective (55–60% yield, eq 2).

Complex 13 was identified by its elemental analysis, IR, MS (Experimental Section), and ^1H and ^{13}C NMR (Table I and II) spectra. The ^1H NMR spectrum of 13 shows two

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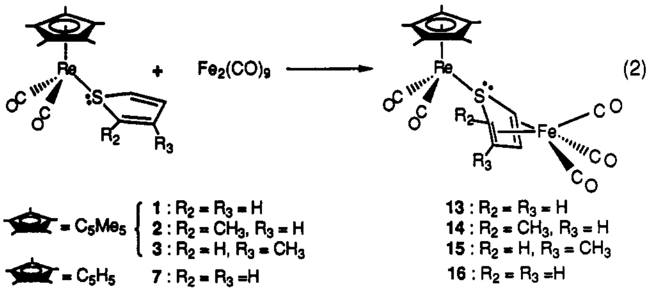
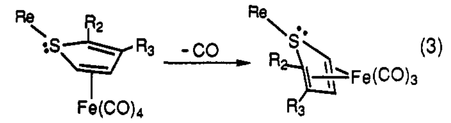


multiplets for the thiophene protons (5.95, 3.56 ppm) which are far upfield compared to those in 1 (7.19, 7.11 ppm). In the ^{13}C NMR spectrum, the two signals (83.9, 57.1 ppm) for the ring carbon atoms in 13 are shifted upfield by 50–70 ppm from those in 1 (138.9, 129.9 ppm) and those in free thiophene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

While the reactions of complexes 2, 3, and 7 with Fe$_2$(CO)$_9$ yield the thiophene-bridged complexes 14, 15, and 16, the α,α'-dimethyl-substituted thiophene (2,5-Me$_2$T and Me$_4$T) complexes 4 and 5 do not react with Fe$_2$(CO)$_9$ under the same conditions. This difference in reactivity can be explained by assuming that the reaction (eq 2) occurs in two steps (eq 3). The first presumably involves η^2-coordination of Fe(CO)$_4$ to the diene part of the ring; subsequent loss of CO leads to η^4-coordination of the diene system. In 4 and 5, the steric and electron-donating properties of the α-methyl groups at both double bonds in the thiophene would inhibit formation of the η^2-intermediate. In the Cp′(CO)$_2$Re(Th) complexes which react with Fe$_2$(CO)$_9$, one of the thiophene double bonds does not contain a methyl group and therefore forms an η^2-complex. While this step-by-step mechanism (eq 3) accounts for the reactivity pattern, it is possible that the reaction (eq 2) proceeds by a concerted mechanism in which all four diene carbons coordinate to iron simultaneously. In this case two or more methyl groups must deactivate the diene to the extent that complexes 4 and 5 do not react.



Although thiophene reacts with Fe$_2$(CO)$_9$ to give thiaferroles and ferroles under vigorous conditions,[25] it does not react with Fe$_2$(CO)$_9$ in THF-d_8 at room temperature for 24 h as determined by ^{1}H NMR spectrometry. Therefore, it appears that S coordination in these complexes disrupts the aromaticity of the thiophene ligand in a way that allows the diene section of it to react with Fe$_2$(CO)$_9$.

Complexation of Fe(CO)$_3$ to the diene significantly affects the rhenium center in the thiophene-bridged complexes. This is evident in the ν(CO) values for the Cp*(CO)$_2$Re group in 13 (1922, 1862 cm^{-1}) which are lower than those in 1 (1934, 1874 cm^{-1}), implying that the sulfur atom in the (η^4-T)Fe(CO)$_3$ ligand is a better donor to Re than thiophene itself. This is consistent with previous observations that the sulfur of the η^4-thiophene in Cp*Ir(η^4-2,5-Me$_2$T) is an unusually strong donor as indicated by its reactions with Lewis acids (BH$_3$, R$^+$),[26] or metal complexes,[27] to form sulfur adducts.

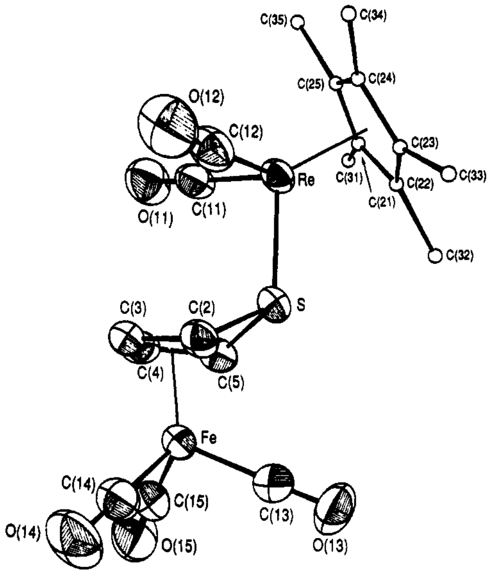


Figure 2. ORTEP drawing of Cp*(CO)$_2$Re(μ_2-η^4(*S*)-T)Fe(CO)$_3$ (13).

Comparison of the Structures of Cp*(CO)$_2$Re(T) (1) and Cp*(CO)$_2$Re(μ_2-η^4(*S*)-T)Fe(CO)$_3$ (13). The structure of 1 (Figure 1) shows that the coordinated thiophene sulfur has a trigonal-pyramidal geometry (i.e., is roughly sp^3 hybridized). The sum of the angles around the S (333.6 (5)°) in 1 is somewhat greater than those in the tetrahydrothiophene (THT) complexes, RhCl$_3$(THT)$_3$ (316.0 (3)°),[28a] CpV(CO)$_3$(THT) (321.7 (5)°),[28b] and *cis*-RuBr$_2$(THT)(L) (322.7 (2)°, L = bis(3-(ethylsulfinyl)propyl) sulfide);[28c] thus, the sulfur geometry is flattened slightly more in the thiophene ligand than in the saturated THT ligand. The Re–S distance of 2.360 (3) Å is somewhat shorter than those (2.396 (4), 2.425 (5), and 2.400 (5) Å) in ReBr$_3$(THT)$_3$[29] and significantly shorter than that (2.480 (2) Å) in Re(S$_2$CNEt$_2$)$_3$(CO).[30] The Re lies out of the thiophene plane such that the angle between the Re–S vector and the vector from S to the midpoint of the C(3)–C(4) bond is 140.4°, which is somewhat larger than that in (PPh$_3$)$_2$Ru(C$_5$H$_4$CH$_2$C$_4$H$_3$S)$^+$ (126°)[9] and those in the S-coordinated DBT of [RuCl$_2${P(4-MeC$_6$H$_4$)$_2$(SC$_{12}$H$_7$)}$_2$] (131°)[31] and Cp(CO)$_2$Fe(DBT)$^+$ (119.4°).[8a] The thiophene ring is planar within experimental error; the dihedral angle between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes is 6.1 (±4.5)°. The C(2)–S and C(5)–S bond distances and the angles within the thiophene ring are essentially the same within experimental error as those in (PPh$_3$)$_2$Ru(C$_5$H$_4$CH$_2$C$_4$H$_3$S)$^{+}$ [9] and free thiophene.[32]

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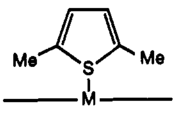
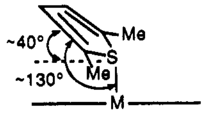
In the structure of 13 (Figure 2),[11] the bridging thiophene ligand that is coordinated to the Re atom via sulfur and to the Fe through the four carbons of the diene system is no longer planar. The thiophene ring is folded with an angle of 143.1 (4)° between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes. This angle is very similar to those in other η^4-thiophene complexes such as $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-}2,5\text{-}Me_2T)Fe(CO)_4$ (142.1 (4)°)[27b] and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (138°).[33] The Re–S distance (2.330 (1) Å) is 0.03 Å shorter than that (2.360 (1) Å) in 1, which is consistent with the sulfur being a better donor in 13 as noted in the discussion of the ν(CO) frequencies of 1 and 13. The sulfur in 13 is pyramidal as indicated by the angle (125°) between the Re–S vector and the vector from S to the midpoint of the line from C(2) to C(5) and the small sum of the angles (327.0 (2)°) around the sulfur. The longer distances for C(2)–C(3) (1.458 (8) Å) and C(4)–C(5) (1.427 (8) Å) as compared to that for C(3)–C(4) (1.379 (9) Å) are often found in η^4-1,3-diene complexes;[34] this pattern of C–C bond distances is just the opposite of that in free thiophene, where C(2)–C(3) and C(4)–C(5) are shorter (1.37 Å) than C(3)–C(4) (1.42 Å).[32] The C(2)–S and C(5)–S distances (1.807 (6), 1.802 (5) Å) are substantially longer than the corresponding distances (1.72 (1), 1.73 (1) Å) in 1 and in free thiophene (1.714 (1) Å)[32] and somewhat shorter than those in $RhCl_3(THT)_3$ (1.823 (1) Å)[28a] and $CpV(CO)_3(THT)$ (1.84 (1) Å).[28b] The C(2)–S–C(5) angle (82.3 (3)°) is more acute than in 1 (92.8 (8)°) and in free thiophene (92.2 (1)°).[32] In general, the geometry (the fold at the C(2)–C(5) line, the elongated C–S bonds, and the small C(2)–S–C(5) angle) of the thiophene in 13 is different from that of free thiophene and the S-coordinated thiophene in 1 but is very similar to that of the η^4-ligands in $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$,[33] $Cp^*Rh(\eta^4\text{-}Me_4T)$,[35] $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-}2,5\text{-}Me_2T)Fe(CO)_4$,[27b] $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-}2,5\text{-}Me_2T)[Mo_2(CO)_4Cp_2]$,[27a] $Cp^*Ir(\mu_2\text{-}\eta^4(S)\text{-}2,5\text{-}Me_2T)[Fe_2(CO)_7]$,[27b] and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot BH_3)$[36] in which the BH_3 is coordinated to the sulfur.

Comments on the Mode of Thiophene Adsorption on HDS Catalysts. Of the various modes that have been proposed for thiophene adsorption on HDS catalysts, S coordination is one of the earliest and most widely suggested. It had generally been assumed that S-bound thiophene would be perpendicularly bonded to the surface (A) and α-methyl groups would sterically weaken S–thiophene coordination. However, it is now[3,8a,9,10] known that the metal does not lie in the thiophene plane and the sulfur is trigonal pyramidal (B), as shown in the crystal structure of 1. This bent arrangement at the sulfur greatly reduces α-methyl steric interactions. Indeed there is evidence to suggest that α-methyl groups actually strengthen the thiophene coordination to a metal center.[23]



A



B

Several studies of thiophene adsorbed on single-crystal surfaces have been reported: on clean Ni(100),[37a] Pt(111),[37b,c] Cu(100),[37d] and Cu(111),[37e] and on clean and sulfided Mo(100),[37f,g] Mo(110),[37h] W(211),[37i] Ni(111),[37j] and Re(0001).[37k] The results indicate that, depending on the metal, thiophene surface coverage, and temperature, the thiophene may be S bonded perpendicular to the surface, S bonded but tilted at an angle of ~40° from the surface (B) or η^5-bonded parallel to the surface. The S-bonded thiophene in $Cp^*(CO)_2Re(T)$ (1) with a Re–thiophene angle of 140° closely represents the tilted species on these surfaces (B) with a M–thiophene angle of ~130°.

Although there is much evidence to support η^5-coordination and activation of thiophene in organometallic complexes and on catalysts,[5] there is no evidence to indicate that S-bound thiophene is activated to undergo reactions which results in C–S bond cleavage. Perhaps a major reason for this lack of reactivity is the generally weak and labile bonding of S-coordinated thiophene in its transition-metal complexes, which has led to its ready displacement from metal centers by potential reactants. In the $Cp'(CO)_2Re(Th)$ series of complexes, however, the thiophene (Th) ligands are not labile and react with $Fe_2(CO)_9$ according to eq 2. In fact, the S coordination activates thiophene to react with "$Fe(CO)_3$", since thiophene itself does not react with $Fe_2(CO)_9$ under very similar conditions. Therefore, it seems possible that on an HDS catalyst, initial adsorption of thiophene through the sulfur atom to a single metal site would activate the diene system to coordinate to an adjacent metal as suggested in structure C. As seen in structure 13, a thiophene coordinated to two metal centers loses its aromatic character and the C–S bonds lengthen. These weakened C–S bonds are perhaps susceptible to cleavage and hydrogenation, although there is no precedent for such reactions at the present time.

C

Supplementary Material Available: Tables containing additional bond angles, least-squares planes, and thermal parameters for $Cp^*(CO)_2Re(T)$ (1) (3 pages); listings of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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