Synthesis and Protonation of the Bridging Benzo[*b*]thiophene (BT) Complexes $[Cp'(CO)_2Re](\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-BT})[Re(CO)_2Cp'']$

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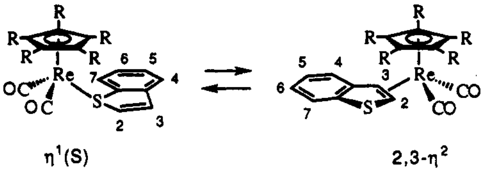
The bimetallic complexes $[Cp'(CO)_2Re](\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-BT})[Re(CO)_2Cp'']$, where Cp′ and Cp″ are η^5-C_5H_5(Cp) or -C_5Me_5(Cp*) and BT = benzo[*b*]thiophene, are prepared by reaction of the monometallic complex $Cp'(CO)_2Re(BT)$ with a catalytic amount of CF_3SO_3H or by the reaction of $Cp'(CO)_2Re(THF)$ with BT. An X-ray structural study of $[Cp(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-BT})$ shows that one Re is η^2-coordinated to the 2,3-olefin of the BT and the other is η^1(S)-coordinated to the sulfur. Infrared and NMR data of these bimetallic complexes suggest that this dual metal coordination to BT enhances the binding abilities of both the sulfur and C2–C3 olefin groups to the Re atoms. When these bimetallic complexes are reacted with 1 equiv of CF_3SO_3H, the complexes protonate exclusively at the Re atom that is η^1(S) bonded to the BT. The protonated complexes are fluxional, and this fluxionality can be explained in terms of *cis–trans* isomerization at the protonated metal center. This same type of fluxionality is observed in the protonated complex $[Cp(CO)_2Re(H)(PPh_3)]O_3SCF_3$.

Introduction

An important aspect of the mechanism of the hydrodesulfurization (HDS) of thiophene compounds is the mode of thiophene coordination on the transition metal catalyst.[2,3] In our studies of the HDS of benzo[*b*]thiophene (BT), we recently reported the compounds $Cp'(CO)_2Re(BT)$[4] (Cp′ is η^5-C_5H_5(Cp) or η^5-C_5Me_5(Cp*)), where the BT coordinates as an equilibrium mixture of η^1(S) and 2,3-η^2 isomers (eq 1). The relative amounts of the isomers in these equilibria can be explained by assuming that the sulfur in the BT is acting as an electron donor to the metal center in the η^1(S) isomer, while the olefin is a π-accepting ligand in the 2,3-η^2 isomer. In an equilibrium solution of **1**, where Cp′ = Cp, the η^1(S) coordination mode is favored over 2,3-η^2 coordination by a ratio of 3:1. When the electron density on the metal is increased by changing Cp′ to Cp*, the Re becomes a poorer acceptor of electron density from sulfur in the η^1(S) isomer but is a better π-back-bonder to the olefin in the 2,3-η^2 isomer; thus, 2,3-η^2 bonding is favored by a ratio of 1.1:1.0 in $Cp^*(CO)_2Re(BT)$. When the BT in $Cp'(CO)_2Re(BT)$ is replaced by 2-MeBT or 3-MeBT, only the η^1(S) isomer is observed because 2-MeBT and 3-MeBT are stronger sulfur-donor ligands, and the olefin is probably also coordinated more weakly for both steric and electronic reasons. Heteroatom donor ability and olefin π-acceptor ability similarly affect equilibria between η^1(Se) and 2,3-η^2 isomers of the selenophene (Sel) complexes $Cp'(CO)_2Re(Sel)$.[5]



(1)

For **1a**, R = H
For **2a**, R = Me

For **1b**, R = H
For **2b**, R = Me

In the present paper, we use the $Cp'(CO)_2Re(BT)$ complexes to prepare the bimetallic compounds $[Cp'(CO)_2Re](\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-BT})[Re(CO)_2Cp'']$, in which one Re is bonded to the sulfur and the other is coordinated to the 2,3-olefin of the BT ligand. An X-ray structural determination of $[Cp(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-BT})$ is presented. Protonation of these complexes is discussed and explained in terms of the electron-donor and electron-acceptor abilities of the BT and the metal.

Experimental Section

General Procedures. All reactions were performed under a nitrogen atmosphere in reagent grade solvents using standard Schlenk techniques.[6] Hexanes and CH_2Cl_2 were distilled under nitrogen from CaH_2; tetrahydrofuran (THF) and diethyl ether were distilled from Na/benzophenone. Triflic acid, CF_3SO_3H, was distilled under argon. The NMR spectra were obtained on a Nicolet NT-300 or Varian VXR-300 spectrometer using a deuterated solvent as an internal lock and internal reference (CD_2Cl_2: δ 5.32 for ^{1}H and δ 53.8 for ^{13}C). Variable temperature NMR spectra were recorded on the Varian instrument. Electron-ionization mass spectra were run on a Finnigan 4000 spectrometer. Infrared spectra of the compounds were recorded in CH_2Cl_2

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(2) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.

(3) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.

(4) (a) Choi, M.-G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005. (b) Choi, M.-G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328.

(5) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7811. (b) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 5651.

(6) (a) *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987. (b) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

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Table I. FTIR Data [ν(CO), cm^{-1}] for the Compounds in CH_2Cl_2

compd	formula	ν(CO)
1a	$Cp(CO)_2Re(\eta^1(S)\text{-}BT)$	1940 (s), 1870 (s)
1b	$Cp(CO)_2Re(2,3\text{-}\eta^2\text{-}BT)$	1975 (s), 1910 (s)
2a	$Cp^*(CO)_2Re(\eta^1(S)\text{-}BT)$	1914 (s), 1844 (s)
2b	$Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}BT)$	1957 (s), 1885 (s)
3	$Cp(CO)_2Re(\eta^1(S)\text{-}2\text{-}MeBT)$	1929 (s), 1870 (s)
4	$Cp(CO)_2Re(PPh_3)$	1944 (s), 1880 (s)
5	$[Cp(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$	1984 (s), 1921 (vs, br), 1850 (s)
6	$[Cp^*(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$	1966 (s), 1904 (s), 1892 (s), 1835 (s)
7	$[Cp(CO)_2Re](\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)[Re(CO)_2Cp^*]$	1971 (s), 1919 (s), 1897 (s), 1848 (s)
8	$(\mathbf{5}H^+)(O_3SCF_3^-)$	2053 (s), 1990 (vs, br), 1919 (s)
9	$(\mathbf{6}H^+)(O_3SCF_3^-)$	2037 (s), 1983 (s), 1971 (s), 1912 (s)
10	$(\mathbf{7}H^+)(O_3SCF_3^-)$	2050 (s), 1980 (vs, br), 1920 (s)
11	$(\mathbf{3}H^+)(O_3SCF_3^-)$	2040 (s), 1970 (s)
12a	$[cis\text{-}Cp(CO)_2HRe(PPh_3)]O_3SCF_3$	(not observed)
12b	$[trans\text{-}Cp(CO)_2HRe(PPh_3)]O_3SCF_3$	2037 (s), 1967 (s)

Table II. ^1H NMR Data (δ) for the Complexes in CD_2Cl_2

complex	BT	Cp or Cp*	Me on BT	Re–H
1a	7.88–7.43 (3 m, 4H), 7.28 (d, 1H),^{a,b} 7.16 (d, 1H)^{a,b}	4.85 (s, 5H)		
1b	7.67 (d, 1H),^{c} 7.33 (d, 1H),^{c} 7.19 (t of d, 1H),^{c,d} 7.10 (t of d, 1H),^{c,d} 5.36 (d, 1H),^{b,e} 5.12 (d, 1H)^{b,e}	5.08 (s, 5H)		
2a	7.77–7.11 (3 m, 6H)	1.81 (s, 15H)		
2b	7.54 (d, 1H),^{f} 7.28 (d, 1H),^{f} 7.13 (t of d, 1H),^{d,f} 7.03 (t of d, 1H),^{d,f} 4.27 (d, 1H),^{b,g} 3.97 (d, 1H)^{b,g}	2.02 (s, 15H)		
3	7.76 (d of d, 1H),^{h,i} 7.58 (d of d, 1H),^{h,i} 7.36 (m, 2H), 7.04 (s, 1H)	4.83 (s, 5H)	2.41 (d, 3H)^{j}	
4^{k}		5.05 (s, 5H)		
5	7.51 (d, 1H),^{c} 7.34 (d, 1H),^{c} 7.25 (t of d, 1H),^{c,d} 7.15 (t of d, 1H),^{c,d} 4.93 (d, 1H),^{b,e} 4.67 (d, 1H)^{b,e}	5.24 (s, 5H), 4.93 (s, 5H)		
6	7.43 (d, 1H),^{f} 7.18 (m, 2H), 7.10 (t of d, 1H),^{d,f} 3.92 (d, 1H),^{b,g} 3.68 (d, 1H)^{b,g}	2.05 (s, 15H), 2.02 (s, 15H)		
7	7.44 (d, 1H),^{c} 7.25 (d, 1H),^{c} 7.22 (t of d, 1H),^{c,d} 7.09 (t of d, 1H),^{c,d} 3.94 (d, 1H),^{b,e} 3.66 (d, 1H)^{b,e}	4.93 (s, 5H), 2.03 (s, 15H)		
8^{n}	7.64–7.25 (3 m, 4H), 5.52 (d, 1H),^{b,e} 4.84 (d, 1H)^{b,e}	5.57 (s, 5H), 5.55 (s, 5H)		–8.67 (s)
9^{n}	7.54–7.19 (3 m, 4H), 3.98 (d, 1H),^{b,e} 3.64 (d, 1H)^{b,e}	2.32 (s, 15H), 2.05 (s, 15H)		–8.38 (s, 1H)
10^{n}	7.56–7.23 (4 m, 4H), 4.09 (d, 1H),^{b,e} 3.79 (d, 1H)^{b,e}	5.49 (s, 5H), 2.06 (s, 15H)		–8.60 (s)
11	7.78–7.48 (3 m, 4H), 7.19 (s, 1H)	5.18 (s)	2.46 (d, 3H)^{j}	–7.87 (s)
12a^{n,o}		5.72 (s)		–7.83 (d)^{l}
12b^{n,o}		5.53 (s)		–8.86 (d)^{m}

^{a} $^1J_{H2-H3}$ = 5.4 Hz. ^{b} H2 or H3 resonance. ^{c} ^1J = 7.8 Hz. ^{d} ^2J = 1.2 Hz. ^{e} $^1J_{H2-H3}$ = 6.0 Hz. ^{f} ^1J = 7.5 Hz. ^{g} $^1J_{H2-H3}$ = 6.3 Hz. ^{h} ^1J = 6.0 Hz. ^{i} ^2J = 1.8 Hz. ^{j} $^2J_{H3-CH_3}$ = 1.2 Hz. ^{k} PPh_3 = 7.40 (m, 18H). ^{l} $^1J_{PH}$ = 41.7 Hz. ^{m} J_{PH} = 14.7 Hz. ^{n} At –60 °C. ^{o} PPh_3 is a broad multiplet.

solution with a Nicolet 710 FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Desert Analytics, Tuscon, AZ.

The following compounds were prepared by literature methods: 2-MeBT,[7] $Cp^*Re(CO)_3$,[8] $CpRe(CO)_3$,[9] $Cp(CO)_2Re(PPh_3)$[10] (**4**), $Cp^*(CO)_2Re(PPh_3)$.[10]

$Cp(CO)_2Re(\eta^1(S)\text{-}BT)$ (1a) and $Cp(CO)_2Re(2,3\text{-}\eta^2\text{-}BT)$ (1b). Compound **1** was prepared by a modified version of the reported synthesis.[4] A solution of $Cp(CO)_2Re(THF)$,[11] prepared by UV irradiation of a THF solution (20 mL) of $CpRe(CO)_3$ (0.20 g, 0.60 mmol) at –16 °C, was stirred with BT (0.25 g, 1.9 mmol) and 6 mL of hexanes[12] at room temperature for 12 h. The solvent was then removed under vacuum, and the residue was chromatographed on a neutral alumina (5% w/w H_2O) column (1 cm × 15 cm). Unreacted $CpRe(CO)_3$ was eluted with hexanes, and then a yellow band containing the product was eluted with hexanes–CH_2Cl_2 (4:1). Slow evaporation of the solvent under vacuum from the yellow eluent at 0 °C gave a moderately air-stable yellow powder of **1** (0.097 g, 38%), which was characterized by its infrared, ^1H NMR, and ^{13}C NMR spectra (Table I–III) by comparison with previously reported data.[4]

$Cp^*(CO)_2Re(\eta^1(S)\text{-}BT)$ (2a) and $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-}BT)$ (2b). Compound **2** was prepared in a manner similar to that described for **1** starting with $Cp^*Re(CO)_3$ (0.20 g, 0.49 mmol) and BT (0.25 g, 1.9 mmol). Product **2** was isolated as a moderately air-stable yellow powder (0.079 g, 31%).[4]

$Cp(CO)_2Re(2\text{-}MeBT)$ (3). Compound **3** was synthesized analogously to compound **1**. Only the η^1(S) form of the compound was formed; product **3** was isolated as a moderately air-stable yellow powder (0.79 g, 29%).[4]

$[Cp(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$ (5). This compound was prepared by first dissolving **1** (0.020 g, 0.045 mmol) in ~1 mL of CH_2Cl_2 in a 25-mL Schlenk flask to give a clear yellow solution. Then, a catalytic amount of CF_3SO_3H (0.1 μL, 0.001 mmol) was added, and the solution was stirred, whereupon the color immediately turned a clear brown. When the reaction is carried out in CD_2Cl_2, a ^1H NMR spectrum of the solution at –60 °C showed near quantitative conversion to **5**. Compound **5** was isolated as a brown solid (0.011 g, 67%) by precipitation from the solution with hexanes at 0 °C. EIMS (70 eV): *m/e* 750 (M^+ based on ^{187}Re). Anal. Calcd for $C_{22}H_{16}O_4Re_2S$: C, 35.28; H, 2.15. Found: C, 34.70; H, 2.10.

Compound **5** was also isolated in less than 5% yield from the synthesis of **1**. After eluting **1** from the alumina column, compound **5** was eluted as a clear light tan band using 3:2 hexanes–CH_2Cl_2. It is helpful to follow the progress of the elution with FT-IR since the intensity of the tan color is very weak.

$[Cp^*(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$ (6). This compound was synthesized following the procedure for **5**. Compound **2** (0.025 g, 0.049 mmol) and a catalytic amount of CF_3SO_3H (0.1 μL, 0.001 mmol) were reacted in 0.55 mL of CD_2Cl_2; a ^1H NMR spectrum of the solution at 20 °C showed near quantitative conversion to

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[7] Shirley, D. A.; Cameron, M. D. *J. Am. Chem. Soc.* **1952**, *74*, 664.

[8] Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.

[9] Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

[10] Angelici, R. J.; Facchin, G.; Singh, M. M. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 275.

[11] Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

[12] Zhuang, J.-M.; Batchelor, R. J.; Einstein, F. W. B.; Jones, R. H.; Hader, R.; Sutton, D. *Organometallics* **1990**, *9*, 2723.

Table III. ^{13}C NMR Data (δ) for the Complexes in CD_2Cl_2

complex	BT[a]	Cp or Cp*	Me on Cp*	CO
1	145.6, 144.4, 139.1, 139.0, 126.6, 126.4, 125.6, 124.1, 123.9, 123.6, 123.3, 122.2, 56.2,[b] 34.2[b]	88.0, 83.8		203.3, 202.5, 200.1
2	145.6, 137.8, 128.1, 126.7, 125.5, 124.6, 123.7, 123.4, 123.2, 122.6, 47.9,[b] 46.6[b]	97.8, 95.9	10.2, 10.4	205.5, 204.4, 204.3
3[c]	152.4, 151.3, 139.7, 127.6, 125.5, 124.4, 124.2, 124.1	83.7		202.2
4[d]		84.2		202.8 (d)[e]
5	147.3, 145.5, 127.5, 127.0, 126.0, 124.8, 56.3,[b] 36.1[b]	88.8, 83.8		203.2, 203.0, 202.0, 200.2
6	147.5, 142.7, 126.7, 126.1, 125.6, 124.6, 60.9,[b] 42.3[b]	99.1, 95.9	10.9, 10.3	207.6, 206.7, 204.5, 204.1
7	147.8, 144.9, 127.0, 126.4, 126.0, 124.0, 61.7,[b] 41.1[b]	99.2, 83.6	10.3	204.8, 203.6, 203.3, 203.0
8[f]	148.0, 135.2, 129.0, 127.6, 125.6, 125.1, 46.0,[b] 32.0[b]	89.3, 88.5		201.8, 199.4, 189.9, 188.9
9[f]	149.7, 131.4, 129.8, 127.1, 126.1, 125.3, 50.3,[b] 38.7[b]	102.9, 100.4	10.9, 10.3	204.0, 203.3, 194.1, 192.6
10[f]	146.8, 143.9, 126.4, 126.3, 125.8, 123.4, 60.3,[b] 40.0[b]	98.6, 83.7	10.1	206.1, 203.6, 203.5, 203.2
12a[f]		90.0		196.0 (d),[g] 190.6 (d)[h]
12b[f]		89.1		189.5 (d)[i]

[a] Some overlap of resonances occurs. [b] C2 or C3. [c] *Me*BT at 14.7. [d] PPh_3 at 138.4 (d), 133.4 (d), 130.0 (d), 128.4 (d). [e] J_{PC} = 8.6 Hz. [f] At −60 °C. [g] $J_{PC(cis)}$ = 19.5 Hz. [h] $J_{PC(trans)}$ = 5.4 Hz. [i] $J_{PC(cis)}$ = 17.7 Hz.

6. Compound **6** was isolated as a brown solid (0.017 g, 78%) in the same manner as **5**. Compound **6** was also isolated in less than 5% yield from the synthesis of **2** in the same way that **5** was isolated from the synthesis of **1**. Anal. Calcd for $C_{32}H_{36}O_4Re_2S$: C, 43.23; H, 4.28. Found: C, 42.50; H, 3.94.

[Cp(CO)$_2$Re](η:η^1(*S*)-μ_2-BT)[Re(CO)$_2$Cp*] (7). This compound was synthesized in a manner similar to that for **1**. A THF solution of Cp(CO)$_2$Re(THF), formed by UV irradiation of CpRe(CO)$_3$ (0.20 g, 0.060 mmol), was stirred with **2** (0.060 g, 0.012 mmol) and 6 mL of hexanes for 12 h. The solvent was then removed under vacuum, and the residue was chromatographed as for **1**. After unreacted CpRe(CO)$_3$ was eluted with hexanes and unreacted **2** with 4:1 hexanes-CH_2Cl_2, compound **7** was eluted with 3:2 hexanes–CH_2Cl_2 as a clear tan solution. The solvent was then removed from the product band under vacuum, the residue was dissolved in 2 mL of CH_2Cl_2, and the resulting solution was cooled to 0 °C. Addition of 40 mL of hexanes precipitated **7** as an air-stable, light cream-colored solid (0.038 g, 40% based on **2**). Anal. Calcd for $C_{27}H_{28}O_4Re_2S$; C, 39.60; H, 3.20. Found: C, 40.01; H, 2.99.

Protonation of Complexes 1, 2, 7, and 3 To Give Complexes 8–11, Respectively. General Procedure. These compounds were prepared in a manner similar to that of **5**, but a stoichiometric amount of CF_3SO_3H was used. For compound **8**, compound **1** (0.020 g, 0.045 mmol) and CF_3SO_3H (2.0 μL, 0.023 mmol) were reacted in 0.55 mL of CD_2Cl_2 (CH_2Cl_2 can also be used) in a 5-mm NMR tube. A ^{1}H NMR spectrum of the solution at −60 °C showed complete conversion to {[Cp(CO)$_2$Re(H)](η^2:η^1(*S*)-μ_2-BT)[Re(CO)$_2$Cp]}O$_3$SCF$_3$ (**8**). Compound **8** was isolated as a brown solid by precipitation from the solution with diethyl ether at 0 °C. Complexes **9–11** were prepared in the same way.

These protonated compounds were insufficiently stable to give satisfactory elemental analyses. Attempts to grow crystals for X-ray structural determination were also unsuccessful. Therefore, they were characterized on the basis of their spectral data, as discussed in the Results and Discussion section.

Reaction of 2 with PPh$_3$ and CF$_3$SO$_3$H. Compound **2** (0.010 g, 0.020 mmol) and PPh_3 (0.1005 g, 0.020 mmol) were dissolved in 0.55 mL of CD_2Cl_2 in a 5-mm NMR tube. The ^{1}H and ^{31}P spectra of the solution were recorded after 30 min at ambient temperature and showed only pure **2** and PPh_3. Then CF_3SO_3H (0.1 μL, 0.001 mmol) was added, and the NMR tube was shaken. There was no apparent change in color. However, after several minutes, the ^{1}H and ^{31}P NMR spectra showed that neither **2** nor **6** were present. The major product was Cp*(CO)$_2$Re(PPh$_3$), which was confirmed by conparison of the ^{1}H and ^{31}P NMR spectra with those of the pure compound.

[Cp(CO)$_2$(H)Re(PPh$_3$)](CF$_3$SO$_3$) (12). Compound **12** was synthesized in a 0.55-mL CD_2Cl_2 solution in a 5-mm NMR tube by reaction of Cp(CO)$_2$Re(PPh$_3$) (**4**) (0.075 g, 0.13 mmol) with CF_3SO_3H (11.7 μL, 0.132 mmol). A ^{1}H NMR spectrum of the solution at ambient temperature showed considerable broadening of the signals. However, when the solution was cooled to −60 °C, the spectrum showed the previously reported[13] **12** present as both the *cis* (**12a**) and *trans* (**12b**) forms, as well as some unprotonated Cp(CO)$_2$Re(PPh$_3$) (**4**).

Table IV. Crystal and Data Collection Parameters for [Cp(CO)$_2$Re]$_2$(η^2:η^1(*S*)-μ_2-BT) (5)

A. Crystal Data	
empirical formula	[Re(CO)$_2$(C$_5$H$_5$)]$_2$(SC$_8$H$_6$)
fw	746.82
lattice params	
a, Å	12.265 (7)
b, Å	11.162 (6)
c, Å	15.816 (5)
β, deg	109.28 (3)
V, Å^3	2044 (2)
space group	$P2_1/c$ (No. 14)
z value	4
D_{calc}, g/cm^3	2.427
μ(MoKα), cm^{-1}	121.20
B. Intensity Measurements	
diffractometer	Rigaku AFC6R
radiation (λ, Å)	MoKα (0.710 69)
temp, °C	23
scan type	ω–2θ
scan rate, deg/min	16.0 (in ω) (2 rescans)
no. of reflns measd	total: 4024 unique: 3837 (R_{int} = 0.103)
corrections	lorentz–polarization absorption (trans factors: 0.60–1.00)
C. Structure Solution and Refinement	
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p factor	0.03
anomalous dispersion	All non-hydrogen atoms
residuals: *R*; R_w	0.044; 0.046
goodness of fit indicator	1.36
max shift/error in final cycle	0.40
max peak in final diff map, e/Å^3	1.35
min peak in final diff map, e/Å^3	−1.38

X-ray Structure Determination of 5. A single crystal of **5** suitable for X-ray diffraction study was obtained by slow diffusion of hexanes into a CH_2Cl_2 solution of **5** at −20 °C. The brown cube-shaped crystals tended to grow in complex twin formations, so the crystal used for data collection was cut from one of these formations. Data collection and reduction parameters are given in Table IV. The structure was solved using a combination of direct methods[14] and a local Fourier program. The non-hydrogen, non-carbon atoms were refined anisotropically. The carbon atoms constrained by the aromatic thiophene ring were also refined anisotropically. The carbon atoms of the cyclopentadienyl rings

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(13) Panosyan, G. A.; Petrovskii, P. V.; Pyshnograyeva, N. I.; Kolobova, N. E.; Setkina, V. N.; Fedin, E. I. *J. Organomet. Chem.* **1976**, *108*, 209.

(14) (a) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42. (b) Deurskens, P. T. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 65625 Ed Nijmegen, Netherlands.

Table V. Selected Intramolecular Distances (Å) for $[Cp(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$ (5)[a]

bond	distance	bond	distance
Re1–S	2.35 (1)	O2AA–C2AA	1.16 (4)
Re1–C1AA	1.84 (4)	O2BB–C2BB	1.12 (4)
Re(1)–C1BB	1.83 (4)	C2–C3	1.35 (5)
Re2–C2AA	1.90 (4)	C3–C8	1.42 (5)
Re2–C2BB	1.85 (4)	C8–C9	1.44 (4)
Re2–C2	2.17 (3)	C8–C4	1.41 (5)
Re2–C3	2.22 (3)	C9–C7	1.40 (4)
S–C2	1.81 (3)	C7–C6	1.36 (4)
S–C9	1.77 (3)	C6–C5	1.34 (6)
O1AA–C1AA	1.23 (4)	C5–C4	1.31 (5)
O1BB–C1BB	1.17 (4)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Table VI. Selected Intramolecular Bond Angles (deg) for $[Cp(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$ (5)[a]

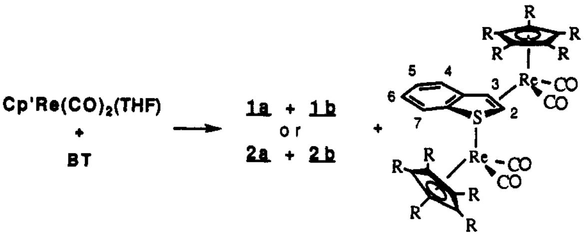
bonds	angle	bonds	angle
S–Re1–C1AA	93(1)	C3–Re2–C2BB	110(1)
S–Re–C1BB	91(1)	C2AA–Re2–C2BB	88(2)
C1AA–Re1–C1BB	88(2)	Re1–C1BB–O1BB	172(3)
Re1–S–C2	114(1)	Re2–C3–C2	71(2)
Re1–S–C9	107(1)	Re2–C3–C8	121(2)
C2–S–C9	90(2)	C3–C8–C9	115(3)
Re2–C2–S	124(1)	C3–C8–C4	136(3)
Re2–C2–C3	74(2)	C9–C8–C4	109(3)
S–C2–C3	114(3)	S–C9–C8	109(3)
Re1–C1AA–O1AA	177(4)	S–C9–C7	127(3)
C2–C3–C8	112(3)	C8–C9–C7	124(3)
Re2–C2AA–O2AA	176(3)	C9–C7–C6	118(4)
Re2–C2BB–O2BB	173(3)	C7–C6–C5	121(4)
C2–Re2–C2AA	110(1)	C6–C5–C4	121(4)
C2–Re2–C2BB	88(1)	C8–C4–C5	127(3)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

and the carbonyl ligands were refined isotropically. These carbons showed effects which could be attributable to slight disorder and/or large thermal motion; they could not be adequately refined anisotropically and somewhat degraded the refinement of the other lighter atoms. Neutral atom scattering factors were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in F_c;[16] the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[17] All direct methods calculations were performed using the TEXSAN crystallographic software package.[18] The Fourier calculations were made using FOUR.[19] Selected bond distances and angles are given in Tables V and VI, respectively.

Results and Discussion

Synthesis of $Cp'(CO)_2Re(BT)$ (1 and 2) and $[Cp'(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$ (5 and 6) Complexes. The reaction of $Cp(CO)_2Re(THF)$ with benzo[*b*]thiophene in THF solution results (eq 2) in the formation of the monometallic compound $Cp(CO)_2Re(BT)$ (1)[4] discussed in the Introduction and a small amount (~5% yield) of the bimetallic compound $[Cp(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$ (5). Compound 1 consists (eq 1) of two isomers, η^1(S) (**1a**) and 2,3-η^2 (**1b**).[4] The ^{1}H NMR spectrum of **1b** (Table II) shows that the H2 and H3 resonances (δ 5.36 and 5.12) are substantially upfield compared to those in free BT (δ 7.33 (H2) and 7.22 (H3)).[20] In the ^{13}C NMR spectrum (Table III) of **1b**, two of the ^{13}C NMR resonances (δ 56.2 and 34.2), presumably those of C2 and C3, are also substantially upfield of those (δ 126.2 (C2) and 123.8 (C3)) in free BT.[21] The ^{1}H and ^{13}C NMR spectra of the bimetallic compound **5** show that the H2 and H3 resonances (δ 4.93 and 4.67) and C2 and C3 resonances (δ 56.3 and 36.1) are very similar to those in the 2,3-η^2 isomer **1b** (see Tables II and III). The X-ray structure determination of **5** (to be discussed in detail later) shows that one Re atom is coordinated to C2 and C3 of the BT above the BT plane and confirms the 2,3-η^2 assignment. The X-ray structure determination also confirms that a $Cp(CO)_2Re$ fragment is η^1(S) bonded to the BT.



For 5, R = H
For 6, R = Me

(2)

The ^{1}H NMR chemical shifts for the Cp ligands in **5** (δ 5.24 and 4.93) can be assigned by comparison with the spectra of isomers **1a** and **1b**. The chemical shift for the Cp in the η^1(S) isomer of **1a** (δ 4.85) is upfield of the resonance for the 2,3-η^2 isomer **1b** (δ 5.08). Similarly, in **5**, the upfield resonance at δ 4.93 can be assigned to the Cp on the Re atom that is η^1(S) bonded to the BT, while the resonance at δ 5.24 may be attributed to the Cp on the Re atom that is 2,3-η^2 bonded to the BT.

In the infrared spectra, ν(CO) values (Table I) of the η^1(S) isomer **1a** occur at 1940 and 1870 cm^{-1} while those of the 2,3-η^2 isomer **1b** are at 1975 and 1910 cm^{-1}. Thus, 2,3-η^2 BT coordination gives ν(CO) values that are about 35–40 cm^{-1} higher than those in the complex in which the BT is S-coordinated.[4] Thus, the ν(CO) bands at 1984 and 1921 cm^{-1} in **5** can be assigned to the 2,3-η^2-coordinated $Re(CO)_2Cp$ and those at 1921 and 1850 cm^{-1} are assigned to the S-coordinated $Re(CO)_2Cp$ group.

The ν(CO) values for the carbonyls on the Re that is S bonded in **5** are about 20 cm^{-1} *lower* than the corresponding values in **1a**. This result suggests that the sulfur in **5** provides more electron density to the metal, thereby increasing π-back-bonding from the metal to the CO π* orbitals and lowering ν(CO). Thus, these ν(CO) values indicate that the sulfur of the BT in **5** is more strongly electron-donating to the Re atom than the BT is in the S bonded monometallic compound **1a**. On the other hand, the ν(CO) values for the carbonyls on the Re that is 2,3-η^2 bonded to the BT are about 10 cm^{-1} *higher* than the corresponding values in **1b**. This indicates that in **5** there is increased π-back-bonding from the Re to the 2,3-η^2 olefin bond of the BT, resulting in less electron density on the Re which increases the ν(CO) values. Thus, in **5** the Re–olefin bond is strengthened by increased π-back-bonding

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(15) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(16) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(17) Cromer, C. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(18) TEXSAN-TEXRAY Structure Analysis Package. Molecular Structure Corp., 1985.

(19) Powell, D. R.; Jacobson, R. A. FOUR: A Generalized Crystallographic Fourier Program. U.S. DOE Report IS-4737; Iowa State University: Ames, IA, 1980.

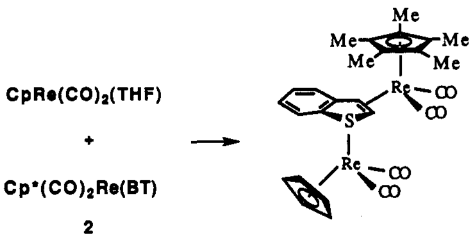
(20) (a) Takahashi, K.; Ito, I.; Matsuki, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2316. (b) Huckett, S. C.; Angelici, R. J.; Ekman, M. E.; Schrader, G. L. *J. Catal.* **1988**, *113*, 36.

(21) Clark, P. D.; Ewing, D. F.; Scrowston, R. M. *Org. Magn. Reson.* **1976**, *8*, 252.

and the Re–S bond is strengthened by enhanced sulfur donation as compared with the monometallic complexes **1a** and **1b**. This flow of electron density from the 2,3-η^2-coordinated Re to the S-coordinated Re is supported by ^{1}H NMR data for the H2 and H3 atoms in the compounds. In **5**, the H2 and H3 NMR resonances (δ 4.93 (d) and 4.67 (d)) are considerably upfield of those in **1b** (δ 5.36 (d) and 5.12 (d)).

The Cp* analogs of **1** and **5** were prepared in the same manner (eq 2) as for **1** from the reaction of $Cp^*(CO)_2Re(THF)$ with BT. Compound **2** also exists in solution as an equilibrium mixture of η^1(S) (**2a**) and 2,3-η^2 (**2b**) isomers (eq 1). The bimetallic compound **6** is also formed in the reaction. As for **5**, the FT-IR and ^{1}H NMR spectroscopic data show that in **6**, the sulfur of the BT is more strongly electron-donating than in the monometallic compound **2a**, and the 2,3-olefin is more π-accepting than in the monometallic compound **2b**. In **6**, the ν(CO) bands for the η^2 bonded metal fragment (1966 and 1892 cm^{-1}) are 7–8 cm^{-1} higher than those in the η^2 isomer **2b** (1957 and 1885 cm^{-1}), while the carbonyl bands for the S bonded metal fragment in **6** (1904 and 1835 cm^{-1}) are 9–10 cm^{-1} lower than those in the η^1(S) isomer **2a** (1914 and 1844 cm^{-1}). Also, in the ^{1}H NMR spectra, the H2 and H3 resonances in bimetallic **6** (δ 3.92 (d), 3.68 (d)) are ~0.3 ppm upfield of those in monometallic **2b** (δ 4.27 (d), 3.97 (d)).

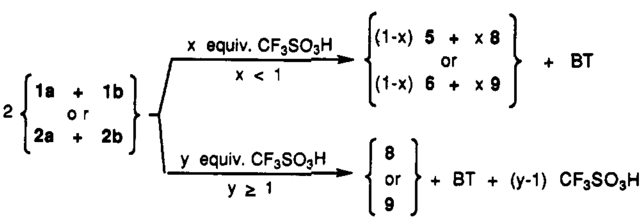
Compound **7**, the bimetallic compound containing one $Cp(CO)_2Re$ fragment and one $Cp^*(CO)_2Re$ fragment is synthesized (eq 3) from the reaction of $Cp(CO)_2Re(THF)$ with **2**. In **7**, the $Cp(CO)_2Re$ fragment is exclusively η^1(S) bonded to the BT, and the $Cp^*(CO)_2Re$ fragment is exclusively 2,3-η^2 bonded to the BT. This bonding assignment is based on ^{1}H NMR and FT-IR data. In the ^{1}H NMR spectrum the Cp resonance for **7** (δ 4.93) is identical to the position of the more upfield Cp resonance of the S bonded $Cp(CO)_2Re$ fragment in **5**, which strongly supports S-coordination by the $Cp(CO)_2Re$ group in **7**. In addition, the H2 and H3 atoms (δ 3.94 and 3.66) are shifted upfield of those in the Cp-containing bimetallic compound **5** (δ 4.93 and 4.67) but closely match those in the Cp*-containing bimetallic compound **6** (δ 3.92 and 3.68). In the FT-IR spectrum of **7**, the ν(CO) values for the CO groups on the S bonded $Cp(CO)_2Re$ fragment (1919 and 1848 cm^{-1}) are nearly the same as those for the S bonded $Cp(CO)_2Re$ fragment in **5** (1921 and 1850 cm^{-1}). In addition, the bands for the $Cp^*(CO)_2Re$ fragment in **7** (1971 and 1897 cm^{-1}) closely match those for the 2,3-η^2 bonded $Cp^*(CO)_2Re$ fragment in **6** (1966 and 1892 cm^{-1}). The only detected isomer of **7** is that in which the $Cp(CO)_2Re$ is bonded to the BT sulfur and the $Cp^*(CO)_2Re$ is bonded to the olefin. There is no evidence for the isomer in which the $Cp(CO)_2Re$ and $Cp^*(CO)_2Re$ fragments are interchanged. Such an isomer would be expected to be less stable because the Cp* ligand would make the $Cp^*(CO)_2Re$ fragment less Lewis acidic for binding to the electron-donating sulfur. At the same time, the less electron-rich $Cp(CO)_2Re$ fragment would be less capable of π-back-bonding to the olefin group.



7

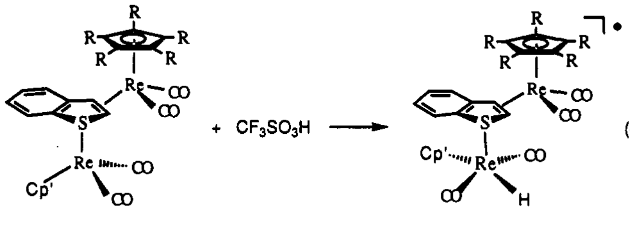
(3)

Scheme I



Reactions of $Cp'(CO)_2Re(BT)$ Complexes with CF_3SO_3H. When 1 equiv of $Cp'(CO)_2Re(BT)$ is reacted with 0.5 equiv or greater of CF_3SO_3H, the protonated bimetallic complex $[Cp'(CO)_2ReH](\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)[Re(CO)_2Cp']$ is formed immediately (Scheme I). If the $Cp'(CO)_2Re(BT)$ complex is reacted with less than 0.5 equiv of CF_3SO_3H, a mixture of the protonated bimetallic complex and the unprotonated bimetallic complex $[Cp'(CO)_2Re]_2(\eta^2{:}\eta^1(S)\text{-}\mu_2\text{-}BT)$ is immediately formed. The bimetallic compounds **5** and **6** are synthesized in quantitative yield by the reaction of **1** and **2**, respectively, with catalytic amounts (1:40) of CF_3SO_3H (Scheme I). Thus, this acid-catalyzed method is far superior to the reaction in eq 2 for the syntheses of **5** and **6**.

The protonated bimetallic complex **8** can also be synthesized (eq 4) by reaction of the bimetallic complex **5** with 1 equiv of acid; **9** can be synthesized from **6** in the same manner. Compound **7** also reacts (eq 4) with 1 equiv of CF_3SO_3H to give **10**. The protonated complexes **8**–**10** are all fluxional (*vide infra*) at room temperature in solution, as indicated by the broad peaks in their ^{1}H and ^{13}C NMR spectra. However, at −60 °C, the peaks are sharp, and the following discussion is based on these low temperature spectra. Compounds **5**–**7** are protonated exclusively at the Re that is S bonded to the BT to give **8**–**10**, respectively. Evidence for this site of protonation is seen in a comparison of the ^{1}H NMR Cp and Cp* resonances of **7** and **10** (Table II). In **7**, the $Cp(CO)_2Re$ fragment is S-bonded to the BT, while the $Cp^*(CO)_2Re$ fragment is 2,3-η^2 bonded (*vide supra*). Upon protonation of **7**, the Cp resonance shifts downfield from 4.93 to 5.49 ppm, while the Cp* resonance shifts only very slightly downfield from 2.03 to 2.06 ppm. This indicates that the S-coordinated $Cp(CO)_2Re$ unit is protonated, despite the fact that the Cp* ligand is more electron-donating than Cp. However, protonation at the S-coordinated Re would strengthen the sulfur–Re donor bond as well as the π-bond from Re to the olefin; these factors are apparently responsible for the observed protonation at the $Cp(CO)_2Re$



(4)

5, 6, 7

8, 9, 10

For **5** and **8**, Cp' = Cp; R = H

For **6** and **9**, Cp' = Cp*; R = Me

For **7** and **10**, Cp' = Cp; R = Me

group. The Cp resonances (4.93 and 5.24 ppm) of **5** shift to 5.55 and 5.57 ppm upon protonation to give **8**. The Cp* resonances of **6** shift from 2.02 and 2.05 to 2.05 and 2.32 ppm upon protonation to give **9**. These downfield shifts of one Cp or Cp* resonance are consistent with the idea that the Cp′(CO)$_2$Re fragment that is S bonded to the BT is protonated.

Only one hydride resonance is observed in the ^{1}H NMR spectra (Table II) of the protonated bimetallic complexes; so, only one metal center is protonated. The protonated bimetallic complexes are stable in an excess of acid, but the second metal center does not protonate. The protonated complexes **8** and **9** can be deprotonated with equimolar diphenylguanidine base to give the unprotonated bimetallic compounds, **5** and **6**, as observed in a ^{1}H NMR spectrum of the solution. Even though the protonated compounds were insufficiently stable to give satisfactory elemental analyses or crystals, their spectra and deprotonations to the neutral bimetallic compounds strongly support the assignment of their structures.

The acid-catalyzed formation (Scheme I) of the bimetallic complexes from **1** or **2** must involve dissociation of the BT from the Cp′(CO)$_2$Re(BT), and this dissociation must be promoted by the acid. Since both **1** and **2** exist as mixtures of the η^1(S) and 2,3-η^2 isomers, likely protonation sites are the metal in the 2,3-η^2 or η^1(S) isomer, or the sulfur atom of the 2,3-η^2 isomer. When **2**, a mixture of **2a** and **2b**, is reacted with a catalytic amount of CF$_3$SO$_3$H in the presence of excess PPh$_3$, Cp*(CO)$_2$Re(PPh$_3$) is formed almost immediately; no **2** remains and no bimetallic complex **5** is formed. The PPh$_3$ effectively traps the Cp*(CO)$_2$Re fragment, and the BT is completely dissociated and uncoordinated. The PPh$_3$ does not react with **2** or **6** during this time frame when no acid is present. Since the interconversion between **2a** and **2b**[4] is much slower than the acid-catalyzed reaction of **2** with PPh$_3$, either the acid must catalyze this interconversion or it must catalyze the substitution of BT by PPh$_3$ in both isomers.

Reaction of the methyl-substituted benzo[*b*]thiophene complex Cp(CO)$_2$Re(2-MeBT) (**3**), which exists as only the S bonded isomer, with CF$_3$SO$_3$H gives the protonated monometallic complex **11**. Complex **3** protonates cleanly at the metal center; no bimetallic compound is formed and 2-MeBT is not dissociated. The compound was insufficiently stable over the time period required to record its ^{13}C NMR spectrum; so, it was not possible to determine if the protonated product had a *cis* or *trans* structure. Attempts to synthesize the bimetallic compound [Cp(CO)$_2$Re](η^2:η^1(*S*)-μ_2-2-MeBT)[Re(CO)$_2$Cp*] from the reaction of **3** with Cp*(CO)$_2$Re(THF) were also unsuccessful. It appears that the 2-methyl group substantially reduces the coordinating ability of the 2,3-olefin, either by making the olefin a poorer π-acceptor or by sterically inhibiting metal–olefin bonding.

Protonation of Cp(CO)$_2$Re(PPh$_3$) (4) and ^{1}H-Coupled ^{13}C NMR Spectra of [Cp(CO)$_2$(PPh$_3$)ReH]O$_3$SCF$_3$ (12) and (8). Compound **4** was synthesized by literature methods[10] analogous to the syntheses of **1** and **2**. When **4** is reacted at room temperature with CF$_3$SO$_3$H in CD$_2$Cl$_2$ solution, an equilibrium mixture of *cis*-[Cp(CO)$_2$(PPh$_3$)Re(H)]O$_3$SCF$_3$ (**12a**) and *trans*-[Cp(CO)$_2$(PPh$_3$)Re(H)]O$_3$SCF$_3$ (**12b**) isomers is formed;[13] in addition, some unprotonated **4** remains.[13] Fluxionality of the complexes in this solution is indicated by the lack of discernible ^{1}H or ^{13}C NMR resonances for **4** and **12** at this temperature. Only broad, overlapping bands are present. However, upon cooling the solution to −60 °C, **4** and isomers of **12** are easily distinguished. Compound **12** exists in a 1:10 ratio of *cis*:*trans* isomers. The *cis* and *trans* isomers of **12** have been reported previously.[13] In the ^{1}H NMR spectrum, the hydride resonance of the *cis* isomer **12a** (δ −7.83 (d, $^1J_{PH}$ = 41.7 Hz)) has a considerably larger J_{PH} coupling constant than the *trans* isomer **12b** (δ −8.86 (d, $^1J_{PH}$ = 14.7 Hz)). In the ^{1}H-coupled, ^{13}C NMR spectrum, the one expected CO resonance of the *trans* isomer **12b** (δ 189.5 (d of d, $^1J_{PC}$ = 17.7 Hz, $^1J_{HC}$ = 13.2 Hz)) is easily detected, but the two CO resonances expected for the minor isomer **12a** (δ 196.0 and 190.6) are barely distinguishable due to the small amount of this isomer present.

Protonation of the bimetallic compound **5** gives the monoprotonated **8**, which exhibits the same type of fluxionality as **12** in solution in its ^{1}H and ^{13}C NMR spectra at room temperature. Only broad overlapping bands are present. Upon cooling a solution of **8** to −60 °C, the ^{1}H and ^{13}C NMR spectra indicate that only one isomer is present, and no unprotonated **5** remains. Since only one hydride resonance (δ −8.67) and two Cp resonances are observed in the ^{1}H NMR spectrum, and only four diastereotopic CO resonances (δ 201.8, 199.4, 189.9, and 188.9) and two Cp resonances (δ 89.3 and 88.5) are observed in the ^{13}C{^{1}H} spectrum, only one isomer is distinguishable. In the ^{1}H-coupled, ^{13}C NMR spectrum of **8**, the two downfield carbonyl resonances remain sharp singlets, while the two upfield resonances become doublets (δ 190.0 (d, $^1J_{HC}$ = 13.4 Hz) and 188.8 (d, $^1J_{HC}$ = 13.9 Hz)). The nearly equal $^1J_{HC}$ values for the carbonyls indicate a *trans* configuration of the COs. In addition, the $^1J_{HC}$ values (13.4 and 13.9 Hz) closely match the $^1J_{HC}$ value (13.2 Hz) for the *trans* carbonyls in **12** and further support the *trans* assignment for the carbonyl groups in **8**.

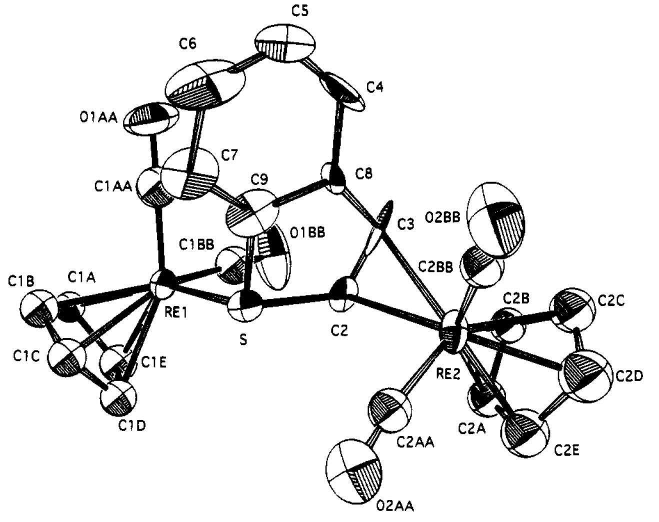
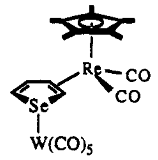


Figure 1. ORTEP drawing of [Cp(CO)$_2$Re]$_2$(η^2:η^1(*S*)-μ_2-BT) (**5**).

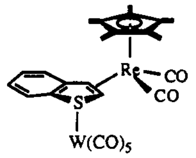
Structure of [Cp(CO)$_2$Re]$_2$(η^2:η^1(*S*)-μ_2-BT) (5). In the structure of **5** (Figure 1) the coordinated BT sulfur has a trigonal-pyramidal geometry; it is roughly sp^3 hybridized. The sum of the angles around the sulfur (311(1)°) in **5** is smaller than that in the S-bonded BT complex Cp*(CO)$_2$Re(η^1(*S*)-3-MeBT) (326(1)°).[4b] The Re1–S distance of 2.35(1) Å is similar to that (2.356(4) Å) of Cp*(CO)$_2$Re(η^1(*S*)-3-MeBT).[4b] The S-coordinated Re lies out of the plane of the BT such that the angle between the Re–S vector and the vector from S to the midpoint of the line between C3 and C8 is 118°. This angle is smaller than those in other S-coordinated thiophene complexes $Cp^*(CO)_2Re(\eta^1(S)$-3-MeBT) (131°)[4b] and $Cp^*(CO)_2Re(\eta^1(S)$-T) (140°) (T = thiophene),[22] but similar to those in $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-2-MeT})^+$ (119.1°)[23] and $Cp(CO)_2Fe(\eta^1(S)\text{-DBT})^+$ (119.4°) (DBT = dibenzothiophene).[24] Another structural aspect of **5** is the lengthening (~0.1 Å) of S–C2 (1.81(3) Å) as compared to the corresponding S–C2 and S–C9 distances in 5-bromo-2,3-dimethylbenzo[*b*]thiophene (1.75(1), 1.741(9) Å),[25] 3-formylbenzo[*b*]thiophene (1.704(5), 1.733(5) Å),[26] $CpRu(\eta^6\text{-BT})^+$ (1.72(1), 1.730(7) Å),[27] and $CpRu(\eta^5\text{-BT}\cdot H)$ (1.723(4), 1.764(3) Å).[28] The other S–C bond (S–C9 = 1.77(3) Å) appears to be only slightly lengthened by comparison. Lengthening of the analogous S–C2 bond in $Cp^*(CO)_2Re(\eta^1(S)$-3-MeBT) (S–C2 = 1.92(2) Å) is also observed.[4b] The lengthening of S–C bonds is particularly interesting since these bonds must be cleaved in BT HDS.

Conclusion

Previously, we showed that selenophene can coordinate to two metal complex fragments in **A**[5] and that benzo[*b*]thiophene can coordinate to Re and W in **B**.[4b] In complexes **5**–**7** (eqs 2 and 3), $Cp'(CO)_2Re$ fragments are coordinated at both the sulfur and the 2,3-olefin bond. Spectroscopic data for these complexes strongly indicate that the BT sulfur is an electron donor atom, whereas the 2,3-olefin is a π electron acceptor. Thus, an electron-rich fragment such as $Cp'(CO)_2Re$ coordinates favorably at the 2,3-olefin as a result of π-back-bonding from the metal to the olefin. This back-bonding also increases electron density on the sulfur, which makes it a better donor toward the $Cp'(CO)_2Re$ fragment on the sulfur. Thus, metal binding at both sites moves electron density from the $Cp'(CO)_2Re$ group coordinated to the olefin to the $Cp'(CO)_2Re$ group coordinated to the sulfur. This makes the η^1(S)-coordinated Re sufficiently basic that it is readily protonated by CF_3SO_3H to give the series of complexes **8**–**10**.



A



B

Supplementary Material Available: Text giving a description of X-ray data collection and structure solution and refinement, tables of *U** values, positional parameters, and bond distances and angles, and a PLUTO drawing of **5** (15 pages). Ordering information is given on any current masthead page.

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(22) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436.

(23) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 1992.

(24) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424.

(25) Hogg, J. H. C.; Sutherland, H. H. *Acta Crystallogr., Sect. B.* **1974**, *30*, 2058.

(26) Pascard, P. R.; Pascard-Billy, C. *Acta Crystallogr., Sect. B* **1972**, *28*, 1926.

(27) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.

(28) Huckett, S. C.; Angelici, R. J. *Organometallics* **1988**, *7*, 1491.