Models for the Homogeneous Hydrodesulfurization of Benzothiophenes. Carbon−Sulfur Bond Cleavage, Hydrogenolysis, and Desulfurization Reactions Mediated by Coordination of the Carbocyclic Ring to Manganese and Ruthenium

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Chemical reduction of a series of (η^6-benzothiophene)$Mn(CO)_3^+$ complexes (**10a**−**c**) under CO affords neutral dimanganese metallathiacyclic complexes (**12a**−**c**), which have a $Mn(CO)_4$ moiety inserted into the C(aryl)−S bond. Reduction of (η^6-benzothiophene)$Ru(C_6Me_6)^{2+}$ in the presence of CO and (η^6-1-Me-naphthalene)$Mn(CO)_3^+$ affords an analogous cationic bimetallic (**15**), which is converted to a neutral cyclohexadienyl complex (**16**) by hydride addition to the carbocyclic benzothiophene ring. The sulfur atom in the metallathiacyclic ring in **12** and **16** is nucleophilic and reacts with electrophiles CF_3SO_3Me, HBF_4, and $W(CO)_5(THF)$ to afford complexes such as **6**, **14**, and **17**. Treatment of **12** with H_2 results in hydrogenolysis of the Mn−C σ bond and formation of the bimetallic $Mn_2(CO)_8(H)(SCH{=}CHPh)$ (**8**), which contains a Mn−Mn bond and bridging hydride and thiolate ligands. Reaction of **6** and **17** with H_2 results in desulfurization of the benzothiophene and formation of a mixture of $Mn(CO)_5SR$ and $[Mn(CO)_4SR]_2$ (R = H, Me). Crystal structures are reported for **9** (R = Me), **12b**, and **16**.

Introduction

Catalytic hydrodesulfurization (HDS) of petroleum feedstocks is an enormously important industrial process, the purpose of which is the removal of sulfur as H_2S by the use of H_2.[1] While most sulfur-containing molecules are susceptible to HDS as currently practiced, thiophenic molecules are resistant to desulfurization, especially substituted benzothiophenes (BTs) and dibenzothiophenes (DBTs).[2] As a consequence, these species constitute a major source of sulfur contamination in fossil fuels. The HDS process involves hydrogenolysis of C−S bonds (to give thiols) and subsequent desulfurization. Hydrogenation of olefinic C=C bonds may also occur. Industrial heterogeneous catalysts contain two types of metals: a *component* (Mo, W) and a *promoter* (Co, Ni, etc.). It has been suggested, but not proven, that thiophene activation occurs at a promoter site while H_2 activation occurs at a component site. Despite the importance of HDS, the mechanistic aspects are at present poorly understood, and for this reason, homogeneous model systems have been developed, especially for thiophenic substrates.[1,3]

A number of nucleophilic 16-electron organometallic fragments containing a promoter-type metal (Ru, Rh, Ir, Pt) have been found to insert into the vinyl carbon−sulfur bond of BT (**1**) to give the metallathiacycle **2** (Chart 1).[4] In some cases, treatment of **2** with H_2 leads to hydrogenolysis of the M−C bond with formation of the thiolate intermediate $ML_n(H)(SR)$. With certain Ru-, Rh-, and Ir-based systems, rate-determining thiol elimination from $ML_n(H)(SR)$ is followed by reinsertion of ML_n into BT so that the overall reaction is the catalytic hydrogenolysis of the C(2)−S bond in BT.[4a,h,5] As for actual desulfurization (or hydrodesulfurization) of thiophenic molecules, multimetallic homogeneous systems, especially when both component and promoter metals are present, are much more effective than are

(1) (a) Sanchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (b) Startsev, A. N. *Catal. Rev.-Sci. Eng.* **1995**, *37*, 353. (c) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801. (d) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073.

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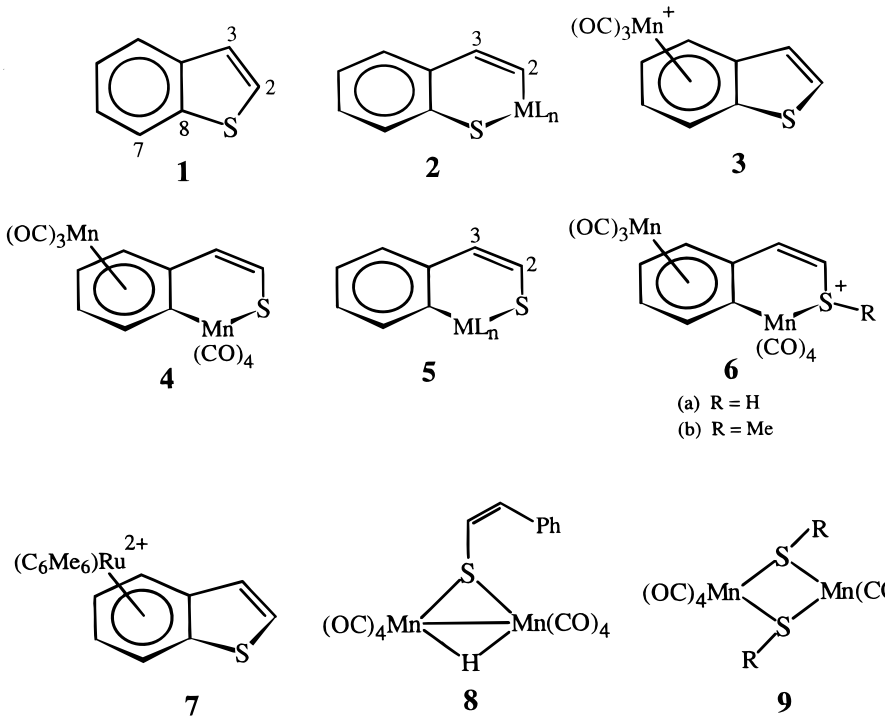
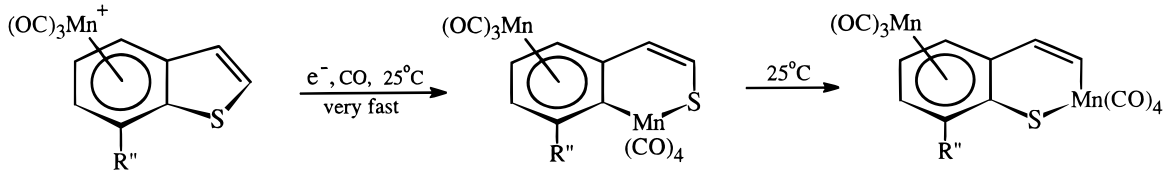
Chart 1



Scheme 1. Sequential Activation of Thiophenic C(aryl)−S and C(vinyl)−S Bonds



monometallic systems. As an example, a recent study[6] found that C−S insertion in BT occurred at a promoter metal (Rh) but desulfurization required the addition of a component metal (W), which reacted to give a bimetallic intermediate from which sulfur was eliminated as WS_2. So far, it has not been possible to make the homogeneous desulfurization process *catalytic* because of the great stability of the M_xS_y products with respect to elimination of H_2S.[7]

We recently demonstrated[8] that coordination of the $Mn(CO)_3^+$ moiety to the carbocyclic ring of BT results in selective activation of the aryl carbon−sulfur bond, C(8)−S. Thus, chemical reduction of **3** under CO led to insertion of $Mn(CO)_4$ into the C(aryl)−S bond to give **4** in high yield. This result was unusual in light of previous studies which invariably had found[4] selective insertion of organometallic fragments into the C(vinyl)−S bond of BT. It was suggested[8] that the formation of **5** instead of **2** requires precoordination of a metal to the carbocyclic ring π-system. The only other known case of C(aryl)−S bond cleavage stems from the reaction of 2-methyl-BT with Cp*Rh(PMe_3), which initially forms **2** as a kinetic product that, due to the steric influence of the 2-methyl substituent, slowly isomerizes to **5**.[9] That steric factors play a major role in C−S bond activation is graphically demonstrated by the chemistry shown in Scheme 1.[10] The isomerization of the initially formed C(aryl)−S insertion product to the C(vinyl)−S insertion product takes place readily at *room temperature* for R″ = Me and Et but does not occur upon prolonged heating when R″ = H. How the reactivity of the sulfur atom in BT is altered by metal insertion into a C−S bond is of paramount importance in HDS chemistry. Free BT is a resonance-stabilized planar molecule with an unreactive sulfur atom. In contrast, the sulfur in **4** is 1.1 Å out of the plane of the carbocyclic ring and is sufficiently nucleophilic so that reaction with electrophiles (R^+) to form **6** is facile.[8]

In the present paper, we further examine the chemistry of a variety of BT complexes containing the organometallic fragments $Mn(CO)_3^+$ and $Ru(C_6Me_6)^{2+}$ coordinated to the carbocyclic ring, as in **3** and **7**. It is shown that insertion of $Mn(CO)_4$ into a C−S bond in these complexes, followed by treatment with H_2, results in hydrogenolysis of the Mn−C bond and formation of a bimetallic product (**8**) that contains bridging hydride and thiolate ligands. In contrast, reaction with H_2 after

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(7) Weak catalytic desulfurization activity has been observed with mononuclear Rh and Ir complexes containing the triphos ligand.[5a,c]

(8) (a) Dullaghan, C. A.; Sun, S.; Carpenter, G. B.; Weldon, B.; Sweigart, D. A. *Angew. Chem.* **1996**, *108*, 234; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 212. (b) Sun, S.; Dullaghan, C. A.; Sweigart, D A. *J. Chem. Soc., Dalton Trans.* **1996**, 4493.

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Chart 2

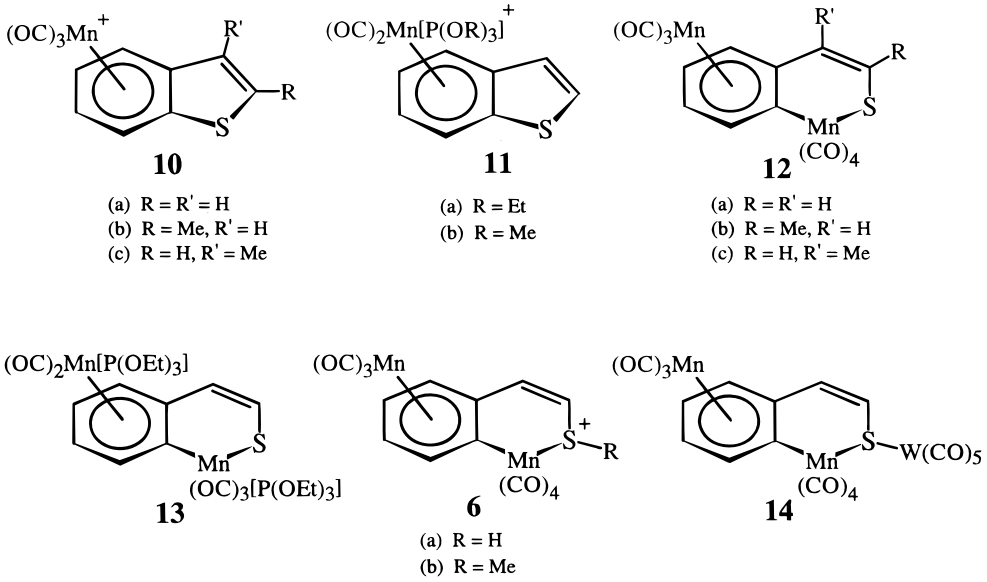


Table 1. Crystallographic Data for Complexes 12b, 9, and 16

	12b	**9** (R = Me)	**16**
formula	$C_{16}H_8Mn_2O_7S$	$C_{10}H_6Mn_2O_8S_2$	$C_{24}H_{25}MnRuO_4S$
fw	454.16	428.15	565.51
temperature	298	298	298
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	8.2343(2)	6.0508(4)	9.0923(2)
b, Å	22.1349(8)	14.2411(10)	13.3934(3)
c, Å	9.7080(4)	9.5560(6)	19.3603(3)
β, deg	99.507(1)	86.933(1)	95.348(1)
V, Å^3	1745.13(10)	785.87(9)	2347.37(8)
Z	4	2	4
d_{calcd}, g cm^{-3}	1.729	1.809	1.600
μ, mm^{-1}	1.602	1.904	1.297
F(000)	904	424	1144
cryst dimens, mm	0.03 × 0.14 × 0.22	0.10 × 0.23 × 0.36	0.21 × 0.21 × 0.18
θ range, deg	1.84−26.76	2.65−23.32	1.85−23.28
no. of reflns collected	9871	3053	8943
no. of indep reflns	3545 (R_{int} = 0.0934)	1084 (R_{int} = 0.0391)	3348 (R_{int} = 0.0364)
data/restraints/params	3543/0/236	1084/0/100	3348/0/286
GOF on F^2	0.941	1.042	1.033
final R indices [$I > 2\sigma I$]	R1 = 0.0782, wR2 = 0.1774	R1 = 0.0492, wR2 = 0.1276	R1 = 0.0322, wR2 = 0.0802
R indices (all data)	R1 = 0.1553, wR2 = 0.2161	R1 = 0.0601, wR2 = 0.1352	R1 = 0.0393, wR2 = 0.0843

the sulfur is methylated or protonated (as in **6**) leads to *desulfurization* of the benzothiophene and formation of $Mn(CO)_5(SR)$ and $[Mn(CO)_4(SR)]_2$ (**9**).

Results

Synthesis and Reduction of Benzothiophene Complexes 10 and 11. The coordination of substituted benzothiophenes to $Mn(CO)_3^+$ to afford **10b,c** (Chart 2) was readily accomplished by following the procedure used previously[8a] for the synthesis of the unsubstituted analogue (**10a**). Treatment of **10a** with $P(OR)_3$ (R = Me, Et) in the presence of Me_3NO induced CO substitution and formation of **11a,b**. Cobaltocene reduction of **10** and **11a** under an atmosphere of CO led to the regioselective insertion of manganese into the C(aryl)−S bond to give **12** and **13**, respectively. The X-ray structure of **12b** was determined (Table 1) and is shown in Figure 1. The most noteworthy feature is a highly nonplanar metallathiacyclic ring, which has C(3) and Mn(2) nearly in the plane of the carbocyclic ring, C(4)−C(9), while C(2) and S(1) are above this plane by 0.47 and 0.88 Å, respectively. By comparison, the displacements of C(2) and S(1) in the unsubstituted analogue (**12a**) are 0.53 and 1.05 Å.[8]

Electrophilic Addition to the Sulfur in Complex 12a. In contrast to the situation in free benzothiophene, the sulfur atom in **12** is significantly nucleophilic. It was shown[8a] in a preliminary communication that methyl triflate reacts cleanly and rapidly with **12a** to give **6b**. Similarly, herein we report that HBF_4 rapidly protonates **12a** in CH_2Cl_2 to afford **6a**, which was identified by an IR spectroscopic comparison to **6b**. Complex **6a** proved too reactive to be isolated in a pure form, and so it was prepared in situ when needed for subsequent hydrogenation studies (vide infra). The addition of the $W(CO)_5$ moiety to the sulfur in **12a** was accomplished by reaction with $W(CO)_5(THF)$. The S−W bond in the product (**14**) was readily cleaved by methyl

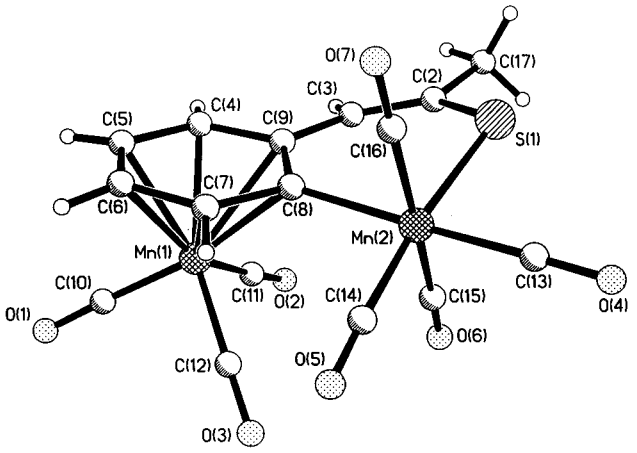
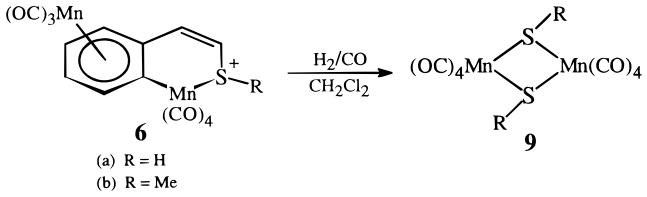


Figure 1. Crystal structure of **12b**. Selected bond distances (Å): Mn(2)−C(8) 2.090(7), Mn(2)−S(1) 2.363(2), S(1)−C(2) 1.723(9), C(2)−C(3) 1.341 (10), C(3)−C(9) 1.434(10), C(8)−C(9) 1.420(11).

triflate (CH_2Cl_2, 8 h) to generate **6b**. That the S−W bond in **14** is rather labile was also indicated by attempted hydrogenation, which led to S−W bond cleavage.

Hydrogenation of Manganese Complexes 12a and 6. Hydrogenation of **12a** at modest pressure and temperature (300 psi, 100 °C) for 3 h resulted in complete loss of the starting complex and hydrogenolysis of the Mn−C σ bond to afford **8** as the only identifiable organometallic product. Complex **8**, with bridging thiolate and hydride ligands, is similar in structure to the products reported[11,12] for hydrogenation reactions of multimetallic manganese complexes of thiophene and dibenzothiophene. Although **8** contains more CO ligands than its precursor (**12a**), the hydrogenation of the latter to the former was found to be mildly inhibited (kinetic factor of ca. 10) when the H_2 contained 5% CO. This suggests that a kinetically important step is initial CO dissociation from the $Mn(CO)_4$ moiety in **12a**, followed by oxidative addition of H_2 at this center.

Complexes **6a** and **6b** differ from **12a** in that the sulfur atom in the metallathiacyclic ring contains a substituent (H and Me, respectively). Hydrogenation of **6a** and **6b** with a 95:5 mixture of H_2:CO led to desulfurization according to eq 1. The organic products



6
(a) R = H
(b) R = Me

9

+ $Mn(CO)_5SR$ + $Mn_2(CO)_{10}$ (1)

were not characterized, but the organometallic products were readily identified (Table 2). Hydrogenation of **6b** produced a mixture of the thiolate complexes $Mn(CO)_5SMe$ and $[Mn(CO)_4SMe]_2$ (**9**), with the former predominating. Both of these complexes were isolated and fully characterized (see Experimental Section).

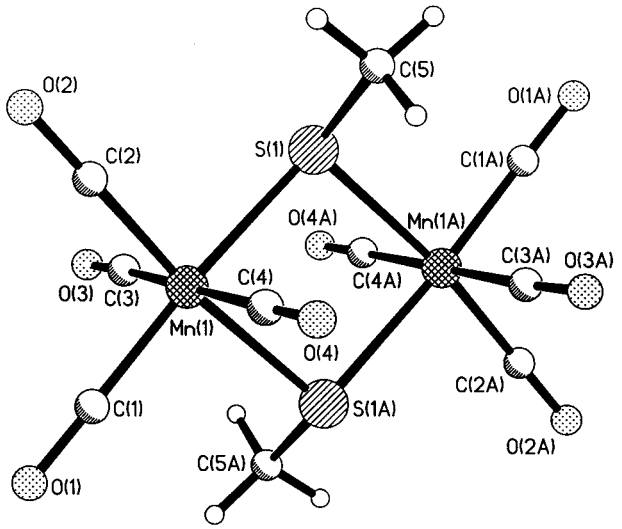


Figure 2. Crystal structure of **9** (R = Me). Selected bond distances (Å) and angles (deg): Mn(1)−S(1) 2.3842(14), Mn(1)−S(1A) 2.3825(14), S(1)−Mn(1)−S(1A) 82.70(5), Mn(1)−S(1)−Mn(1A) 97.30(5).

Although $Mn(CO)_5SMe$ has been previously described[13] as very unstable, we found that it could be stored unchanged for weeks at −20 °C under CO. At room temperature in solution in the absence of CO, it decomposes within several hours. An X-ray diffraction study (Table 1) confirmed that the known[14] dimer $[Mn(CO)_4SMe]_2$ (**9**) was formed from the hydrogenation of **6b**. As shown in Figure 2, $[Mn(CO)_4SMe]_2$ crystallizes as the anti isomer, with structural features similar to those reported[14b] previously for $[Mn(CO)_4S(p\text{-tolyl})]_2$. In analogy to the behavior of **6b**, hydrogenation of **6a** produced a mixture of $Mn(CO)_5SH$ and $[Mn(CO)_4SH]_2$. The major product was the known[15] dimer $[Mn(CO)_4SH]_2$ (**9**), which was isolated in solution by extraction of the reaction mixture with pentane. Its IR spectrum was identical to that reported[15] previously. Similarly, by comparison to its known[16] IR spectrum, $Mn(CO)_5SH$ was detected as a minor component (ca. 25%) but could not be isolated. That $Mn(CO)_5SH$ could not be isolated is to be expected in view of its reported[16] rapid conversion to $[Mn(CO)_4SH]_2$. Interestingly, hydrogenation of **6a** in the presence of excess acid (HBF_4) led to the generation of H_2S, which was verified by formation of PbS as the gases were passed through an aqueous solution of $Pb(OAc)_2$.

Activation of Benzothiophene with Ruthenium. Coordination of the $Ru(C_6Me_6)^{2+}$ moiety to the carbocyclic ring of BT to give **7** was readily accomplished by following a general procedure[17] for the synthesis of $Ru(arene)(C_6Me_6)^{2+}$. Cobaltocene reduction of **7** in the presence of $[(1\text{-Me-naphthalene})Mn(CO)_3]BF_4$ under CO led to insertion of $Mn(CO)_4$ into the C(aryl)−S bond to afford the bimetallic **15** (Chart 3). The sulfur atom in

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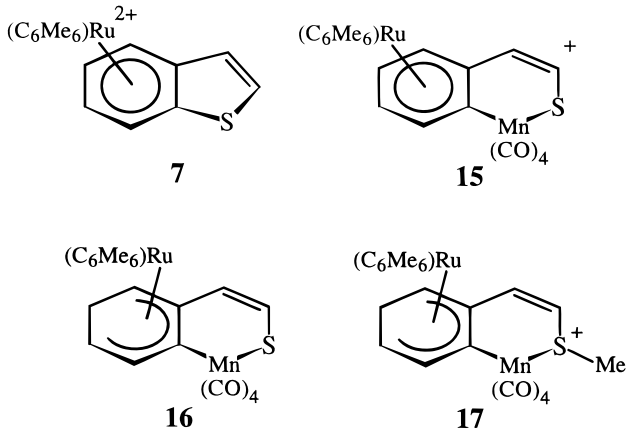
(16) Küllmer, V.; Vahrenkamp, H. *Chem. Ber.* **1976**, *109*, 1560.
(17) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87.

Table 2. Products of Hydrogenation Reactions of 6a,b and 17[a]

reactant	reaction conditions[b] (temp, pressure, time)	product distribution[c] $Mn(CO)_5SR$	$[Mn(CO)_4SR]_2$	$Mn_2(CO)_{10}$
6a	110 °C, 640 psi, 3 h	minor	major	none
6a	110 °C, 640 psi, 30 h	minor	major	minor
6b	85 °C, 500 psi, 1 h		no reaction	
6b	125 °C, 540 psi, 2 h	major	minor	minor
6b	100 °C, 540 psi, 14 h[d]	major	minor	none
17	86 °C, 500 psi, 9.5 h	major	major	minor
17	85 °C, 500 psi, 8.5 h[d]	major	none	minor
17	90 °C, 500 psi, 11 h[d]	major	none	minor
17	90 °C, 500 psi, 24 h[d]	minor	none	major

[a] The solvent was CH_2Cl_2 in all cases. [b] The hydrogenation gas consisted of a 95:5 mixture of H_2:CO. [c] R = Me for all reactions except those of **6a**, for which R = H. The combined yield for the product distribution in the individual reactions was in the 70−80% range. [d] Solutions contained a ca. 5-fold excess of methyl triflate.

Chart 3



15 was found to be unreactive toward electrophiles, which we ascribe to the overall positive charge. To increase the reactivity of the sulfur atom, **15** was converted to the neutral complex **16** by adding hydride to the carbocyclic ring. Hydride addition to **15** occurred regioselectively at the C(5) position to afford **16** as the major product. ^{1}H NMR spectra of the unpurified product mixture indicated that addition occurred to a minor extent at the C_6Me_6 ring to give the neutral η^5-hexamethylcyclohexadienyl isomer of **16**. The structure of **16** was confirmed by single-crystal X-ray diffraction. Figure 3 and Table 1 provide the structural details. As found with **12b** (Figure 1), the metallathiacyclic ring in **16** is highly nonplanar. The respective bond distances in the two structures are quite similar, but the metallathiacyclic rings are skewed differently—**12b** has the sulfur 0.88 Å above the plane defined by the six carbocyclic carbons, whereas in **16** the sulfur is 0.98 Å below the plane defined by the five dienyl carbocyclic carbons.

As anticipated, the sulfur atom in **16** readily underwent methylation to give **17** as a stable salt. Hydrogenation of **17** with a 95:5 mixture of H_2:CO resulted in desulfurization and formation of $Mn(CO)_5SMe$ and $[Mn(CO)_4SMe]_2$, along with a trace amount of $Mn_2(CO)_{10}$ (Table 2). With an excess of methyl triflate present, the hydrogenations produced mainly $Mn(CO)_5SMe$, although at longer reaction times the amount of $Mn_2(CO)_{10}$ increased.

Discussion

Insertion into the C(aryl)−S Bond of Benzothiophene. The results show that coordination of $Mn(CO)_3^+$ or $Ru(C_6Me_6)^{2+}$ to the carbocyclic ring in benzothiophene selectively activates the C(aryl)−S bond to reductive insertion of a $Mn(CO)_4$ fragment. As noted above, studies of C−S bond scission in free benzothiophene induced by organometallic nucleophiles invariably found[4] the C(vinyl)−S bond to be the one activated. Our work suggests that this activation is easily shifted in favor of C(aryl)−S bond scission by precoordination of a metal to the carbocyclic ring. Once this coordination is in place, cleavage of a C−S bond can be effected via organometallic nucleophiles or via reductive insertion. The former approach is the subject of a forthcoming paper,[18] and the latter is described herein.

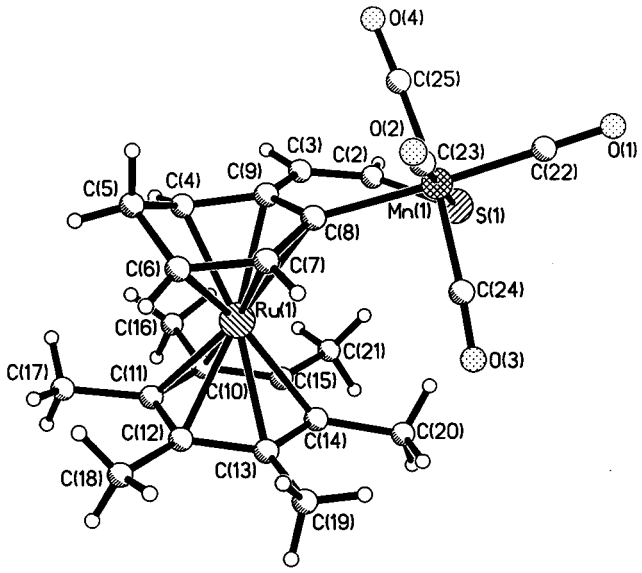


Figure 3. Crystal structure of **16**. Selected bond distances (Å): Mn(1)−C(8) 2.085(4), Mn(1)−S(1) 2.3667(12), S(1)−C(2) 1.720(5), C(2)−C(3) 1.340 (6), C(3)−C(9) 1.447(6), C(8)−C(9) 1.434(5).

Insertion of $Mn(CO)_4$ into the C(aryl)−S bond according to eqs 2 and 3 was found to occur when the manganese complex **10** is reduced under CO to give **12** and when the ruthenium complex **7** is reduced under CO in the presence of (1-Me-naphthalene)$Mn(CO)_3^+$ to give **15**. At least superficially, the mechanism(s) of reactions **10** → **12** and **7** → **15** would appear to be rather complex. It is possible, however, to postulate a simple

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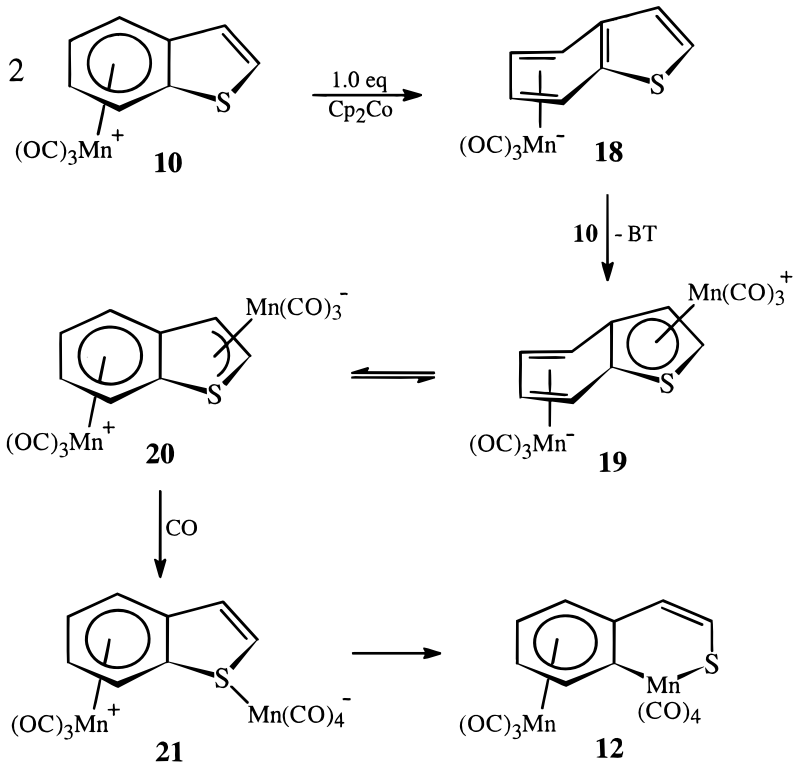
Scheme 2. Possible Mechanism for Reductive Insertion into the C(aryl)−S Bond of BT

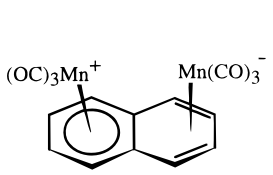


$$(\eta^6\text{-BT})\underset{\mathbf{10}}{\text{Mn(CO)}_3^+} \xrightarrow[\text{CO}]{1\ e^-} \mathbf{12} \qquad (2)$$

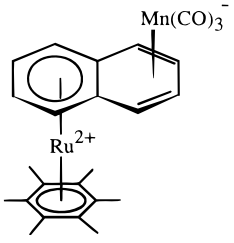
$$(\eta^6\text{-BT})\underset{\mathbf{7}}{\text{Ru}(C_6Me_6)^{2+}} + \text{(1-Me-naphthalene)Mn(CO)}_3^+ \xrightarrow[\text{CO}]{2e^-} \mathbf{15} \qquad (3)$$

and reasonable mechanism that is based on an analogy to the known[8b,19] behavior of manganese and ruthenium naphthalene complexes. This mechanism, shown in Scheme 2 for reaction **10** → **12**, is predicated on the assumption that benzothiophene and naphthalene are similar with respect to binding metals via their 10-electron π-systems. The first step in Scheme 2 is the reduction of $(\eta^6\text{-BT})Mn(CO)_3^+$ (**10**) to $(\eta^4\text{-BT})Mn(CO)_3^-$ (**18**), which mimics the well-established[20] reduction of $(\eta^6\text{-naphthalene})Mn(CO)_3^+$ to $(\eta^4\text{-naphthalene})Mn(CO)_3^-$. Although reduction of **10** to **18** requires two electrons, the actual synthesis of **12** from **10** (eq 2) was found to work best when only 1 equiv of cobaltocene is used. It is assumed that one reducing equivalent added to **10** would generate 0.5 equiv of **18**, leaving a 0.5 equiv of **10** unreacted. The alternative is one-electron reduction of all of **10** to the 19-electron species $(\eta^6\text{-BT})Mn(CO)_3$. The former scenario seems much more likely because one-electron reduction of $(\eta^6\text{-naphthalene})Mn(CO)_3^+$ is known[8] to give an equimolar mixture of the η^6-cation and the η^4-anion.

The key step in the mechanism in Scheme 2 is the reaction of the anion **18** with unreacted starting material **10** to liberate free BT and afford the bimetallic zwitterions **19**/**20**. This reaction is nothing more than ligand substitution of the carbocyclic ring of BT in **10** by the electron-rich thiophenic ring in **18**. It is likely that this process is favored by facile slippage of the carbocyclic ring in **10** from η^6 to η^4 to η^2 as the thiophene ring in **18** coordinates to the metal in **10** via an associatively activated pathway. This type of chemistry has been documented[8b,19,21] for $(\eta^6\text{-naphthalene})Mn(CO)_3^+$, which is known to undergo rapid ring slippage and which can react with $(\eta^4\text{-naphthalene})Mn(CO)_3^-$ to yield the stable structurally characterized zwitterion **22**.



22



23

Complex **22** is clearly analogous to zwitterions **19**/**20** in Scheme 2. At this stage, it is postulated that complex **20** undergoes ligand substitution of the vinyl C=C bond by CO to give the η^1-S complex **21**. Although η^1-S coordination from benzothiophene to a metal is rather weak, it has been demonstrated with iron and rhenium systems.[22] Furthermore, it is believed[4e,9,23] that η^1-S coordination generally precedes C−S bond scission. Accordingly, it is suggested that insertion of the electron-

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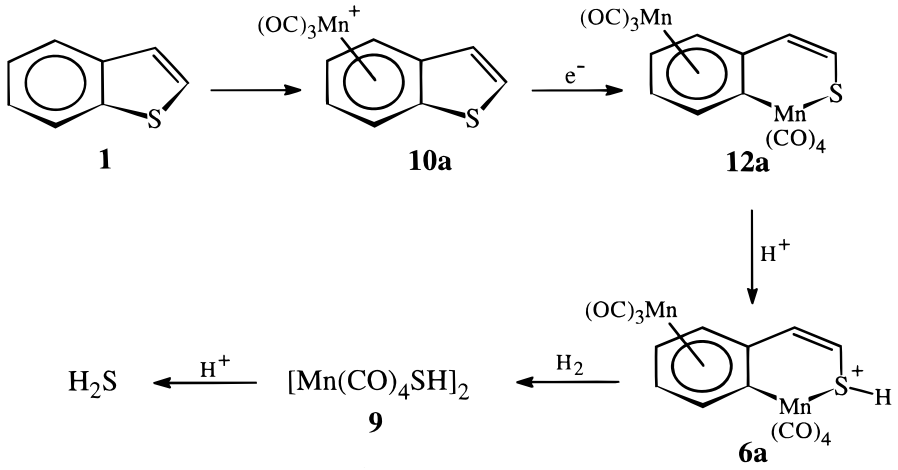
Scheme 3. Manganese-Mediated Hydrodesulfurization of Benzothiophene



rich $Mn(CO)_4$ fragment in **21** into the C(aryl)−S bond, activated by $Mn(CO)_3^+$ coordination to the carbocyclic ring, occurs to complete the overall reaction.

Essentially the same mechanism is proposed for manganese insertion into the ruthenium complex according to eq 3. In this case, two-electron reduction of **7** occurs to give (η^4-BT)Ru(C_6Me_6), which contains an electron-rich thiophene ring that displaces the 1-Me-naphthalene from (η^6-1-Me-naphthalene)$Mn(CO)_3^+$. The initial product is a cationic complex analogous to **19**, which subsequently undergoes insertion into the C(aryl)−S bond to give **15**. Precedent for this proposal comes from the reaction of (η^4-naphthalene)Ru(C_6Me_6) with (η^6-naphthalene)$Mn(CO)_3^+$, which affords the cationic bimetallic complex **23**.[8b,19]

Hydrogenation and Desulfurization Studies. The organometallic product obtained from the hydrogenation of **12a** is the interesting bimetallic complex **8**. The basic structural unit MM′(H)(SR) found in **8**, with bridging hydride and thiolate ligands, has been suggested as a possible intermediate in HDS reactions.[6,24,25] Two recent examples of this type of bimetallic unit, RhW(H)(SR)[6] and Ir_2(H)(SR),[25] in which the bridging thiolate is derived from benzothiophene, were shown to undergo desulfurization to ethylbenzene upon hydrogenation. These studies and others[26,27] suggest that hydrodesulfurization is facilitated by coordination of the thiolate sulfur to two or more metal centers. This is likely the case because multimetallic coordination weakens the C−S bond to homolytic cleavage. Although hydrogenation studies of the manganese bimetallic **8** have yet to be completed, it is noteworthy that the species $Mn_2(CO)_8$(H)(SR) is formed under mild hydrogenation conditions from bimetallic precursors of all three of the relevant thiophenic molecules—thiophene,[11] benzothiophene (**12a**), and dibenzothiophene.[12]

Given that hydrogenation of **12a** results in hydrogenolysis of the Mn−C σ bond and formation of a bimetallic with a bridging thiolate, we reasoned that methylation (or protonation) of the nucleophilic sulfur in **12a** or **16** prior to hydrogenation could lead to desulfurization. Indeed, **6** and **17** reacted with a 95:5 mixture of H_2:CO as in eq 1 to give a mixture of $Mn(CO)_5SR$ and $[Mn(CO)_4SR]_2$ (R = H, Me; Table 2). Although the organic products of this reaction were not isolated and identified, it is clear that desulfurization of the benzothiophene moiety occurred. The mechanism of desulfurization is unknown, but the nature of the products suggest that the metal fragment coordinated to the carbocyclic ring is not directly involved in product formation.

Perhaps the most interesting hydrogenation reaction is that involving the protonated complex **6a**. Without excess acid present, the major product is $[Mn(CO)_4SH]_2$, while hydrogenation in the presence of HBF_4 generates H_2S. The overall sequence of reactions is summarized in Scheme 3. While incomplete in that not every organic/inorganic product has been quantified, this scheme shows that benzothiophene can be hydrodesulfurized using manganese-based chemistry. $Mn(CO)_3^+$ coordination activates the benzothiophene to reductive insertion, which activates the sulfur to protonation and subsequent desulfurization upon hydrogenation. Once the manganese is coordinated, the only reagent required is H_2 or its constituents (H^+, e^-).

Although the hydrogenolysis/desulfurization reactions discussed above are presently stoichiometric, the possibility of catalysis is being explored. Mechanistic studies of the insertion, hydrogenation, and desulfurization reactions described herein are in progress.

Experimental Section

Materials. Most reagents were obtained from commercial sources and used without further purification. Published

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procedures were used to synthesize 2-methylbenzothiophene,[9] $W(CO)_5THF$,[6] $[(C_6Me_6)RuCl_2]_2$,[17] [(1-methylnaphthalene)Mn$(CO)_3]BF_4$,[21] and [(benzothiophene)Mn$(CO)_3]BF_4$ (**10a**).[21] The synthesis of bimetallics **12a** and **6a** was previously communicated.[8a] Cobaltocene and Me_3NO were purchased from Strem and Aldrich, respectively. Neutral alumina (Aldrich, 150 mesh, Brockmann I) for column chromatography was used as received ("activated") or deactivated by mixing with 10 wt % water. FAB MS and HR MS were performed at Brown University. Elemental analyses were done by National Chemical Consulting, Inc., Tenafly, NJ.

Crystal Structure Determinations. The crystal structures of **12b**, **9** (R = Me), and **16** were determined with a Siemens P4 diffractometer equipped with a CCD area detector and controlled by SMART version 4 software. Data reduction was carried out by SAINT version 4 and included profile analysis; this was followed by absorption correction by use of the program SADABS. Data were collected at 25 °C with Mo Kα radiation. The structures were determined by direct methods and refined on F^2 using the SHELXTL version 5 package. Hydrogen atoms were introduced in ideal positions, riding on the carbon atom to which they are bonded; each was refined with isotropic temperature factors 20−50% greater than that of the ridden atom. All other atoms were refined with anisotropic thermal parameters.

Synthesis of Benzothiophene Complexes 10b,c. These complexes were prepared by a procedure previously described for **10a**.[8a] In a typical synthesis, $AgBF_4$ (215 mg, 1.1 mmol) was added to $Mn(CO)_5Br$ (275 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) and the reaction mixture was stirred for 10 min at room temperature in the absence of light. Next, 1.5 mmol (222 mg) of the desired benzothiophene was added and the mixture refluxed for 3 h. The volume was then reduced to 5 mL, and the product was precipitated as the BF_4^- salt by the addition of Et_2O. Reprecipitation from acetone with Et_2O afforded pure product as a bright yellow powder. For [**10b**]BF_4: yield 89%; IR (CH_2Cl_2) ν_{CO} = 2072 (s), 2014 (s, br) cm^{-1}; ^{1}H NMR (250 MHz, $CD_3C(O)CD_3$) δ 8.01 (d, J = 7.1 Hz, H7), 7.64 (d, J = 7.0 Hz, H4), 7.52 (s, H3), 6.78 (m, H5,6), 2.77 (s, Me). Anal. Calcd for $C_{12}H_8O_3Mn_1S_1B_1F_4$: C, 38.51; H, 2.16. Found: C, 38.59; H, 2.19. For [**10c**]BF_4: yield 74%; IR (CH_2Cl_2) ν_{CO} = 2072 (s), 2014 (s, br) cm^{-1}; ^{1}H NMR (250 MHz, $CD_3C(O)CD_3$) δ 8.29 (s, H2), 8.13 (d, J = 6.9 Hz, H7), 7.69 (d, J = 6.3 Hz, H4), 6.88 (m, H5,6), 2.66 (s, Me). Anal. Calcd for $C_{12}H_8O_3Mn_1S_1B_1F_4$: C, 38.51; H, 2.16. Found: C, 38.14; H, 2.16.

Synthesis of Complexes 11a,b. Anhydrous Me_3NO (83 mg, 1.1 mmol) was added to a stirring suspension of **10a** (360 mg, 1.0 mmol) and $P(OR)_3$ (1.0 mmol) in CH_2Cl_2 (25 mL) at room temperature under N_2. The initial red color quickly disappeared, and the solution became orange-yellow. The volume was then reduced to 3 mL and filtered through a small pad of Celite. The product crystallized as a deep yellow solid upon addition of Et_2O. For [**11a**]BF_4: yield 62%; IR (CH_2Cl_2) ν_{CO} = 2012 (s), 1966 (s) cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.06 (d, J = 5.6 Hz, H2), 7.43 (d, J = 6.3 Hz, H3), 7.05 (d, J = 6.8 Hz, H4), 6.97 (d, J = 6.3 Hz, H7), 6.13 (t, J = 6.4 Hz, H5), 6.04 (t, J = 6.3 Hz, H6), 3.98 (m, CH_2), 1.34 (t, J = 7.0 Hz, Me). Anal. Calcd for $C_{16}H_{21}O_5Mn_1S_1B_1P_1F_4$: C, 38.57; H, 4.26. Found: C, 38.42; H, 4.31. For [**11b**]BF_4: yield 49%; IR (CH_2Cl_2) ν_{CO} = 2012 (s), 1968 (s) cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.08 (d, J = 5.5 Hz, H2), 7.45 (d, J = 6.3 Hz, H3), 7.11 (d, J = 6.7 Hz, H4), 7.03 (d, J = 6.6 Hz, H7), 6.17 (t, J = 5.7 Hz, H5), 6.10 (t, J = 6.3 Hz, H6), 3.70 (d, J = 11.6 Hz, Me). Anal. Calcd for $C_{13}H_{15}O_5Mn_1S_1B_1P_1F_4$: C, 34.23; H, 3.32. Found: C, 33.94; H, 3.31.

Synthesis of Complexes 12b,c and 13. Cobaltocene (59 mg, 0.31 mmol) and the BF_4^- salt of **10b,c** or **11a** (0.3 mmol) were combined in CH_2Cl_2 (10 mL) and the mixture was stirred under CO at room temperature for 20 min and then passed through deactivated neutral alumina with CH_2Cl_2 as the eluant. After the solvent was removed under vacuum, the resulting red-purple solid was washed with pentane and dried. For **12b**: yield 85%; IR (CH_2Cl_2) ν_{CO} = 2072 (m), 2049 (s), 1993 (s, br), 1929 (m) cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 6.83 (d, J = 6.3 Hz, H7), 6.11 (s, H3), 6.00 (t, J = 6.6 Hz, H5), 5.42 (d, J = 6.2 Hz, H4), 5.39 (t, J = 6.6 Hz, H6), 2.29 (s, Me). Anal. Calcd for $C_{16}H_8O_7Mn_2S_1$: C, 42.30; H, 1.78. Found: C, 42.06; H, 1.71. For **12c**: yield 81%; IR (CH_2Cl_2) ν_{CO} = 2074 (m), 2049 (s), 1993 (s, br), 1931 (m) cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.50 (s, H2), 6.88 (dd, J = 7.8, 1.5 Hz, H7), 6.05 (ddd, J = 7.5, 6.5, 1.5 Hz, H5), 5.73 (dd, J = 6.9, 1.2 Hz, H4), 5.53 (dt, J = 6.2, 1.1 Hz, H6), 2.10 (s, Me). Anal. Calcd for $C_{16}H_8O_7Mn_2S_1$: C, 42.30; H, 1.78. Found: C, 42.20; H, 1.69. For **13**: yield 48%; IR (hexanes) ν_{co} = 2018 (s), 1983 (m), 1944 (s, br), 1928 (m, sh), 1920 (m) cm^{-1}; ^{1}H NMR (250 MHz, $CD_3C(O)CD_3$) δ 7.12 (d, J = 9.8 Hz, H2), 6.81 (d, J = 6.8 Hz, H7), 6.07 (d, J = 10.0 Hz, H3), 5.87 (d, J = 6.0 Hz, H4), 5.38 (m, H6,5), 4.10−3.76 (m, CH_2), 1.33 (t, J = 7.0 Hz, Me), 1.24 (t, J = 7.0 Hz, Me). Anal. Calcd for $C_{25}H_{36}O_{11}P_2Mn_2S_1$: C, 41.91; H, 5.08. Found: C, 41.68; H, 5.03.

Synthesis of Complex 14. $(THF)W(CO)_5$ (257 mg, 0.65 mmol, 2.0 equiv) was added to a solution of **12a** (141 mg, 0.32 mmol) in CH_2Cl_2 (15 mL) under N_2. The reaction was refluxed for 1 h and cooled to room temperature, and the volume was reduced to 3 mL under vacuum. The concentrated CH_2Cl_2 solution was loaded onto a deactivated Al_2O_3 column. A hexanes:Et_2O (5:1) solution was used to elute free $W(CO)_6$, while the product was eluted with Et_2O. For **14**: yield 33%; IR (CH_2Cl_2) ν_{co} = 2085 (w), 2066 (w), 2056 (s), 2006 (s, br), 1927 (s), 1890 (m, br) cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.16 (d, J = 9.9 Hz, H2), 6.77 (d, J = 6.5 Hz, H7), 6.17 (d, J = 10.0 Hz, H3), 6.10 (d, J = 5.9 Hz, H4), 5.64 (m, H6,5). Anal. Calcd for $C_{20}H_6O_{12}W_1Mn_2S_1$: C, 31.44; H, 0.79. Found: C, 31.60; H, 0.92. MS FAB: 764 (M^+), 652 ($M^+ - 4CO$), 624 ($M^+ - 5CO$), 440 ($M^+ - W(CO)_5$). HR MS: M^+ (m/z) calcd 763.7850, obsd 763.7840.

Hydrogenation of 12a to Produce 8. The complex **12a** (44 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL) and placed in a Parr high-pressure bomb reactor. The reactor was purged twice with H_2, refilled with H_2 (300 psi), and placed in an oil bath at, typically, 100 °C for 3 h. The bomb was then immediately cooled to room temperature and adjusted to atmospheric pressure. The solution was concentrated in vacuo, and purification was performed by silica gel TLC with pentane as the eluant. For **8**: yield 32%; IR (CH_2Cl_2) ν_{co} = 2101 (w), 2072 (s), 2016 (vs), 2005 (s, sh), 1973 (s) cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.97 (d, J = 7.4 Hz, Ph), 7.50−7.34 (m, Ph), 7.01 (d, J = 10.2 Hz, H2 or H3), 6.24 (d, J = 10.3 Hz, H2 or H3), −15.83 (s, −H−). Anal. Calcd for $C_{16}H_8O_8Mn_2S_1$: C, 40.87; H, 1.72. Found: C, 40.78; H, 1.90. MS FAB: 470 (M^+), 386 ($M^+ - 3CO$), 358 ($M^+ - 4CO$), 330 ($M^+ - 5CO$). HR MS: M^+ (m/z) calcd 469.8701, obsd 469.8686.

Synthesis and Hydrogenation of 6a,b. The reaction of methyl triflate with **12a** cleanly affords the methylated product **6b**, as described previously.[8a] Similarly, the addition of HBF_4 to **12a** in CH_2Cl_2 rapidly and quantitatively produced **6a**, as judged by IR spectra. Attempted purification of **6a** via chromatographic procedures led to deprotonation and reversion to starting material **12a**. For **6a**: IR (CH_2Cl_2) ν_{co} = 2093 (m), 2066 (s), 2022 (vs), 1975 (m) cm^{-1}. Hydrogenations of **6a,b** with H_2/CO mixtures (95:5) were performed in CH_2Cl_2 with a Parr bomb reactor, as described above for the hydrogenation of **12a**. After the reactions were terminated, IR spectra were used to identify the organometallic products; the results are given in Table 2. The hydrogenation products, as determined by IR, generally consisted of a mixture of $Mn(CO)_5SR$ and [Mn$(CO)_4SR]_2$, with the former predominating with **6b** (R = Me) and the latter with **6a** (R = H); the combined yield of the two products was in the 70−80% range. A trace amount of $Mn_2(CO)_{10}$ could sometimes be detected. In the reaction of **6b** with H_2/CO (540 psi) at 100 °C for 14 h, the major product, $Mn(CO)_5SMe$, was isolated in 68% yield by extraction into hexanes.

Although this complex is reported[13] to be very unstable with respect to CO loss and dimerization, we found that it can be stored for several weeks at −20 °C under CO without decomposition. At room temperature in hexane under nitrogen, $Mn(CO)_5SMe$ decomposes within several hours with loss of CO to unidentified products. For $Mn(CO)_5SMe$: IR (CH_2Cl_2) ν_{co} = 2141 (w), 2056 (vs), 2010 (s) cm^{-1}; ^1H NMR (250 MHz, CD_2Cl_2) δ 1.26 (s, Me). Anal. Calcd for $C_6H_3O_5Mn_1S_1$: C, 29.77; H, 1.25; S, 13.24. Found: C, 30.15; H, 1.34; S, 13.11. MS FAB: 242 (M^+), 227 (M^+ − Me), 214 (M^+ − CO), 199 (M^+ − Me − CO), 195 (M^+ − SMe). The dimer $[Mn(CO)_4SMe]_2$ was isolated from the mixture of hydrogenation products by column chromatography on activated Al_2O_3 (which destroys $Mn(CO)_5SMe$). Hexanes was used to elute minor impurities and diethyl ether to elute $[Mn(CO)_4SMe]_2$, which is a known[14] compound.

Synthesis of Complex 7. $[(C_6Me_6)RuCl_2]_2$ (254 mg, 0.38 mmol) and $AgBF_4$ (304 mg, 1.56 mmol) were combined in acetone (20 mL) and stirred for 30 min at room temperature. The reaction mixture was filtered and concentrated to 2 mL. Benzothiophene (140 mg, 1.04 mmol) and CF_3CO_2H (5 mL) were then added, and the reaction mixture was refluxed for 2 h. Upon cooling, the red solution was added dropwise to a large excess of Et_2O. The white precipitate of **[7]**$[BF_4]_2$ was collected and dried in vacuo. For **[7]**$[BF_4]_2$: yield 97%; ^1H NMR (250 MHz, $CD_3C(O)CD_3$) δ 8.93 (d, J = 5.7 Hz, H2), 7.98 (m, H7), 7.77 (d, J = 5.7 Hz, H3), 7.72 (m, H4), 7.05 (m, H5,6), 2.41 (s, C_6Me_6). Anal. Calcd for $C_{20}H_{24}Ru_1B_2F_8S_1$: C, 42.06; H, 4.24. Found: C, 41.90; H, 4.09. HR MS: M^+ (m/z) calcd 398.0642, obsd 398.0630.

Synthesis of Complex 15. **[7]**$[BF_4]_2$ (354 mg, 0.62 mmol), [(1-Me-naphthalene)$Mn(CO)_3$]BF_4 (309 mg, 0.84 mmol), and Cp_2Co (322 mg, 1.70 mmol) were mixed under N_2 at −78 °C. CH_2Cl_2 (40 mL) was added, and the reaction was allowed to warm to −20 °C. CO was slowly bubbled through the solution, and the mixture was stirred for 1 h. The volume was reduced to 10 mL, and the solution was loaded onto a deactivated Al_2O_3 column. CH_2Cl_2 was used to elute impurities, and the deep red product was then eluted with CH_2Cl_2/ acetone (2:1). The product was further purified by washing a CH_2Cl_2 solution with H_2O and precipitating with Et_2O. For **[15]**BF_4: yield 37%; IR (CH_2Cl_2) ν_{co} = 2074 (s), 2000 (vs), 1978 (vs), 1944 (s) cm^{-1}; ^1H NMR (250 MHz, CD_2Cl_2) δ 7.82 (d, J = 9.4 Hz, H2), 6.43 (d, J = 5.8 Hz, H7), 6.18 (dt, J = 6.0, 1.0 Hz, H6), 5.90 (m, H3,5), 5.48 (d, J = 6.2 Hz, H4), 2.39 (s, C_6Me_6). Anal. Calcd for $C_{24}H_{24}O_4Mn_1Ru_1B_1F_4S_1$: C, 44.26; H, 3.71. Found: C, 44.10; H, 4.00. HR MS: M^+ (m/z) calcd 564.9820, obsd 564.9810.

Hydride Addition to 15 to Produce 16. Bu_4NBH_4 (139 mg, 0.54 mmol) and **[15]**BF_4 (274 mg, 0.42 mmol) were mixed under N_2 at −78 °C. CH_2Cl_2 (5 mL) was added, and the reaction was stirred for 5 min at −78 °C and warmed to room temperature. After reducing the volume to ca. 1 mL, the CH_2Cl_2 solution was loaded onto a deactivated Al_2O_3 column. Pentane was used to elute impurities, and the yellow product was then eluted with Et_2O:pentane (1:1). For **16**: yield 30%; IR (CH_2Cl_2) ν_{co} = 2058 (m), 1975 (vs), 1961 (s, sh), 1915 (s) cm^{-1}; ^1H NMR (250 MHz, CD_2Cl_2) δ 6.78 (d, J = 9.5 Hz, H2), 5.12 (d, J = 9.5 Hz, H3), 4.71 (d, J = 5.5 Hz, H7), 2.38 (m, 2H), 2.26 (m, 2H), 2.16 (s, C_6Me_6). Anal. Calcd for $C_{25}H_{25}O_4Mn_1Ru_1S_1$: C, 50.97; H, 4.46. Found: C, 50.87; H, 4.57. A crystal of **16** suitable for X-ray diffraction was grown by slow diffusion of pentane into a diethyl ether solution at −20 °C.

Methyl Triflate Addition to 16 to Produce 17. CF_3SO_3Me (25 μL, 0.22 mmol) was added to a solution of **16** (85 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) under N_2. The reaction was stirred for several minutes and warmed to room temperature. The solution was then evaporated to dryness, and the residue was washed with Et_2O. The product was loaded onto a deactivated Al_2O_3 column and eluted first with CH_2Cl_2 to remove impurities and then with CH_2Cl_2:acetone (1:1) to afford the yellow product. For **[17]**CF_3SO_3: yield 70%; IR (CH_2Cl_2) ν_{co} = 2087 (m), 2004 (vs), 1996 (s, sh), 1968 (s) cm^{-1}; ^1H NMR (250 MHz, CD_2Cl_2) δ 6.34 (d, J = 9.6 Hz, H2), 5.74 (d, J = 9.7 Hz, H3), 4.64 (d, J = 5.7 Hz, H7), 2.69 (s, Me), 2.61 (m, 2H), 2.49 (m, 1H), 2.31 (m, 1H), 2.20 (s, C_6Me_6). Anal. Calcd for $C_{26}H_{28}O_7F_3Mn_1Ru_1S_2$: C, 42.80; H, 3.87. Found: C, 42.62; H, 3.71. HR MS: M^+ (m/z) calcd 581.0133, obsd 581.0144.

Hydrogenation of Complex 17. Hydrogenations were performed as described above for complexes **6a** and **6b**, with the results given in Table 2.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **9** (R = Me), **12b** and **16** (35 pages). Ordering information is given on any current masthead page.

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