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Models for the Homogeneous Hydrodesulfurization of Thiophenes: Manganese-Mediated Carbon−Sulfur Bond Cleavage and Hydrogenation Reactions

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Chemical reduction of a series of (η^5-thiophene)$Mn(CO)_3^+$ complexes (**3a**−**d**) under an atmosphere of CO affords dimanganese metallathiacyclic complexes (**4a**−**d**), which have a $Mn(CO)_4$ moiety regioselectively inserted into a C−S bond. Reaction of **4** with H_2, the rate of which is strongly influenced by substituents on the thiophene ring, leads to hydrogenolysis of the Mn−C σ-bond and formation of $(OC)_3Mn(\mu\text{-}H)(\mu\text{-}SCRCHCHCHR')Mn(CO)_3$ (**8**; R, R′ = H, Me), which contains bridging hydride and thiolate ligands and a Mn−Mn bond. The addition of PhMgBr to **3** occurs at the sulfur to give zwitterionic complexes (**6a**−**c**, **14**), which undergo regioselective hydrogenolysis of a C−S bond and, in some cases, partial desulfurization with concomitant formation of $(OC)_4Mn(\mu\text{-}H)(\mu\text{-}SPh)Mn(CO)_4$ (**5a**). Crystal structures are reported for complexes **4b**,**d**, **5a**, **8d**, **10**, **12c**, and **14b**,**c**. It is suggested that the reactions reported herein may be relevant to the general problem of hydrodesulfurization (HDS) of thiophenic molecules.

Introduction

Due to the great importance of hydrodesulfurization (HDS) in petroleum refining, a considerable amount of research has been directed to the study of homogeneous model systems that may mimic some of the chemical steps occurring during the heterogeneously catalyzed industrial process.[1] Thiophenic molecules are of particular interest in this regard due to their reluctance to undergo desulfurization, thus accounting for their relative abundance in fossil fuels. In the case of simple thiophenes (**1**) (Chart 1), work has been directed at activation of the heterocyclic ring to nucleophilic attack as well as to C−S and C−H bond cleavage.[2,3] The strategies used to induce scission of a C−S bond in **1** include (1) coordination of a metal to the thiophene π-system followed by nucleophilic attack at the ring,[2a,3d,4] (2) coordination of a metal followed by reduction and subsequent addition of an electrophile,[3e,5] and, most commonly, (3) generation of an electron-rich 16-electron fragment that reacts directly with **1** by oxidative addition to a C−S bond to afford the generic metallathiacycle **2** (or analogous species).[2,3]

This paper is concerned with the use of manganese to facilitate C−S bond scission in thiophenes. The $Mn(CO)_3^+$ moiety is readily coordinated to thiophenes in an η^5-fashion as shown in structure **3**.[6] Nucleophiles are known to react with **3** by adding to a ring carbon or the sulfur atom without causing C−S bond cleavage. In contrast to this behavior, chemical reduction of **3** leads to C−S bond scission and formation of the bimetallic

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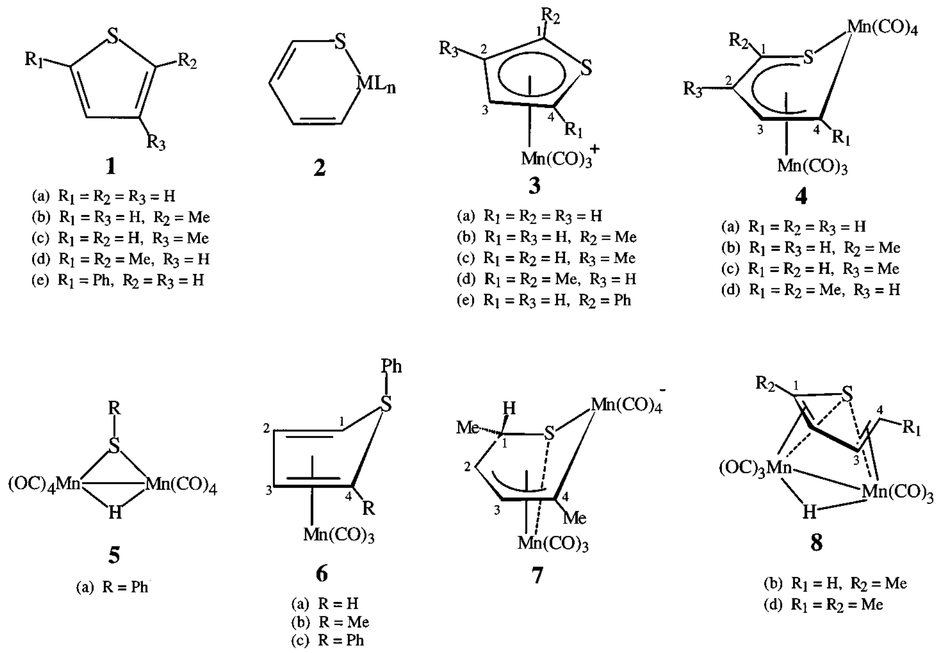
Chart 1

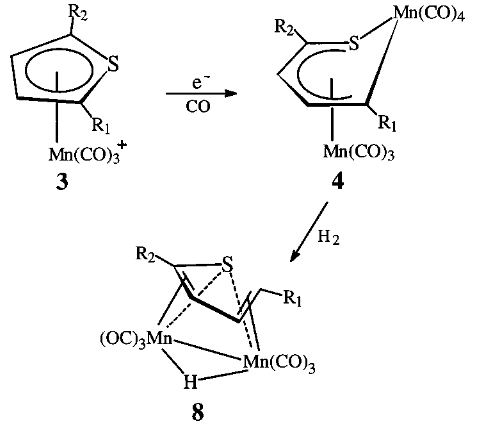


4.[7] In this paper various aspects of the transformation **3** → **4** are discussed. In addition, it is shown that the reaction of **4** with H_2 in certain cases results in hydrogenolysis of the Mn−C σ-bond and formation of a dimanganese complex (**5**) which contains bridging hydride and thiolate ligands. Further, it is demonstrated that **5a** (R = Ph) can also be obtained as one of the major products of hydrogenation of **6**, which is prepared by addition of PhMgBr to **3**. The bimetallic structural unit $Mn_2(H)(SR)$ in **5** is of particular interest because of its similarity to species suggested to occur with heterogeneous HDS catalysts.[2c,8]

Results and Discussion

Reduction of (η^5-Thiophene)$Mn(CO)_3{}^+$ Complexes 3a−d. Cobaltocene reduction of **3a**−**d** at room temperature under an atmosphere of CO occurred rapidly according to Scheme 1 to afford good yields of the bimetallic **4**, which contains a $Mn(CO)_4$ moiety inserted into a C−S bond. (The synthesis and X-ray structure of **4a** were previously communicated.[7]) The X-ray structures of **4b**,**d** were determined and found to be virtually identical to that of **4a**. Figure 1 shows the structure of **4b**, and Table 1 gives a summary of the crystallographic data. The S1−C2−C3−C4−C5 dienyl segment π-bonded to $Mn(CO)_3$ is highly planar, with mean deviations (Å) being: **4a**, 0.030; **4b**, 0.038; **4d**, 0.046. The $Mn(CO)_4$ fragment is situated about 1.2 Å above the dienyl plane, which is folded about the S1−Mn2−C5 plane at the following angles (deg): **4a**, 46.5; **4b**, 45.3; **4d**, 47.7. Complexes **4b**,**c** were formed as single isomers, indicating that **3** → **4** is a highly regioselective process. It is noteworthy that $Mn(CO)_4$ prefers to insert into an unsubstituted C−S bond, but when there is no alternative, as in **3d**, insertion to give **4d** still takes place smoothly. In contrast to this, Bianchini[21] and Maitlis[9] found that the nucleophiles (triphos)Rh(H) and $Pt(PEt_3)_3$, respectively, insert cleanly into the unsubstituted C−S bond in 2-methylthiophene but are unreactive toward 2,5-dimethylthiophene. They ascribe these great reactivity differences to steric constraints.

Scheme 1



While the mechanism of formation of **4** by reduction of **3** has yet to be established, it is clear that there must be a transfer of a $Mn(CO)_n$ moiety from one thiophene molecule to another. Such a transfer is known[10] to occur rapidly when (η^6-naphthalene)$Mn(CO)_3{}^+$ is reduced with 1 equiv of cobaltocene and is believed to involve displacement of naphthalene from the cationic complex by the initially formed nucleophilic anion (η^4-naphthalene)-$Mn(CO)_3{}^-$ to give a bimetallic complex, (η^6,η^4-naphthalene)$Mn_2(CO)_5$. The key mechanistic feature of this reaction is the ease with which naphthalene can slip

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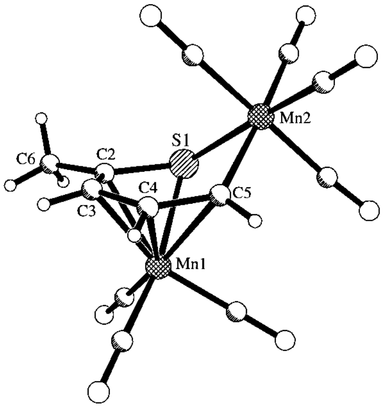


4b

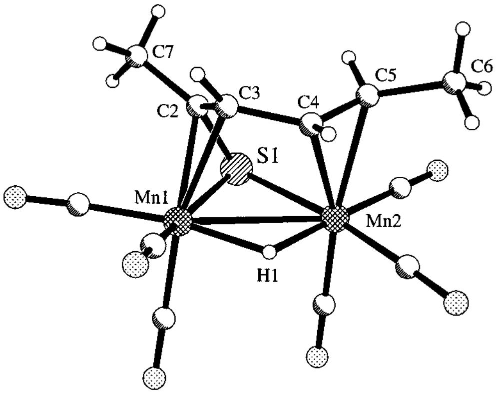
Figure 1. Crystal structure of **4b**. Selected bond distances (Å) and angles (deg) are Mn1−S1 2.364(2), Mn2−S1 2.334(2), Mn2−C5 2.046(5), Mn1−C2 2.164(4), Mn1−C3 2.156(4), Mn1−C4 2.163(4), Mn1−C5 2.395(5), S1−C2 1.746(5), C2−C3 1.395(6), C3−C4 1.436(6), C4−C5 1.367(6), C2−C6 1.489(6); S1−Mn2−C5 80.10(14), Mn2−S1−C2 110.7(2), S1−C2−C3 120.9(4), C2−C3−C4 124.4(4), C3−C4−C5 125.2(4), C4−C5−Mn2 127.8(4).

Table 1. Crystallographic Data for Complexes 4b,d

	4b	4d
formula	$C_{12}H_6Mn_2O_7S$	$C_{13}H_8Mn_2O_7S$
fw	404.11	418.13
temperature	298	298
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	9.244(2)	8.4712(3)
b, Å	27.160(4)	9.1029(3)
c, Å	12.289(2)	12.4490(5)
α, deg		70.367(1)
β, deg	104.099(14)	86.933(1)
γ, deg		63.062(1)
V, Å^3	2992.4(9)	800.47(5)
Z	8	2
d_{calcd}, g cm^{-3}	1.794	1.735
μ, mm^{-1}	1.856	1.737
$F(000)$	1600	416
cryst dimens, mm	0.28 × 0.39 × 0.42	0.40 × 0.36 × 0.35
θ range, deg	1.87−25.00	1.75−23.38
no. of reflns collected	6601	2960
no. of indept reflns	5259 (R_{int} = 0.0385)	2119 (R_{int} = 0.0537)
data/restraints/ parameters	5258/0/399	2119/0/208
GOF on F^2	0.875	1.109
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0454$, $R_{2w} = 0.0987$	$R_1 = 0.0401$, $R_{2w} = 0.1096$
R indices (all data)	$R_1 = 0.0819$, $R_{2w} = 0.1097$	$R_1 = 0.0418$, $R_{2w} = 0.1125$

from η^6- to η^4-bonding. Application of the broad features of this chemistry to the thiophene reactions presently under consideration suggests as a plausible possibility that initial electron transfer to **3** generates (η^4-thiophene)-$Mn(CO)_3^-$, which attacks and displaces the thiophene from **3** to give a bimetallic intermediate that ultimately transforms to **4**. The known[1d,11] ease with which thiophenes can bind to a metal in an η^4-fashion with a concomitant increase in the nucleophilicity of the (nonplanar) sulfur atom lends credence to this possibility.

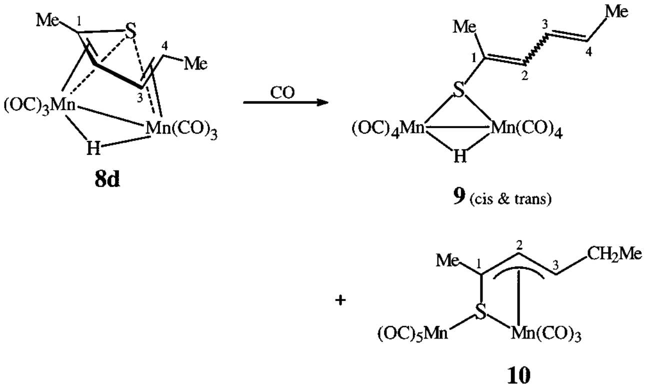
Complex **4d** was found to be unreactive toward triflic acid, from which one may conclude that the sulfur is essentially nonbasic. This is not surprising since the sulfur in **4d** is, in effect, three-coordinate. (Quite different behavior is obtained with the manganese metallathiacycle analog of benzothiophene.[7]) Reaction of **4d** with $[Bu_4N][BH_4]$ in CH_2Cl_2 occurred cleanly to afford a hydride addition product, tentatively assigned structure **7** based on spectroscopic data.



8d

Figure 2. Crystal structure of **8d**. Selected bond distances (Å) and angles (deg) are Mn1−Mn2 2.817(1), Mn1−S1 2.303(1), Mn2−S1 2.317(1), Mn1−H1 1.665(39), Mn2−H2 1.628(38), Mn1−C2 2.159(4), Mn1−C3 2.205(4), Mn2−C4 2.256(4), Mn2−C5 2.307(4), S1−C2 1.756(4), C2−C3 1.378(5), C3−C4 1.467(5), C4−C5 1.373(5), C5−C6 1.503(6), C2−C7 1.503(5); Mn1−S1−Mn2 75.16(4), Mn1−H1−Mn2 118(2), S1−Mn1−Mn2 52.65(3).

Scheme 2



Hydrogenation Reactions of Complex 4. The unsubstituted complex **4a** failed to react with H_2 at 500 psi and 80 °C over 24 h. Increasing the temperature to 110 °C led to uncharacterized decomposition. In contrast, under the same experimental conditions (500 psi, 80 °C, 24 h), **4b** converted in 61% yield to the bridging hydride complex **8b**, as shown in Scheme 1. Similarly, hydrogenation of **4d** gave **8d** (81% yield) at temperatures as low as 60 °C. The X-ray structure of **8d** is illustrated in Figure 2. The bridging diene thiolate ligand is bonded to each manganese through the sulfur and a carbon−carbon double bond. In the presence of CO at 500 psi, **8d** reacted as illustrated in Scheme 2; complex **9** results from simple CO substitution for the diene part of the thiolate ligand and was formed as a 1:1 mixture of cis:trans isomers. The formation of **10** is more complicated and features a hydride migration to C4. The structure of **10** was verified by X-ray diffraction (Figure 3, Table 2). The relative amounts of **9** and **10** formed were found to depend markedly on the temperature. Thus, the **9**:**10** ratio varied from 10:1 at 80 °C to 0.4:1 at 110 °C (see Experimental Section).

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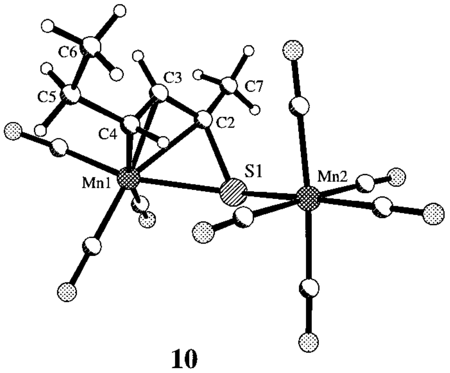


10

Figure 3. Crystal structure of **10**. Selected bond distances (Å) and angles (deg) are Mn1−S1 2.352(2), Mn2−S1 2.441(2), Mn1−C2 2.097(5), Mn1−C3 2.118(5), Mn1−C4 2.174(5), S1−C2 1.781(6), C2−C3 1.401(8), C3−C4 1.392(7), C4−C5 1.508(8), C5−C6 1.510(9), C2−C7 1.507(8); Mn1−S1−Mn2 134.28(7), Mn1−S1−C2 59.1(2), C2−C3−C4 123.7(5), C3−C2−C7 122.7(5), C3−C4−C5 120.3(5).

Table 2. Crystallographic Data for Complexes 8d and 10

	8d	**10**
formula	$C_{12}H_{10}Mn_2O_6S$	$C_{14}H_{10}Mn_2O_8S$
fw	392.14	448.16
temperature	298	298
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P1$
a, Å	14.1457(3)	9.1376(2)
b, Å	6.7369(1)	13.1185(1)
c, Å	31.9820(7)	16.8912(4)
α, deg		81.093(1)
β, deg	92.127(1)	88.082(1)
γ, deg		69.679(1)
V, Å^3	3045.73(10)	1875.41(6)
Z	8	4
d_{calcd}, g cm^{-3}	1.794	1.587
μ, mm^{-1}	1.815	1.493
F(000)	1568	896
cryst dimens, mm	0.10 × 0.24 × 0.34	0.15 × 0.26 × 0.28
θ range, deg	1.89−24.72	1.22−23.29
no. of reflns collected	10637	7953
no. of indept reflns	4951 ($R_{int} = 0.0449$)	5144 ($R_{int} = 0.0393$)
data/restraints/ parameters	4951/0/387	5132/6/450
GOF on F^2	1.121	1.162
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0442$, $R_{2w} = 0.1086$	$R_1 = 0.0496$, $R_{2w} = 0.1095$
R indices (all data)	$R_1 = 0.0521$, $R_{2w} = 0.1149$	$R_1 = 0.0633$, $R_{2w} = 0.1274$

Exposure of pure samples of **9** and **10** to CO (acetone solution, 500 psi, 100 °C) gave no reaction with the former (3 h) and $Mn_2(CO)_{10}$ with the latter (12 h), suggesting that **9** and **10** are formed via distinctly separate pathways and do not interconvert.

The reaction of **4b** or **4d** with H_2 results in hydrogenolysis of the Mn−C4 bond and loss of a CO ligand. Significantly, it was found that hydrogenation of **4d** was *completely inhibited* when the H_2 contained 5% CO. One interpretation of these results is that rate-limiting CO dissociation from the $Mn(CO)_4$ moiety occurs prior to oxidative addition of H_2 at this center, which is then followed by reductive elimination of C4-H and rearrangement to the structure shown. The observed reactivity of **4** with hydrogen follows the order **4d** > **4b** >> **4a**. It is likely that this order is due mainly to steric constraints that are relaxed upon CO dissociation as **4** converts to **8**.

Table 3. Isolated Yields of the Products of Hydrogenation Reactions of 6 and Related Complexes (Scheme 3)

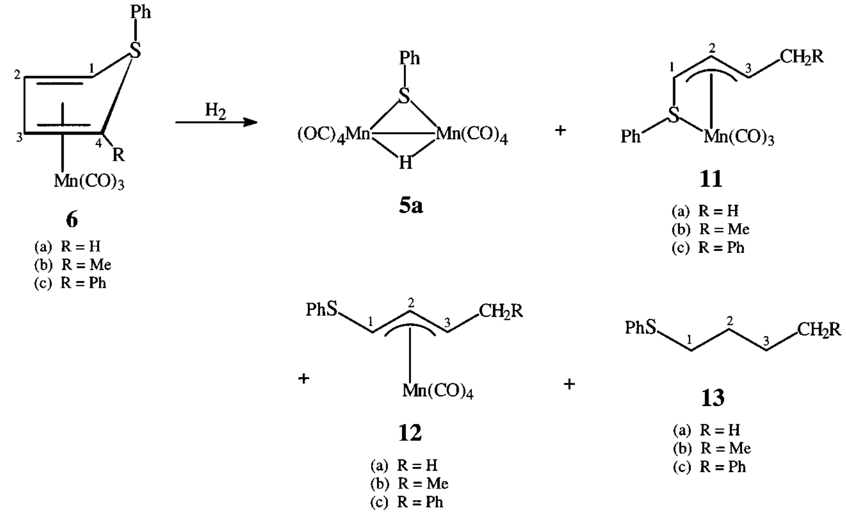
reactant	solvent	reaction conditions (temp (°C), pressure (psi), time (h))	isolated yields (%)			
			5a	**11**	**12**	**13**
6a	CH_2Cl_2	45, H_2 (700), 24	48	23	6	7
6b	CH_2Cl_2	45, H_2 (700), 24	5	23	8	34
6c	CH_2Cl_2	45, H_2 (700), 24	18	39	3	
6a	THF	25, H_2 (700), 96		60	14	
6b	THF	25, H_2 (700), 96		69	4	
6c	THF	25, H_2 (700), 96		63	10	
6a	CH_2Cl_2	25, H_2 (500), CO (250), 36			95	
5a	CH_2Cl_2	40, H_2 (450), CO (150), 24	no reaction			
11a−c	CH_2Cl_2	25, CO (450), 24			>90	
11a	CH_2Cl_2	40, H_2 (600), 120	8	21	19	25[a]
11c	CH_2Cl_2	80, H_2 (700), 48				90

[a] Also isolated from this reaction was a 16% yield of PhSSPh.

Catalytic HDS involves several essential steps: (1) cleavage and eventual hydrogenolysis of the C−S bonds, generally with concomitant hydrogenation of olefinic bonds, (2) extraction of the sulfur from metal-containing intermediates, and (3) recycling of the catalyst. With thiophene analogs, a number of metal fragments are known to insert into C−S (and/or C−H) bonds to give **2** or related species.[1−3] The metals most commonly utilized for this process are the heavier transition metals: Ru, Rh, W, Ir, and Pt. Studies with bimetallic systems[2c,g,h,3c,e,g,j] led to suggestions that C−S bond cleavage (and desulfurization) is facilitated by the presence of two metals, perhaps in analogy to the industrial Mo/Co HDS catalyst. Reactions **3** + e^- → **4**, **4** + H_2 → **8**, and **8** + CO → **9** + **10** provide evidence that electron transfer and availability of bimetallic sites play a role in the ring opening as well as subsequent hydrogenolysis and desulfurization of thiophene. Complexes **8** and **9**, which feature bridging hydride and thiolate ligands, may be of general significance in this regard. Thus, the $Mn_2(H)(SR)$ structural unit found in **8** and **9** is analogous to two others recently reported to occur with heavier transition metal systems in model HDS studies: RhW(H)(SR)[8] and Ir_2(H)(SR).[3j] Bimetallic intermediates of this type may be present on the heterogeneous HDS catalyst surfaces.[2c,8]

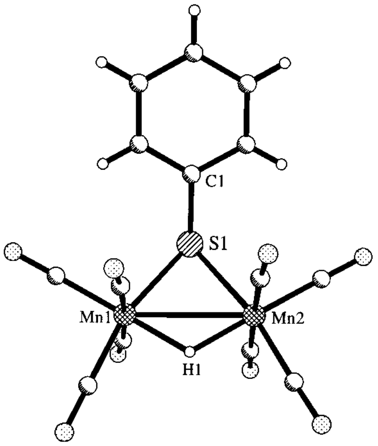
Hydrogenation and Related Reactions of Complexes 6a−c. It was demonstrated[6b,c] previously that a range of nucleophiles add to the thiophene ring in **3**. The site of attack is most often a carbon atom, but in some cases nucleophilic addition occurs at the sulfur to afford neutral zwitterionic complexes such as **6**. In the present work, the reaction of **6** with hydrogen was examined. The results are summarized in Scheme 3 and tabulated in Table 3. Hydrogenations were performed in two solvents—CH_2Cl_2 and THF. In all cases, regioselective hydrogenolysis of the S−C4 bond occurred to give substantial amounts of **11** and **12**. In addition, in CH_2Cl_2, there was partial desulfurization to the bridging hydride complex **5a** as well as demetalation to the alkyl phenyl sulfide **13**. The bimetallic complex **5a** contains the $Mn_2(H)(SR)$ structural unit and is very similar to **8** and **9**, which were obtained from hydrogenation of bimetallic **4**. The structure of **5a** was confirmed by X-ray diffraction (Figure 4, Table 4). Complex **5a** proved to be unreactive toward a mixture of H_2 and CO over 24 h (Table 3) and probably constitutes a thermodynamic sink in the chemistry depicted in Scheme

Scheme 3



3. When **6a** was reacted with H_2 (500 psi) in the presence of CO (250 psi), essentially complete conversion to **12a** took place. The η^4-species **11** readily underwent displacement of the sulfur ligand to give **12** when treated with CO (450 psi) for 24 h. Similarly, the sulfur in **11a** was cleanly substituted by $P(OEt)_3$ when reacted at room temperature for 30 min. Under N_2 in THF, **12** very slowly lost CO and reverted back to **11**; the **12a** → **11a** conversion was more conveniently and rapidly effected by reacting **12a** with Me_3NO. (Crystal structure of **12c** is shown in Figure 5.)

In order to further investigate the regioselectivity of hydrogenolysis of the S−C bond, complexes **14b,c** were prepared (Chart 2). Both were characterized by an X-ray crystal structure determination. The structure of **14c** is shown in Figure 6 (see also Table 5). Treatment of **14** with H_2 (600 psi) at 25 °C proceeded very much as observed for **6** (Scheme 3). Thus, **5a** was formed, along with products analogous to **11**−**13**. With **14c** the S−C scission occurred at S−C4 to give **15**, but with **14b** bond cleavage occurred predominantly at S−C1 to yield **16**. This suggests, as one might expect, that the electronic effect of substituents at C2 and C3 can determine which S−C bond is broken.



5a

Figure 4. Crystal structure of **5a**. Selected bond distances (Å) and angles (deg) are Mn1−Mn2 2.8939(5), Mn1−S1 2.3313(7), Mn2−S1 2.3276(7), Mn1−H1 1.789(27), Mn2−H1 1.689(26), S1−C1 1.792(3); Mn1−S1−Mn2 76.80(2), Mn1−H1−Mn2 117(1), S1−Mn1−Mn2 51.54(2).

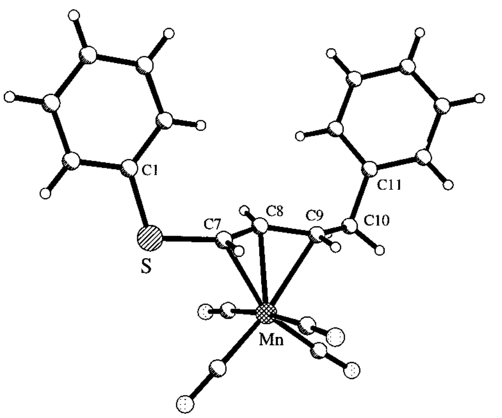
Table 4. Crystallographic Data for Complexes 5a and 12c

	5a	12c
formula	$C_{14}H_6Mn_2O_8S$	$C_{20}H_{15}MnO_4S$
fw	444.13	406.32
temperature	298	293
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	9.1614(2)	10.684(2)
b, Å	13.0295(1)	10.789(2)
c, Å	14.2989(2)	17.160(2)
α, deg		
β, deg	90.989(1)	103.336(14)
γ, deg		
V, $Å^3$	1706.58(5)	1924.7(6)
Z	4	4
d_{calcd}, g cm^{-3}	1.729	1.402
μ, mm^{-1}	1.640	0.815
$F(000)$	880	832
cryst dimens, mm	0.25 × 0.38 × 0.40	0.40 × 0.35 × 0.30
θ range, deg	2.11−23.25	2.25−24.93
no. of reflns collected	6465	2131
no. of indept reflns	2353 ($R_{int} = 0.0400$)	2024 ($R_{int} = 0.0353$)
data/restraints/ parameters	2353/0/230	2024/0/235
GOF on F^2	0.986	1.120
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0314$, $R_{2w} = 0.0772$	$R_1 = 0.0486$, $R_{2w} = 0.1177$
R indices (all data)	$R_1 = 0.0351$, $R_{2w} = 0.0790$	$R_1 = 0.0529$, $R_{2w} = 0.1211$

A plausible (partial) mechanism for the hydrogenation of **6** is given in Scheme 4. In this mechanism, slippage from η^4- to η^2-bonding of the thiophene ring permits oxidative addition of H_2. The zwitterionic nature of **6**, with the negative charge located on the metal, should facilitate this process. Subsequent hydride migration and S−C4 bond cleavage generate the allylic complex **11**. Complexes **12** and **13** (Scheme 3) can easily be envisioned to arise from further reactions of **11**, as the last two entries in Table 3 indicate.

Conclusions

In this study we report that coordination of $Mn(CO)_3^+$ to the thiophene ring to give **3** results in activation of a C−S bond to reductive cleavage, affording the bimetallic **4**. Reaction of **4** with H_2 results in hydrogenolysis of the Mn−C σ-bond and opening of the thiophene ring to afford a dimanganese species (**8**) containing bridging



12c

Figure 5. Crystal structure of **12c**. Selected bond distances (Å) and angles (deg) are Mn−C7 2.183(5), Mn−C8 2.101(4), Mn−C9 2.250(5), S−C7 1.750(5), S−C1 1.767(5), C7−C8 1.398(6), C8−C9 1.389(6), C9−C10 1.513(6), C10−C11 1.519(6); S−C7−C8 120.4(4), C7−C8−C9 124.6(4), C8−C9−C10 123.9(4).

Chart 2

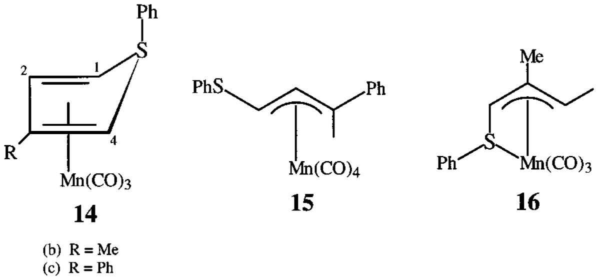
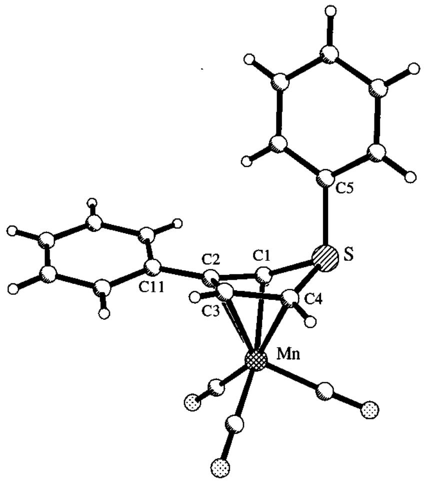


Table 5. Crystallographic Data for Complexes 14b,c

	14b	14c
formula	$C_{14}H_{11}MnO_3S$	$C_{19}H_{13}MnO_3S$
fw	314.23	376.29
temperature	293	293
wavelength, Å	0.71073	0.71073
cryst syst	triclinic	triclinic
space group	P1	P1
a, Å	8.2710(14)	8.6656(6)
b, Å	8.7630(6)	10.4706(9)
c, Å	9.7890(6)	10.9134(8)
α, deg	100.510(4)	115.652(6)
β, deg	92.419(13)	95.117(6)
γ, deg	94.040(6)	104.313(6)
V, Å^3	694.76(13)	842.81(11)
Z	2	2
d_{calcd}, g cm^{-3}	1.502	1.483
μ, mm^{-1}	1.099	0.920
F(000)	320	384
cryst dimens, mm	0.40 × 0.20 × 0.20	0.60 × 0.30 × 0.30
θ range, deg	2.12−24.97	2.12−25.97
no. of reflns collected	2617	3171
no. of indept reflns	2431 ($R_{int} = 0.0100$)	2956 ($R_{int} = 0.0081$)
data/restraints/ parameters	2430/0/172	2954/0/217
GOF on F^2	1.112	1.114
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0548$, $R_{2w} = 0.1541$	$R_1 = 0.0566$, $R_{2w} = 0.1419$
R indices (all data)	$R_1 = 0.0687$, $R_{2w} = 0.1671$	$R_1 = 0.0689$, $R_{2w} = 0.1535$

hydride and thiolate ligands. In a complementary series of reactions, the zwitterionic complex **6**, formed via nucleophilic addition of a phenyl group to the sulfur in **3**, was found to undergo regioselective hydrogenolysis of a C−S bond.



14c

Figure 6. Crystal structure of **14c**. Selected bond distances (Å) and angles (deg) are Mn−C1 2.115(3), Mn−C2 2.112(3), Mn−C3 2.090(3), Mn−C4 2.110(4), C1−C2 1.443(4), C2−C3 1.402(4), C3−C4 1.429(5), S−C1 1.756(3), S−C4 1.756(4), S−C5 1.806(4), C2−C11 1.478(4); C1−S−C4 86.1(2), C5−S−C1 109.2(2), C5−S−C4 109.4(2), S−C1−C2 110.7(2), C1−C2−C3 109.0(3), C2−C3−C4 111.6(3), C3−C4−S 110.0(2).

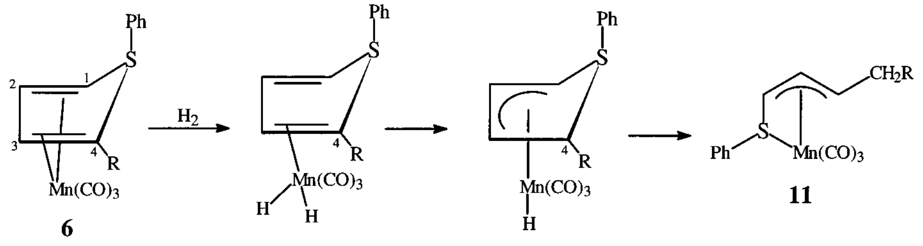
Experimental Section

Crystal Structure Determinations. The crystal structures of **4b**,**d**, **5a**, **8d**, **10,** and **14b** were determined with a Siemens P4 diffractometer equipped with a CCD area detector and controlled by SMART, version 4, software. (The structures of **12c** and **14c** were determined with an Enraf-Nonius CAD4 diffractometer.) 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 was 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. All of the crystals reported herein were grown from pentane solutions.

Synthesis of [(η^5-R$_1$,R$_2$,R$_3$-thiophene)Mn(CO)$_3$]BF$_4$ (3a−e). These complexes were prepared by a procedure previously described for **3a**,**d**.[6] In a typical synthesis, $AgBF_4$ (1.1 mmol) was added to $Mn(CO)_5Br$ (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. At this stage 1.5 mmol of the thiophene of interest (**1a**−**e**) was added and the mixture refluxed for 3 h. The volume was then reduced to 5 mL, and the product 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 **3b**: yield 63%. IR (acetone): ν_{CO} = 2072 (s), 2008 (s, br) cm^{-1}. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.05 (d, *J* = 3.7 Hz, H4), 6.94 (t, *J* = 3.4 Hz, H3), 6.80 (d, *J* = 2.9 Hz, H2), 2.67 (s, Me). Anal. Calcd for $C_8H_6O_3Mn_1S_1B_1F_4$: C, 29.66; H, 1.87. Found: C, 29.71; H, 1.88. For **3c**: yield 68%. IR (acetone): ν_{CO} = 2072 (s), 2014 (s), 2000 (s) cm^{-1}. ^{1}H NMR (250 MHz, $CD_3C(O)CD_3$): δ 7.04 (br, 1H), 6.94 (br, 1H), 6.81 (br, 1H), 2.67 (s, Me). Anal. Calcd for $C_8H_6O_3Mn_1S_1B_1F_4$: C, 29.66; H, 1.87. Found: C, 29.38; H, 1.80. For **3e**: yield 82%. IR (CD_2Cl_2): ν_{CO} = 2064 (s), 2010 (s) cm^{-1}. ^{1}H NMR (250 MHz, CD_3NO_2): δ 7.72 (m, 2H, Ph), 7.66 (m, 1H, Ph), 7.59 (m, 2H, Ph), 7.08 (s, H4), 6.90 (m, H2,3). Anal. Calcd for $C_{13}H_8O_3Mn_1S_1B_1F_4$: C, 40.43; H, 2.07; S, 8.31. Found: C, 40.24; H, 1.91; S, 8.58.

Synthesis of Complexes 4a−d. Cobaltocene (0.31 mmol) and [**3b**−**d**]BF$_4$ (0.30 mmol) were combined in CH_2Cl_2, and the

Scheme 4



mixture was stirred at room temperature for 20 min under a CO atmosphere. The solvent was removed *in vacuo* and the product extracted with CH_2Cl_2. The CH_2Cl_2 solution was then passed through neutral alumina (deactivated with 10% water) with CH_2Cl_2 as eluant. After the solvent was removed under vacuum, the resulting orange-yellow solid was washed with pentane and dried. For **4b**: yield 65%. IR (hexanes) $\nu_{CO} = 2080$ (m), 2036 (vs), 1997 (s), 1991 (vs), 1975 (m), 1961 (vs) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ 6.74 (d, $J = 5.5$ Hz, H2), 5.92 (dd, $J = 10$, 5.5 Hz, H3), 5.00 (d, $J = 10.5$ Hz, H4), 2.45 (s, Me). Anal. Calcd for $C_{12}H_6O_7Mn_2S_1$: C, 35.67; H, 1.50. Found: C, 35.81; H, 1.44. HR MS: M^+ (*m*/*z*) calcd 403.8596, obsd 403.8607. Spectral data for **4c**: yield 72%. IR (hexanes): $\nu_{CO} = 2079$ (m), 2037 (vs), 1998 (s), 1991 (vs), 1977 (m), 1960 (vs) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ 6.40 (s, H1), 6.26 (d, $J = 10$ Hz, H3), 5.31 (d, $J = 10$ Hz, H4), 2.28 (s, Me). Anal. Calcd for $C_{12}H_6O_7Mn_2S_1$: C, 35.67; H, 1.50. Found: C, 35.71; H, 1.46. MS FAB: 404 (M^+), 348 ($M^+ - 2CO$), 320 ($M^+ - 3CO$), 292 ($M^+ - 4CO$), 264 ($M^+ - 5CO$). HR MS: M^+ (*m*/*z*) calcd 403.8596, obsd 403.8605. For **4d**: yield 84%. IR (hexanes): $\nu_{CO} = 2079$ (m), 2033 (vs), 1995 (s), 1991 (vs), 1969 (m), 1958 (vs) cm^{-1}. ^1H NMR (250 MHz, $CD_3C(O)CD_3$): δ 7.05 (d, $J = 5.5$ Hz, H2), 5.62 (d, $J = 5$ Hz, H3), 2.52 (s, Me), 2.22 (s, Me). Anal. Calcd for $C_{13}H_8O_7Mn_2S_1$: C, 37.34; H, 1.93. Found: C, 37.30; H, 1.90. MS FAB: 418 (M^+), 362 ($M^+ - 2CO$), 334 ($M^+ - 3CO$), 306 ($M^+ - 4CO$). HR MS: M^+ (*m*/*z*) calcd 417.8753, obsd 417.8754.

Addition of Hydride to Complex 4d. Bu_4NBH_4 (0.06 mmol) was added to **4d** (0.05 mmol) in CH_2Cl_2 (8 mL) at 0 °C under N_2. The reaction mixture was stirred for 20 min as the temperature increased to ca. 25 °C. IR spectra at this point indicated that there was a clean conversion to a single product. The resulting orange solution was concentrated and chromatographed through an alumina column with CH_2Cl_2 as the eluant. Solvent removal afforded a thermally unstable product assigned structure **7** based on NMR data. For **7**: yield 87%. IR (CH_2Cl_2): $\nu_{CO} = 2079$ (m), 1971 (vs), 1950 (br, s), 1894 (br, s), 1863 (m, sh) cm^{-1}. ^1H NMR (250 MHz, $CD_3C(O)CD_3$): δ 4.90 (d, $J = 8.3$ Hz, H3), 3.79 (dd, $J = 8.2$, 4.4 Hz, H2), 3.44 (m, 8H, Bu), 3.28 (m, H1-exo), 2.48 (s, Me4), 1.88 (d, $J = 7.4$ Hz, Me1), 1.80 (m, 8H, Bu), 1.42 (m, 8H, Bu), 0.97 (m, 12H, Bu).

Hydrogenation of 4b,4d. The complex (0.1 mmol) was dissolved in CH_2Cl_2 (10 mL) and placed in a Parr high-pressure bomb reactor. The reactor was purged (×2) with H_2, refilled with H_2 (500 psi), and placed in an oil bath at typically 90 °C for 18 h (**4b**) or 4 h (**4d**). The bomb was immediately cooled to room temperature and adjusted to atmospheric pressure. The solution was concentrated *in vacuo*, and purification was performed on silica gel TLC with pentane as the eluant. The products **8b**,**d** were crystallized from a concentrated pentane solution at −20 °C. For **8b**: yield 61%. IR (hexanes): $\nu_{(CO)} = 2054$ (s), 2022 (s), 1983 (s), 1969 (s), 1956 (s), 1950 (s) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ 4.91 (m, H2), 3.94 (dd, $J = 12$, 8 Hz, H3), 2.27 (d, $J = 8$ Hz, H4), 2.21 (s, Me), 1.76 (d, $J = 13$ Hz, H4′), −14.51 (s, -H-). For **8d**: yield 81%. IR (hexanes): $\nu_{(CO)} = 2051$ (s), 2019 (s), 1979 (s), 1964 (s), 1951 (s), 1948 (s) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ 4.73 (s, H2), 3.84 (d, $J = 12$ Hz, H3), 2.64 (m, $J = 12$, 6 Hz, H4), 2.20 (s, Me), 1.50 (d, $J = 6$ Hz, Me), −14.48 (s, -H-). Anal. Calcd for $C_{12}H_{10}O_6Mn_2S_1$: C, 36.75; H, 2.57. Found: C, 36.68; H, 2.60. FAB MS: 392 (M^+), 336 ($M^+ - 2CO$), 308 ($M^+ - 3CO$), 280 ($M^+ - 4CO$). HR MS: M^+ (*m*/*z*) calcd 391.8965, obsd 391.8960.

Reaction of Complex 8d with CO. In a typical experiment, **8d** was dissolved in acetone (10 mL) and placed in the bomb reactor, which was purged (×2) with CO (30 atm), refilled with CO (30 atm), and placed in an oil bath at variable temperatures for varying times. The bomb was immediately cooled to room temperature and adjusted to atmospheric pressure. The solution was concentrated *in vacuo*; separation and purification of the products (**9** and **10**) was performed on silica gel TLC with pentane as the eluant. The product ratio **9**:**10** depended on temperature and time in the following manner: 10:1, 80 °C, 14 h; 5:3, 95 °C, 2 h; 2:5, 110 °C, 0.5 h. The combined yield of **9** and **10** was in the range 70−75%. For **9:** obtained as a 1:1 mixture of *cis* and *trans*. IR (hexanes): $\nu_{CO} = 2098$ (w), 2067 (s), 2014 (s), 2005 (s), 2000 (s), 1974 (s) cm^{-1}. IR (CH_2Cl_2): $\nu_{CO} = 2098$ (w), 2068 (s), 2011 (vs), 2000 (s, br), 1969 (s, br) cm^{-1}. (The IR spectra of the *cis*- and *trans*-isomers are indistinguishable.) ^1H NMR (250 MHz, CD_2Cl_2): *cis*-isomer δ 6.94 (dd, $J = 14.4$, 11 Hz, H3), 6.42 (d, $J = 10.9$ Hz, H2), 5.81 (m, $J = 14.4$, 6.6 Hz, H4), 1.69 (d, $J = 6.6$ Hz, Me), 1.26 (s, Me), −16.07 (-H-); *trans*-isomer δ 6.83 (dd, $J = 15.9$, 9.6 Hz, H3), 6.07 (d, $J = 15.9$ Hz, H2), 5.62 (m, H4), 2.29 (s, Me), 2.09 (d, $J = 10.6$ Hz, Me), −16.14 (-H-). Anal. Calcd for $C_{14}H_{10}O_8Mn_2S_1$: C, 37.52; H, 2.25. Found: C, 37.41; H, 2.30. MS FAB: 448 (M^+), 392 ($M^+ - 2CO$), 336 ($M^+ - 4CO$), 280 ($M^+ - 6CO$). HR MS: M^+ (*m*/*z*) calcd 447.8858, obsd 447.8858 For **10**, IR (hexanes): $\nu_{CO} = 2115$ (m), 2036 (vs), 2004 (vs), 1933 (s), 1918 (s) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ 5.11 (d, $J = 9.8$ Hz, H2), 2.51 (s, Me), 2.17 (m, $-CH_2-$), 1.27 (t, $J = 7.4$ Hz, Me), 1.10 (dt, $J = 9.7$, 7.4 Hz, H3). Anal. Calcd for $C_{14}H_{10}O_8Mn_2S_1$: C, 37.52; H, 2.25. Found: C, 37.68; H, 2.44. MS FAB: 448 (M^+), 420 ($M^+ - CO$), 364 ($M^+ - 3CO$), 264 ($M^+ - 7CO$). HR MS: M^+ (*m*/*z*) calcd 447.8858, obsd 447.8839.

Synthesis and Hydrogenation Reactions of Complexes 6a−c. The following typical procedure was used to synthesize **6**. To a solution of **3** (0.40 mmol) in THF (10 mL), was added PhMgBr (2.0 equiv) at 0 °C under N_2. The reaction mixture was stirred for 30 min and allowed to warm to room temperature. To this solution were added diethyl ether (50 mL) and water (30 mL). The organic layer was collected, dried over $MgSO_4$, concentrated, and chromatographed on a silica gel column with *n*-hexane and diethyl ether (2:1) as eluant to give the product as a yellow solid. Complex **6a** was reported previously.[6b] IR (acetone solution evaporated onto a NaCl plate): $\nu_{CO} = 1994$ (s), 1885 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44 (m, 5H), 5.36 (s, 2H), 2.79 (s, 2H). Anal. Calcd for $C_{13}H_9O_3MnS_1$: C, 52.01; H, 3.02; S, 10.66. Found: C, 52.13; H, 3.11; S, 10.65. For **6b**: yield 45%. IR (NaCl): $\nu_{CO} = 1987$ (s), 1885 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.5−7.2 (m, 5H), 5.32 (t, $J = 2.8$ Hz, H2), 4.98 (dd, $J = 1.2$, 2.7 Hz, H3), 2.65 (dd, $J = 1.0$, 2.7 Hz, H1), 1.73 (s, Me). HR MS: M^+ (*m*/*z*) calcd 313.9809, obsd 313.9750. For **6c**: yield 34%. IR ($CDCl_3$): $\nu_{CO} = 2000$ (s), 1912 (s), 1889 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4−7.1 (m, 2Ph), 5.72 (dd, $J = 1.2$, 2.9 Hz, H3), 5.42 (t, $J = 2.9$ Hz, H2), 2.94 (dd, $J = 1.2$, 2.7 Hz, H1). Anal. Calcd for $C_{19}H_{13}O_3MnS_1$: C, 60.64; H, 3.46; S, 8.53. Found: C, 60.69; H, 3.65; S, 8.88.

Hydrogenation reactions of **6a−c** were performed in THF at room temperature and in CH_2Cl_2 at various temperatures.

A steel pressure bomb was used, and the total pressure of H_2 was in the range 600−750 psi. A typical procedure was as follows: complex **6a**−**c** (0.80 mmol) in THF (10 mL) was placed in a 100-mL volume bomb reactor. The reactor was purged with N_2 for 10 min and then pressurized with H_2 to 700 psi. The reaction was stirred for 4 days at room temperature. After releasing the H_2, the solution was filtered and concentrated. Product separation and purification was achieved using preparative silica gel TLC with Et_2O:hexanes (1:10) as eluant or silica gel flash column chromatography with hexane as eluant. Analogous experiments were also performed wth CH_2Cl_2 as the solvent. In these cases, the solvent was stripped after reaction and the resultant mixture chromatographed on a silica gel column. The phenyl alkyl sulfide (**13**) shown in Scheme 2 as well as PhSSPh (Table 3) were isolated and identified by ^1H NMR and MS. The organometallic products **11a**−**c** were obtained as a roughly 1:1 mixture of diastereomers (A + B) resulting from *exo*- and *endo*-orientations of the phenyl group on the chiral sulfur atom.

For **5a**, IR (hexanes): ν_{CO} = 2100 (w), 2070 (m), 2020 (vs), 2004 (s), 1974 (s, br) cm^{-1}. IR (CH_2Cl_2): ν_{CO} = 2102 (w), 2072 (s), 2019 (vs), 2002 (s), 1971 (s, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.57 (m, 2H, Ph), 7.23 (m, 3H, Ph), −15.97 (s, -H-). Anal. Calcd for $C_{14}H_6O_8Mn_2S_1$: C, 37.86; H, 1.36; S, 7.22. Found: C, 38.18; H, 1.35; S, 7.26. For **11a**: A + B isomers. IR (hexanes): ν_{CO} = 2016 (s), 1938 (vs), 1927 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): A isomer δ 7.0−7.25 (m, 5H, Ph), 5.23 (m, H1,2), 1.67 (d, J = 6.3 Hz, Me), 1.50 (m, H3); B isomer δ 7.26−7.45 (m, Ph), 5.47 (dd, J = 3.8, 1.0 Hz, H1), 5.04 (dd, J = 9.5, 3.8 Hz, H2), 1.72 (d, J = 5.9 Hz, Me), 1.32 (m, H3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.50, 18.98, 54.03, 57.76, 66.17, 69.42, 91.47, 101.11, 128.82, 129.11, 129.37, 129.62, 129.81, 130.24, 141.30. Anal. Calcd for $C_{13}H_{11}O_3Mn_1S_1$: C, 51.66; H, 3.67; S, 10.6. Found: C, 51.44; H, 3.74; S, 10.9. HR MS: M^+ (m/z) calcd 301.9816, obsd 301.9818. For **11b**: A + B isomers. IR (hexanes): ν_{CO} = 2015 (s), 1939 (vs), 1927 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): A isomer δ 7.0−7.27 (m, Ph), 5.24 (m, H1,2), 1.97 (m, CH_2), 1.47 (dt, J = 9.5, 6.7 Hz, H3), 0.97 (t, J = 7.4 Hz, Me); B isomer δ 7.20−7.45 (m, Ph), 5.50 (d, J = 4.0 Hz, H1), 5.04 (dd, J = 9.5, 4.0 Hz, H2), 1.97 (m, CH_2), 1.30 (dt, J = 9.5, 6.7 Hz, H3), 1.18 (t, J = 7.4 Hz, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.93, 17.23, 27.13, 27.26, 54.22, 66.60, 69.78, 75.17, 90.22, 99.64, 124.81, 129.02, 129.40, 129.66, 129.97, 130.35, 141.30. Anal. Calcd for $C_{14}H_{13}O_3Mn_1S_1$: C, 53.17; H, 4.14. Found: C, 53.30; H, 4.15. HR MS: M^+ (m/z) calcd 315.9962, obsd 315.9963. For **11c**: A + B isomers. IR (hexanes): ν_{CO} = 2005 (s), 1939 (vs), 1926 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): A isomer δ 6.8−7.40 (m, Ph, Ph), 5.30 (m, H1,2), 3.38 (m, CH_2), 1.68 (m, H3); B isomer δ 7.10−7.40 (m, Ph, Ph), 5.53 (dd, J = 4.1, 1.2 Hz, H1), 5.17 (dd, J = 9.4, 4.1 Hz, H2), 3.08 (m, CH_2), 1.44 (m, H3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.39, 39.82, 55.03, 63.03, 70.50, 71.11, 90.65, 100.36, 124.93, 125.91, 126.19, 127.64, 128.11, 128.24, 128.55, 128.90, 129.14, 129.44, 129.75, 129.94, 130.21, 130.41, 142.29, 142.56. Anal. Calcd for $C_{19}H_{15}O_3Mn_1S_1$: C, 60.32; H, 4.00. Found: C, 60.60; H, 4.00. HR MS: M^+ (m/z) calcd 378.0118, obsd 378.0122.

For **12a**, IR (hexanes): ν_{CO} = 2052 (w), 1999 (s), 1976 (vs), 1960 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.15−7.38 (m, Ph), 4.90 (dd, J = 11.4, 9.5 Hz, H2), 3.08 (dq, J = 11.4, 6.0 Hz, H3), 2.96 (d, J = 9.5 Hz, H1), 1.80 (d, J = 6.0 Hz, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.65, 46.78, 63.59, 101.44, 125.62, 126.38, 128.86, 141.30. Anal. Calcd for $C_{14}H_{11}O_4Mn_1S_1$: C, 50.92; H, 3.36. Found: C, 51.20; H, 3.36. HR MS: M^+ (m/z) calcd 301.9806, obsd 301.9812. For **12b**, IR (hexanes): ν_{CO} = 2052 (w), 1999 (s), 1977 (vs), 1966 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.17−7.35 (m, Ph, Ph), 4.88 (dd, J = 11.9, 9.4 Hz, H2), 3.08 (ddd, J = 11.9, 7.2, 5.0 Hz, H3), 2.96 (d, J = 9.4 Hz, H1), 2.14 (m, -CH_2), 1.98 (m, -CH_2), 1.17 (t, J = 7.40 Hz, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.93, 27.36, 46.67, 72.07, 99.39, 125.60, 126.34, 128.88, 141.30. Anal. Calcd for $C_{15}H_{13}O_4Mn_1S_1$: C, 52.33; H, 3.81. Found: C, 52.40; H, 3.83. HR MS: M^+ (m/z) calcd 343.9911, obsd 343.9907. For **12c**, IR (hexanes): ν_{CO} = 2050 (w), 2000 (s), 1976 (vs), 1962 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.17−7.37 (m, Ph, Ph), 4.92 (t, J = 10 Hz, H2), 3.46 (dd, J = 14.0, 3.0 Hz, H3), 3.18 (m, -CH_2), 3.04 (d, J = 9.4 Hz, H1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.05, 47.64, 67.90, 100.02, 125.70, 126.40, 126.87, 128.49, 128.82, 128.93, 140.03, 140.97. Anal. Calcd for $C_{20}H_{115}O_4Mn_1S_1$: C, 59.11; H, 3.72; S, 7.89. Found: C, 58.66; H, 3.51; S, 7.62. HR MS: M^+ (m/z) calcd 378.0118, obsd 378.0117. For **13a**, ^1H NMR ($CDCl_3$): δ 7.3−7.1 (m, Ph), 2.92 (t, J = 7.4 Hz, H1), 1.63 (m, H2), 1.45 (m, H3), 0.92 (t, J = 7.4 Hz, Me). HR MS: M^+ (m/z) calcd 166.0816, obsd 166.0824.

Reaction of Complex 11a with $P(OEt)_3$. $P(OEt)_3$ (0.1 mL, 0.66 mmol) and **11a** (0.10 g, 0.33 mmol) were dissolved in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 30 min at room temperature, after which the solution was concentrated and chromatographed on silica gel with hexane as the eluant. The solvent was removed *in vacuo*, and the product, which contains a $P(OEt)_3$ group substituted for the thioether ligand, was obtained in quantitative yield. IR (hexanes): ν_{CO} = 2010 (s), 1944 (vs), 1924 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.38 (m, Ph), 7.28 (m, Ph), 7.08 (m, Ph), 4.85 (dd, J = 11.2, 8.9 Hz, H2), 4.06 (m, P-OCH_2-), 2.90 (m, H3), 2.59 (dd, J = 14.6, 8.9 Hz, H1), 1.71 (d, J = 6.1 Hz, Me), 1.29 (t, J = 7.0, P-OCH_2*Me*). Anal. Calcd for $C_{19}H_{26}O_6P_1Mn_1S_1$: C, 48.92; H, 5.60. Found: C, 48.90; H, 5.67. HR MS: M^+ (m/z) calcd 468.0560, obsd 468.0576.

Synthesis and Reactions of 14b,c. These complexes were synthesized by the same procedure used for the synthesis of **6a**−**c**. For **14b**: yield 46%. IR (hexanes): ν_{CO} = 1998, 1918, 1911 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.40 (m, Ph), 7.30 (m, Ph), 5.18 (s), 2.74 (d, J = 2.1 Hz), 2.62 (t, J = 2.7 Hz). Anal. Calcd for $C_{14}H_{11}O_3Mn_1S_1$: C, 53.51; H, 3.53. Found: C, 53.60; H, 3.50. For **14c**: yield 44%. IR (CH_2Cl_2): ν_{CO} = 1989, 1907, 1898 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.50 (m, Ph), 7.35 (m, Ph), 5.76 (dd, J = 2.7, 1.4 Hz), 3.24 (dd, J = 2.9, 1.4 Hz), 2.85 (t, J = 2.9 Hz). Anal. Calcd for $C_{14}H_{11}O_3Mn_1S_1$: C, 60.64; H, 3.46; S, 8.53. Found: C, 60.48; H, 3.41; S, 8.86. For **15**: yield 32%. IR (hexanes): ν_{CO} = 2060 (w), 2005 (s), 1972 (s), 1957 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.6−7.2 (m, 10H, Ph), 4.93 (d, J = 10.3 Hz, 1H), 3.96 (d, J = 10.3 Hz, 1H), 2.30 (s, Me). For **16**: yield 57%. IR (hexanes): ν_{CO} = 2010, 1933, 1920 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): one diastereomer δ 7.3−7.0 (m, Ph), 5.11 (s, 1H), 2.03 (s, Me), 1.61 (d, J = 6.1 Hz, Me), 1.36 (m, 1H); other diastereomer δ 7.6−7.3 (m, Ph), 5.29 (s, 1H), 2.06 (s, Me), 1.69 (d, J = 6.1 Hz, Me), 1.11 (m, 1H). Anal. Calcd for $C_{14}H_{13}O_3Mn_1S_1$: C, 53.17; H, 4.14. Found: C, 52.51; H, 3.87.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **4b**,**d**, **5a**, **8d**, **10**, **12c**, and **14b**,**c** (97 pages). Ordering information is given on any current masthead page.

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