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Models for the Homogeneous Hydrodesulfurization of Benzothiophene: Sequential Insertion of Manganese into the C(aryl)−S and C(vinyl)−S Bonds, Followed by Metallathiacycle Ring Contraction

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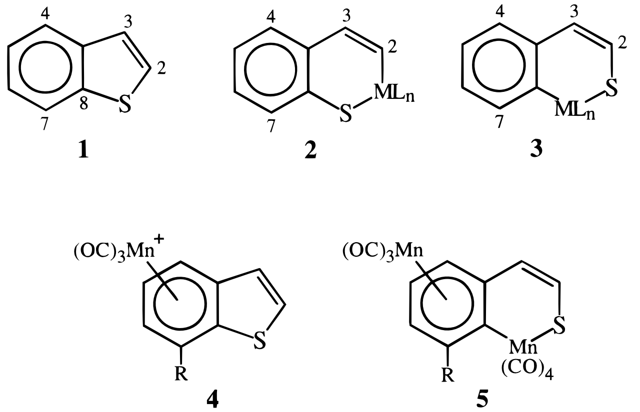
Summary: Coordination of $Mn(CO)_3{}^+$ *to the carbocyclic ring of benzothiophenes activates the C(aryl)−S bond to reductive cleavage, affording metallathiacycle* **5**. *When the 7-R substituent in* **5** *is methyl or ethyl (but not hydrogen), rapid C(vinyl)−S bond scission ensues to give isomer* **6**, *which subsequently undergoes a metallathiacycle ring contraction to yield complex* **7**.

Hydrodesulfurization (HDS) of petroleum is one of the largest volume industrial chemical processes, the main purpose of which is the removal of sulfur and conversion to H_2S.[1] Most aliphatic and acyclic sulfur compounds are adequately treated by current technology. However, unsaturated heterocycles of the thiophenic type, especially substituted benzothiophenes (BTs) and dibenzothiophenes (DBTs),[2] are resistant to the usual HDS conditions and, as a consequence, constitute much of the residual sulfur in fossil fuels. A key step in HDS is the cleavage of the C−S bonds, and this is thought[3] to be facilitated by precoordination of a metal in the catalyst to the sulfur, which is then followed by insertion into the C−S bond. In homogeneous model studies of BT (**1**), a variety of nucleophilic metal fragments have been shown[3c,d,4] to insert at the vinylic carbon−sulfur bond to afford **2**, Chart 1. The preference for cleavage at C(2), rather than at the aryl carbon−sulfur bond, C(8)−S, has been attributed[3d] to selective weakening of the C(2)−S bond via η^1-S precoordination.

Chart 1



Recent studies show that cleavage of the C(aryl)−S bond in **1** to give metallathiacycle **3** can, in fact, be accomplished by strategies based on either steric and/or electronic effects. Thus, 2-methyl-BT reacts with $Cp^*Rh(PMe_3)$ to give **2** as the kinetic product, which, due to the steric influence of the methyl group, converts upon prolonged heating to the thermodynamically favored **3**.[5] With regard to electronic effects, we have shown[6] that selective activation of the C(aryl)−S bond in **1** occurs when the $Mn(CO)_3{}^+$ fragment is precoordinated to the carbocyclic ring to give the π-bonded BT complex **4** (R = H; hereafter labeled "**4**(H)"). Chemical reduction of **4**(H) leads to rapid and high-yield formation of **5**(H), with no trace of insertion into the C(vinyl)−S bond. In a similar vein, precoordination of $Ru(C_6Me_6)^{2+}$ to **1** was also found to activate the C(aryl)−S bond.[7] The suggestion was made that C(aryl)−S bond cleavage in BT may *require* initial coordination to the carbocyclic ring and that bimetallic species such as **5**(H), produced upon electron transfer or nucleophilic attack, play an important role in subsequent hydrogenolysis and desulfurization.[6,7] Indeed, there are a number of model studies suggesting[8] that important steps in HDS chemistry of thiophenes are facilitated when two metals are available, perhaps in analogy to the industrial heterogeneous catalysts (Mo/Co, etc.).

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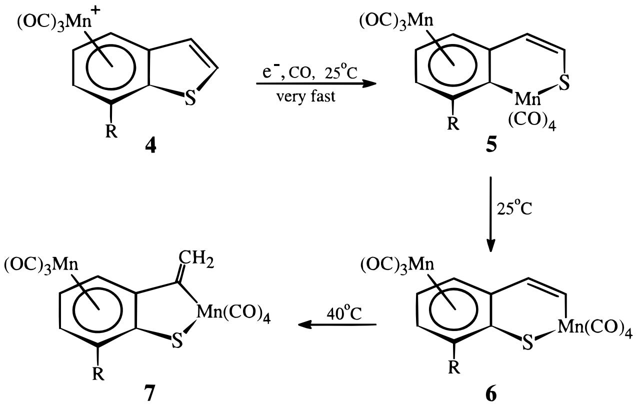
Scheme 1. Activation of Thiophenic C(aryl)−S and C(vinyl)−S Bonds and Metallathiacycle Ring Contraction



In this communication, we demonstrate that C(aryl)−S bond cleavage in **4** is the kinetically favored pathway even when the thermodynamically favored product involves C(vinyl)−S cleavage. This, as well as a novel metallathiacycle ring contraction reaction that may be of general significance in HDS chemistry, are illustrated in Scheme 1.

Benzothiophenes occurring in petroleum are generally highly substituted and, as a result, are more resistant to HDS than is unsubstituted BT. In order to probe these important "substituent" effects on C−S bond scission, we undertook a study of complexes **4** substituted at the 7-position with methyl and ethyl groups. Herein, we demonstrate that substitution at the C(7) carbon has a profound effect on the chemistry related to C−S bond activation. The manganese tricarbonyl complexes of 7-Me-BT and 7-Et-BT were readily synthesized by a standard method[9,10] in which $Mn(CO)_5Br$ in CH_2Cl_2 is treated with $AgBF_4$, followed by addition of the benzothiophene. In analogy with the previously observed facile conversion of **4**(H) to **5**(H), it was anticipated that reduction of **4**(Me) and **4**(Et) would produce the bimetallics **5**(Me) and **5**(Et), although at a lower rate reflective of steric inhibition in the vicinity of the C(aryl)−S bond. Indeed, cobaltocene reduction of **4**(Me) and **4**(Et) under CO produced the red-purple C(aryl)−S insertion products **5** in high yield, as summarized in Scheme 1.[12] However, **5**(Me) and **5**(Et) were formed as *kinetic* products which, in CH_2Cl_2 solution at room temperature, cleanly isomerized to the orange C(vinyl)−S insertion analogues **6**(Me) and **6**(Et) with a half-life of circa 6 and 0.5 h, respectively.[13] By comparison, **5**(H), which lacks a substituent at C(7), undergoes no detectable reaction in 24 h. Surprisingly, it was also found that in refluxing CH_2Cl_2 or Et_2O over 2 h **6**(Me) and **6**(Et) react further via an unprecedented metallathiacycle ring contraction to afford **7**(Me) and **7**(Et).[14]

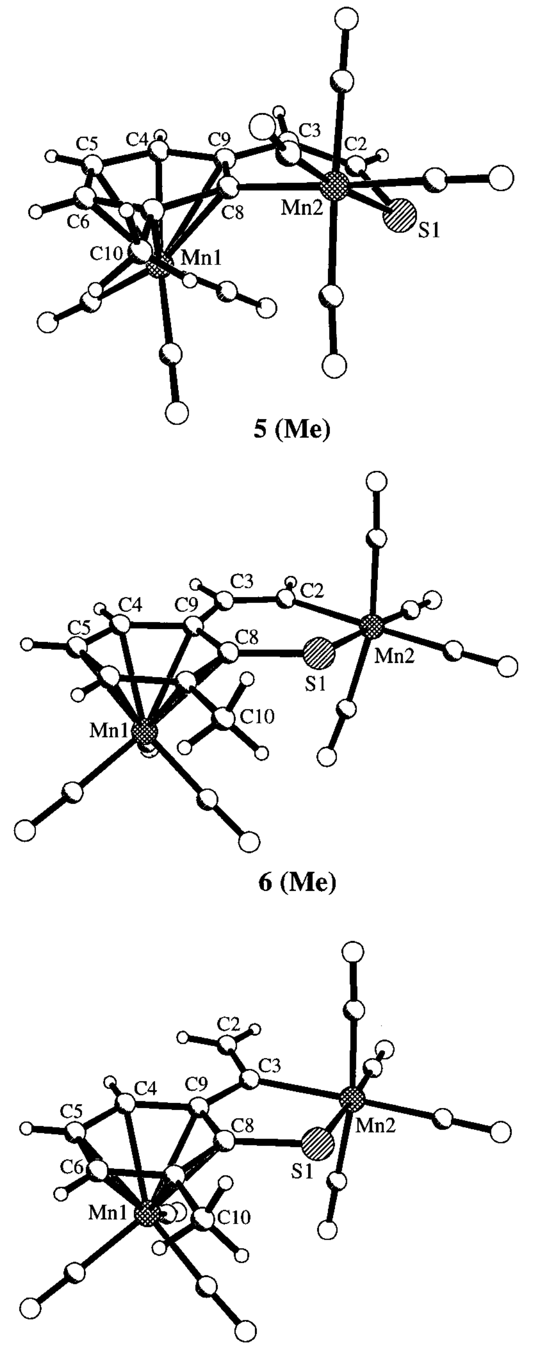


Figure 1. Crystal structures of **5**(Me), **6**(Me), and **7**(Me). Selected bond distances (Å) for **5**(Me): Mn2−C8 2.122(6), Mn2−S1 2.384(2), S1−C2 1.694(9), C2−C3 1.358(11), C3−C9 1.485(10). Bond distances (Å) for **6**(Me): Mn2−C2 2.039(4), Mn2−S1 2.348(1), S1−C8 1.722(4), C2−C3 1.333(5), C3−C9 1.453(5). Bond distances (Å) for **7**(Me): Mn2−C3 2.105(4), Mn2−S1 2.365(1), S1−C8 1.738(3), C2−C3 1.310(6), C3−C9 1.526(5).

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(10) **4**(R): All reaction vessels were flame dried under nitrogen. $AgBF_4$ (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 7-Me-BT or 7-Et-BT, prepared by a published method,[11] 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 diethyl ether. Reprecipitation from CH_2Cl_2 with diethyl ether afforded pure product as a bright yellow powder. **4**(Me)·BF_4: yield 79%; IR (CH_2Cl_2) ν_{CO} 2074 (s), 2012 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.30 (d, J = 5.6 Hz, H2), 7.69 (d, J = 5.6 Hz, H3), 7.33 (d, J = 6.8 Hz, H4), 6.59 (t, J = 6.5 Hz, H5), 6.38 (d, J = 6.0 Hz, H6), 2.93 (s, Me). Anal. Calcd: C, 38.51; H, 2.16. Found: C, 38.07; H, 1.85. **4**(Et)·BF_4: yield 84%; IR (CH_2Cl_2) ν_{CO} 2074 (s), 2012 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.28 (d, J = 5.4 Hz, H2), 7.69 (d, J = 5.5 Hz, H3), 7.37 (d, J = 6.5 Hz, H4), 6.60 (t, J = 6.2 Hz, H5), 6.35 (d, J = 5.8 Hz, H6), 3.19 (m, CH_2), 1.56 (t, J = 7.5 Hz, Me). Anal. Calcd: C, 40.21; H 2.60. Found: C, 40.48; H 2.45.

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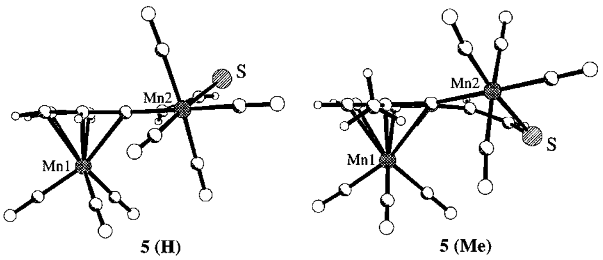

5 (H) **5 (Me)**

Figure 2. A comparison of **5**(H) and **5**(Me) viewed along the edge of the carbocyclic plane.

A transformation of this type has not been previously observed or postulated in HDS chemistry.

The chemistry discussed above and outlined in Scheme 1 was verified by X-ray structural studies of **5**(Me), **6**(Me), and **7**(Me), the results of which are shown in Figure 1.[15] Figure 2 gives a comparative structural view of **5**(Me) and the previously reported **5**(H).[6] In both cases, the metallathiacyclic rings are highly nonplanar, but in very different manners. For example, in **5**(H), the ring is twisted such that the sulfur is 1.04 Å above the plane defined by the carbocyclic atoms, whereas in **5**(Me), the ring is flipped in an opposite sense such that the sulfur is 0.96 Å below this plane. It appears that **5**(Me) adopts this conformation to avoid contact between a carbonyl group and the 7-methyl substituent, which, as a consequence, renders **5**(Me) thermodynamically unstable with respect to isomerization to **6**(Me). The conversion **5**(R) → **6**(R) is surprisingly facile, with the observed rate order R = Et > Me being in agreement with the idea that the reaction is driven by steric constraints imposed by the 7-R substituent. In contrast to the case with **5**(Me), the metallathiacyclic ring in **6**(Me) is fairly planar (mean deviation 0.057 Å), with the sulfur 0.16 Å above the plane defined by the carbocyclic atoms.

A completely unexpected result of the present study was the observation that **6**(R) cleanly transforms to **7**(R) after 2 h in refluxing CH_2Cl_2. The resultant five-membered metallathiacyclic ring in **7**(Me) is approximately planar (mean deviation 0.054 Å) with the sulfur and manganese atoms on opposite sides of the mean plane and 0.06 Å away from it. The mechanism of the transformation **6**(R) → **7**(R) is presently unclear, although it was found that the same product is obtained in CD_2Cl_2 and Et_2O, indicating that the exocyclic methylene hydrogens on C(2) in **7**(Me) originate from the thiophene ring and not the solvent.

The results presented herein indicate that metal coordination to the carbocyclic ring in benzothiophenes favors C(aryl)−S over C(vinyl)−S bond scission, even when the latter is the thermodynamic product. This may be true as well for heterogeneously catalyzed HDS reactions of BTs. Preliminary work[16] shows that precoordination of a variety of metal fragments to the carbocyclic ring of BTs leads to enormous increases in the rate of C−S bond cleavage via metal insertion reactions. The metallathiacycle ring contractions **6**(R) → **7**(R) appears to be a new reaction type in HDS chemistry, the significance of which is yet to be determined. Mechanistic studies and hydrogenation reactions related to **5**(R), **6**(R), and **7**(R) are underway.

Acknowledgment. This work was supported by grants from the National Science Foundation (Grant Nos. CHE-9400800 and CHE-9705121) and the Petroleum Research Fund, administered by the American Chemical Society.

Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **5**(Me), **6**(Me), and **7**(Me) (32 pages). Ordering information is given on any current masthead page.

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[12] **5**(R): Cobaltocene (0.31 mmol) and **4**(R)·BF_4 (0.30 mmol) were combined in CH_2Cl_2 (10 mL), and the mixture was stirred 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. **5**(Me): yield 85%; IR (CH_2Cl_2) ν_{CO} 2072 (m), 2047 (s), 1991 (s, br), 1927 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47 (d, J = 9.7 Hz, H2), 6.26 (d, J = 9.7 Hz, H3), 6.00 (t, J = 6.6 Hz, H5), 5.55 (d, J = 7.0 Hz, H4), 5.52 (d, J = 6.8 Hz, H6), 2.77 (s, Me). Anal. Calcd: C, 42.30; H, 1.78. Found: C, 42.68; H, 1.55. **5**(Et): yield 86%; IR (CH_2Cl_2) ν_{CO} 2072 (m), 2047 (s), 1993 (s, br), 1927 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52 (d, J = 9.5 Hz, H2), 6.28 (d, J = 9.5 Hz, H3), 5.96 (t, J = 6.5 Hz, H5), 5.57 (d, J = 6.5 Hz, H4), 5.52 (d, J = 6.6 Hz, H6), 3.30 (m, CH_2), 2.97 (m, CH_2), 1.36 (t, J = 7.6, Me).

[13] **6**(R): Complex **5**(R) (0.10 mmol) was dissolved in CH_2Cl_2 (10 mL) under nitrogen at room temperature. The conversion to **6**(R) was monitored via IR, with approximate half-lives being 6 h for R = Me and 0.5 h for R = Et. After the reaction was complete, the volume was reduced to 2 mL and the solution passed through alumina with CH_2Cl_2 as the eluant. Crystals of **6**(Me) suitable for X-ray diffraction were grown by cooling a 1:1 Et_2O:pentane solution. **6**(Me): yield 85%; IR (CH_2Cl_2) ν_{CO} 2068 (m), 2047 (s), 1975 (s, br), 1931 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.68 (d, J = 12 Hz, H2), 7.22 (d, J = 12 Hz, H3), 5.82 (d, J = 6.5 Hz, H4), 5.78 (d, J = 6.5 Hz, H6), 5.43 (t, J = 6.3 Hz, H5), 2.55 (s, Me). Anal. Calcd: C, 42.30; H, 1.78. Found: C, 42.12; H, 2.02. **6**(Et): yield 76%; IR (CH_2Cl_2) ν_{CO} 2066 (m), 2047 (s), 1975 (s, br), 1931 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.57 (d, J = 12 Hz, H2), 7.33 (d, J = 12 Hz, H3), 5.93 (d, J = 6.4 Hz, H4), 5.87 (d, J = 6.4 Hz, H6), 5.53 (t, J = 6.2 Hz, H5), 3.23 (m, CH_2), 2.77 (m, CH_2), 1.35 (t, J = 7.6 Hz, Me).

[14] **7**(R): Complex **6**(R) (0.10 mmol) was dissolved in CH_2Cl_2 (10 mL), and the solution was refluxed under nitrogen for 2 h. The volume was then reduced to 2 mL and passed through neutral alumina with CH_2Cl_2 as the eluant. Crystals of **7**(Me) suitable for X-ray diffraction were grown by cooling a pentane solution. **7**(Me): yield 82%; IR (CH_2Cl_2) ν_{CO} 2068 (m), 2047 (s), 1975 (s, br), 1931 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.57 (s, CH), 6.51 (d, J = 7.6 Hz, H4), 6.00 (s, CH), 5.87 (d, J = 6.5 Hz, H6), 5.46 (t, J = 6.3 Hz, H5), 2.54 (s, Me). FAB-MS: *m/z* 454 (M^+), 370 ($M^+ - 3CO$), 342 ($M^+ - 4CO$), 87 ($M^+ - Mn - 4CO$). HRMS: *m/z* calcd 453.8752, found 453.8762. Anal. Calcd: C, 42.30; H, 1.78. Found: C, 41.83; H, 2.06. **7**(Et): yield 86%; IR (CH_2Cl_2) ν_{CO} 2066 (m), 2047 (s), 1975 (s, br), 1931 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 6.57 (s, CH), 6.54 (d, J = 6.4 Hz, H4), 5.98 (s, CH), 5.88 (d, J = 5.8 Hz, H6), 5.47 (t, J = 6.4 Hz, H5), 3.10 (m, CH_2), 2.81 (m, CH_2), 1.36 (t, J = 6.4 Hz, Me).

[15] The crystal structures of **5**(Me), **6**(Me), and **7**(Me) 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 a 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. **5**(Me): crystal dimensions 0.16 × 0.15 × 0.07 mm, crystal system triclinic, space group $P1$, $a = 9.8508(2)$ Å, $b = 14.2111(3)$ Å, $c = 14.9125(4)$ Å, $\alpha = 117.853(1)°$, $\beta = 90.655(1)°$, $\gamma = 106.487(1)°$, $V = 1744.14(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.730$ g cm^{-3}, $\mu = 1.603$ mm^{-1}, θ range 1.57−24.64°, 471 variables refined with 5715 independent reflections to final R indices ($I > 2\sigma(I)$) of R = 0.0649 and wR2 = 0.1471, and GOF = 1.091. The unit cell contains two independent molecules, which are similar except that molecule 2 (with 20 added to the atom numbers of molecule 1) shows evidence of disorder in the S(21)−C(22)−C(23) region and in the C(35)−O(25) carbonyl group. **6**(Me): crystal dimensions 0.20 × 0.20 × 0.05 mm, crystal system monoclinic, space group $P2_1/c$, $a = 9.7032(5)$ Å, $b = 13.8228(8)$ Å, $c = 13.6898(8)$ Å, $\beta = 105.881(1)°$, $V = 1766.1(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.708$ g cm^{-3}, $\mu = 1.583$ mm^{-1}, θ range 2.14−23.37°, 236 variables refined with 2530 independent reflections to final R indices ($I > 2\sigma(I)$) of R = 0.0379 and wR2 = 0.0807, and GOF = 0.993. **7**(Me): crystal dimensions 0.56 × 0.12 × 0.07 mm, crystal system monoclinic, space group $C2/c$, $a = 28.9521(3)$ Å, $b = 8.06810(10)$ Å, $c = 18.7138(2)$ Å, $\beta = 123.729(1)°$, $V = 3635.51(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.660$ g cm^{-3}, $\mu = 1.538$ mm^{-1}, θ range 1.69−26.33°, 236 variables refined with 3509 independent reflections to final R indices ($I > 2\sigma(I)$) of R = 0.0467 and wR2 = 0.1043, and GOF = 0.980.

[16] Camiletti, C.; Dullaghan, C. A.; Zhang, X.; Meng, Q.; Carpenter, G. B.; Sweigart, D. A. Unpublished results.