Models for Homogeneous Deep Hydrodesulfurization. Intramolecular CO Substitution by the Sulfur in $[(\eta^6\text{-2-methylbenzothiophene})Mn(CO)_3]^+$ and $[(\eta^6\text{-dibenzothiophene})Mn(CO)_3]^+$ after Regiospecific Insertion of Platinum into a C−S Bond

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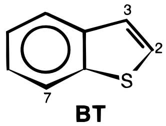
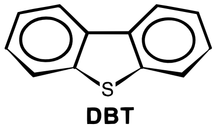
Summary: Coordination of $Mn(CO)_3^+$ to a carbocyclic ring of sterically congested thiophenes activates a C−S bond to regiospecific insertion of platinum. The resulting metallathiacycles contain a nucleophilic sulfur atom that undergoes spontaneous intramolecular CO substitution at the manganese center.

The removal of sulfur as H_2S from petroleum feedstocks is a major industrial process known as hydrodesulfurization (HDS).[1] Unsaturated heterocycles containing the thiophene nucleus are resistant to HDS and, as a consequence, comprise most of the sulfur contamination in fossil fuels. Desulfurization requires cleavage of the C−S bonds by insertion of a metal catalyst, followed by hydrogenolysis of the M−C bonds. Thiophenes are relatively unreactive because the conjugated sulfur atom is only very weakly nucleophilic toward a metal. In addition, steric factors play a major role, as evidenced by the fact that benzothiophenes (BT's) and dibenzothiophenes (DBT's) with alkyl substituents near the sulfur are especially difficult to treat.[2] Successful processing of these species is termed "deep hydrodesulfurization".



BT



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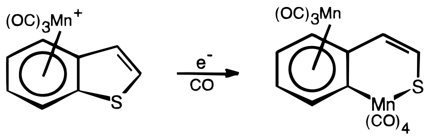
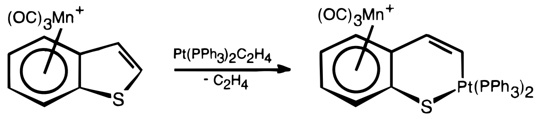


(1)



(2)

We recently demonstrated that η^6 coordination of an electrophilic metal fragment to the carbocyclic ring in BT or DBT activates the C−S bonds in the adjacent heterocyclic ring to cleavage upon reduction or upon attack by metal nucleophiles.[3] Equations 1 and 2 illustrate specific reactions with BT that occur within seconds at room temperature but do not proceed at all in the absence of the $Mn(CO)_3^+$ precoordination.[4] Of the two C−S bonds in BT, C(aryl)−S and C(vinyl)−S, we reasoned that precoordination selectively activates C(aryl)−S, thus accounting for the regiospecificity indicated in eq 1. That the C(vinyl)−S bond is broken in eq 2 is thought to be due to greater steric congestion at the C(aryl)−S bond that is manifest with the bulky $Pt(PPh_3)_2$ nucleophile. To test this hypothesis and, more importantly, to investigate the influence of steric factors on C−S bond cleavage reactions that model deep hydrodesulfurization, we examined the reactions of η^6-coordinated 2-MeBT and DBT with the weak nucleophile $Pt(PPh_3)_2(C_2H_4)$. As is documented below, the C−S bond nearer the $Mn(CO)_3^+$ moiety is preferentially cleaved in these sterically congested systems and, in a surprising development, it was found that the nucleo-

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[1] (a) Topsøe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysis*; Springer: Berlin, 1996. (b) *Petroleum Chemistry and Refining*; Speight, J. G., Ed.; Taylor & Francis: Washington, DC, 1998. (c) Startsev, A. N. *Catal. Rev.-Sci. Eng.* **1995**, *37*, 353. (d) Sanchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (e) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073. (f) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801. (g) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (h) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259. (i) Angelici, R. J. *Bull. Soc. Chim. Belg.* **1995**, *104*, 265. (j) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109.

[2] (a) Shih, S. S.; Mizrahi, S.; Green, L. A.; Sarli, M. S. *Ind. Eng. Chem. Res.* **1992**, *31*, 1232. (b) Vasudevan, P. T.; Fierro, J. L. G. *Catal. Rev.-Sci. Eng.* **1996**, *38*, 161. (c) Kabe, T.; Akamatsu, K.; Ishihara, A.; Otsuki, S.; Godo, M.; Zhang, Q.; Qian, W. *Ind. Eng. Chem. Res.* **1997**, *36*, 5146. (d) Vicic, D. A.; Jones, W. D. *Organometallics* **1998**, *17*, 3411. (e) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 7606. (f) Gates, B. C.; Topsøe, H. *Polyhedron* **1997**, *16*, 3213. (g) Myers, A. W.; Jones, W. D.; McClements, S. M. *J. Am. Chem. Soc.* **1995**, *117*, 11704. (h) Bianchini, C.; Casares, J. A.; Jimenez, M. V.; Meli, A.; Moneti, S.; Vizza, F.; Herrera, V.; Sanchez-Delgado, R. *Organometallics* **1995**, *14*, 4850. (i) Bianchini, C.; Jimenez, M. V.; Meli, A.; Moneti, S.; Vizza, F.; Herrera, V.; Sanchez-Delgado, R. A. *Organometallics* **1995**, *14*, 2342. (j) Meyers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905. (k) Bianchini, C.; Casares, J. A.; Masi, D.; Meli, A.; Pohl, W.; Vizza, F. *J. Organomet. Chem.* **1997**, *541*, 143.

[3] (a) Dullaghan, C. A.; Sun, S.; Carpenter, G. B.; Weldon, B.; Sweigart, D. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 212. (b) Sun, S.; Dullaghan, C. A.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4493. (c) Dullaghan, C. A.; Zhang, X.; Walther, D.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **1997**, *16*, 5604. (d) Zhang, X.; Dullaghan, C. A.; Watson, E. J.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **1998**, *17*, 2067. (e) Dullaghan, C. A.; Zhang, X.; Greene, D. L.; Carpenter, G. B.; Sweigart, D. A.; Camiletti, C.; Rajaseelan, E. *Organometallics* **1998**, *17*, 3316. (f) Zhang, X.; Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A.; Meng, Q. *Chem. Commun.* **1998**, 93. (g) Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A.; Choi, D. S.; Lee, S. S.; Chung, Y. K. *Organometallics* **1997**, *16*, 5688. (h) Zhang, X.; Watson, E. J.; Dullaghan, C. A.; Gorun, S. G.; Sweigart, D. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2206.

[4] In the original report of eq 2[3e] the nucleophile used was $Pt(PPh_3)_3$ instead of $Pt(PPh_3)_2C_2H_4$. The latter nucleophile, which gives the same product as the former, was subsequently found to be more generally useful in reactions of thiophenic complexes.

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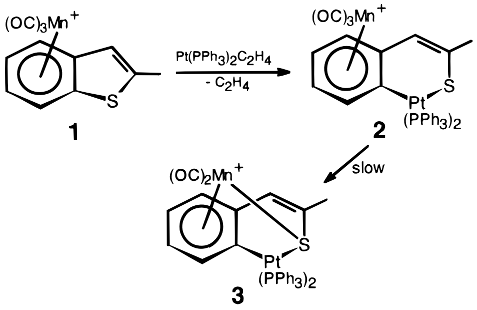
Scheme 1. Regiospecific Insertion of Pt into a C(aryl)−S Bond and Subsequent CO Substitution by the Sulfur



philicity of the sulfur atom in the resulting metallathiacyclic ring is so great that it spontaneously attacks the manganese and displaces a CO ligand.

We previously reported[3e] that (η^6-2-MeBT)Mn(CO)$_3^+$ (**1**) reacts rapidly with Pt(PPh$_3$)$_3$ to give a complex that was postulated on the basis of ^{31}P NMR data to be the product of C(aryl)−S insertion, as shown in the first reaction in Scheme 1. In the present work, attempts to grow crystals of **2** suitable for X-ray diffraction were unsuccessful; therefore, it was decided to synthesize the corresponding Mn(CO)$_2$P(OEt)$_3$ complex in the hope of obtaining adequate crystals. Thus, stirring [**2**]BF$_4$ under N$_2$ at room temperature in CH$_2$Cl$_2$ containing 2 equiv of P(OEt)$_3$ led to a slow transformation ($t_{1/2} \approx 10$ h) to a dicarbonyl species that, surprisingly, did not contain P(OEt)$_3$. The same complex could be obtained within minutes by treating **2** with 1 equiv of Me$_3$NO or by simply allowing a solution of **2** to sit (without P(OEt)$_3$) overnight.[5] An X-ray structure[6] of the product showed it to be **3**, in which the sulfur in the metallathiacyclic ring of **2** had displaced a CO ligand from Mn(CO)$_3$. Figure 1 gives the structure of the cation in [**3**]BF$_4$.

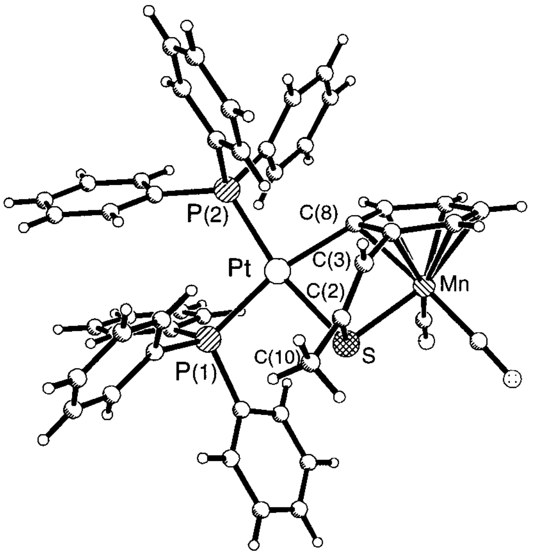


Figure 1. Structure of the cation in [**3**]BF$_4$. Selected bond lengths (Å) and angles (deg): Pt(1)−P(1) = 2.3182(11), Pt(1)−P(2) = 2.2806(10), Pt(1)−C(8) = 2.092(4), Pt(1)−S(1) = 2.3945(11), S(1)−C(2) = 1.817(5), S(1)−Mn(1) = 2.3487(14), C(2)−C(3) = 1.312(7), C(3)−C(9) = 1.492(6), C(8)−C(9) = 1.470(6), C(2)−C(10) = 1.504(7); P(1)−Pt(1)−P(2) = 100.40(4), P(1)−Pt(1)−S(1) = 92.01(4), P(2)−Pt(1)−C(8) = 91.89(12), C(8)−Pt(1)−S(1) = 76.15(12), Pt(1)−S(1)−Mn(1) = 90.81(4), Pt(1)−S(1)−C(2) = 90.77(15), S(1)−C(2)−C(3) = 116.4(4), C(2)−C(3)−C(9) = 116.3(4), C(3)−C(9)−C(8) = 119.7(4), Pt(1)−C(8)−C(9) = 119.1(3).

These results are significant for several reasons. (1) They show that insertion into the C(aryl)−S bond in BT's is possible even with bulky nucleophiles, provided a metal is precoordinated to the carbocyclic ring and there is a substituent in the 2-position. (2) The sulfur atom in the metallathiacyclic ring in **2** possesses a greatly enhanced nucleophilicity compared to that in free BT. The sulfur's nucleophilic character is so pronounced that external tertiary phosphite cannot compete with the intramolecular ring closure in the CO substitution reaction shown in Scheme 1. Preliminary work[7] suggests that the sulfur atom is more nucleophilic in general when the metal, whether Pt or Mn, is inserted into the C(aryl)−S as opposed to the C(vinyl)−S bond.

Interestingly, it was found that a solution of [**3**]BF$_4$ in a mixture of CH$_2$Cl$_2$ and Et$_2$O under N$_2$ for 2 months deposits crystals of the dimer [(PPh$_3$)$_2$PtS]$_2$, which was determined by X-ray crystallography to have the expected bridging sulfide structure.[8] This shows that 2-MeBT can be desulfurized via the cooperative interactions of manganese and platinum.

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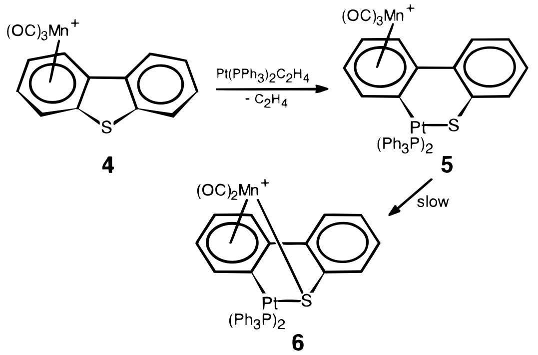
(5) Synthesis of [**3**]BF$_4$: Me$_3$NO (0.055 mmol) was added to a solution of [**2**]BF$_4$ (0.055 g, 0.050 mmol) in CH$_2$Cl$_2$ (5 mL) under N$_2$ at room temperature. There was an immediate color change from yellow to red. After 10 min, the solution was concentrated and the product precipitated with diethyl ether. Purification was effected by reprecipitation from diethyl ether. Yield: 60%. IR (CH$_2$Cl$_2$): ν_{CO} 1989 (s), 1944 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.51−7.27 (m, 30H), 7.07 (s, H3), 6.58 (d, J = 6 Hz, H4), 5.18 (t, J = 5.5 Hz, H7), 4.87 (t, J = 6 Hz, H6), 4.71 (t, J = 6 Hz, H5), 1.41 (s, Me). ^{31}P NMR (CD$_2$Cl$_2$): δ 22.28 (dd, J_{P-P} = 13 Hz, J_{P-Pt} = 3420 Hz), 16.73 (dd, J_{P-P} = 13 Hz, J_{P-Pt} = 2310 Hz). Anal. Calcd for C$_{47}$H$_{38}$O$_2$SP$_2$MnPtBF$_4$: C, 52.97; H, 3.56. Found: C, 52.70; H, 3.63.

(6) The crystal structure of [**3**]BF$_4$ was determined with a Siemens P4 diffractometer equipped with a CCD area detector and controlled by SMART version 5 software. Data reduction was carried out by SAINT version 5 and by SADABS and included profile analysis and an empirical absorption correction. The structure was determined by direct methods and refined on F^2 using the SHELXTL version 5 package. Thirty-one of the 38 expected hydrogen atoms appeared in a difference map. Each hydrogen was introduced in an ideal position, riding on the atom to which it is bonded, and refined with isotropic temperature factors 20% greater than that of the ridden atom. All other atoms were refined with anisotropic displacement parameters. Crystal data: 25 °C, Mo Kα radiation, crystal dimensions 0.28 × 0.24 × 0.20 mm, triclinic crystal system, space group $P\bar{1}$, a = 10.9549(5) Å, b = 13.2328(7) Å, c = 15.4405(9) Å, α = 80.429(2)°, β = 88.043(2)°, γ = 81.572(2)°, V = 2183.2(2) Å^3, Z = 2, ρ_{calcd} = 1.621 g cm^{-3}, μ = 3.666 mm^{-1}, θ range 1.88−27.88°, 533 variables refined with 10 243 independent reflections to final R indices ($I > 2\sigma(I)$) of R1 = 0.0392 and wR2 = 0.0922, and GOF = 1.080.

(7) Watson, E. J.; Li, H.; Sweigart, D. A. Unpublished results.

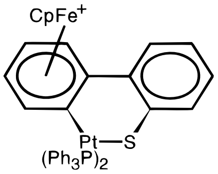
(8) The crystal structure of [(PPh$_3$)$_2$PtS]$_2$ was determined as described in ref 6 for [**3**]BF$_4$. The structure was determined by direct methods and refined on F^2 using the SHELXTL version 5 package. Only a few of the 30 expected hydrogen atoms appeared in a difference map, because the scattering was dominated by the heavier atoms. Each hydrogen was introduced in an ideal position, riding on the atom to which it is bonded, and refined with isotropic temperature factors 20% greater than that of the ridden atom. All other atoms were refined with anisotropic displacement parameters, except for the disordered solvent molecules. The molecule is located on a 2-fold rotation axis, so that only half is independent. There was clear evidence for some disordered solvent in the crystal; however, no discrete solvent molecules could be recognized. The solvent was modeled by two clusters of six carbon atoms, which fit neatly into gaps between the [(PPh$_3$)$_2$PtS]$_2$ molecules. Crystal data: 25 °C, Mo Kα radiation, crystal dimensions 0.46 × 0.26 × 0.15 mm, monoclinic crystal system, space group $C2/c$, a = 17.2348(13) Å, b = 18.2934(15) Å, c = 20.4947(16) Å, β = 91.325(3)°, V = 6459.9(9) Å^3, Z = 8, ρ_{calcd} = 1.694 g cm^{-3}, μ = 4.539 mm^{-1}, θ range 1.62−26.45°, 385 variables refined with 6636 independent reflections to final R indices ($I > 2\sigma(I)$) of R1 = 0.0590 and wR2 = 0.1500, and GOF = 1.117.

Scheme 2. Regiospecific Insertion of Pt into a C−S Bond in DBT and Subsequent CO Substitution by the Sulfur



Dibenzothiophenes are even more resistant to hydrodesulfurization than are benzothiophenes. We previously reported[3e] that (η^6-DBT)Mn(CO)$_3^+$ readily inserts Pt(PPh$_3$)$_2$ into a C−S bond. It was thought likely that the C−S bond broken was the one farther removed from the coordinated carbocyclic ring. We now report that this conclusion was incorrect. The chemistry that applies to (η^6-DBT)Mn(CO)$_3^+$ is remarkably similar to that found for (η^6-2-MeBT)Mn(CO)$_3^+$ and is summarized in Scheme 2. Thus, a CH$_2$Cl$_2$ solution of the insertion product **5** was found to convert slowly ($t_{1/2} \approx 3.5$ days) to **6**, which could also be generated rapidly by adding Me$_3$NO to induce the CO substitution.[9]

Although crystals of **6** suitable for X-ray diffraction could not be grown, the regiochemistry was established by reacting (η^6-DBT)FeCp$^+$ with Pt(PPh$_3$)$_2$(C$_2$H$_4$) and examining crystals of the resulting insertion product **7**. The crystals of **7** were of poor quality and produced broad reflections, so that it was not possible to get good integrated intensities. Nevertheless, the atom connectivities were established unequivocally. As can be seen, the platinum inserts into the C−S bond nearer the FeCp$^+$ moiety, and it is probable that the same regioselectivity obtains with **5**. Another strong indication of the regiochemistry in **5** and **6** is provided by the observation that **2** readily converts to **3**, but the isomer of **2** (sans the 2-Me group) having the platinum inserted into the C(vinyl)−S bond (eq 2) decomposes rather than undergoing CO substitution by the sulfur upon treatment with Me$_3$NO. From molecular models, it appears that a sulfur bonded to the carbocyclic ring containing the Mn(CO)$_3^+$ fragment is ill-positioned to form a bond to the manganese. The conclusion is that **6** indeed has the platinum situated as indicated.



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Conclusion. The conclusion from this work is that remote activation by precoordination to the carbocyclic ring of 2-substituted benzothiophenes and dibenzothiophenes selectively activates the C−S bond nearer the coordinated metal to cleavage by nucleophilic reagents. That this methodology works with such sterically congested thiophenic systems renders it a reasonable model for deep hydrodesulfurization. The metallathiacyclic complexes formed in this manner contain a highly nucleophilic sulfur atom.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for [**3**]BF$_4$ and [(PPh$_3$)$_2$-PtS]$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] Synthesis of [**6**]BF$_4$: the procedure was identical with that described above for [**3**]BF$_4$. Yield: 50%. IR (CH$_2$Cl$_2$): ν_{CO} 1991 (s), 1947 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.57−7.06 (m, Ph, H6−8), 6.71 (d, J = 5 Hz, H5), 6.10 (d, J = 8 Hz, H4), 5.49 (t, J = 8 Hz, H1), 5.04 (t, J = 6 Hz, H2), 4.70 (t, J = 6 Hz, H3). ^{31}P NMR (CD$_2$Cl$_2$): δ 16.54 (dd, J_{P-P} = 12 Hz, J_{P-Pt} = 3410 Hz), 15.60 (dd, J_{P-P} = 12 Hz, J_{P-Pt} = 2300 Hz). Anal. Calcd for C$_{50}$H$_{38}$O$_2$SP$_2$MnPtBF$_4$: C, 54.51; H, 3.45. Found: C, 54.29; H, 3.58. MS FAB: 1014 (M$^+$).