Insertion of manganese into a C–S bond of dibenzothiophene: a model for homogeneous hydrodesulfurization

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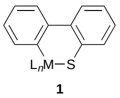
Coordination of $Mn(CO)_3{}^+$ to a carbocyclic ring of dibenzothiophene activates a C–S bond to reductive cleavage, affording a novel tetramanganese metallathiacycle 5 that reacts with H_2 to form a dimanganese complex 9 containing bridging hydride and thiolate ligands; methylation of 5 followed by hydrogenation results in desulfurization of the dibenzothiophene and formation of $[Mn(CO)_5(SMe)]$.

Much of the research in the field of catalytic hydrodesulfurization (HDS) has focused on the problem of sulfur removal from thiophenic molecules.[1] Benzothiophene (BT) and dibenzothiophene (DBT) are of particular interest in this regard because their substituted derivatives are difficult to desulfurize and, as a consequence, are relatively abundant in fossil fuels.[2] A key step in HDS is cleavage of the C–S bonds by insertion of a metal. A recent study indicates that the energy barrier to metal insertion is considerably greater for DBT than for BT, or for thiophene itself.[3] This higher barrier to C–S cleavage in DBT (which is probably steric in origin) most likely accounts for the relatively small number of published reports of metal insertion into DBT to give metallathiacycle **1**. Nevertheless, there are reports of metal-promoted scission of the C–S bonds in DBT to give characterizable organometallic products with systems based on Rh, Ir, Pt and Co.[3,4] We recently showed[5,6] that precoordination of a $Mn(CO)_3{}^+$ fragment to the carbocyclic ring in BT or the η^5 π-system of thiophene activates the C–S bonds to facile electron-transfer induced cleavage, affording the bimetallic metallathiacycles **2** and **3**, respectively. Here, we show that a C–S bond in the dibenzothiophene complex $[(\eta^6\text{-DBT})Mn(CO)_3]^+$ **4** is also activated and that chemical reduction leads (in part) to the novel metallathiacycle **5**, the multimetallic nature of which may be relevant to hydrogenolysis and desulfurization reactions occurring with industrial heterogeneous HDS catalysts (Mo/Co, *etc.*).[7] The reactions of **5** with H_2 and electrophilic reagents were investigated and are described below.

Reduction of **4**$[BF_4]$[8] with cobaltocene or Na/Hg produced as the major product an isomeric mixture of the yellow bis(cyclohexadienyl) complexes $[(\eta^5\text{-DBT})Mn(CO)_3]_2$, an example of which is shown as structure **6**.† Isomers of **6** occur because the dienyl rings can couple at various sites. Analogous ring-coupled dimeric cyclohexadienyl complexes are known to result from the reduction of $[(\text{arene})Mn(CO)_3]^+$ (arene = benzene, mesitylene).[9] Far more interesting is a dark red minor product that was isolated† and shown by X-ray crystallography to be **5**.‡ The yield of **5** was only *ca.* 10%, but this improved to > 20% when $[Mn_2(CO)_{10}]$ was added to the reaction mixture. The structure of **5**, illustrated in Fig. 1, shows that precoordination of $Mn(CO)_3{}^+$ to a carbocyclic ring of DBT provides sufficient activation so that manganese can insert into the adjacent C–S bond. The transformation **4** $\rightarrow$ **5** is initiated by electron transfer, probably by a mechanistic pathway that depends on the known[10] ease with which ring slippage and arene ligand displacement occur with conjugated polyarene complexes of $Mn(CO)_3{}^+$.

A novel feature of **5** is the coordination of the sulfur to three metal atoms. The sulfur atom in the metallathiacyclic ring acts as a bridging ligand to $Mn_2(CO)_8$, in analogy to the bridging sulfur in $[Mn_2(CO)_8\{S(CH_2)_4\}]$, which is obtained by the reaction of tetrahydrothiophene and $[Mn_2(CO)_{10}]$.[11] Thus, the sulfur atom in **5** has significantly enhanced donor properties in comparison to the sulfur in free DBT. An attempt was made to remove the $Mn_2(CO)_8$ fragment from **5** by ligand substitution with CO at room temp., but this was unsuccessful. However, treatment of **5** in CH_2Cl_2 with HBF_4 in CH_2Cl_2 led to a change from red to yellow; after chromatography on neutral alumina, a low yield (17%) of a thermally unstable red complex was obtained that is assigned structure **7** based on comparison of spectroscopic data to that of **2** (R = H). It is likely that the initial yellow product in this reaction contained a protonated sulfur, which converted to **7** during the chromatographic procedure. In a similar vein, the reaction of **5** with methyl triflate afforded a good yield of the methylated complex **8**.§ An X-ray structural study of **8**$[CF_3SO_3]$ was plagued by disorder in the triflate anion, but the data were sufficient to establish the structure unequivocally.¶ Complex **5** has a highly non-planar metallathiacyclic ring. The twist angle between the arene rings in **5**, as measured by the C(2)–C(3)–C(9)–C(8) torsion angle, is



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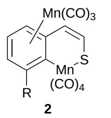

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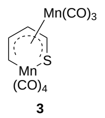

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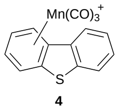

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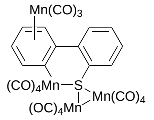

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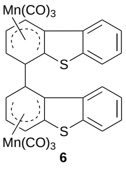

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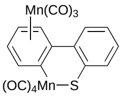

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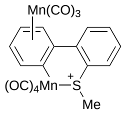

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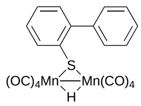

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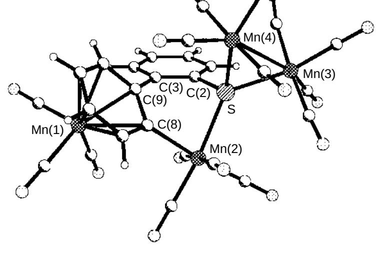

Fig. 1 Crystal structure of **5**. Selected bond distances (Å) and angles (°): Mn(2)–S 2.408(1), Mn(2)–C(8), 2.095(4), Mn(3)–S 2.301(1), Mn(4)–S 2.320(1), Mn(3)–Mn(4), 2.773(1), C(2)–S 1.804(4), C(2)–C(3) 1.394(6), C(3)–C(9) 1.499(6), C(8)–C(9) 1.447(6), S–Mn(3)–Mn(4) 53.43(3), Mn(3)–S–Mn(4) 73.76(4), S–Mn(4)–Mn(3) 52.81(3), S–Mn(2)–C(8) 80.82(11).

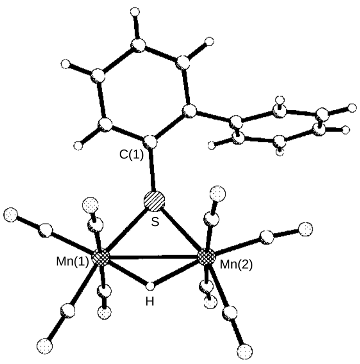

Fig. 2 Crystal structure of **9**. Selected bond distances (Å) and angles (°): Mn(1)–S 2.315(14), Mn(2)–S 2.346(2), Mn(1)–H 1.66(4), Mn(2)–H 1.75(4), Mn(1)–Mn(2) 2.883(1), S–C(1) 1.801(5), Mn(1)–S–Mn(2) 75.71(4), Mn(1)–H–Mn(2) 115(2). The twist angle between the arene rings in the thiolate ligand is 54°.

47.1(6)° and is somewhat larger than the 30–40° range found by Myers *et al.*[4j] for a series of dibenzothiophenes having the (η-C_5Me_5)Rh(PMe_3) fragment inserted into a C–S bond.

Reaction of **5** with H_2 at 500 psi and 97 °C for 3 h led to clean hydrogenolysis of the Mn–C σ-bond to afford complex **9**, which features bridging hydride and biphenyl thiolate ligands, and a Mn–Mn bond.‖ The structure and relevant intramolecular parameters for **9** are given in Fig. 2.** Interestingly, the bimetallic structural unit $Mn_2(H)(SR)$ found in **9** also forms when the manganese thiophene and benzothiophene bimetallics **2** and **3** are hydrogenated.[5b,12] Analogous bridging species containing the fragment $Ir_2(H)(SR)$ and RhW(H)(SR) have very recently been reported in model HDS studies of thiophene and benzothiophene complexes.[7c,13] The structural unit $M_2(H)(SR)$ is significant because of a possible relationship to species occurring on the surface of heterogeneous HDS catalysts.[7,13] Preliminary hydrogenation experiments with **8** under conditions similar to those used with **5** gave [$Mn(CO)_5(SMe)$] rather than **9** as the major organometallic product.†† This shows that complete desulfurization of DBT can be achieved by alkylation of the multimetallic intermediate **5** (or **7**).

In conclusion, we have demonstrated that coordination of $Mn(CO)_3^+$ to a carbocyclic ring of dibenzothiophene activates a C–S bond to reductive cleavage, affording the tetrametallic species **5**. Hydrogenation of **5** produces the bridging hydride **9**, while methylation of **5** followed by hydrogenation results in desulfurization of the DBT with the concomitant formation of [$Mn(CO)_5(SMe)$].

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Footnotes and References

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† Cobaltocene (47 mg, 0.249 mmol) was added to a suspension of **4**[BF_4] (105 mg, 0.256 mmol) in CH_2Cl_2 (5 ml) and the mixture stirred under N_2 for 30 min at room temp. The solvent was then stripped and the residue chromatographed on deactivated neutral alumina with pentane to elute [$Mn_2(CO)_{10}$], free DBT and unidentified trace products, then with Et_2O to elute **6** (and its isomers, collectively labeled '**6**'), and finally with CH_2Cl_2 to elute **5**. The isolated yields of **6** and **5** were 45 and 5 mg, respectively. When [$Mn_2(CO)_{10}$] was added to the reaction mixture (215 mg, 0.551 mmol), the yield of **5** increased to 20 mg. The presence of an atmosphere of CO had no discernable effect on the product distribution. IR, NMR, MS and elemental analysis data for **5**–**9** and [$Mn(CO)_5(SMe)$] are available upon request from the authors.

‡ Crystal dimensions 0.11 × 0.20 × 0.34 mm, crystal system triclinic, space group $P\bar{1}$, a = 10.0482(3), b = 10.1494(3), c = 16.3738(5) Å, α = 73.532(1), β = 78.792(1), γ = 78.268(1)°, U = 1551.19(8) Å^3, Z = 2, D_c = 1.765 g cm^{-3}, μ = 1.730 mm^{-1}, θ range 2.09–26.45°, 424 variables refined with 6139 independent reflections to final R indices [$I > 2\sigma(I)$] of R = 0.0587 and wR_2 = 0.1160 and GOF = 1.113. CCDC 182/678.

§ Methyl triflate (100 μl, 0.883 mmol) was added to **5** (22 mg, 0.027 mmol) in CH_2Cl_2 (5 ml) and the solution was stirred for 18 h at room temp. under N_2, during which time it changed from red to yellow. The solution was then filtered through cotton wool and concentrated. Diethyl ether was added to precipitate the product as a yellow powder in a yield of 86% (15 mg, 0.023 mmol).

¶ The crystal structure of **8**[CF_3SO_3] was determined as described in footnote ‡. However, owing to low intensities and disorder in the triflate anion, the structure refined only to R = 0.140. Nevertheless, the atom connectivity indicated in structure **8** is unequivocal.

‖ Complex **5** (25 mg, 0.030 mmol) in dry CH_2Cl_2 (2 ml) was placed in a Parr bomb and treated with H_2 at 500 psi and 97 °C for 3 h. (A gas mixture consisting of 95% H_2 and 5% CO gave the same results.) After cooling to room temp., the product was purified by TLC on silica gel with pentane eluent. A bright yellow band separated cleanly, from which **9** was isolated in 87% yield (13.8 mg, 0.0265 mmol) as a yellow oil.

** Crystal dimensions 0.22 × 0.14 × 0.09 mm, crystal system triclinic, space group $P\bar{1}$, a = 7.1767(1), b = 15.3254(1), c = 19.6549(1), α = 90.363(1), β = 93.210(1), γ = 95.236(1)°, U = 2149.21(3) Å^3, Z = 4, D_c = 1.608 g cm^{-3}, μ = 1.316 mm^{-1}, θ range 1.68 to 24.83°, 567 variables refined with 7224 independent reflections to final R indices [$I > 2\sigma(I)$] of R = 0.0549 and wR_2 = 0.0889, and GOF = 1.005.

†† Complex **8** in CH_2Cl_2 was pressurized to 550 psi with H_2–CO (95 : 5) at 97 °C for 9 h. After solvent removal, the product, [$Mn(CO)_5(SMe)$], was extracted into hexanes.

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