Organometallic models of catalytic hydrodesulfurization: $Re_2(CO)_{10}$-promoted cleavage of C–S bonds in benzothiophene

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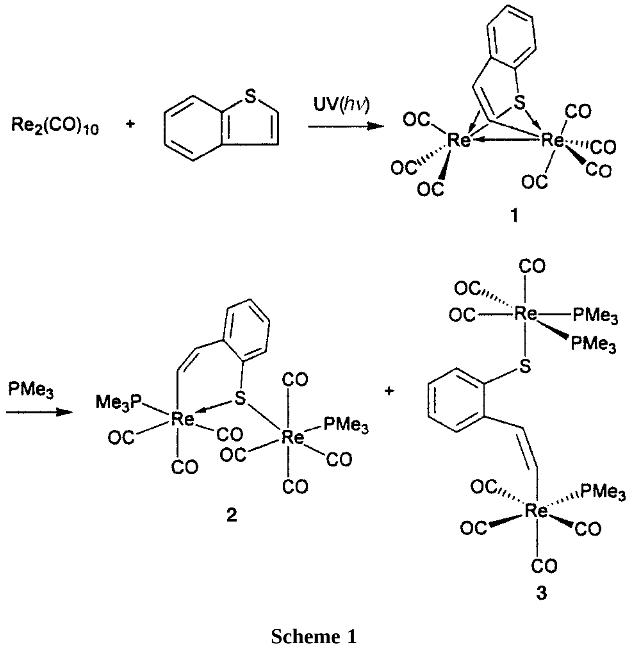
Ultraviolet photolysis of hexanes solutions containing $Re_2(CO)_{10}$ and benzothiophene (BT) give the C–S cleavage product $Re_2(CO)_7[\eta^2(C2,C3)\text{-}\mu_2(C2,S)\text{-BT}]$ 1 which reacts with PMe_3 at room temperature to yield two phosphine-substituted products, 2 and 3, in which the fragmented BT ligand is partially displaced from the metals; molecular structures of 1, 2 and 3 are models for possible intermediates in the HDS of BT on catalyst surfaces.

Heterogeneous catalytic hydrodesulfurization (HDS), the commercial process used for the removal of sulfur from organosulfur compounds present in petroleum-based feedstocks, is important in industry and for the environment.[1,2] Typically, the sulfur in crude petroleum is present in the form of organic thiols, sulfides, disulfides and thiophenes. It is the thiophenic molecules, however, such as benzothiophene (BT) that are the most difficult to desulfurize under current hydrotreating conditions.[3] In order to improve the efficiency of current HDS catalytic systems, much needs to be learned about intermediates that are present on transition-metal sulfide-based catalysts during the HDS of benzothiophene.

The present paper reports preliminary results of reactivity studies of $Re_2(CO)_{10}$ with BT under mild conditions to produce the C–S cleavage product **1** containing a Re–Re backbone. Upon addition of PMe_3 to **1**, two unexpected phosphine substitution products are formed (**2** and **3**) in which both the C–S and Re–Re bonds have been cleaved (Scheme 1).

Complex **1** was prepared by UV photolysis (Hanovia 450 W, medium pressure Hg lamp) of a stirred hexanes solution containing $Re_2(CO)_{10}$ and 2 equiv. of BT in a quartz reaction vessel under nitrogen for 24–36 h at 10 °C. The progress of the reaction was monitored by IR spectroscopy of samples taken during the reaction. The IR bands corresponding to $Re_2(CO)_{10}$ [ν_{CO} (hexanes): 2071w, 2015s, 1977m cm^{-1}]^4 were gradually replaced by those of **1** [ν_{CO} (hexanes): 2099m, 2043s, 2027s, 1981s, 1977s, 1957m, 1947s cm^{-1}]. Solvent removal, followed by extraction with CH_2Cl_2 and column chromatography on silica gel packed in hexanes, produced orange **1** in 30–45% yield.†‡



Scheme 1

The molecular structure of **1** was confirmed by single crystal X-ray structure analysis (Fig. 1). It contains a bridging BT ligand in which the vinylic C–S bond of the BT has been cleaved, and three CO ligands have been displaced from the $Re_2(CO)_{10}$. The sulfur bridges both Re atoms asymmetrically with distances of 2.506(2) Å for Re(1)–S and 2.431(3) Å for Re(2)–S. The vinyl carbon also bridges the two Re atoms asymmetrically acting as a η^1-ligand to Re(1) and η^2 to Re(2) with distances of 2.142(10) Å for Re(1)–C(8) and 2.208(10) Å for Re(2)–C(8). The Re–Re distance [2.8945(7) Å] is shorter than that in $Re_2(CO)_{10}$ [3.0413(11) Å].[5] Other previously reported dinuclear complexes, prepared by quite different methods, that contain a similar bridging BT ligand are $Fe_2(CO)_5(PPh_3)(C_8H_6S)$[6] and $[Cp^*Co]_2(\mu\text{-}C_8H_6S)$.[7]

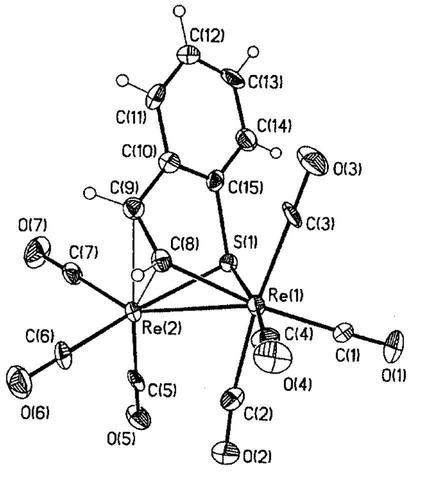


Fig. 1 Molecular structure of **1** in the solid state. Selected bond lengths (Å) and angles (°): Re(1)–Re(2) 2.8945(7), Re(1)–S, 2.506(2), Re(2)–S 2.431(3), Re(1)–C(8) 2.142(10), Re(2)–C(8) 2.208(10), Re(2)–C(9) 2.413(11), C(8)–C(9) 1.370(14), S–C(15) 1.805(11), Re(2)–S–Re(1) 71.77(7), Re(1)–C(8)–Re(2) 83.4(3), C(8)–Re(2)–S 82.8(3), C(8)–Re(1)–S 82.3(3), C(8)–C(9)–C(10) 126.6(10).

The addition of PMe_3 (1–5 equiv.) (1 M in toluene) to a toluene solution of **1** at room temperature causes an immediate change from orange to pale yellow with no evolution of CO. Solvent removal, extraction with CH_2Cl_2, and fractional crystallization of the crude residue produced yellow crystals of **2** and white **3**. Both complexes have been characterized spectroscopically‡ and by X-ray structure analysis of their single crystals.

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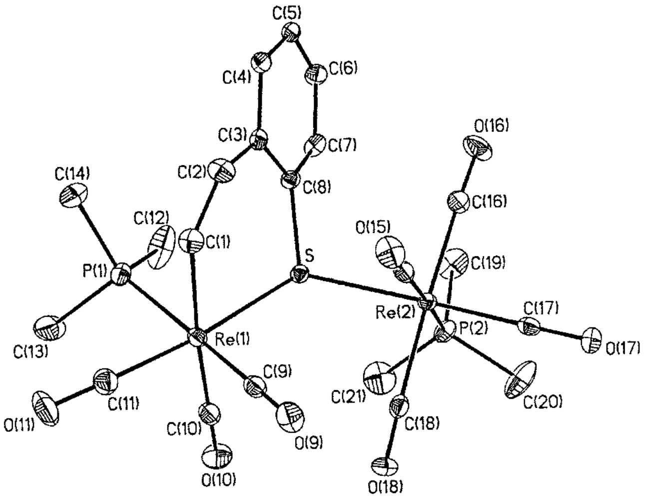


Fig. 2 Molecular structure of **2** in the solid state. Selected bond lengths (Å) and angles (°): Re(1)··Re(2) 4.2874(3), Re(1)–S 2.5027(9), Re(2)–S 2.5320(9), C(8)–S 1.796(3), Re(1)–C(1) 2.169(3), C(1)–C(2) 1.343(5), Re(1)–S–Re(2) 116.76(3), C(1)–Re(1)–S 86.51(10), Re(1)–S–C(8) 109.94(12), Re(2)–S–C(8) 105.40(12), P(1)–Re(1)–S 87.24(3), P(2)–Re(2)–S 88.04(3).

The X-ray structure of **2** (Fig. 2) shows that the C(1)–C(2) double bond is no longer η^2-coordinated and the Re–Re bond has been cleaved. Both Re atoms are pseudo-octahedral and each contains a PMe_3 ligand. The S bridges both Re atoms almost symmetrically with distances of 2.5027(9) Å for Re(1)–S and 2.5320(9) Å for Re(2)–S.

A single crystal X-ray analysis of **3** (Fig. 3) shows that there are no single atom bridges between the two Re centers nor is there a metal–metal bond. The Re centers are pseudo-octahedral with respect to the C–Re–C angles between Re and adjacent CO ligands. The Re(1)–C(1) distance is 2.205(3) Å which is longer than that in either **1** or **2**. The Re(2)–S distance is 2.5086(9) Å which is similar to those in both **1** and **2**.

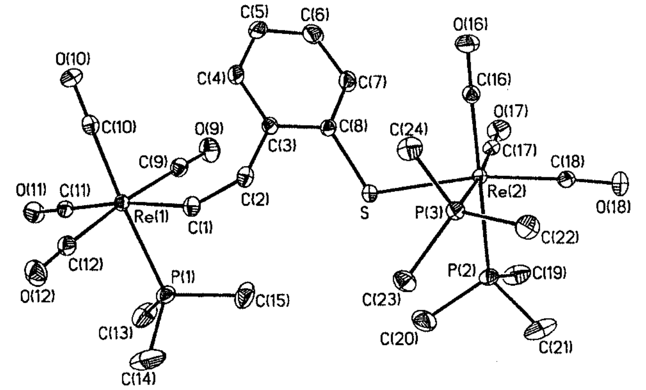
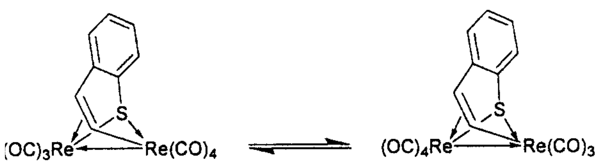


Fig. 3 Molecular structure of **3** in the solid state. Selected bond lengths (Å) and angles (°). Re(1)–C(1) 2.205(3), Re(2)–S 2.5086(9), C(1)–C(2) 1.327(4), S–C(8) 1.769(3), C(2)–C(3) 1.479(4), Re(1)–C(1)–C(2) 134.8(3), C(8)–S–Re(2) 113.18(12), P(2)–Re(2)–S 84.54(3), C(1)–C(2)–C(3) 129.8(3), C(1)–Re(1)–P(1) 82.44(8).

In the reaction (Scheme 1) of **1** with PMe_3, the relative amounts of **2** and **3** formed are the same whether 1 or 5 equiv. of PMe_3 are used. This means that the tri-phosphine product **3** is not formed from the bis-phosphine product **2** even in the presence of an excess of PMe_3. Therefore **2** and **3** must form by independent pathways. The structures of **2** and **3** are also fundamentally different from each other because the terminal vinyl carbon is bound to the $Re(CO)_3$ unit in **2** whereas in **3** it is coordinated to the $Re(CO)_4$ group. The formation of these products may be understood in terms of a mechanism that involves two forms of **1** resulting (Scheme 2) either from a "flip-flop" of the vinyl group from one Re to the other, as proposed for related bridging thiophene complexes $\{Fe_2(CO)_6(C_8H_6S)$,[6] $[(C_5Me_5)Co]_2(\mu\text{-}C_4H_4S)$[8] and $[(dippe)Ni]_2(\mu\text{-}C_8H_6S)$[9]$\}$, or the migration of a CO group from one Re to the other.



1 **1′**

Scheme 2

The reaction of isomer **1′** with 2 equiv. of PMe_3 would lead to product **2** in which the olefin is displaced and the Re–Re bond is cleaved, leaving the terminal vinyl carbon coordinated to the $Re(CO)_3$ unit. On the other hand, the reaction of isomer **1** with 3 equiv. of PMe_3 would lead to product **3** with the vinyl carbon bonded to the $Re(CO)_4$ moiety while undergoing Re–olefin, Re–S and Re–Re bond cleavages. An attempt to detect the two isomers of **1** by low temperature (−50 °C, CD_2Cl_2 solvent) ^1H NMR spectroscopy showed only the same isomer that is present in the room temperature spectrum.‡ However, variable temperature ^{13}C NMR spectra of **1** (−50 °C to +20 °C) showed that the CO ligands are fluxional. Thus, while the two isomers are not detected by the NMR studies, a low concentration of the highly reactive **1′** would reasonably account for the formation of **2**.

The reactions in Scheme 1 are of special interest because they indicate the variety of ways that a bridging, C,S-cleaved BT ligand can bind to two metal centers. Were C–S cleavage to occur on a HDS catalyst, all three forms of BT represented in compounds **1**–**3** would be potential modes of BT adsorption on the catalyst surface.

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Notes and references

† Satisfactory elemental analyses were obtained for **1**–**3**.

‡ *Selected spectroscopic data*: for **1**: ^1H NMR (CD_2Cl_2, 300 MHz) δ 8.63 (d, 1 H, J = 11.4 Hz), 7.11 (m, 2 H), 7.05 (dt, 1 H, J_1 7.5, J_2 1.5 Hz), 7.00 (d, 1 H, J 11.4 Hz), 6.93 (dt, 1 H, J_1 7.2, J_2 1.5 Hz). IR (hexanes) ν_{CO}: 2099m, 2043s, 2027s, 1981s, 1977s, 1957m, 1947s cm^{-1}. For **2**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 8.06 (dd, 1 H, J_1 14.1, J_2 2.4 Hz), 7.44 (dd, 1 H, J_1 14.1, J_2 3.6 Hz), 7.26 (d, 1 H, J 7.8 Hz), 7.00 (m, 2 H), 6.87 (m, 1 H), 1.87 (d, 9 H, PMe_3, J 9.3 Hz), 1.19 (d, 9 H, PMe_3, J 8.4 Hz). IR (CH_2Cl_2) ν_{CO}: 2100w, 2003s, 1953m, br, 1896m, br, 1873m, br cm^{-1}. For **3**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.89 (dd, 1 H, J_1 13.5, J_2 3.9 Hz), 7.43 (dd, 1 H, J_1 7.8, J_2 1.2 Hz), 7.21 (d, 1 H, J 7.2 Hz), 6.99 (dt, 1 H, J_1 7.5, J_2 1.5 Hz), 6.92 (m, 2 H), 1.62 (m, 27 H, $3PMe_3$). IR(CH_2Cl_2) ν_{CO} 2079w, 2018s, 1978s(sh), 1972s, 1933s, 1893s cm^{-1}.

CCDC 182/1551. See http://www.rsc.org/suppdata/cc/a9/a909161k/ for crystallographic files in .cif format.

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