

Hydrogenation and Carbon–Sulfur Bond Hydrogenolysis of Benzothiophene Promoted by $\text{Re}_2(\text{CO})_{10}$ and $\text{H}_4\text{Re}_4(\text{CO})_{12}$

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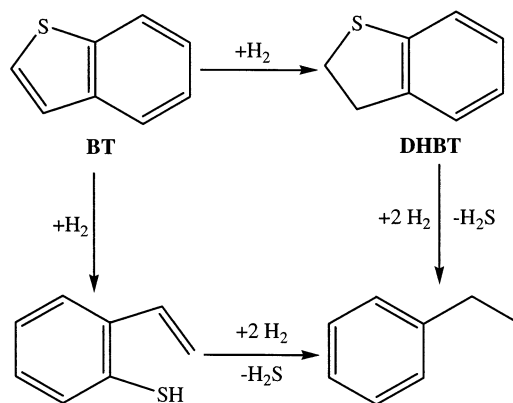
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In the search for metal complexes that promote the cleavage of C–S bonds in thiophenes, we observe that the reaction of $\text{Re}_2(\text{CO})_{10}$ and benzothiophene (BT) under a hydrogen atmosphere gives the trinuclear cluster $\text{Re}_3(\mu\text{-H})_2(\mu_3\text{-S-2-EtC}_6\text{H}_4)(\mu\text{-2,3-DHBT})(\text{CO})_9$ (**1**), which contains a hydrogenated BT ligand and a thiolate ligand resulting from the hydrogenation and cleavage of a C–S bond in BT. A detailed study of the reaction shows that $\text{Re}_2(\text{CO})_{10}$ initially reacts with H_2 to give $\text{H}_3\text{Re}_3(\text{CO})_{12}$, which subsequently converts to $\text{H}_4\text{Re}_4(\text{CO})_{12}$, which finally reacts with BT to give **1**.

The hydrodesulfurization (HDS) of organosulfur compounds that are present in petroleum feedstocks is an important industrial process that uses heterogeneous catalysts such as Co- or Ni-promoted MoS_2 supported on alumina under high temperatures (300 °C) and pressures (10–90 atm) of H_2 , as shown for benzothiophene in Scheme 1.^{1,2} The efficient HDS of thiophenic compounds, such as benzothiophene (BT) and dibenzothiophene (DBT), continues to be challenging.³ In an attempt to understand the HDS process of these compounds, homogeneous transition metal complexes have been investigated as models for the binding, hydrogenation, C–S bond cleavage, and hydrogenolysis of thiophenes on HDS catalysts.^{4,5} Many of these studies involved single-metal or dinuclear complexes, but there are few studies of C–S bond hydrogenolysis that are promoted by metal clusters.⁶ The trinuclear $\text{Fe}_3(\text{CO})_{12}$ reacts with BT in refluxing benzene to give a dinuclear benzothiaferrole $\text{Fe}_2(\text{CO})_6(\text{SC}_8\text{H}_6)$.⁷ On the other hand, $\text{Ru}_3(\text{CO})_{12}$ reacts with

Scheme 1. Pathways Proposed for the Catalytic HDS of Benzothiophene



BT in refluxing THF to give the cluster $\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)^8$ containing the desulfurized BT, while the related $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ reacts with BT to give trinuclear clusters containing BT ligands in which C–H cleavage has occurred.⁹ Curtis¹⁰ showed that the homogeneous sulfido cluster $\text{Cp}_2\text{Mo}_2\text{Co}_2(\text{CO})_4\text{S}_3$ desulfurizes thiophene stoichiometrically (at 150 °C, 15 atm of H_2) to give desulfurized organic products and the cluster $\text{Cp}_2\text{Mo}_2\text{Co}_2(\text{CO})_4\text{S}_4$, which contains the extruded sulfur, in 90% yield. Suzuki¹¹ demonstrated that $(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ reacts with BT at 50 °C to give the μ_3 -sulfido- μ_3 -alkylidene cluster $(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_2(\mu_3\text{-S})(\mu_3\text{-CCH}_2\text{Ph})$; the reaction with DBT gives biphenyl quantitatively and the sulfido-containing cluster $(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_3(\mu_3\text{-S})$ in 84% yield at 110 °C. In this communication, we report the hydrogenolysis of BT upon reaction with $\text{Re}_2(\text{CO})_{10}$ under 1 atm of H_2 pressure to give a trinuclear Re cluster containing partially hydrogenated and hydrogenolyzed BT ligands. A

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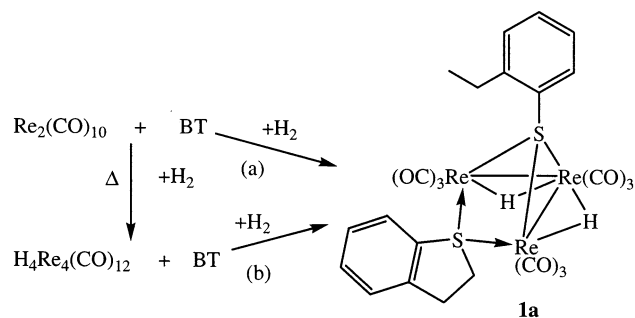
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Scheme 2. Reactions of $\text{Re}_2(\text{CO})_{10}$ and $\text{H}_4\text{Re}_4(\text{CO})_{12}$ with BT under H_2



unique aspect of this reaction is the initial conversion of $\text{Re}_2(\text{CO})_{10}$ to $\text{H}_4\text{Re}_4(\text{CO})_{12}$, which subsequently reacts with BT to give the cluster product containing hydrogenated and hydrogenolyzed BT ligands.

When a decane solution of $\text{Re}_2(\text{CO})_{10}$ and excess BT was refluxed under a H_2 atmosphere for 5 days, the off-white complex $\text{Re}_3(\mu\text{-H})_2(\mu_3\text{-S-2-EtC}_6\text{H}_4)(\mu\text{-2,3-DHBT})(\text{CO})_9$ (**1**) (2,3-DHBT = 2,3-dihydrobenzothiophene) was produced in 80% yield (Scheme 2, reaction a).¹² Recrystallization of **1** gave a mixture of colorless crystals and an off-white powder. An X-ray diffraction study of the crystals (**1a**) hand-picked from the mixture yielded the trimetallic structure (Figure 1) containing three pseudo-octahedral Re atoms with relatively long Re(1)–Re(2) (3.1020(4) Å) and Re(2)–Re(3) (3.1093(4) Å) bonds indicating the presence of bridging hydride ligands that were not located in the X-ray refinement. Rhenium complexes that contain a Re–Re single bond typically have shorter Re–Re distances as observed in the structures of $\text{Re}_2(\text{CO})_{10}$ (3.0413(11) Å),¹³ $\text{Re}_2(\text{CO})_9(3\text{-MeBT})$ (3.0343(4) Å),¹⁴ and $\text{Re}_2(\text{CO})_8(\text{PMe}_2\text{Ph})_2$ (3.044(1) Å)¹⁵ compared to those Re complexes that have a bridging hydride ligand such as $\text{Re}_2(\text{CO})_8(\mu\text{-H})(\mu\text{-2-S-naphthyl})$ (3.0934(10) Å),¹⁶ $[\text{Re}_3(\mu\text{-H})(\text{CO})_{12}]^{2-}$ (3.125(3) Å),¹⁷ and $[\text{Re}_3(\text{CO})_9(\mu\text{-H})_3(\mu_3\text{-S}^t\text{Bu})]^-$ (average Re–Re distance of 3.091(1) Å).¹⁸ The presence of the bridging hydride ligands was supported by the ^1H NMR spectrum of **1a** in CD_2Cl_2 which showed only one hydride signal (δ –11.05) indicating the rapid interchange of these two bridging hydrides. The Re(1) and Re(3) atoms are bridged by the sulfur atom of a 2,3-DHBT ligand. The Re_3 unit is capped nearly symmetrically by the sulfur atom of a 2-ethylthiophenolate ($2\text{-EtC}_6\text{H}_4\text{S}^-$) ligand.

A ^1H NMR study¹² of the crystal–powder mixture of **1** showed duplicate sets of signals for all of the protons in the

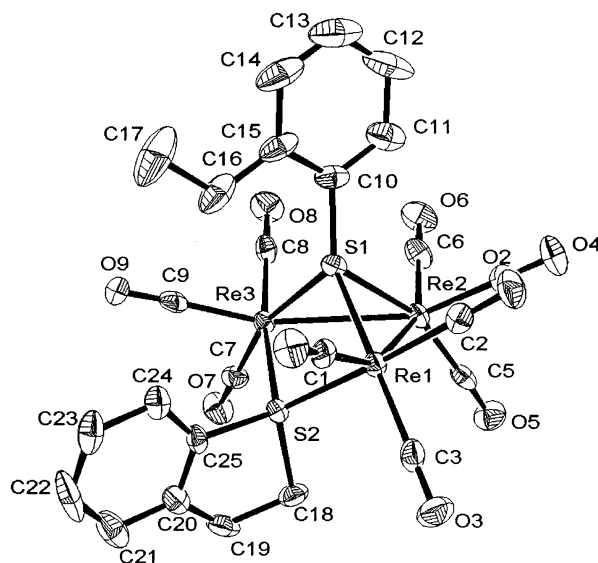


Figure 1. Molecular structure of **1a** with 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Re(1)–Re(2), 3.1020(4); Re(2)–Re(3), 3.1093(4); Re(1)–S(1), 2.4673(16); Re(1)–S(2), 2.4765(16); Re(2)–S(1), 2.4188(17); Re(3)–S(1), 2.4693(16); Re(3)–S(2), 2.4823(16); S(2)–C(18), 1.835(6); S(1)–C(10), 1.763(4); C(18)–C(19), 1.534(8); Re(1)–Re(2)–Re(3), 76.463(9); Re(1)–S(1)–Re(2), 78.81(5); Re(1)–S(1)–Re(3), 102.27(5); Re(2)–S(1)–Re(3), 78.99(5); Re(1)–S(2)–Re(3), 101.64(5); C(18)–S(2)–C(25), 91.9(3); Re(1)–S(2)–C(18), 114.4(2); Re(3)–S(2)–C(25), 114.7(2).

molecule, suggesting the presence of two isomers, formed in approximately equal amounts, which could not be separated by chromatography. The ^1H NMR spectrum of the hand-picked crystals allowed the assignment of peaks to isomer **1a** in the spectrum of the mixture. It also allowed the assignment of peaks to the other isomer **1b**. The similarity of their ^1H NMR spectra suggests that the structure of **1b** is very similar to that of **1a**, whose structure was established crystallographically (Figure 1). We therefore suggest that **1b** has a structure in which the arene ring of the 2,3-DHBT ligand is directed away from S(1), rather than toward it as in **1a**.

During the reaction of $\text{Re}_2(\text{CO})_{10}$ with BT and H_2 , a series of intermediates were detected by IR spectroscopy. In the initial stages of the reaction, ν_{CO} bands corresponding only to $\text{Re}_2(\text{CO})_{10}$ were observed (2070w, 2014s, 1976m cm^{-1}), but after ca. 2 h these bands were replaced with those corresponding to $\text{H}_3\text{Re}_3(\text{CO})_{12}$ (2093m, 2030s, 2008s, 1982m cm^{-1}), which has been reported in the reaction of $\text{Re}_2(\text{CO})_{10}$ with H_2 .¹⁹ After a further 24 h, the $\text{H}_3\text{Re}_3(\text{CO})_{12}$ cluster converted into $\text{H}_4\text{Re}_4(\text{CO})_{12}$ (2041s, 1987s cm^{-1}), which then converted into **1** within 4 days. The formation of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ was confirmed by its preparation from $\text{Re}_2(\text{CO})_{10}$ and H_2 (1 atm), as previously reported.²⁰ The observation that $\text{H}_4\text{Re}_4(\text{CO})_{12}$ was formed in the step immediately preceding the formation of **1** suggests that $\text{H}_4\text{Re}_4(\text{CO})_{12}$ is the species that reacts with BT. Indeed, when $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and BT were

(12) Selected spectroscopic data for **1a**: ^1H NMR (CD_2Cl_2) 300 MHz: δ 7.68–7.22 (m, 8H), 4.25 (t, 2H, J = 6.9 Hz), 3.55 (q, 2H, J = 7.5 Hz), 3.43 (t, 2H, J = 6.9 Hz), 1.61 (t, 3H, J = 7.5 Hz), –11.05 (s, 2H, $\mu\text{-H}$). For **1**: IR (decane): ν_{CO} , cm^{-1} 2057vw, 2037vs, 2024m, 1966m, 1941m. Anal. Calcd (found) for $\text{C}_{25}\text{H}_{19}\text{O}_9\text{Re}_3\text{S}_2$: C, 27.65 (27.64); H, 1.76 (1.71).

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reacted under the same conditions as those in the reaction of $\text{Re}_2(\text{CO})_{10}$, BT, and H_2 , complex **1** was produced and the reaction was complete within 48 h, confirming the intermediacy of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ in the formation of **1** from $\text{Re}_2(\text{CO})_{10}$, BT, and H_2 (Scheme 2).

In order to test for the possibility that the hydrogenolysis of BT could occur catalytically, $\text{Re}_2(\text{CO})_{12}$ was reacted with 100 equiv of BT in refluxing decane under 1 atm of H_2 . Samples taken during the reaction contained unreacted BT and the hydrogenated product 2,3-DHBT as determined by GC. After 6.5 days, 3.47 mol of 2,3-DHBT was produced for each mole of $\text{Re}_2(\text{CO})_{10}$ used, and ethylbenzene was detected in very low concentration (<0.1 mol %). Although there is some catalytic formation of 2,3-DHBT, complex **1** is not part of the catalytic system. This was shown by the observation that BT was not converted to DHBT or ethylbenzene when **1** was reacted for 6 days with excess BT under reaction conditions identical to those used in the formation of **1**; also no new organometallic products were observed by IR spectroscopy. Thus, the hydrogenation of BT to DHBT must be catalyzed by either an unidentified Re complex that

was not detected spectroscopically or Re metal which perhaps forms during the course of the reaction in unobservable amounts.

In conclusion, we have demonstrated that the reaction of BT with $\text{Re}_2(\text{CO})_{10}$ under H_2 proceeds through $\text{H}_3\text{Re}_3(\text{CO})_{12}$ and then $\text{H}_4\text{Re}_4(\text{CO})_{12}$, which reacts with BT to give the trinuclear cluster $\text{Re}_3(\mu\text{-H})_2(\mu_3\text{-S-2-EtC}_6\text{H}_4)(\mu\text{-2,3-DHBT})(\text{CO})_9$ (**1**) containing BT molecules that have undergone hydrogenation and C–S bond hydrogenolysis. These investigations suggest that other hydride clusters may be useful models for the catalytic hydrodesulfurization of thiophenes.

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Supporting Information Available: Crystallographic files for the structure of **1a**. Preparative details and spectroscopic data for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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