Thiophene Activation by Iron and Rhodium Complexes

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Hydrodesulfurization (HDS) is the industrial process used to remove sulfur from petroleum products [1]. Sulfur-containing organic compounds, from simple alkyl thiols to complex heteroaromatics, are typically desulfurized and hydrogenated over a $Mo,Co/Al_2O_3$ catalyst at high H_2 pressures and temperatures. Despite the industrial importance of the HDS reaction, the specific mechanism of the process is not fully understood. The mechanism most often referred to involves hydrogen transfer from an OH (SH) group on the catalyst surface to a sulfur-bound thiophene resulting in C-S bond cleavage [2].

One approach to HDS research involves the study of organometallic compounds that mimic catalyst structure, or that undergo reactions similar to those thought to occur during HDS. In early work, Stone and coworkers discovered that thiophenes and iron carbonyls react to give the ring-opened products, thiaferroles and ferroles (eq. 1) [3]. For example, the reaction
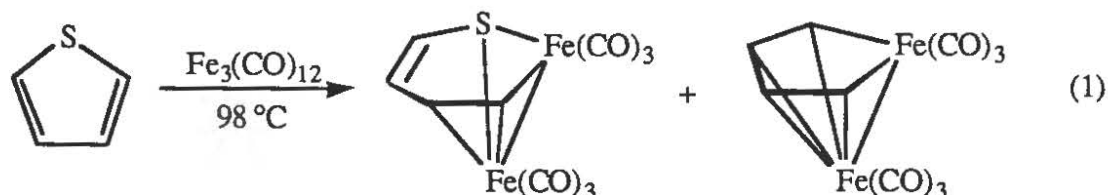
of benzothiophene with $Fe_3(CO)_{12}$ results in a 49% yield of the benzothiaferrole, $Fe_2(C_8H_6S)(CO)_6$ (1). A crystal structure of a PPh_3 derivative of 1 consists of a normal metal-metal bonded $Fe_2(CO)_6$ subunit spanned unsymmetrically by what may be viewed as a derivative of 2-mercaptostyrene [4]. The structure of 1 in solution was studied by variable-temperature ^{13}C NMR spectroscopy. One carbonyl resonance is observed at 20°C, and this requires the interchange of the three carbonyls on each iron as well as the equivalencing of the two iron centers via the "flip-flop" of the organic ligand.

We have found that carbonylation of solutions of 1 gives a homogeneous solution of $Fe(CO)_5$ and benzothiophene. Benzothiophene is also generated upon flash vacuum thermolysis of 1. Hydrogenation of a solution of 1 gives an insoluble iron-containing solid and a series of ethylbenzene derivatives identified by gc/MS. Free benzothiophene was not detected. The fact that 1 is so thermally stable sparked our interest in the properties of the corresponding thiaferroles. Both $Fe_2(2-MeC_4H_3S)(CO)_6$ and Fe_2-$(2,5-Me_2C_4H_2S)(CO)_6$ give the corresponding ferrole complexes when heated. This demonstrates that α-protons are not involved in the desulfurization event.

Ruthenium (η^6-arene) complexes are known to undergo a hapticity change ($\eta^6 \rightarrow \eta^4$) upon reduction [5]. Several η^5-thiophene complexes are known [6] but η^4-thiophene species had not been previously reported. Following unsuccessful attempts to reduce $[(C_5H_5)Ru(TMT)]^+$ [7] and $[(TMT)_2Ru]^{2+}$ [8] (TMT = C_4Me_4S), we found that $[(C_5Me_5)Rh(TMT)]^{2+}$ reacts with cobaltocene to give $(C_5Me_5)Rh(\eta^4-TMT)$, 2 [9].

The ^1H NMR spectrum of **2** shows only one peak for the Cp* ligand and two peaks for the η^4-TMT ligand. High symmetry is again indicated by the ^{13}C NMR spectrum. Although all of the ring carbons exhibit Rh-C coupling, one resonance is shifted approximately 50 ppm upfield from the range expected for aromatic ring shifts. We used an NMR heteronuclear correlation technique and a labeling study to assign the shifts and found that the upfield resonance originates from the methyl groups closest to the sulfur (2,5-positions) in the η^4-TMT ring. A crystallographic study by Skaugset and Wilson confirms its assignment. As expected, the sulfur atom is oriented away form the rhodium atoms, and is displaced out of the plane of the carbon atoms in the TMT ring.

The η^4-TMT ligand is readily replaced with carbon monoxide to give the known Cp*Rh(CO)$_2$ and free TMT, and it desulfurizes upon treatment with Fe$_3$-(CO)$_{12}$ to give the ferrole Cp*Rh(C$_4$Me$_4$)Fe(CO)$_3$, **3**. An X-ray crystal structure of **3** shows that the Fe(CO)$_3$ fragment is incorporated in the C$_4$Me$_4$ ring (Figure 1). The corresponding thiaferrole complex was not isolated. Thermolysis of **2** in aromatic solvents produces two major products which were separated using gel permeation chromatography. The dark green fraction was tentatively identified as "[(η^5-TMT)Rh]$_2$S$_4$" following spectroscopic characterization. The red fraction is believed to be an ionic compound. A crystal of this latter compound grown from a crude mixture of these two products was studied by X-ray diffraction methods. The centrosymmetric cation consists of four CpRh(η^4-TMT) units, identical to **2**, surrounding a "bare" Rh atom (Figure 2). The sulfur in each unit is bound to the central Rh atom in a square planar fashion creating a "pinwheel" structure.

A new HDS mechanism may be suggested on the basis of the work described above. After thiophene binds to a catalyst surface, presumably in an η^5-configuration, it is possible that electron transfer from the metal catalyst (rather than hydrogen) cleaves the C-S bonds. Our work supports the concept that activation occurs via reduction by electrons instead of anions [10]. There is strong evidence for the formation of metallacycles during thiophene decomposition on single crystal metal surfaces [11].
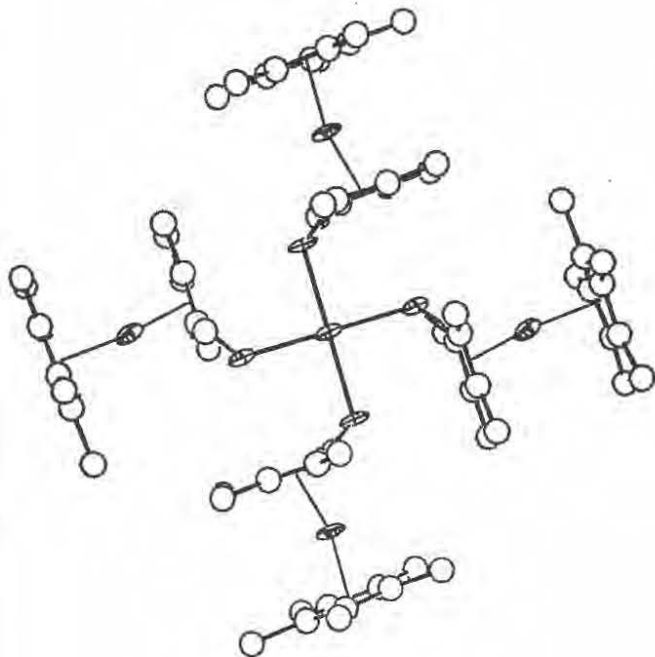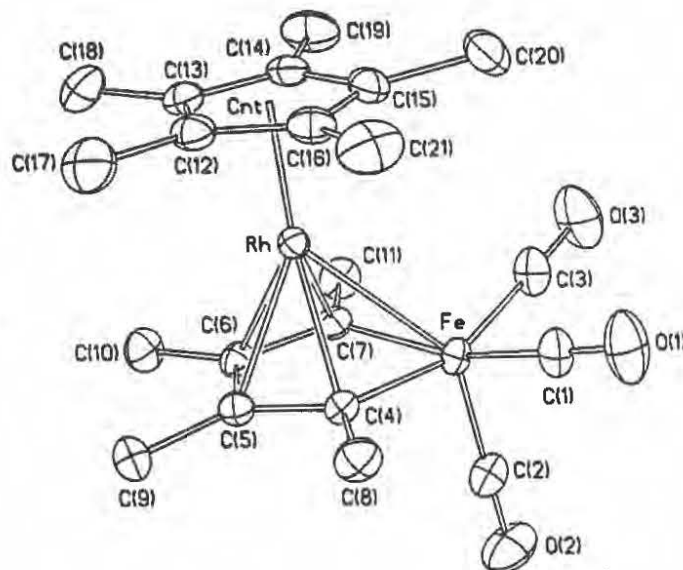

Figure 1

Figure 2

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