Progress Report for

NSF Grant CHE-9816365

for the period
February 1, 1999-January 31, 2000
(year 1 of 3)

Studies of Carbon-Sulfur Bond Cleavage by Homogeneous Transition Metal Complexes

William D. Jones, P.I.

Department of Chemistry
University of Rochester
Rochester, NY  14627
716-275-5493
A. Introduction

Cleavage of the C-S bond is an important step in the removal of sulfur from thiophene in the hydrodesulfurization (HDS) process.\(^1\) Thiophene and its benzo derivatives represent abundant sulfur-containing impurities in coal and petroleum feedstocks, and are among the most difficult to desulfurize.\(^2,3\) In the coming years, environmental regulations will require that the present levels of sulfur in fuels (300ppm) be dropped to approximately 30ppm, and industry does not have in place the technology to achieve this level. Consequently, alternative catalysts for HDS are now being considered.

Homogeneous transition metal complexes are ideal for probing the mechanism for this process by allowing analysis of specific steps in the proposed HDS cycle.\(^4,5,6\) In addition, such complexes can show reactivity patterns that differ from commercial HDS catalysts. Many obstacles will have to be overcome to make these systems usable in any real process, including supporting the homogeneous species on a heterogeneous support. In this report, we summarize our studies of homogeneous C-S bond cleavage that have appeared since the termination of our prior grant in December of 1997. (The project was renewed in February of 1999.) These investigations show promising results for a new generation of HDS catalysts.

B. New Binuclear Complexes for C-S bond Cleavage

We have examined a number of new complexes for cleavage of C-S bonds. The goal has been to probe binuclear metal polyhydrides with the notion that the hydride ligands would already be present on the metal center to effect reduction of the thiophene. Furthermore, the presence of two adjacent metal centers will better serve to model a real Co/MoS\(_2\) heterogeneous catalyst. The active centers in these systems are proposed to be small MoS\(_2\) rafts with sulfur vacancies around the edge of the crystal (Figure 1).\(^7\) We have already seen C-S activation with diiridium, dirhodium, and dicobalt systems that mimic these sites, with bridging hydrides, thiolates, and sulfides in the organometallic derivatives.

![Figure 1. Illustration of some of the different types of coordinatively unsaturated sites which are possible at the \(\overline{1}010\) (a-e) and \(10\overline{1}\) (f-j) edges of MoS\(_2\).](image)

The dimeric nickel hydride \([(Cy_2PCH_2CH_2PCy_2)NiH]_2\) has been reported in the literature as a convenient source of the L\(_2\)Ni fragment.\(^8\) We have discovered that the related isopropylphosphine derivative not only inserts into C-S bonds but also desulfurizes dibenzothiophene.
The complex [(dippe)NiH]₂ reacts with thiophene, benzothiophene, and dibenzothiophene to give the C-S insertion adduct of (dippe)Ni⁰ (Eq 1). We have made several observations that characterize this system:

(1) these C-S insertion reactions are reversible, as it is possible to displace one thiophene with another (Eq 2);

(2) the insertion adducts react with more (dippe)Ni⁰ to give [(dippe)Ni]₂(µ-thiophene) insertion adducts similar to that seen earlier with cobalt (Eq 3);⁹ a similar dinuclear adduct is seen with benzothiophene, but not dibenzothiophene;

(3) with dibenzothiophene, the initial C-S insertion adduct reacts further to give desulfurized products (see below);

(4) both 4-methyldibenzothiophene and 4,6-dimethyl-dibenzothiophene react with [(dippe)NiH]₂ to give desulfurized products.

This latter observation is quite important in that no other homogeneous or even heterogeneous catalyst is active for desulfurization of 4,6-dialkyldibenzothioephes.

We have reported the results of the desulfurization of dibenzothiophene with [(dippe)NiH]₂.¹⁰ Following formation of the initial insertion adduct, the reaction continues to result in the formation of several organometallic products as shown in Scheme 1. Reaction of desulfurized species 4 with hydrogen at room temperature gives a mixture of both [(dippe)₂NiH]₂ and biphenyl (Eq 4). The above observations are consistent with the following conclusions: (1) the insertion into the dibenzothiophene C-S bond is reversible, (2) the nickel complex is capable of cleaving both C-S bonds, thereby effecting desulfurization of the dibenzothiophene, and (3) the reaction is potentially capable of becoming catalytic, since the starting dinuclear dihydride is regenerated (bridging sulfido complex 5 must also be recycled for this).
Another important result that we have obtained pertains to the activation and desulfurization of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. As mentioned above, \([(\text{dippe})\text{NiH}]_2\) reacts with these substrates as indicated in the Table below. 4-methylDBT gives in isolable C-S insertion adduct, but 4,6-dimethylDBT gives no such adduct and reacts only at elevated temperatures (90 °C) to give 3,3'-bitoly1. The analogous platinum hydrido dimer, however, reacts to give an isolable C-S insertion adduct that has been structurally characterized. *This represents the first example of a clean C-S cleavage of 4,6-dimethyldibenzothiophene.* Only one report of a low yield (15%) desulfurization of 4,6-dimethyldibenzothiophene using Ni$^0$ reducing agents plus acid has appeared in the literature,$^{11}$ and one report of cleavage of the hindered C-S bond of 4-methyldibenzothiophene has appeared.$^{12}$ Furthermore, heating this compound with H$_2$ or more \([(\text{dippe})\text{PtH}]_2\) results in the desulfurization of the thiophene altogether (Eq 5).$^{13}$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>equivs of [Ni(dippe)H]$_2$</th>
<th>Temp (°C)</th>
<th>Time (hrs)</th>
<th>Product (% yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Substrate" /></td>
<td>1.5</td>
<td>25</td>
<td>29</td>
<td><img src="image2" alt="Product" /> (99%)</td>
</tr>
<tr>
<td><img src="image3" alt="Substrate" /></td>
<td>1.5</td>
<td>25</td>
<td>120</td>
<td><img src="image4" alt="Product" /> (90%)</td>
</tr>
<tr>
<td><img src="image5" alt="Substrate" /></td>
<td>1.5</td>
<td>90</td>
<td>21</td>
<td><img src="image6" alt="Product" /> (46%)</td>
</tr>
</tbody>
</table>
With dibenzothiophene, a possible mechanism is shown in Scheme 2. It is reasonable that a similar µ-thiolato species to that shown in Eq 3 is formed and that extrusion of sulfur leads to the metallacycle and a terminal nickel sulfido complex. The sulfido species is unstable and is trapped by another (dippe)Ni⁰ fragment to give the observed dimeric product. A full report on these studies has appeared.¹⁴

The proposed mechanism for this desulfurization involves the intermediacy of a terminal nickel sulfido complex, although no such species are known. We have provided independent evidence for the existence of such species in the loss of benzene from Ni(dippe)(Ph)(SH) (Scheme 3). The reaction is first order, consistent with the formation of (dippe)Ni=S which then dimerizes. The intermediate can be trapped by 1,3-dipolar addition using a nitrone. As further evidence that there is a competition between dimerization of the sulfido intermediate and trapping by the nitrone, the ratio of products was found to be dependent on nitrone concentration.¹⁵
We have also found that the dinuclear ruthenium hydride [Cp*RuH2]2 reacts with thiophene to give a ring-opened product (Eq 6). 2-methylthiophene reacts similarly. No incorporation of the hydrogen into the product is observed.\textsuperscript{16}

\begin{equation}
\begin{array}{c}
\text{RuRu} \\
25^\circ\text{C} \\
S R \\
H \\
Ru Ru \\
H \\
1 \\
, R = H \\
3 \\
, R = \text{Me}
\end{array}
\end{equation}

The reactivity of the iridium dimer [Cp*IrH3]2 with nitrogen containing heterocycles has also been examined. N-methyl pyrrole reacts to give a product of C-H activation and olefin coordination as shown in Eq 7. A trace amount of a second zwitterionic product was also obtained. Both compounds were characterized by X-ray diffraction.\textsuperscript{17}

\begin{equation}
\begin{array}{c}
\text{N} \\
\text{Ir} \\
\text{H} \\
\text{Ir} \\
\text{H} \\
\text{H} \\
\text{HH} \\
\text{4} \\
+ \text{trace:}
\end{array}
\end{equation}

C. Bond Activation using Tethered Complexes.

Earlier work with Cp*Rh(PMe3) complexes showed that one limitation with these derivatives is their lack of long term thermal stability. When these compounds are subjected to temperatures in excess of 80-100 °C for periods of greater than a week, substantial quantities of Cp*Rh(PMe3)\textsubscript{2} are formed. This complex can only be formed by the decomposition of half of the initial rhodium complex(es) present, and is quite inert toward further reaction. One theory for the formation of this product is that loss of phosphine from Cp*Rh(PMe3)XY compounds occurs on a limited basis under these conditions (control experiments show that PMe3 is not generally labile in these derivatives), and that the free PMe3 reacts with coordinatively unsaturated [Cp*Rh(PMe3)] to give the dead-end product.

We have prepared a new class of thermally stable analogs of these compounds by working with tethered phosphine derivatives. The ligand (C\textsubscript{5}H\textsubscript{4}SiMe\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}) has been reported in the literature by Schore,\textsuperscript{18} and we have found that it reacts with [RhClL\textsubscript{2}]\textsubscript{2} where L = CO or C\textsubscript{2}H\textsubscript{4} to give (C\textsubscript{5}H\textsubscript{4}SiMe\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})RhL (Eq 8). The ethylene complex has been structurally characterized and confirms that the phosphine is chelated to the same metal center as the C\textsubscript{5}H\textsubscript{4} ring (see Figure at right). Earlier complexes containing this ligand were found to bridge two metal centers. Other tethered ligands in the literature include C\textsubscript{5}Me\textsubscript{4}HCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2},\textsuperscript{19} C\textsubscript{5}H\textsubscript{5}CH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2},\textsuperscript{20} and C\textsubscript{5}Me\textsubscript{4}HCH\textsubscript{2}CH\textsubscript{2}NMe\textsubscript{2}.\textsuperscript{21}
We have identified two modes of reactivity for these types of adducts. In one reaction, the coordinated phosphine can be displaced by a strong nucleophile, such as PMe3 (Eq 9). In a second reaction, oxidative addition with concomitant ethylene loss is observed. The diiodide can be converted to the dihydride, as shown in Scheme 4.

Furthermore, the dihydride was found to be capable of activating certain C-H bonds. Irradiation in benzene provides no evidence for C-H bond activation, yet irradiation in C6F6 leads to the η^2-arene complex, indicating that dihydrogen is photolabile. C-H activation does occur with C6F5H indicating that the fragment is capable of oxidative addition to arene C-H bonds, provided the product is stable. With benzene, activation probably occurs but the adduct is labile.
D. Statement of Funds Estimated to be Unobligated.

None of the funds allocated for the current project year will remain unobligated at the end of the current year.

E. Publications appearing during the first year of this grant:


F. References and Notes


(2) "Current state of the problem of the study of organosulfur compounds from petroleums,"


(12) A report has recently appeared in the literature in which the (Et3P)2Pt fragment is believed to have inserted non-specifically into the C-S bonds of 4-methyl dibenzothiophene forming a 1:1 mixture of thiametallacycle isomers. The C-S insertion complexes were not structurally characterized, but were found to release 3-methylbiphenyl under desulfurization conditions. See: Iretskii, A.; Garcia, J. J.; Picazo, G.; Maitlis, P. M. Catal. Letters 1998, 51, 129-131. We believe this report to be incorrect, and instead reflects reactivity with an isomeric impurity in the dibenzothiophene substrate.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Title</th>
<th>Authors</th>
<th>Journal</th>
<th>Volume</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>(21)</td>
<td>“Rhodium and Iridium Complexes with the 1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadieny ligand,”</td>
<td>Jutzi, P.; Kristen, M. O.; Neumann, B.; Stammler, H.-G.</td>
<td>Organometallics</td>
<td>1994</td>
<td>13, 3854-3861.</td>
</tr>
</tbody>
</table>