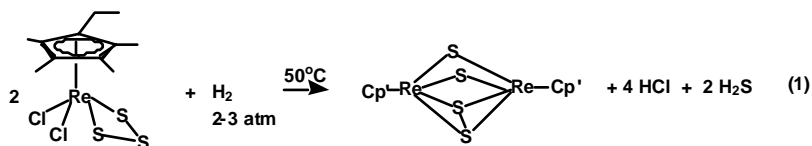


## Summary of Results

**Introduction.** The research project proposed to synthesize new metal complexes with sulfido, disulfido and other types of reactive sulfur ligands, and to explore the joint reactivity of metal and sulfur ligands with hydrogen and organic molecules. The overall objective was to investigate reaction pathways relevant to those observed for the heterogeneous metal sulfide catalysts which promote hydrogen activation, hydrogenation-dehydrogenation of organic substrates, and hydrogenolysis of carbon-heteroatom bonds.<sup>1</sup> Particular emphasis was placed on CpRe derivatives (where Cp might be C<sub>5</sub>H<sub>5</sub> or alkylated versions) so that comparisons could be made with the previously studied CpMo complexes, which showed extensive reactivity at the sulfur ligands.<sup>2</sup> Heterogeneous rhenium sulfides generally show higher catalytic activity than molybdenum sulfides, and this is attributed, in part, to the weaker Re-S bond strength, relative to the molybdenum-sulfur bond.<sup>3</sup> In our studies of discrete Re-sulfide complexes, we have also observed evidence for weaker Re-S bonds relative to the molybdenum systems. In addition we have characterized novel hydrogen activation by rhenium sulfido complexes, as well as carbon-hydrogen, carbon-sulfur and metal sulfur bond cleavage reactions.

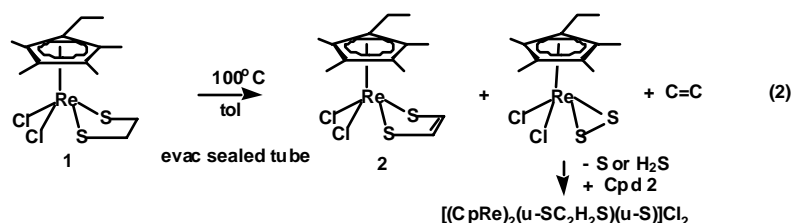
During this project period work supported by a previous DOE grant was also completed in which the activation of pyrrole heterocycles by metal complexes was studied. As detailed in the final report for that project, several types of metal-pyrrole complexes were synthesized, and regioselective activations toward both nucleophilic and electrophilic reagents were identified.

**Hydrogen Activation.** The complex Cp'ReCl<sub>2</sub>S<sub>3</sub> was synthesized in ca 70% yield and characterized by an X-ray diffraction study which confirms that the complex contains a  $\eta^2$ -trisulfide ligand. The cyclic voltammogram of Cp'ReCl<sub>2</sub>S<sub>3</sub> shows a wide window of redox stability with an irreversible reduction wave at -0.97 V and an irreversible oxidation at +1.03 V vs Fc. Nevertheless, the complex undergoes a facile reaction with hydrogen at 50°C as shown in Eq. 1.



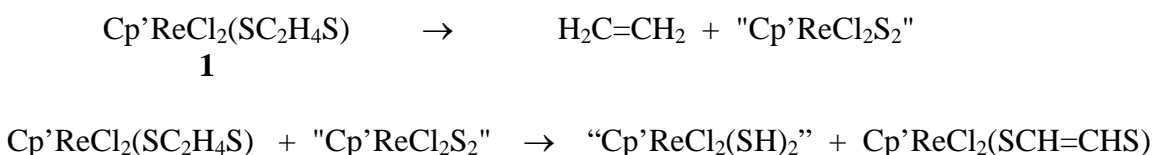
This reaction is of interest because it is the first example of the hydrogenolysis of a discrete metal polysulfide complex to produce H<sub>2</sub>S, a reaction also observed for heterogeneous rhenium sulfides. The reaction contrasts with those of related Cp-molybdenum complexes with sulfide ligands, which also activate hydrogen, but generally form hydrosulfido products without H<sub>2</sub>S elimination.

**C-H and C-S Cleavage Reactions.** New mononuclear Cp'Re(dithiolate) complexes such as Cp'ReCl<sub>2</sub>(SC<sub>2</sub>H<sub>4</sub>S), **1**, have been prepared and characterized and have been found to display a very interesting range of reactions. The thermal reaction of **1** involves the dehydrogenation of the alkanedithiolate ligand to form Cp'ReCl<sub>2</sub>(SCH=CHS), **2** as well as a competing elimination of olefin from the dithiolate ligand in **1** as summarized in Eq. 2.



Kinetic data for the thermal reactions of **1** and related derivatives in  $d^8$ -toluene were obtained by NMR spectroscopy and the thermal reaction of **1**, followed through 3 half lives, was found to be first order in **1**. Rate constants were determined over a temperature range of 80 to 108°C. An Eyring plot provided the following activation parameters:  $\Delta H^\ddagger = 121 \pm 5 \text{ kJ/mol}$  and  $\Delta S^\ddagger = -24 \pm 12 \text{ J/mole K}$ .

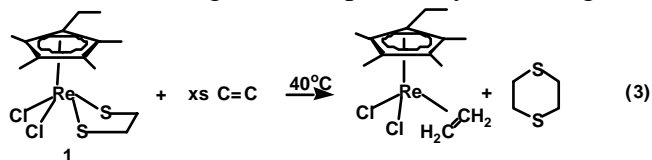
On the basis of kinetic and related studies, the mechanism is proposed to involve a sequential series of reactions as shown in Scheme 1.



Scheme 1

In this scheme, the olefin extrusion reaction is proposed to produce a reactive Re-disulfide or Re-bis(sulfido) intermediate which serves as an oxidant for the dithiolate complex **1**. The ability of the bis sulfido complex to dehydrogenate hydrocarbons is a unique feature and several additional dehydrogenation reactions with this system have been characterized, including the oxidation of other dithiolate complexes, of tetrahydronaphthalene and of cyclohexadiene. Precedents for the role of metal sulfides in dehydrogenation reactions have been reported for heterogeneous metal sulfide surfaces.<sup>13</sup> This work has begun to provide information about the electronic and structural features necessary for such reactivity.

**Carbon Sulfur Bond Formation.** When the thermal reaction of **1** was carried out in the presence of excess dry ethene a new reaction was observed as shown in Eq. 3.<sup>5</sup> The dithiolate ligand is displaced by incoming olefin to form the organic product,



1,4-dithiane. The Re product is identified as  $\text{Cp'Re(alkene)Cl}_2$  on the basis of NMR and mass spectroscopic data. Similar reactions with alkynes have been found to form unsaturated 6-membered rings and reactions with 1,3 dithiolate complexes form the organic 7-membered rings. To our knowledge the formation of cyclic bis-thioethers by the reactions of an alkene or alkyne with a discrete dithiolate metal complex has not been reported previously.

Reactions of the rhenium dithiolate complexes with other metal fragments have been studied as a pathway to heteronuclear clusters. For example, the first example of a

Pt<sub>2</sub>ReS<sub>2</sub> complex and examples of Re/Ag/S coordination polymers have been synthesized and characterized.

**Conclusions.** A series of new rhenium complexes with sulfido, disulfido, and thiolate ligands have been synthesized and characterized. The complexes have shown novel patterns of reactivity at the sulfur ligands that include hydrogen activation and addition, dehydrogenations, and carbon-sulfur bond formation. Systematic studies of sulfur ligand reactivity as the coligands in these rhenium complexes were varied have established electronic features that favor the novel ligand based reactivity. This series of complexes provides a model system for aspects of rhenium-sulfide surface reactivity, and have led to the suggestion of new mechanistic possibilities.

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