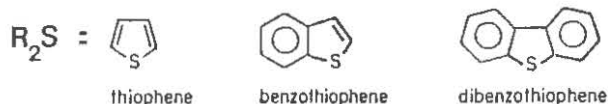
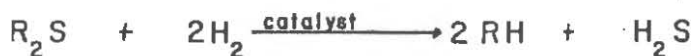


# Synthesis of Molecular Models of Hydrodesulfurization Catalysts

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The removal of thiophenes and dibenzothiophenes from petroleum by catalytic hydrodesulfurization (HDS) is becoming increasingly important to fossil fuel processing. The reaction is catalyzed by a cobalt-molybdenum sulfide (eq. 1) and is believed to involve

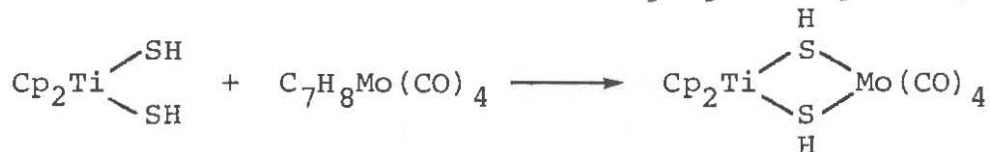


thiophene coordination to the metal surface and subsequent hydrogen transfer from an M-SH (metallothiol) unit to the bound substrate [1]. Transition metal complexes with SH or thiophene ligands may be thought of as molecular analogs of these surface species.

## I. Metallothiols

The reactivity of the metallocithiols  $Cp_2M(SH)_2$  ( $M = Ti, W$ ) [2,3] was observed to differ depending on the metal center. While the titanium compound was relatively unreactive, the tungsten compound was readily alkylated by methyl iodide.  $Cp_2W(SH)_2$  also reacted with a methyl isonitrile ligand of  $[Pd(CH_3NC)_2dppf](PF_6)_2$  to afford the dithiocarbamate complex  $[Cp_2WS_2CN(H)CH_3]PF_6$  [4]. This reaction does not occur with uncoordinated methyl isonitrile and illustrates a bimetallic activation of the substrate. The palladium product of this reaction was identified as  $[Pd(CH_3NC)dppf]_2(PF_6)_2$  [5].

The compound  $Cp_2Ti(SH)_2$  functions as a bidentate ligand to form mixed-metal derivatives with bridging SH ligands (eq. 2) [6].



Dynamic NMR spectroscopy established the inversion barrier at sulfur is similar to other ( $\mu$ -SR) derivatives ( $74 \text{ kJ}\cdot\text{mol}^{-1}$ ).

The reactivity of the dimeric Ti-Mo compound increased in relation to the monomeric titanium precursor.  $Cp_2Ti(SH)_2Mo(CO)_4$  was readily alkylated to afford  $Cp_2Ti(SR)_2Mo(CO)_4$ , and reacted with activated olefins to afford the conjugate addition products. The increased reactivity of the thiol groups of the bimetallic compound may be related to the observed bimetallic effect of the HDS catalyst.

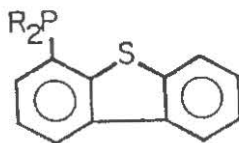
## II. Metal-Thiophene Complexes

In order to induce thiophene coordination to a metal center, several transition metal complexes of the substituted cyclopentadiene ThCpH were prepared and studied spectroscopically. Although



no interaction of thiophene was seen in several complexes of titanium and molybdenum, the compound (ThCp)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl reacts with silver (I) salts to afford a cationic complex whose spectroscopic characteristics are consistent with an S-bound thiophene unit.

The chelating phosphine ligand tol<sub>2</sub>PDBT reacted with Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>



R = 4-MePh; tol<sub>2</sub>PDBT

to afford the transition metal derivative RuCl<sub>2</sub>(tol<sub>2</sub>PDBT)<sub>2</sub>, which was characterized by single crystal x-ray diffraction [7]. This is the first unambiguous example of a metal complex with an S-bound thiophene.

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