

MECHANISTIC STUDIES RELATED TO THE METAL CATALYZED  
HYDROGENATION OF CARBON MONOXIDE TO HYDROCARBONS

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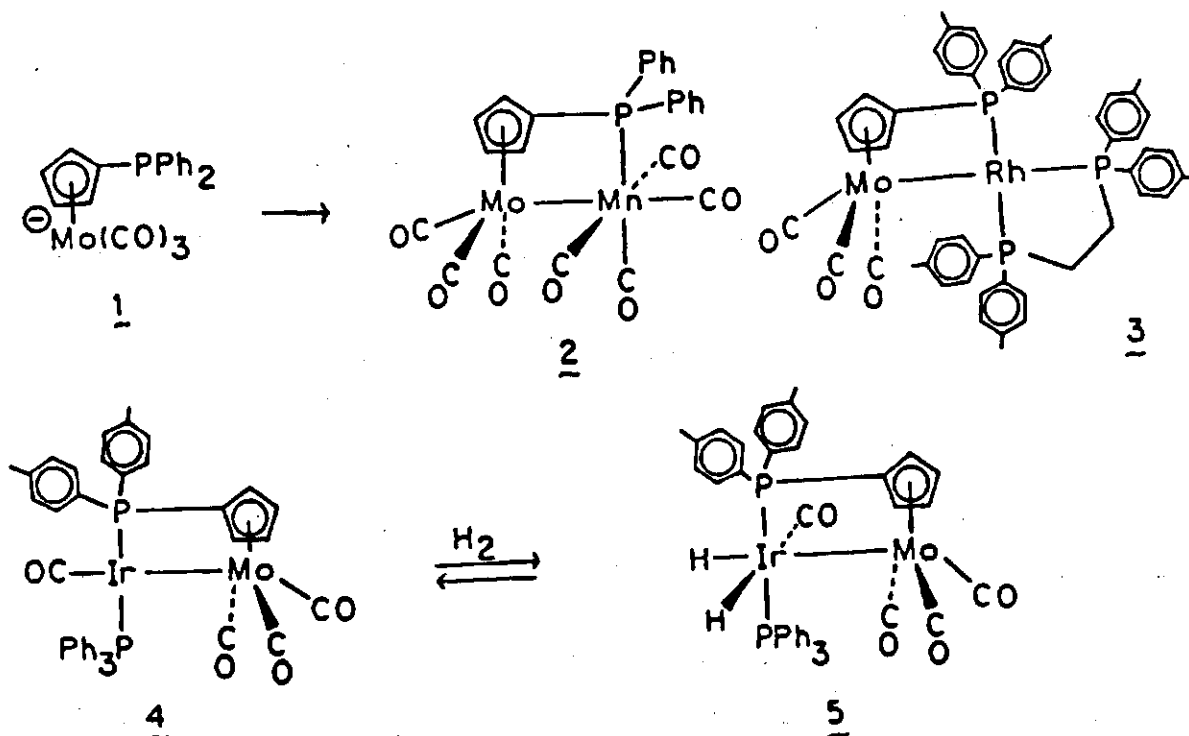
Research Scope and Objectives

The synthesis of organometallic compounds which contain functional groups similar to those proposed in homogeneous and heterogeneous catalyzed carbon monoxide reduction is being carried out so that the properties and reactions of these species can be studied. This basic information should contribute to the understanding and eventual design of catalysts for the reduction of carbon monoxide. In addition, new heterobimetallic complexes are being synthesized as potential CO hydrogenation catalysts.

Description of Research Effort

A series of compounds containing  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  groups bridging between two iron atoms have been synthesized as models for surface species in the reduction of CO on metal surfaces. The bridging methylene diiron compound  $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$  reacts with  $(\text{C}_6\text{H}_5)_3\text{C}^+\text{PF}_6^-$  to produce  $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH})]^+\text{PF}_6^-$ , the first methylidyne complex in which a  $\text{CH}$  unit bridges between two metals. This methylidyne complex reacts with CO to produce the bridging acylium complex  $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHCO})]^+\text{PF}_6^-$ . The methylidyne complex reacts with ethylene to add its  $\mu\text{-CH}$  bond across the carbon-carbon double bond of ethylene to give the propylidyne complex  $[(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}_2\text{CH}_3)]^+\text{PF}_6^-$ . Reaction of 1,2-disubstituted alkenes with the methylidyne complex leads to the formation of equilibrating mixtures of bridging alkylidyne complexes and bridging vinyl complexes.

For the past several years, we have been attempting to synthesize heterobimetallic dihydrides which contain both a hydridic early transition metal hydride and an acidic late transition metal hydride in the same molecule. We believe that such molecules might be new homogeneous catalysts for the hydrogenation of CO. Our approach has been to prepare heterobimetallic compounds held together both through a metal-metal bond and a heterodifunctional ligand, and to investigate the reactivity of these compounds with hydrogen in an attempt to form heterobimetallic dihydrides.



Reaction of molybdenum anion **1** with  $[(\text{CO})_4\text{MnBr}]_2$  give **2**, which has been characterized spectrally and by X-ray crystallography. Neither the Mo-Mn nor the related Mo-Re compound shows any evidence for metal hydride formation when heated under high pressures of  $\text{H}_2$ . The Mo-Mn and Mo-Re bonds of these heterobimetallic compounds can be protonated by  $\text{CF}_3\text{SO}_3\text{H}$ , giving cationic species with bridging hydrides. Attempted dihydride formation by reaction of these monohydrides with  $\text{LiHBEt}_3$  resulted in deprotonation instead of hydride addition.

Since **2** is coordinatively saturated, prior ligand loss or metal-metal bond rupture would have been required to create a site for addition of hydrogen. We therefore prepared several coordinatively unsaturated Rh-Mo compounds such as **3** which we thought would be capable of facile oxidative addition of  $\text{H}_2$ . Surprisingly, **3** is also unreactive towards  $\text{H}_2$ . We believe that **3** may be reacting rapidly and reversibly with  $\text{H}_2$  to form a thermodynamically unstable dihydride.

Since third row metals often form stronger bonds than their second row counterparts, we decided to prepare some Ir-Mo compounds to compare their reactivity to the Rh-Mo compounds. As expected, the Ir-Mo compounds such as **4** reacted with  $\text{H}_2$  to form isolable iridium dihydrides such as **5**.

### Future Research

Structural modifications that would lead to reductive elimination of M-H from  $\text{M}^{\text{II}}-\text{MH}_2$  to produce  $\text{M}^{\text{I}}\text{H}-\text{MH}$  are currently under investigation. In addition, synthesis of Zr-Fe, Zr-Ru and Zr-Co cobalt compounds are being studied.