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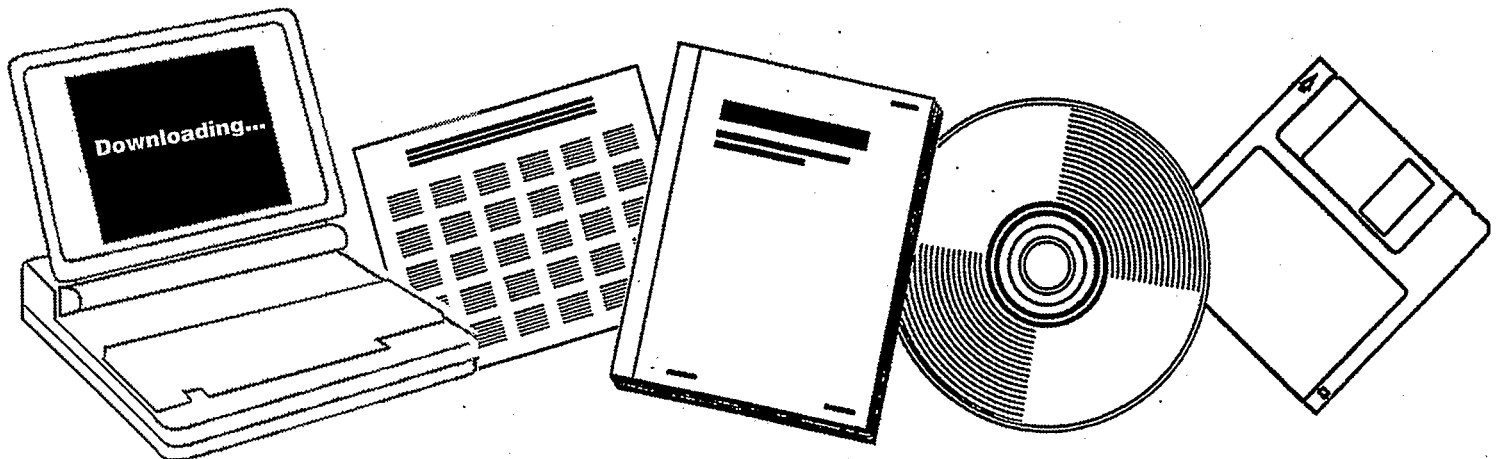
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**MECHANISTIC STUDIES RELATED TO THE METAL
CATALYZED REDUCTION OF CARBON MONOXIDE TO
HYDROCARBONS. FINAL REPORT, APRIL 1,
1977-JUNE 30, 1984**

WISCONSIN UNIV.-MADISON

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National Technical Information Service

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

Final Report for the Period

from April 1, 1977 to June 30, 1984

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DE84 007963

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ABSTRACT

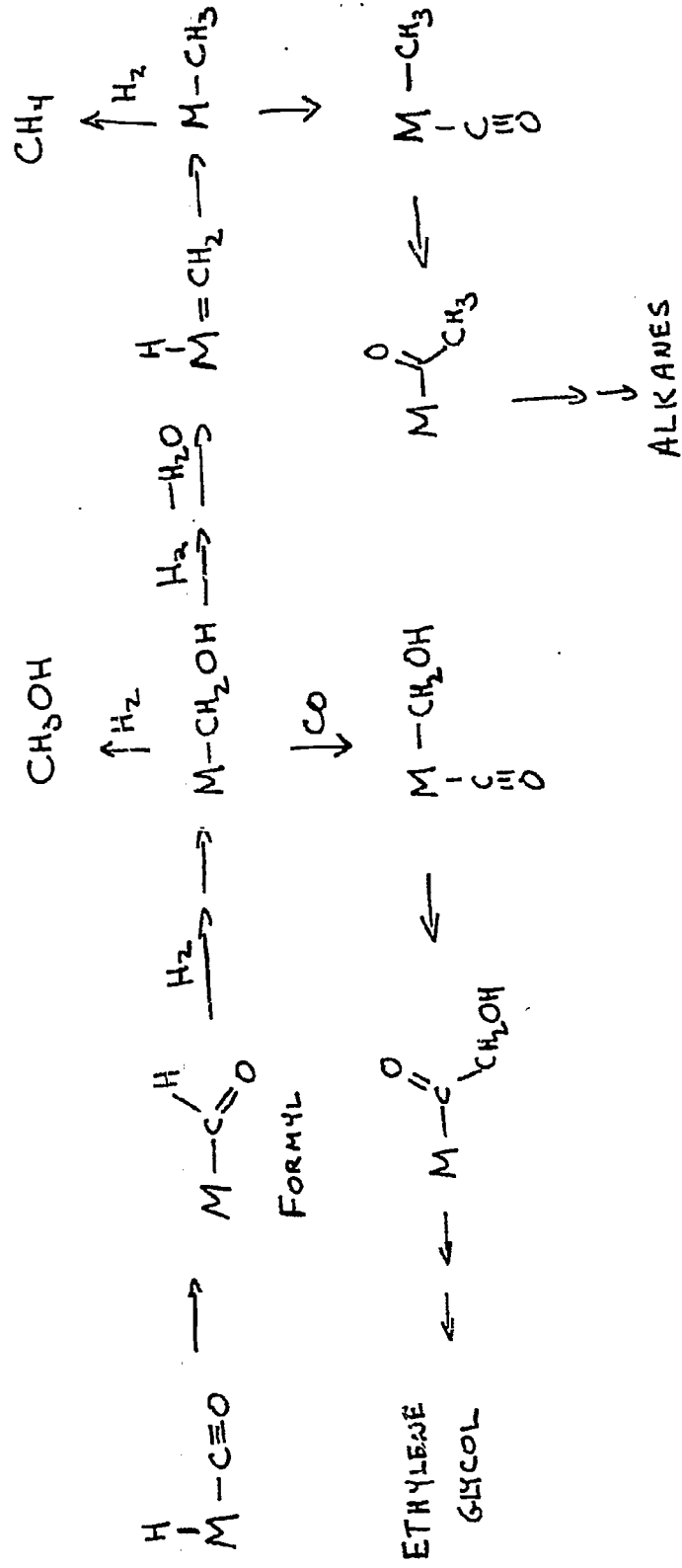
Studies of compounds related to proposed intermediates in the hydrogenation of carbon monoxide over homogeneous and heterogeneous catalysts have been carried out. The synthesis, structure, and reactions of metal formyl compounds have been investigated. The synthesis and desproportionation reactions of hydroxymethyl metal compounds have been explored. Reactions involving interconversion of η^5 - and η^1 - C_5H_5 organometallic compounds have been discovered. New synthetic routes to bimetallic compounds with bridging hydrocarbon ligands have been developed. The first bimetallic compound with a bridging CH ligand has been prepared. The hydrocarbation reaction in which the CH bond of a bridging methylidyne complex adds across a carbon-carbon double bond has been discovered. New heterobimetallic compounds linked by a heterodifunctional ligand and heterobimetallic compounds with directly bonded early and late transition metals have been synthesized in a search for new CO hydrogenation catalysts.

INTRODUCTION

Our research on the mechanism of the metal catalyzed hydrogenation of CO has been supported continuously by the Department of Energy since April 1977. To date, this work has resulted in 23 publications and five submitted papers. In this report, I will concentrate on communicating the major themes of our research and the evolution of the research program. Four main topics will be covered: (1) the chemistry of metal formyl and hydroxymethyl metal compounds related to intermediates proposed in the homogeneous hydrogenation of CO, (2) the interconversion of $\eta^5\text{-C}_5\text{H}_5$ and $\eta^1\text{-C}_5\text{H}_5$ organometallic compounds serendipitously discovered in the course of other work, (3) bimetallic compounds with bridging hydrocarbon ligands related to intermediates proposed in the heterogeneous reduction of CO and (4) the synthesis of heterobimetallic compounds linked by heterodifunctional ligands as possible new catalysts for CO hydrogenation. The highlights of this research have included (1) the synthesis and characterization of metal formyl complexes (2) the synthesis of the first hydroxymethyl metal compound (3) the development of a new synthesis for bridging methylene metal complexes (4) the synthesis of the first bridging methylidyne complex (5) the discovery of the hydrocarbation reaction in which the C-H bond of a bridging methylidyne complex adds across the carbon-carbon double bond of an alkene (6) the discovery of reactions involving η^5 to η^1 interconversions of cyclopentadienyl metal complexes (7) the development of syntheses of heterobimetallic compounds linked by heterodifunctional ligands and (8) the synthesis of compounds with direct metal-metal bonds between an early and a late transition metal.

A. Formyl and Hydroxymethyl Metal Compounds

When we began this work, the mechanism of CO hydrogenation with both homogeneous and heterogeneous catalysts was thought to proceed via formyl, and hydroxymethyl metal compounds as shown in Scheme 1. The homogeneous reduction of CO

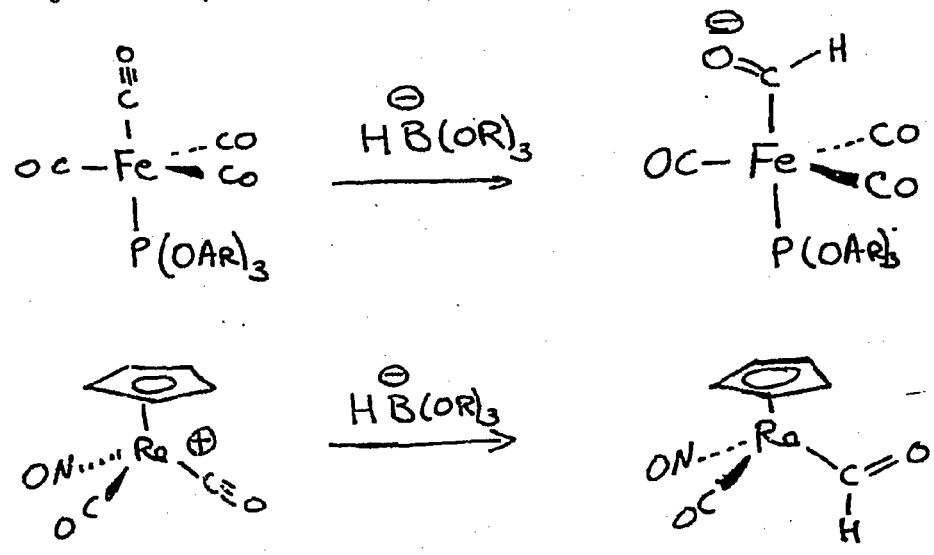


Scheme 1

to ethylene glycol and to other oxygenated products is still considered to take place by this mechanism. The heterogeneous reduction of CO has now been demonstrated to proceed by a very different route involving initial CO bond cleavage (dissociative chemisorption).

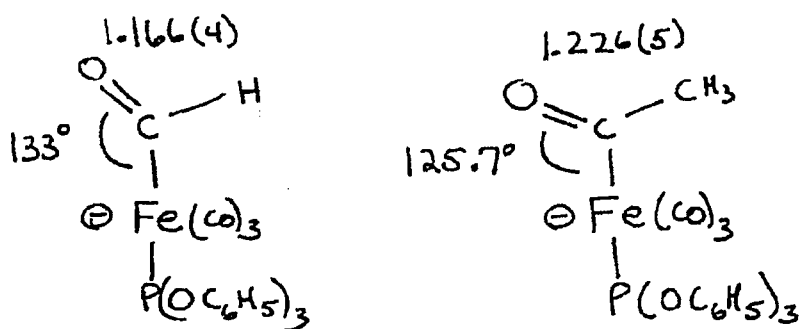
The insertion of CO into metal-carbon bonds is a very well known and facile process. In contrast, the insertion of CO into a metal-hydrogen bond to give a metal formyl complex has not been observed until very recently. (Wayland has seen insertion of CO into the rhodium hydrogen bond of a porphyrin complex but this is apparently a special case). To ascertain the reasons for the failure to observe metal formyl complexes in the reactions of metal hydrides with CO, we developed a new synthesis of metal formyl compounds and studied their properties. We have summarized our research on metal formyl compounds on several occasions.^{3,5,8}

We developed a new synthesis of metal formyl compounds from the addition of trialkoxyborohydrides to metal carbonyls and used this synthesis to prepare isolable metal formyl compounds including $(ArO)_3P(CO)_3FeCHO^-$,^{3,15,25} $(CO)_5Re-Re(CO)_4CHO^-$, and $(C_5H_5)Re(CO)(NO)CHO^-$.²

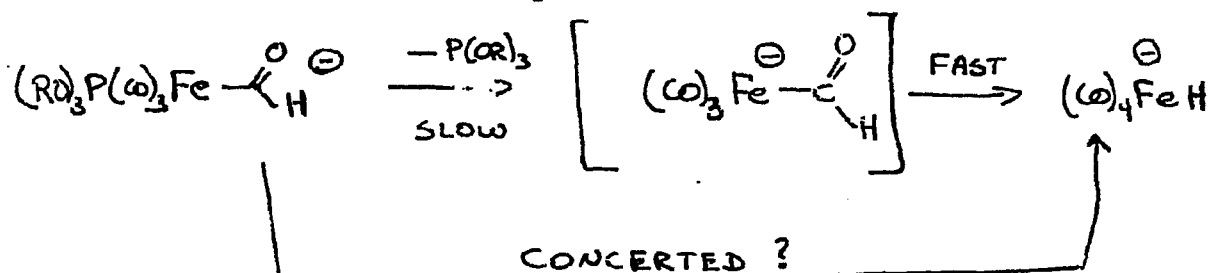


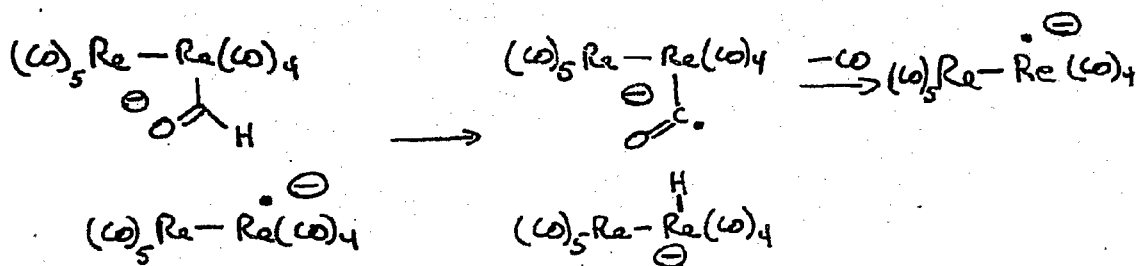
We have determined the structure of a closely analogous pair of metal formyl and metal acetyl complexes. The structures of the two complexes are remarkably similar; the very different chemistry displayed by formyl and acetyl complexes

cannot be due to structural differences. The only significant differences are that the 1.166(4) Å C=O bond length of the formyl ligand is substantially shorter than the 1.226(5) Å C=O bond length of the acetyl ligand and that the 133.0(3)° Fe-C-O angle of the formyl complex is substantially wider than the 125.7(3)° Fe-C-O angle of the acetyl complex. These structural differences might be related to the hydride donor ability¹ of formyl complexes since the formyl ligand is converted to a linear carbonyl ligand with a shortened C-O bond in the course of these reactions.



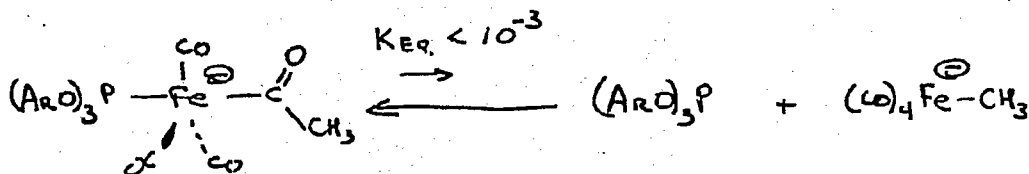
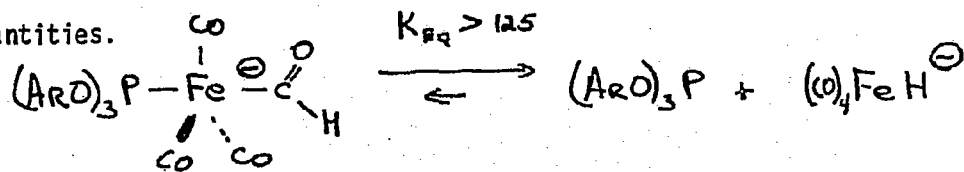
Formyl complexes display a wide range of kinetic reactivity. In some cases, such as $(RO)_3P(CO)_3FeCHO^-$ and $(RO)_3P(CO)_3FeCOCH_3^-$, the formyl and acetyl complexes both show high kinetic stability and are stable to $-70^\circ C$.^{3,5} In other cases, such as $C_5H_5(CO)_2RuCHO$ ($t_{1/2} = 2h$ at $-90^\circ C$) and $C_5H_5(CO)_2RuCOCH_3$ ($t_{1/2} = 15h$ at $150^\circ C$),⁸ the formyl complexes are much less stable than the corresponding acetyl complexes. For $(RO)_3P(CO)_3FeCHO^-$, we observed smooth first order decomposition to $(CO)_4FeH^-$ and $(RO)_3P$ and no inhibition by added phosphite.^{3,5,8} This is consistent either with loss of phosphite followed immediately by hydride migration to iron or with concerted loss of phosphite and hydride migration. For $(CO)_5ReRe(CO)_4CHO^-$, we noted that the compound was light sensitive.¹ Recently, in collaboration with Jay Kochi at Indiana, a radical chain mechanism for decomposition was established for $(CO)_5ReRe(CO)_4CHO^-$.²¹





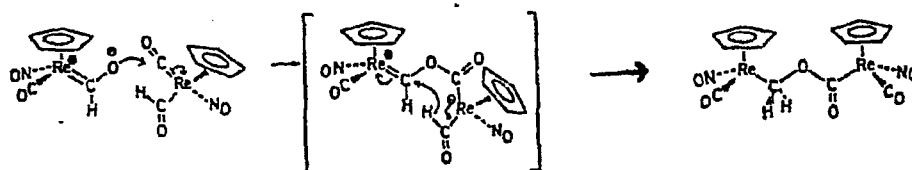
We attempted to measure the relative thermodynamic stabilities of a pair of analogous formyl and acetyl metal compounds but were only able to obtain limits of their differences in stability.^{3,5,8} Metal formyl compounds are thermodynamically much less stable than the corresponding metal acetyl compounds. For example, $(\text{CH}_3\text{CH}_2)_4\text{N}^+[(\text{ArO})_3\text{P}](\text{CO})_3\text{FeCHO}^-$ is completely converted (> 99.8%) to $(\text{CO})_4\text{-FeH}^-$ upon heating to 70° C. Therefore, the equilibrium constant $K_{\text{eq}} = [(\text{ArO})_3\text{P}][\text{FeH}^-]/[\text{FeCHO}]$ must be greater than 125M. By contrast, $(\text{CH}_3\text{-CH}_2)_4\text{N}^+(\text{CO})_4\text{FeCH}_3^-$ reacts with $(\text{ArO})_3\text{P}$ to give only $(\text{CH}_3\text{CH}_2)_4\text{N}^+[(\text{ArO})_3\text{P}](\text{CO})_3\text{FeCOCH}_3^-$. The equilibrium constant $K_{\text{eq}} = [(\text{ArO})_3\text{P}][\text{FeCH}_3^-]/[\text{FeCOCH}_3^-]$ was estimated to be less than 10^{-3}M .

The difference in equilibrium constant for insertion of CO into an FeH and an Fe-CH₃ bond is therefore greater than 1.25×10^5 which corresponds to a free energy difference of at least 7.5 kcal mole⁻¹. The greatly different thermodynamic stabilities of metal acyl and metal formyl compounds is mainly attributable to the greater strength of M-H bonds (estimated 50-60 kcal mole⁻¹) compared with M-CH₃ bonds (estimated 30-40 kcal mole⁻¹). The failure to observe metal formyl species in the reactions of metal hydrides with CO is now understandable in light of the low thermodynamic stability of metal formyl compounds. However, it is entirely possible that metal catalyzed CO reduction might proceed by formation and subsequent reduction of metal formyl species which are never present in detectable quantities.

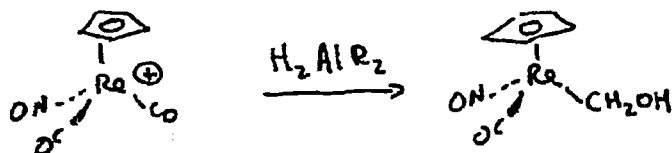


The availability of metal formyl compounds has allowed their chemical reactivity to be determined.¹ Our group and Gladysz's group independently discovered that metal formyl compounds can act as hydride donors to electrophiles such as ketones, alkyl halides, metal carbene complexes, and metal carbonyl compounds. For example, $(\text{CH}_3\text{CH}_2)_4\text{N}^+[(\text{C}_6\text{H}_5\text{O})_3\text{P}](\text{CO})_3\text{FeCHO}^-$ reacts with 2-butanone to give a 95% yield of 2-butanol, with $n\text{-C}_7\text{H}_{15}\text{I}$ to give a 71% yield of heptane, and with $(\text{CO})_5\text{W}(\text{OCH}_3)\text{C}_6\text{H}_5$ to give $(\text{CO})_5\text{WCH}(\text{OCH}_3)\text{C}_6\text{H}_5^-$.

The hydride donor ability of formyl complexes can lead to disproportionation reactions of the formyl compounds. For example, $\text{C}_5\text{H}_5(\text{CO})(\text{NO})\text{ReCHO}$ undergoes spontaneous disproportionation upon sitting at room temperature to produce the dimeric metalloester shown below.^{4,6} The disproportionation is proposed to proceed by an intramolecular pathway.

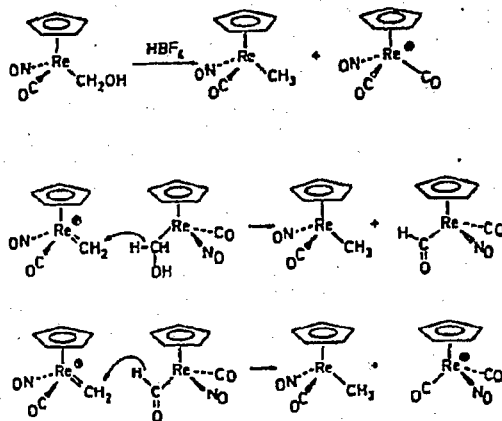


The hydrolysis of this metalloester led to the first synthesis of a hydroxymethyl metal compound.^{4,6} Later we developed a better route to the hydroxymethyl metal compound by $\text{Li}^+ \text{H}_2\text{AlEt}_2^-$ reduction of $\text{C}_5\text{H}_5\text{Re}(\text{CO})_2(\text{NO})^+$.⁶



Hydroxymethyl metal compounds like formyl complexes showed a strong tendency to undergo disproportionation reactions. For example, treatment of

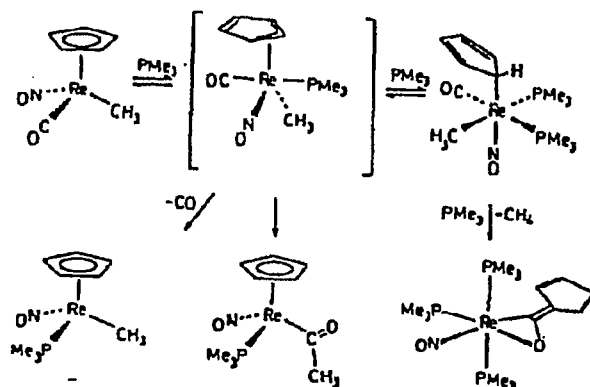
$C_5H_5(CO)(NO)ReCH_2OH$ with strong acid led to disproportionation to a rhenium methyl compound and a rhenium carbonyl.⁸



B. $\eta^5 \rightleftharpoons \eta^1-C_5H_5$ Interconversions.

All attempts to carbonylate this hydroxymethyl compound failed. This is probably unrelated to the nature of the hydroxymethyl group since the related methyl compound $C_5H_5(CO)(NO)ReCH_3$ also failed to undergo carbonylation even at $150^\circ C$ and 800 psi CO. The reaction of these compounds with PMe_3 was studied in an attempt to induce migration of the hydroxymethyl or methyl groups to CO.

We were surprised to find that two equivalents of PMe_3 added to $C_5H_5Re(CO)(NO)CH_3$ and that the $\eta^5-C_5H_5$ ligand slipped to an $\eta^1-C_5H_5$ unit.⁷ We found that the rate of reaction depended on $[Re]$ and $[PMe_3]$; this requires an intermediate monophosphene complex -- presumably an $\eta^3-C_5H_5$ intermediate. The addition of PMe_3 was completely reversible at room temperature. At higher temperatures, phosphene substitution took place to give a mixture of PMe_3 substituted acetyl and methyl complexes. When very high concentrations of PMe_3 were used, the formation of these substitution products was inhibited and a new compound -- a cyclopentadienylidene ketene complex -- was formed.¹⁸

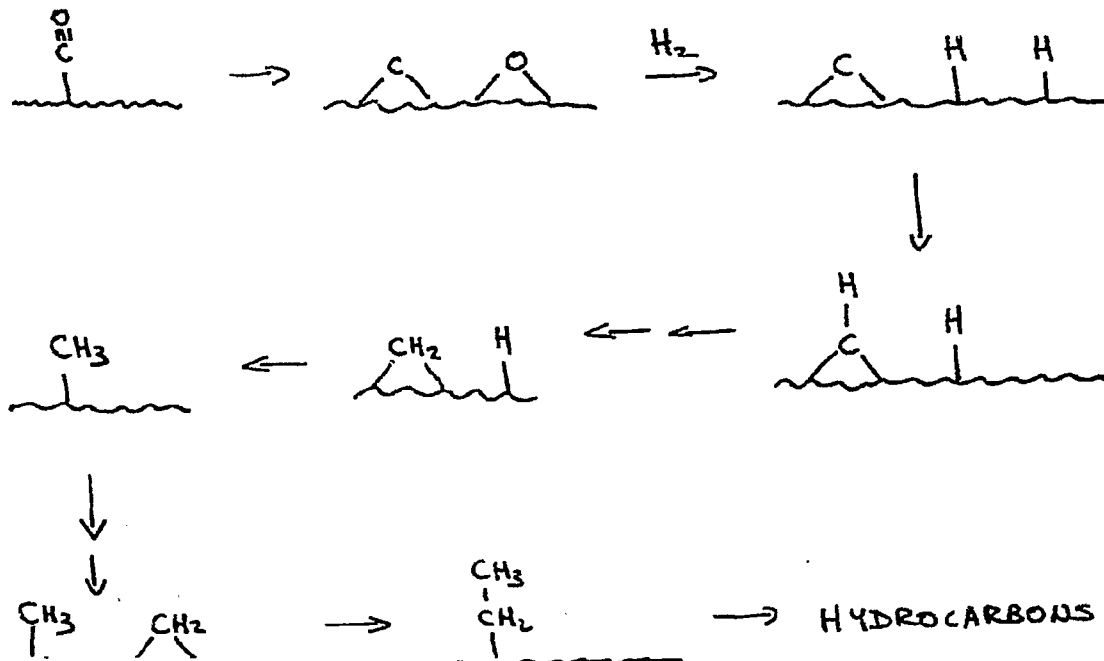


We have observed similar $\eta^1\text{-C}_5\text{H}_5$ metal compounds in the reaction of PMe_3 with $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$,⁸ $\text{C}_5\text{H}_5\text{W}(\text{CO})_2\text{NO}$,⁹ and $\text{C}_5\text{H}_5\text{Re}(\text{CO})_3$.¹⁷

While this chemistry of $\eta^5\text{-C}_5\text{H}_5$ and $\eta^1\text{-C}_5\text{H}_5$ is not directly related to CO hydrogenation, it does point out a new kind of basic transformation which should have broad implications in organometallic chemistry.

C. Bimetallic Complexes with Bridging Hydrocarbon Ligands.

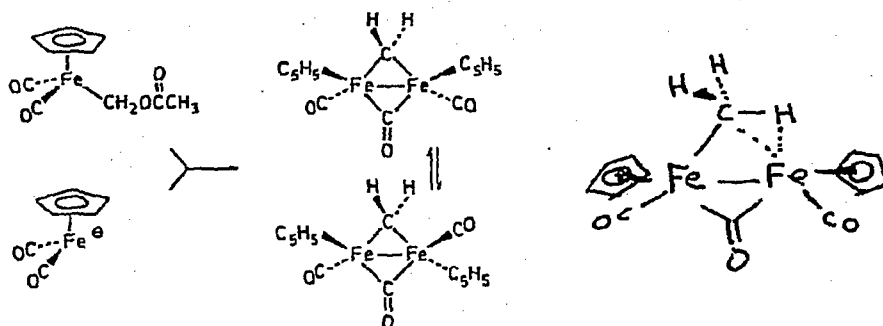
The mechanism of reduction of CO to hydrocarbons on some heterogeneous catalysts has now been shown to proceed by initial carbon-oxygen bond cleavage to give surface carbides. The surface carbides are then proposed to be hydrogenated to surface bound CH, CH₂, and CH₃ species. Carbon-carbon bond formation is thought to proceed via coupling of surface bound CH₃ and CH₂ units.



Scheme 2

Because of this proposed mechanism, we became interested in studying the synthesis and reactions of bimetallic complexes with bridging hydrocarbon ligands.^{20,22} This metal complex chemistry should be related to the surface chemistry in Fischer-Tropsch reactions.

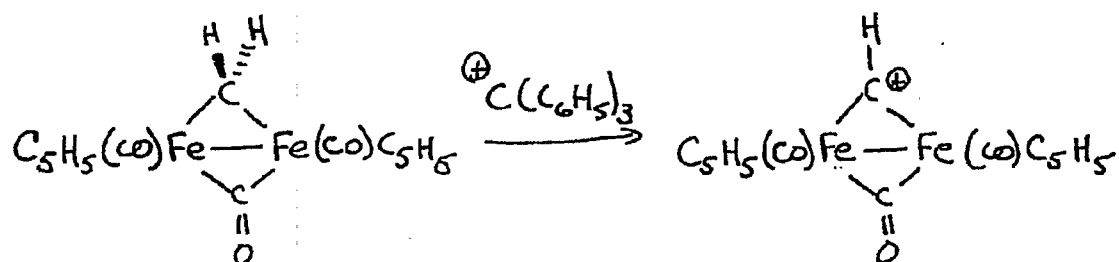
We developed a new synthesis of bridging methylene complexes by reaction of an organometallic anion with an organometallic compound with a leaving group on the carbon bonded to the metal. Reaction of $C_5H_5(CO)_2Fe^-$ with $C_5H_5(CO)_2FeCH_2OAc$ gave a good yield of bridging methylene complex $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-CH_2)$.¹⁰ The reaction is undoubtedly more complex than a simple nucleophilic displacement since $[C_5H_5Fe(CO)_2]_2$ is always isolated as a side product, indicating the possible involvement of odd-electron species such as $C_5H_5(CO)_2Fe$.



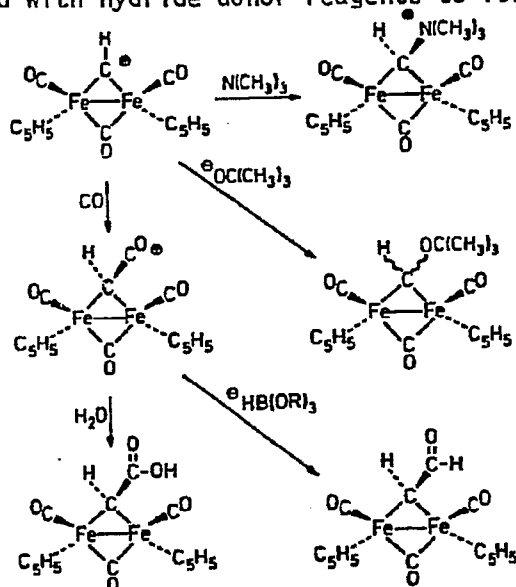
Protonation of the bridging methylene compounds produces a bridging methyl compound. NMR studies established that the methyl group is unsymmetrically bonded to the two iron centers and that there is a specific interaction of one iron atom with one of the CH bonds of the bridging methyl group.

Reaction of the bridging methylene compound with $C(C_6H_5)_3^+$ led to hydride abstraction and the isolation of the first doubly bridging methylidyne complex.¹⁰ This methylidyne complex can be thought of as a secondary carbocation stabilized by two strongly electron donating iron groups. The two iron groups lend greater

stabilization to the carbocation than the three phenyl groups of the trityl cation from which the methylidyne complex was prepared.

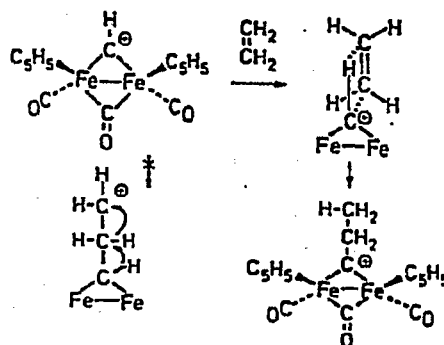


In spite of its thermodynamic stability, the methylidyne complex is remarkably reactive toward nucleophiles. It forms simple adducts with amines and with alcohols.¹³ The methylidyne complex even reacts with CO in a new carbon-carbon bond forming reaction to produce a bridging acylium complex whose X-Ray structure was determined in collaboration with Prof. Victor Day of Nebraska.¹³ The acylium complexes react with water to form an acid and with hydride donor reagents to form an aldehyde.



The most remarkable reaction of the bridging methylidyne complex is its reaction with alkenes.¹² The methylidyne complex reacts rapidly with ethylene at -30°C to give a bridging propylidyne complex in $> 70\%$ isolated yield. This reaction involves an unprecedented addition of a carbon hydrogen bond of the carbyne complex

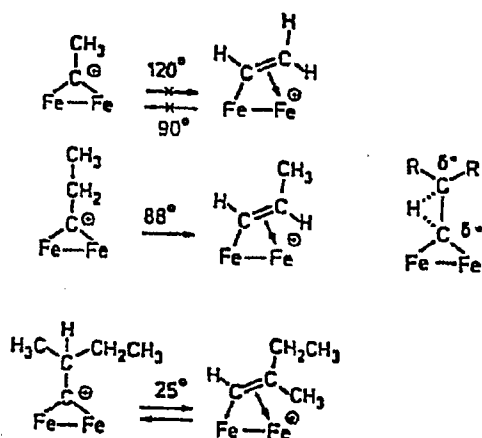
across the carbon-carbon double bond of ethylene. This similarity of this reaction to the hydroboration reaction has caused us to call the new reaction "hydrocarbation." As in the case of hydroboration, no oligomerization takes place. That is, the μ -CH and BH bonds readily add to alkenes but μ -C-R and B-R bonds don't.



Hydrocarbation is regiospecific: the methylidyne carbon always adds to the less substituted carbon and hydrogen is transferred to the more substituted carbon of the alkene.¹³ The reaction has also been demonstrated to involve cis addition of carbon and hydrogen to the alkene.^{20,22}

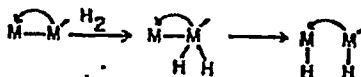
The reaction of the methylidyne complex with 1,2 disubstituted alkenes such as 2-butene gives a mixture of alkylidyne complexes formed by C-H addition to the alkene and of bridging vinyl complexes. Labeling experiments and low temperature studies have shown that the vinyl complexes arise from rearrangement of the initially formed alkylidyne complexes.²⁷

In independent studies of the rearrangement of bridging alkylidyne complexes to bridging vinyl complexes, we have found that the rate of rearrangement is accelerated greatly by carbon substituents on the carbon α to the carbyne carbon atom. Thus, the ethylidyne complex with no α carbon substituents does not rearrange at all at 88° C; the pentylidyne complex with one α carbon substituent rearranges slowly at 88° C; and the cyclohexyl substituted carbyne complex with two α -carbon substituents rearranges rapidly at -13° C.

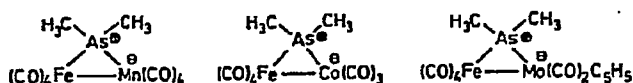


D. Heterobimetallic Compounds

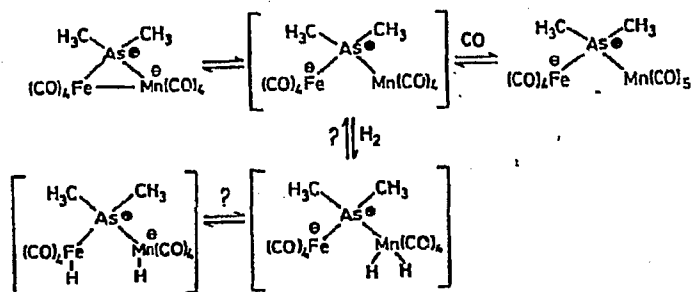
Heterobimetallic metal dihydrides which possess both a hydridic M-H bond and an acidic M-H bond are potentially excellent reducing agents for polar molecules like CO. Compounds possessing a hydridic M-H bond to an early transition metal and an acidic M-H bond to a late transition metal are prime candidates for powerful hydrogenation catalysts and might be available from reaction of H₂ with metal-metal bonds. However, since synthetic methods for making the desired precursors with directly bonded early and late transition metals are just beginning to be developed, our early efforts have centered on making bimetallic compounds between metals having smaller electronegativity differences. Our initial approach has been to prepare heterobimetallic compounds linked by a heterodifunctional ligand and to investigate the reactions of these compounds with H₂ as a possible route to heterobimetallic dihydrides. Linking the two metal centers through a bridging ligand maximizes the opportunity for the resulting metal hydrides to act cooperatively to reduce polar molecules.



The first bimetallic compounds we investigated as possible CO hydrogenation catalysts were the arsenic bridged bimetallic compounds shown below.



Vahrenkamp had previously synthesized these compounds and proposed that their ligand substitution reactions proceeded by initial metal-metal bond cleavage followed by trapping the coordinatively unsaturated metal with an incoming ligand. We set out to trap the proposed unsaturated intermediate with H_2 as a possible route to heterobimetallic dihydrides.¹¹ However, these arsenic bridged bimetallic compounds showed no evidence for interaction with H_2 or for activity as hydrogenation catalysts. In subsequent investigations, we found that the rate of reaction of PMe_3 with $(\text{CO})_4\text{Fe}(\mu\text{-AsMe}_2)\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ depended on the concentrations of both reactants.⁹ This implies that substitution reactions do not proceed by initial metal-metal bond cleavage and may explain why no reaction with H_2 was seen.

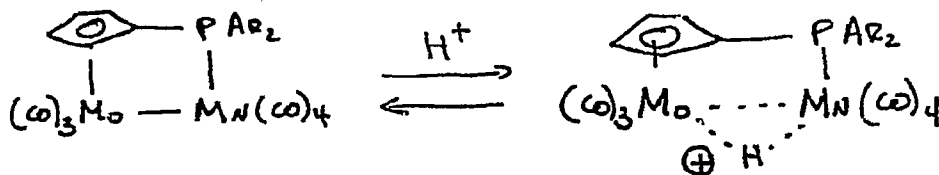


We next set out to prepare heterobimetallic compounds linked by a hetero-difunctional ligand.

We first prepared $(Ar_2P-C_5H_4)Mo(CO)_3^-$ which can be viewed as a difunctional chelate ligand with phosphine and metal anion donor groups capable of binding to a second metal center.¹⁴ Reaction of this molybdenum anion with the bridging metal halides $[(CO)_4MnBr]_2$ and $[(CO)_4ReBr]_2$ led to good yields of the heterobimetallic compounds shown below. The X-ray structure of the Mn-Mo compound indicated some ring strain.

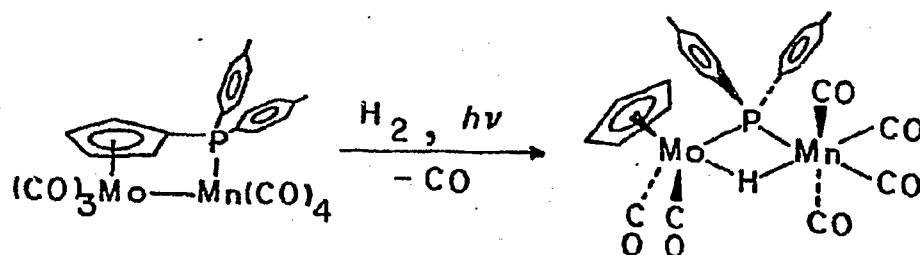


All attempts to add H_2 thermally to the Mo-Mn or Mo-Re compounds failed. For example, the Mo-Mn compound is stable to $170^\circ C$ under 1200 psi H_2 .¹⁴ In another attempt to make a heterobimetallic dihydride, the metal-metal bond of the Mo-Mn compound was protonated with strong acid to give a cationic bridging metal hydride.¹⁹ Attempted hydride addition to the cation failed to produce a dihydride; instead, H_2 evolved and the starting Mo-Mn compound was regenerated.

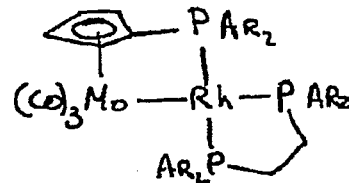
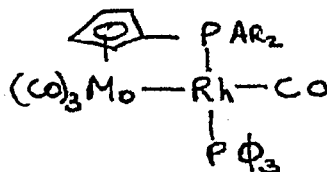
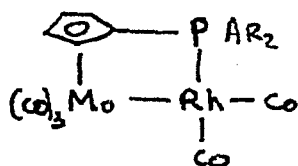


The failure of the Mo-Mn and Mo-Re compounds to react with H_2 even under forcing conditions is probably related to their coordinative saturation. These

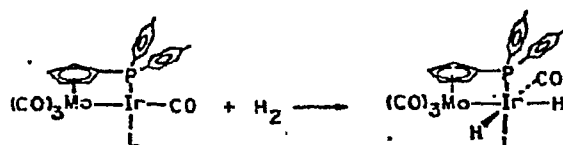
compounds would probably have to undergo less of a ligand or metal-metal bond rupture before reacting with H_2 . In an effort to generate a reactive site on the Mo-Mn compound, photolysis in the presence of H_2 was studied.²⁶ Once again, we failed to observe a heterobimetallic dihydride; instead, a novel reaction occurred in which the phosphorus-cyclopentadienyl bond was cleaved and $(CO)_4Mn[\mu-P(C_6H_4-CH_3)_2](\mu-H)Mo(CO)_2C_5H_5$ was formed.



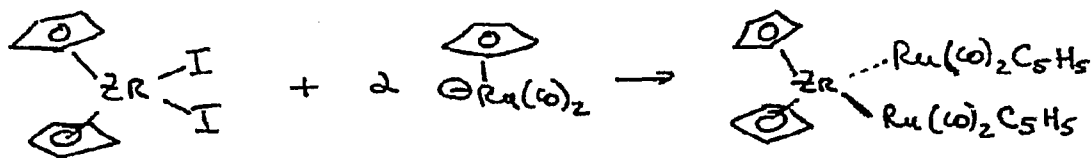
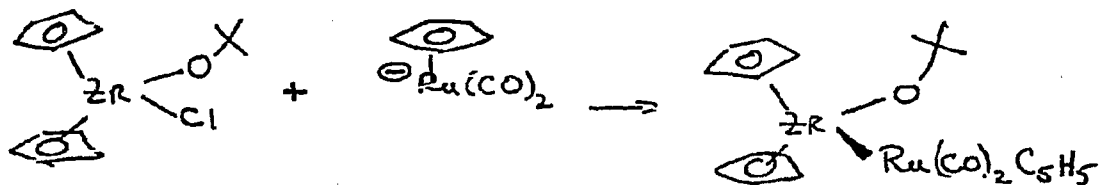
We next attempted to synthesize heterobimetallic compounds in which one of the metals was coordinatively unsaturated and capable of undergoing facile oxidative addition of H_2 . Rh(I)-Mo compounds were studied initially because ordinarily Rh(I) is reactive toward H_2 . The Rh-Mo compounds shown below were synthesized but all three compounds failed to react with H_2 .²⁴ IR evidence indicated that the Rh-Mo bond was highly polarized Rh^+-Mo^- . The failure of the Rh-Mo compounds to react with H_2 is probably related to the relatively electropositive nature of Rh in these compounds.



Ir(I) compounds are normally much more reactive toward H_2 than their Rh(I) counterparts because hydrogen forms substantially stronger bonds to third row elements like Ir than to second row elements like Rh. Indeed, we found that Mo-Ir compounds added H_2 to give iridium dihydrides.²⁴ Thus we have now succeeded in adding H_2 to a heterobimetallic compound but we have a long way to go before arriving at a CO hydrogenation catalyst. First, we need to develop reactions such as elementation of a metal hydride from a M^1-MH_2 system to arrive at a heterobimetallic dihydride M^1H-MH . Second, we need to work with bimetallic compounds with greater electronegativity differences between the metal centers to arrive at a compound possessing one hydridic M-H and one acidic M-H group.



To overcome the second problem, we have developed syntheses of bimetallic compounds with bonds between early and late transition metals. Reaction of $C_5H_5Ru(CO)_2^-$ with $(C_5H_5)_2(t-BuO)Zr-Cl$ produced a high yield of the first compound with a direct bond between zirconium and ruthenium.¹⁶ More recently, we have synthesized a compound with two rutheniums bonded to zirconium.²⁸



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