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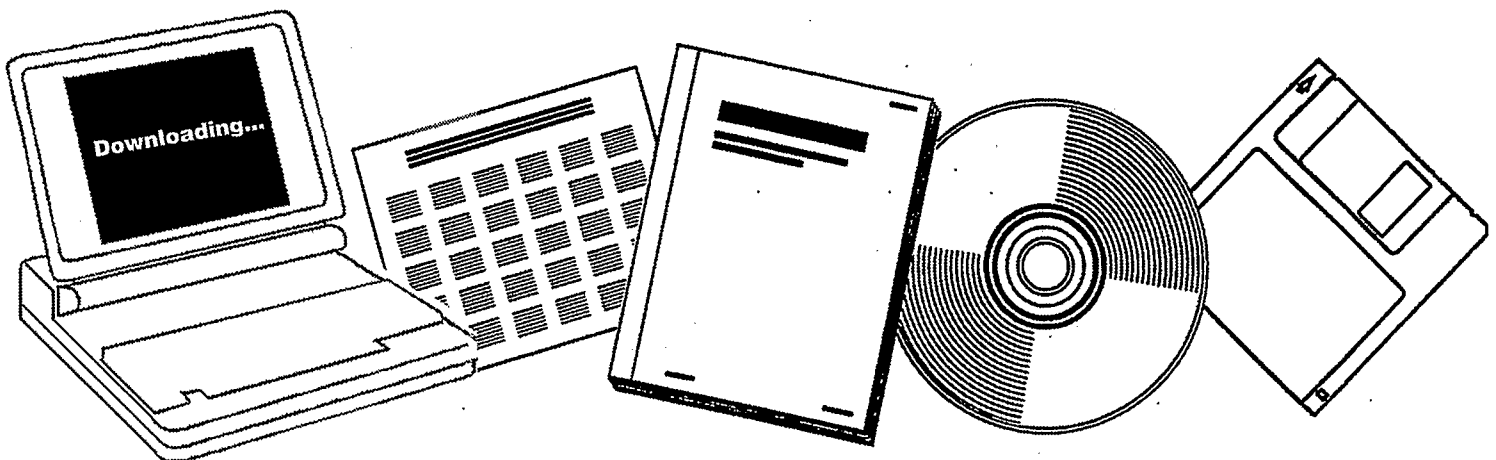
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**MECHANISTIC STUDIES RELATED TO THE METAL
CATALYZED REDUCTION OF CARBON MONOXIDE TO
HYDROCARBONS. PROGRESS REPORT, APRIL 1,
1980-JANUARY 31, 1982**

WISCONSIN UNIV.-MADISON

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

Progress Report for the Period
from April 1, 1980 to January 31, 1982

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ABSTRACT

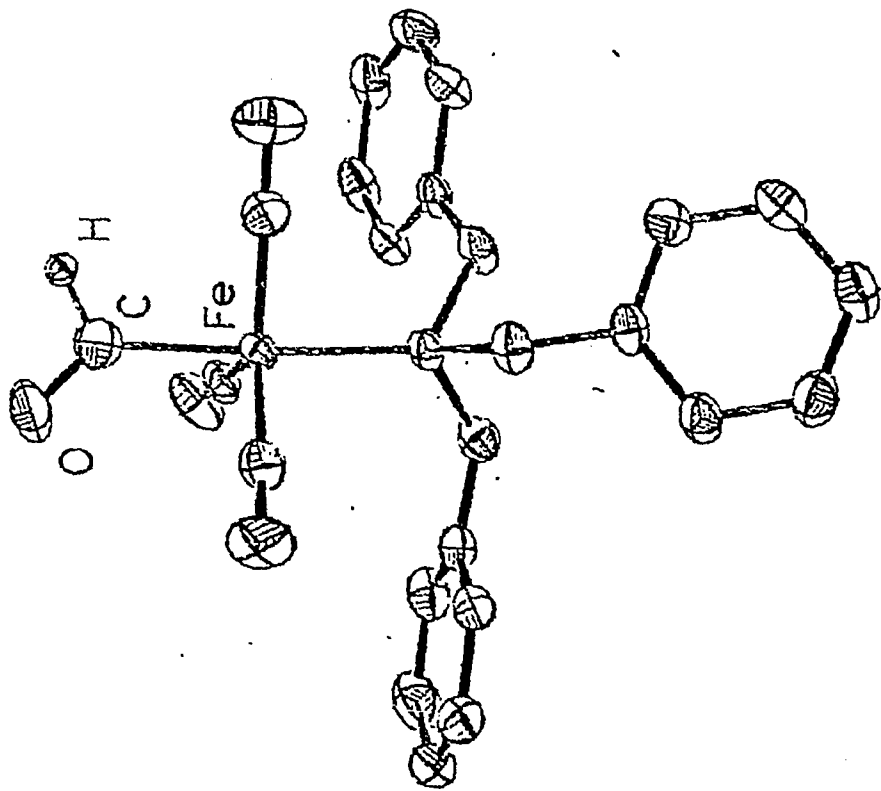
The crystal structures of analogous metal formyl and metal acetyl complexes have been determined and the differences analyzed. New heterobimetallic compounds have been prepared for study as possible carbon monoxide hydrogenation catalysts. The synthesis of related bridging methyl, methylene, and methylidyne complexes has been achieved. Several new types of chemical reactions have been discovered including $\eta^5\text{-C}_5\text{H}_5 \rightleftharpoons \eta^1\text{-C}_5\text{H}_5$ rearrangements and addition of C-H bonds to alkenes.

1. Metal Formyl Complexes

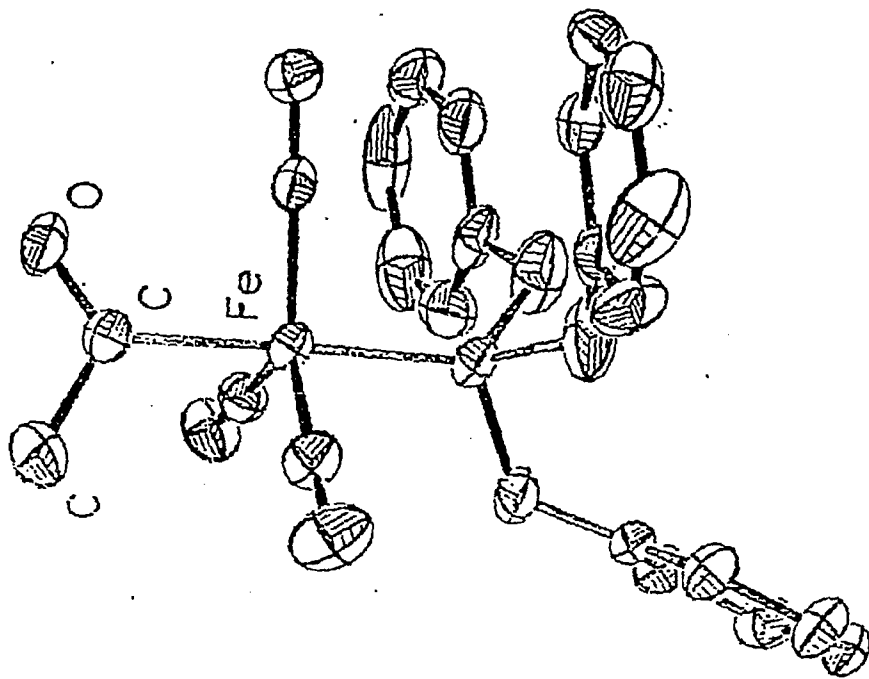
Metal Formyl Complexes have been proposed as key intermediates in homogeneously catalyzed hydrogenation of carbon monoxide. To determine the key features which distinguish metal formyl compounds from metal acetyl compounds, we have synthesized metal formyl and closely related metal acetyl complexes and are studying their structures and reactions¹.

STRUCTURE. During the past year, we completed X-ray crystal structures of exactly analogous metal formyl and acetyl compounds $N(CH_2CH_3)_4^+$ $(CO)_3[(C_6H_5O)_3P]FeCOR^-$ ($R=H, CH_3$)². The structures are very similar; the major difference being a 90° rotation of the acetyl ligand relative to the phosphite ligand.

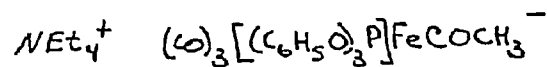
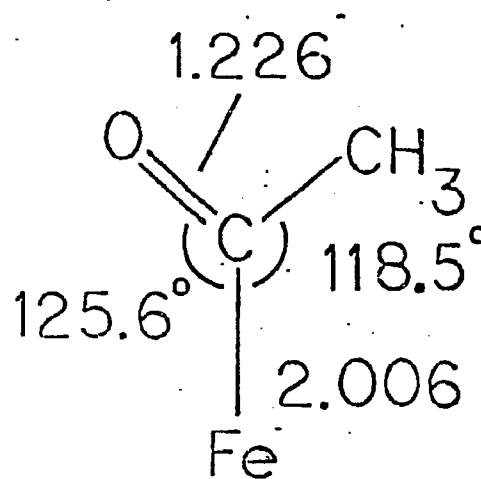
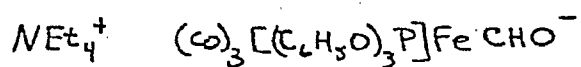
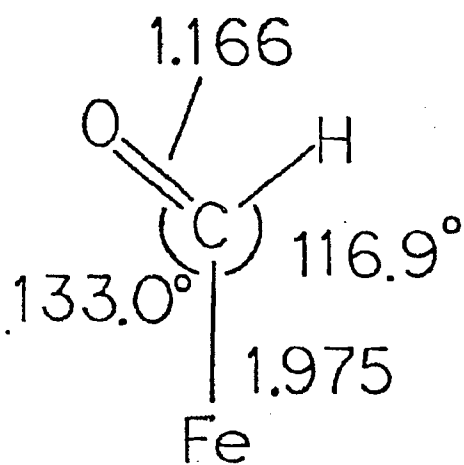
To a first approximation, there is little structural difference between this metal formyl and this metal acetyl complex. The geometries about the acyl groups detailed below points up two significant differences between formyl and acetyl complexes: first, the Fe-CH-O angle is 7.4° wider in the formyl complex than in the acetyl complex; second, the carbon-oxygen bond of the formyl ligand is 0.06 Å shorter than in the acetyl ligand. It is tempting to note that the formyl ligand is a hydride donor in its chemical reactions and that the formyl group is converted to a terminal CO ligand in these reactions. The wider Fe-CH-O angle and shorter C=O bond may be a ground state reflection of this type of reactivity. For both structures, R is less than 5% and so these bond length differences



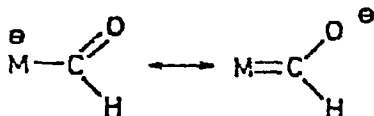
$NEt_4^+ [Co_3(CO)_3(C_6H_5O)_3P]FeCHO^-$



$NEt_4^+ [Co_3(CO)_3(C_6H_5O)_3P]FeCOCH_3^-$



quite significant. The C=O bond of the formyl ligand (1.166 Å) is nearly as short as the average terminal CO bond lengths (1.160 Å) but this short formyl bond does not give rise to a high frequency IR band. The formyl HC=O stretch appears at 1580 cm⁻¹ while the acetyl CH₃C=O stretch appears at 1587 cm⁻¹. These low RC=O stretches indicate extensive electron donation from iron and the importance of resonance structure contributors with C=O single bond character. We do not at all understand why the formyl HC=O bond is so short particularly since its IR frequency is 1580 cm⁻¹.

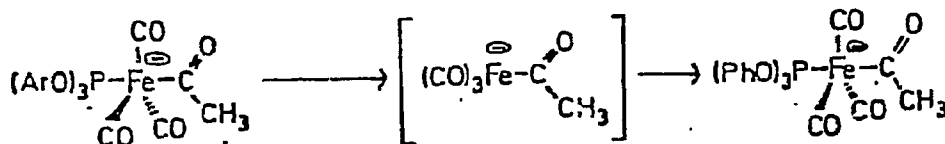
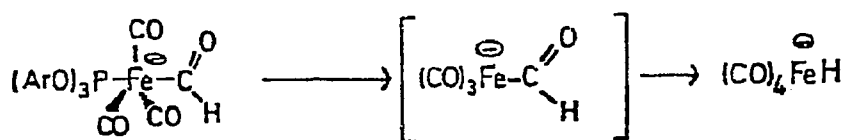


REACTIVITY. The thermal decomposition of the phosphite substituted metal formyl compound shown below occurs at 67.3°C with a half-life of 1.1 hr. The reaction is clearly first order in formyl compound and the rate is independent of added phosphite ligand. Initially we believed that this reaction occurred in two steps - a slow loss of phosphite followed by a very rapid migration of hydrogen from the formyl ligand to iron. Such two step mechanisms are very common for metal acetyl compounds. However, we now have reason to suspect that phosphite loss and hydride migration may be concerted. If the slow step in the conversion of the formyl complex to metal hydride were loss of phosphite ligand, the reaction should have been faster in the presence of Lewis acid cations which would stabilize the four coordinate metal acyl intermediate. Such Lewis acid stabilization of a 4-coordinate metal acyl intermediate was responsible for 10,000 fold rate enhancement of phosphite exchange of the corresponding

acetyl compound. However, the Li^+ and NEt_4^+ salts of the formyl compounds decompose at approximately the same rate (NEt_4^+ is 1.7 times faster than Li^+). This absence of a salt effect may be the result of a concerted decomposition that avoids a 4-coordinate acyl intermediate. To test for a concerted mechanism, we have prepared a deuterated formyl complex and are now determining the kinetic isotope effect for the reaction. We have found that ^{31}P NMR will provide a convenient method of following the rate of reaction.

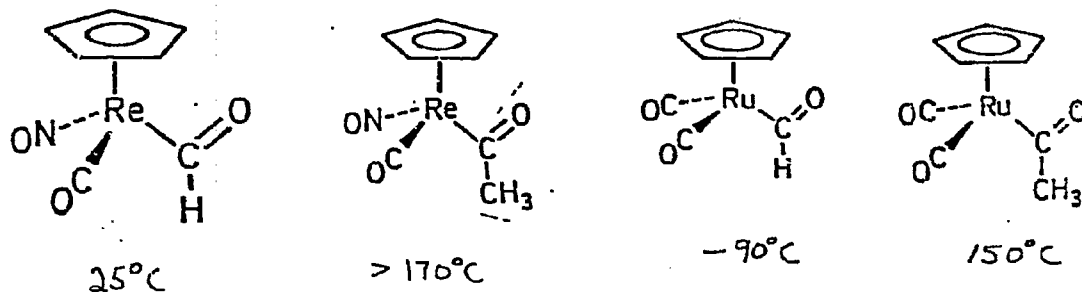
Relative Rate Data for Formyl and Acetyl Compounds

	$(\text{CH}_3\text{CH}_2)_4\text{N}^+$	Li^+
Formyl + Hydride	1.0	0.58
Phosphite Exchange of Acetyl	0.02	520

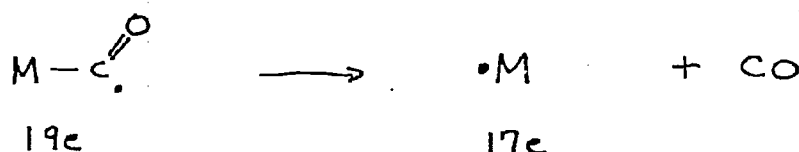
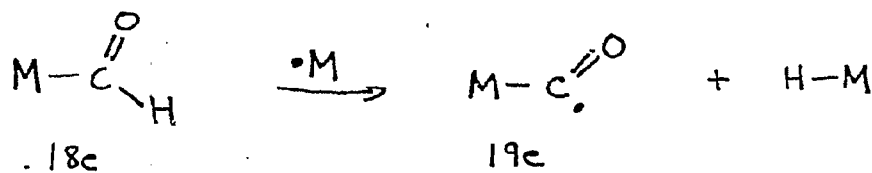


We now have two pairs of compounds where the kinetic stability of the formyl compound is much less than that of the corresponding acetyl complex. $(\text{C}_5\text{H}_5)(\text{CO})(\text{NO})\text{ReCHO}$ decomposes at room temperature slowly but the related acetyl complex is stable to over 170°C . Similarly $(\text{C}_5\text{H}_5)(\text{CO})_2\text{RuCHO}$

decomposes rapidly at -90°C but $(\text{C}_5\text{H}_5)(\text{CO})_2\text{RuCOCH}_3$ decarbonylates only upon heating to 150°C .

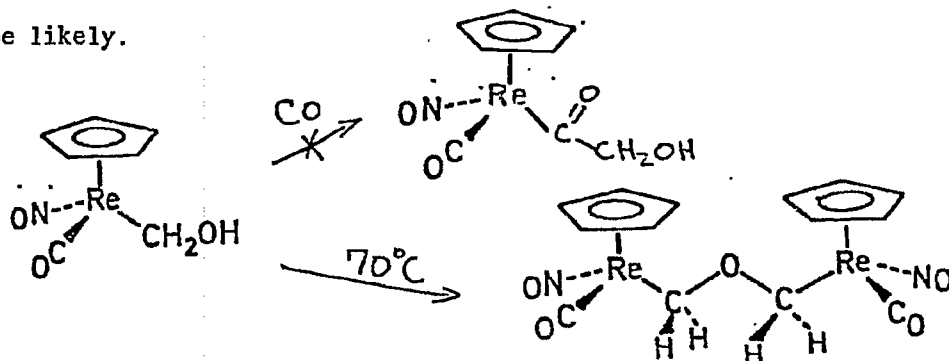


Clearly, some formyl complexes have very different mechanisms of decarbonylation that are unavailable to metal acetyl complexes. One possible mechanism would be a radical chain decomposition pathway:



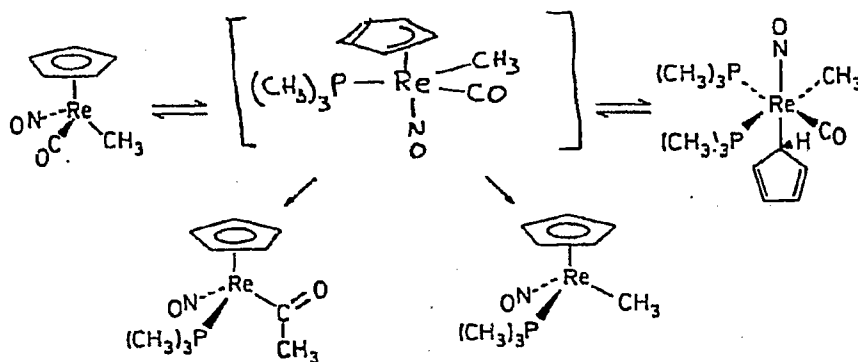
2. Hydroxymethyl Metal Compounds

Earlier we had prepared a hydroxymethyl rhenium compound $(\text{C}_5\text{H}_5)(\text{CO})(\text{NO})\text{ReCH}_2\text{OH}$ and had attempted to study the insertion of CO into the $\text{Re}-\text{CH}_2\text{OH}$ bond^{3,4}. However, the $(\text{C}_5\text{H}_5)(\text{CO})(\text{NO})\text{Re}-\text{R}$ system is very unreactive towards CO; no reaction of methyl compound was observed even upon heating to 170°C . The hydroxymethyl compound underwent dehydration to give an ether dimer at 70°C long before any CO insertion would be likely.

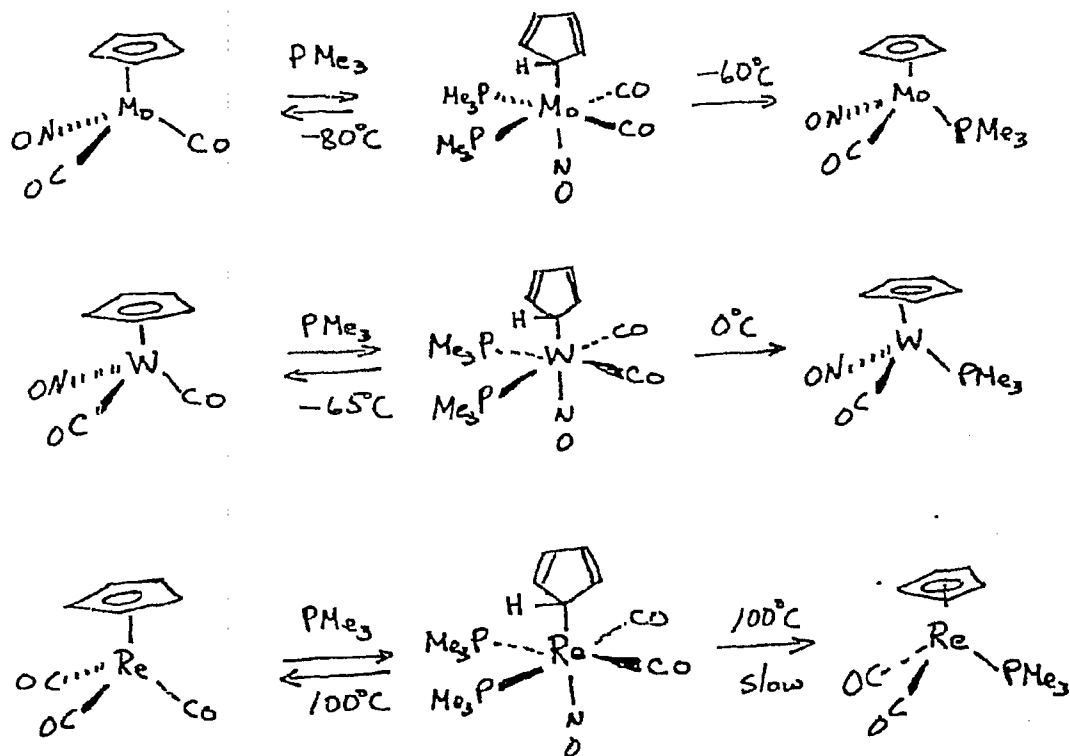


3. $\eta^5\text{-C}_5\text{H}_5 \rightleftharpoons \eta^1\text{-C}_5\text{H}_5$ Rearrangements

In the course of studying the reaction of $(\text{C}_5\text{H}_5)(\text{CO})(\text{NO})\text{ReCH}_2\text{OH}$ with PMe_3 in the hope of inducing a migration of the CH_2OH group to CO, we noted a reaction which produced the unstable $(\eta^1\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})[\text{PMe}_3]_2\text{ReCH}_2\text{OH}$. Subsequently, we found that the corresponding methyl compound also added two moles of PMe_3 to give an $\eta^1\text{-C}_5\text{H}_5$ complex. We have isolated and characterized $(\eta^1\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})[\text{PMe}_3]_2\text{ReCH}_3$ by spectral means and by X-ray crystallography⁵. The $\eta^1\text{-C}_5\text{H}_5$ compound can be converted back to the starting $\eta^5\text{-C}_5\text{H}_5$ compound by removal of PMe_3 under vacuum. On heating to 90°C , the $\eta^1\text{-C}_5\text{H}_5$ complex is converted to $(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PMe}_3)\text{ReCOCH}_3$ and to $(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PMe}_3)\text{ReCH}_3$. A common intermediate in all of these reactions is probably an $\eta^3\text{-C}_5\text{H}_5$ derivative.

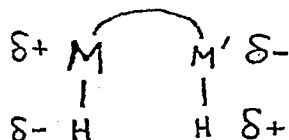


We are exploring the generality of the $\eta^5\text{-C}_5\text{H}_5 \rightleftharpoons \eta^1\text{-C}_5\text{H}_5$ rearrangement and have found several other examples of this kind of interconversion. The least stable $\eta^1\text{-C}_5\text{H}_5$ compound we've detected is $(\eta^1\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NO})(\text{PMe}_3)_2\text{Mo}$ which is formed at -78°C and has a half-life of 45 min at -57°C ⁶. The most stable $\eta^1\text{-C}_5\text{H}_5$ compound we've prepared is $(\eta^1\text{-C}_5\text{H}_5)(\text{CO})_3(\text{PMe}_3)_2\text{Re}$ which is stable at 100°C .

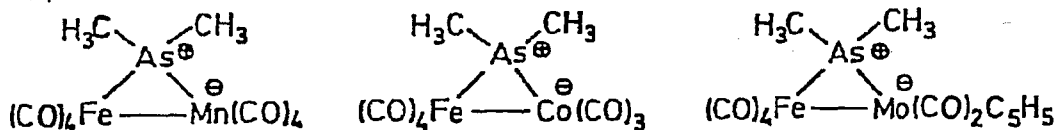


4. Heterobimetallic Dihydrides

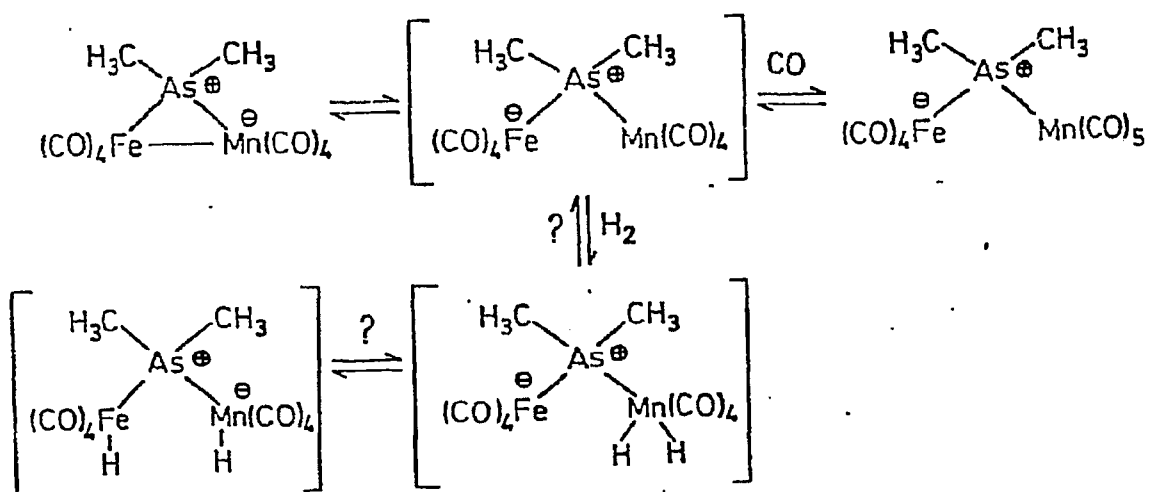
For the effective reduction of carbon monoxide to hydrocarbons, we now believe that a catalyst which can act both as a hydride donor and as a Lewis acid may be required. We plan to synthesize molecules which contain both a hydridic (H^-) transition metal hydride and an acidic (H^+) transition metal hydride. Such a system could successively transfer H^- and H^+ to reduce CO and maintain electronic neutrality. Regeneration of the metal hydrides by reaction with H_2 is also crucial. Early transition metal hydrides are hydridic in nature and could serve as the source of H^- . The metal hydrides of the later transition metals (e.g., Fe, Co, etc.) are relatively acidic and could serve as a source of H^+ . Thus, a bimetallic metal dihydride which possesses a hydridic hydrogen and an acidic hydrogen would be an attractive catalyst for CO reduction.



The first systems we studied as possible sources of heterobimetallic dihydrides were a series of arsenic bridged bimetallic compounds first prepared by Vahrenkamp⁹.



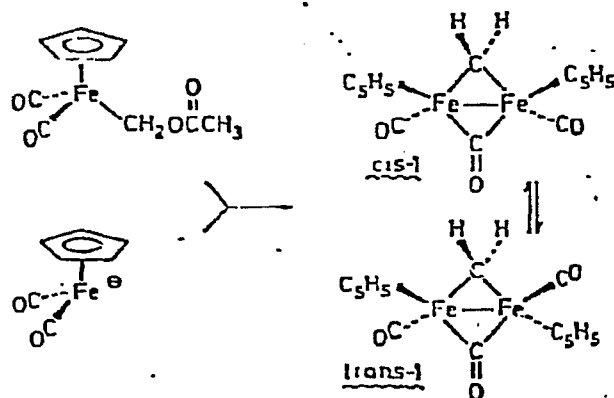
Vahrenkamp had reported that the metal-metal bond of these compounds could break spontaneously to generate a vacant coordination site and that the substitution chemistry of the compounds could be explained in terms of such a coordinatively unsaturated intermediate. We hoped to intercept the proposed intermediate with H_2 and to generate a heterobimetallic dihydride. However, all of the compounds were inert to H_2 to over $100^\circ C$ and failed to act as CO hydrogenation catalysts. The only evidence we obtained for interaction of H_2 with the bimetallic compounds was the observation of alkene isomerization and hydrogenation reactions at high temperature.



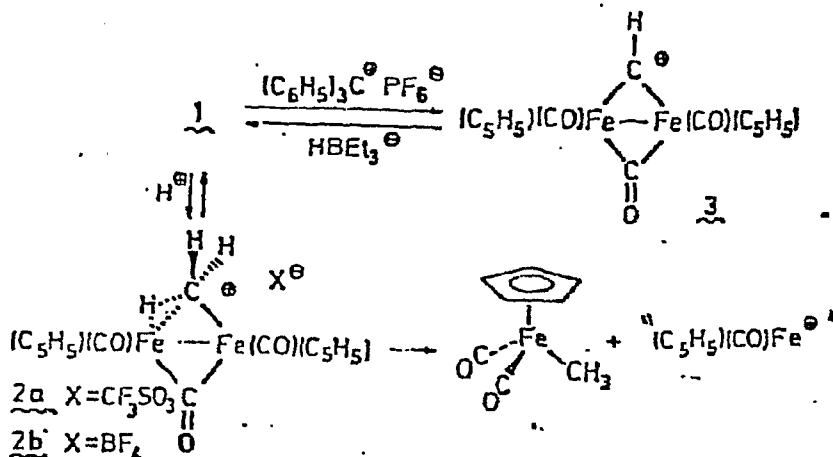
We now have reason to doubt our initial assumption that metal-metal bond cleavage in these systems is the pathway for ligand substitution. We have found¹¹ that the rate of reaction of the Mo-Fe compound with PMe_3 depends on both $[PMe_3]$ and $[Mo-Fe]$. This observed 2nd order kinetics argues for attack of ligand on the metal-metal bond rather than for prior metal-metal bond dissociation.

5. Bridging Methyl, Methylene and Methylidyne Complexes

Many research groups have been studying bridging CH_2 metal compounds. Pettit has pointed out the relationship of these compounds to intermediates in the heterogeneously metal catalyzed hydrogenation of CO ¹². We have developed a convenient synthesis of a bridging iron methylene complex by reaction of $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{OAc}$ with $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2^- \text{K}^+$ ¹³. The resulting bridging methylene complex can be made in large quantities and can be purified by a special procedure we've developed that combines Soxhlet extraction with column chromatography.

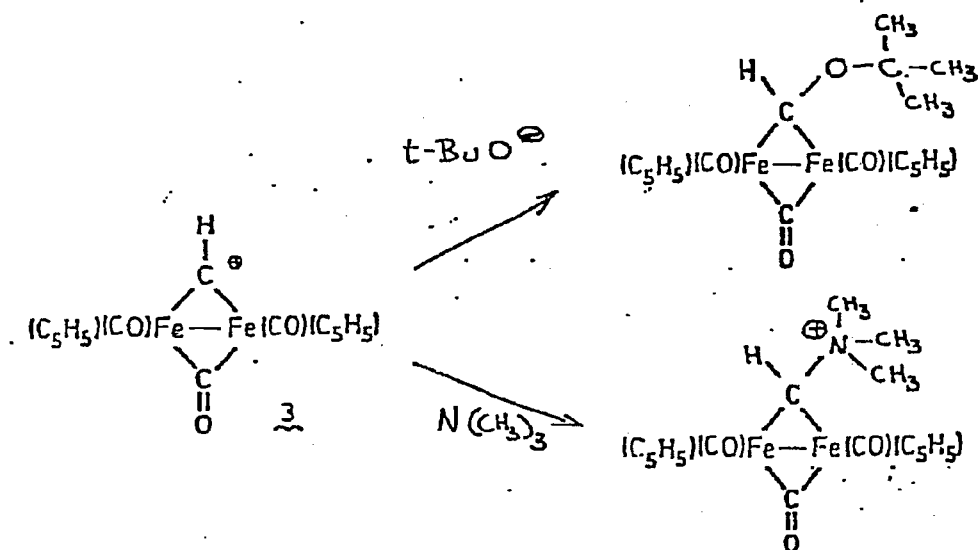


The bridging methylene compound can be reversibly protonated to give a bridging methyl complex. Using techniques first developed by Shapley, we have shown that while the three protons of the methyl group and the two iron centers are equivalent on the NMR time scale at -86°C , there is a specific interaction of one of the methyl hydrogens with one of the iron atoms on an instantaneous time scale.

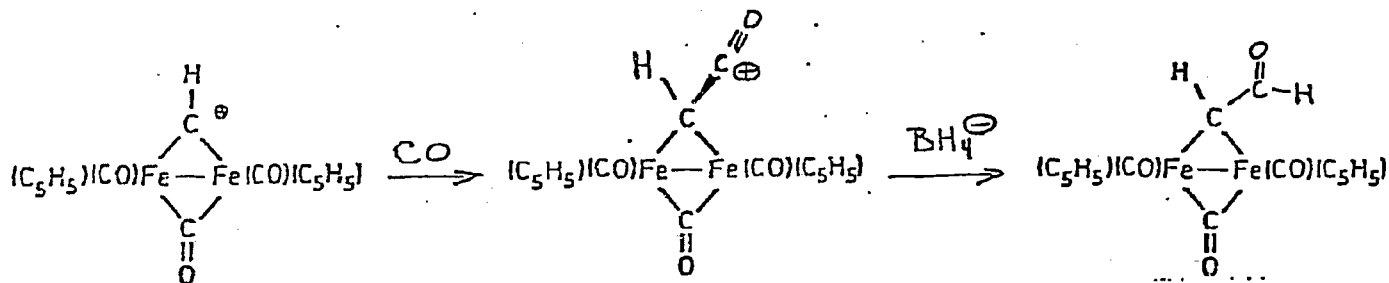


Reaction of the bridging methylene complex with $\text{C}(\text{C}_6\text{H}_5)_3^+ \text{BF}_4^-$ produces a bridging methylidyne complex which was characterized by the extreme down field chemical shifts of the methylidyne proton ($\delta 22.8$) and carbon ($\delta 490.2$). This is the first methylidyne complex in which the methylidyne bridges between two metals.

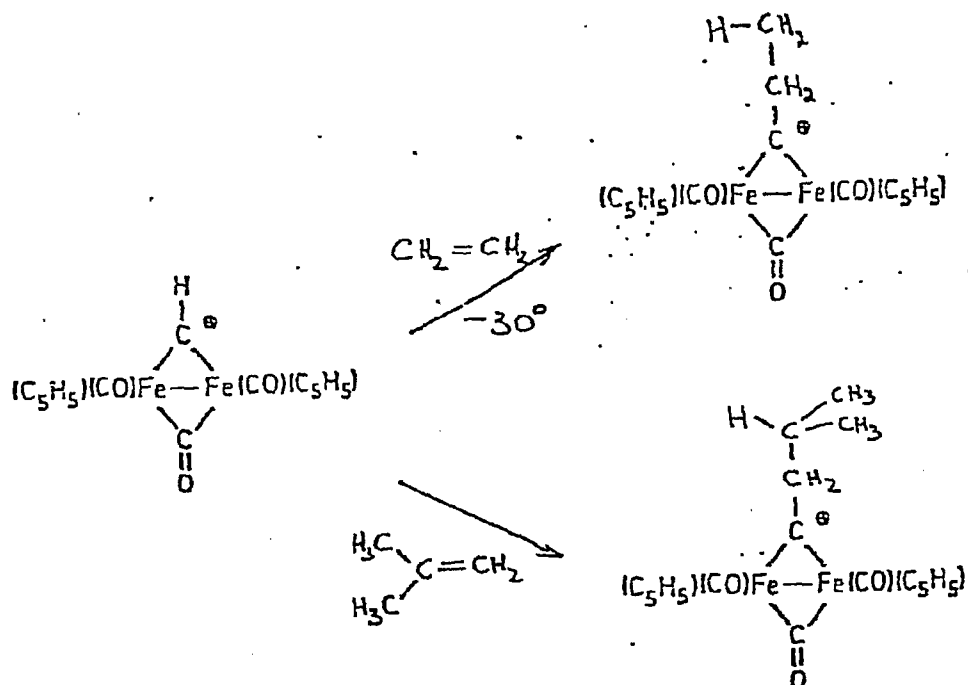
Reactions of a Bridging Methylidyne Complex with Nucleophiles. The cationic methylidyne complex can be viewed as a relatively stable carbonium ion. It is certainly more stable than the triphenylmethyl cation from which it was prepared. Extensive electron donation from the two iron centers must be responsible for the stability of the methylidyne complex. In spite of its thermodynamic stability, the bridging methylidyne complex is kinetically very reactive towards nucleophiles. For example, reaction with $(\text{CH}_3)_3\text{CO}^- \text{K}^+$ or trimethylamine gives high yields of nucleophilic adducts.



The bridging carbyne complex reacts with CO to give an acylium species. The structure of the acylium species has been determined in collaboration with Professor Victor Day at the University of Nebraska. On treatment with $NaBH_4$ the acylium species is converted to an aldehyde:



Hydrocarbation. The most remarkable reaction of the bridging methyldiyne complex is its reaction with ethylene. The methyldiyne complex reacts rapidly with ethylene at -30°C to give a bridging propyldiyne complex. The reaction involves the addition of the carbon hydrogen bond of the carbyne complex across the carbon-carbon double bond of ethylene. The similarity of this reaction to the hydroboration reaction has caused us to call the new reaction "hydrocarbation". The hydrocarbation and hydroboration reactions show similar regiochemistry for addition to alkenes. Reaction of the carbyne complex with isobutylene gives a 3-methylbutyldiyne complex. We are now studying the stereochemistry of these addition reactions and their application in organic synthesis.



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