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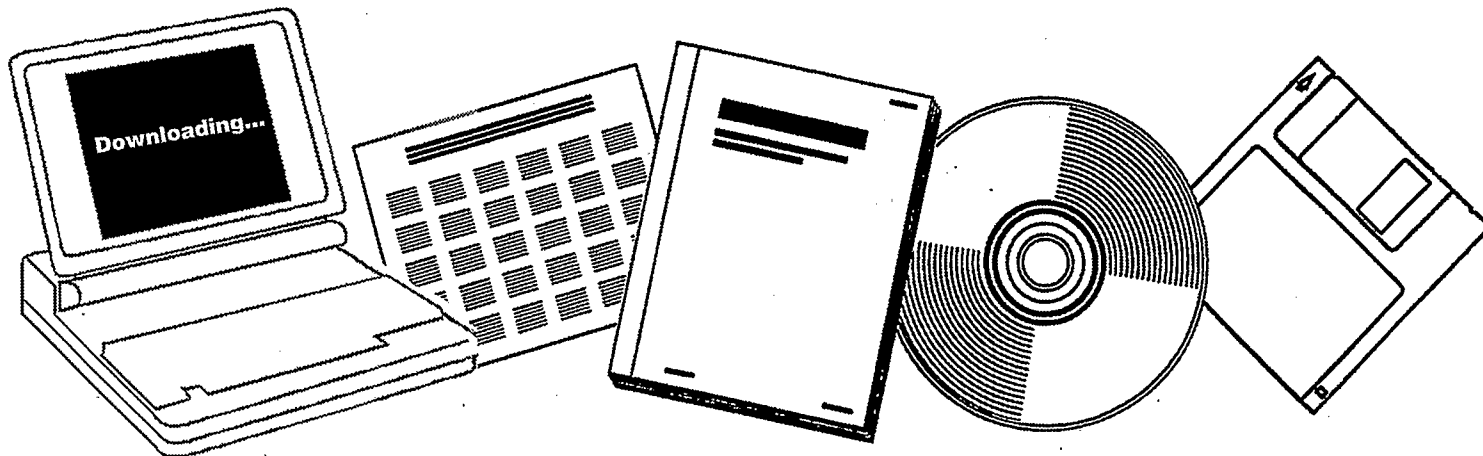
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MECHANISTIC STUDIES RELATED TO THE METAL CATALYZED REDUCTION OF CARBON MONOXIDE TO HYDROCARBONS. PROGRESS REPORT, APRIL 1, 1978-MARCH 31, 1979.

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

Progress Report
 for Period April 1, 1978 to March 31, 1979

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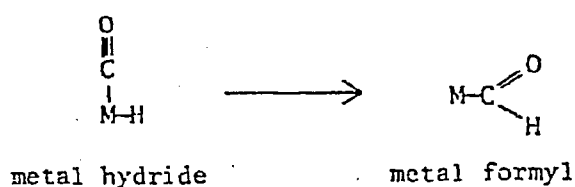
Abstract

The stoichiometric reactions of metal complexes which parallel probable steps in the metal catalyzed reduction of CO are being investigated. It is hoped that the study of these model reactions will lead to an understanding of the structural factors influencing these individual reaction steps. The information obtained should be useful in the design and discovery of homogeneous catalysts for the reduction of CO to hydrocarbons.

We have studied metal formyl complexes which may be involved in the initiation step in CO reduction and have compared metal formyl compounds with metal acetyl compounds. We have found that the structure and kinetic stability of metal formyl compounds are very similar to metal acetyl compounds. However, metal formyl compounds are thermodynamically much less stable than metal acetyl compounds towards decarbonylation. Hydride donation reactions of metal formyl compounds have been discovered. A neutral metal formyl compound has been discovered and its reactions have been investigated.

I. Metal Formyl Complexes

Metal formyl complexes have been proposed as important intermediates in the metal catalyzed reduction of CO by H₂.¹ While the insertion of CO into alkyl and aryl carbon metal bonds is well known,² the insertion of CO into a metal hydrogen bond to give a metal formyl complex has not been observed.³

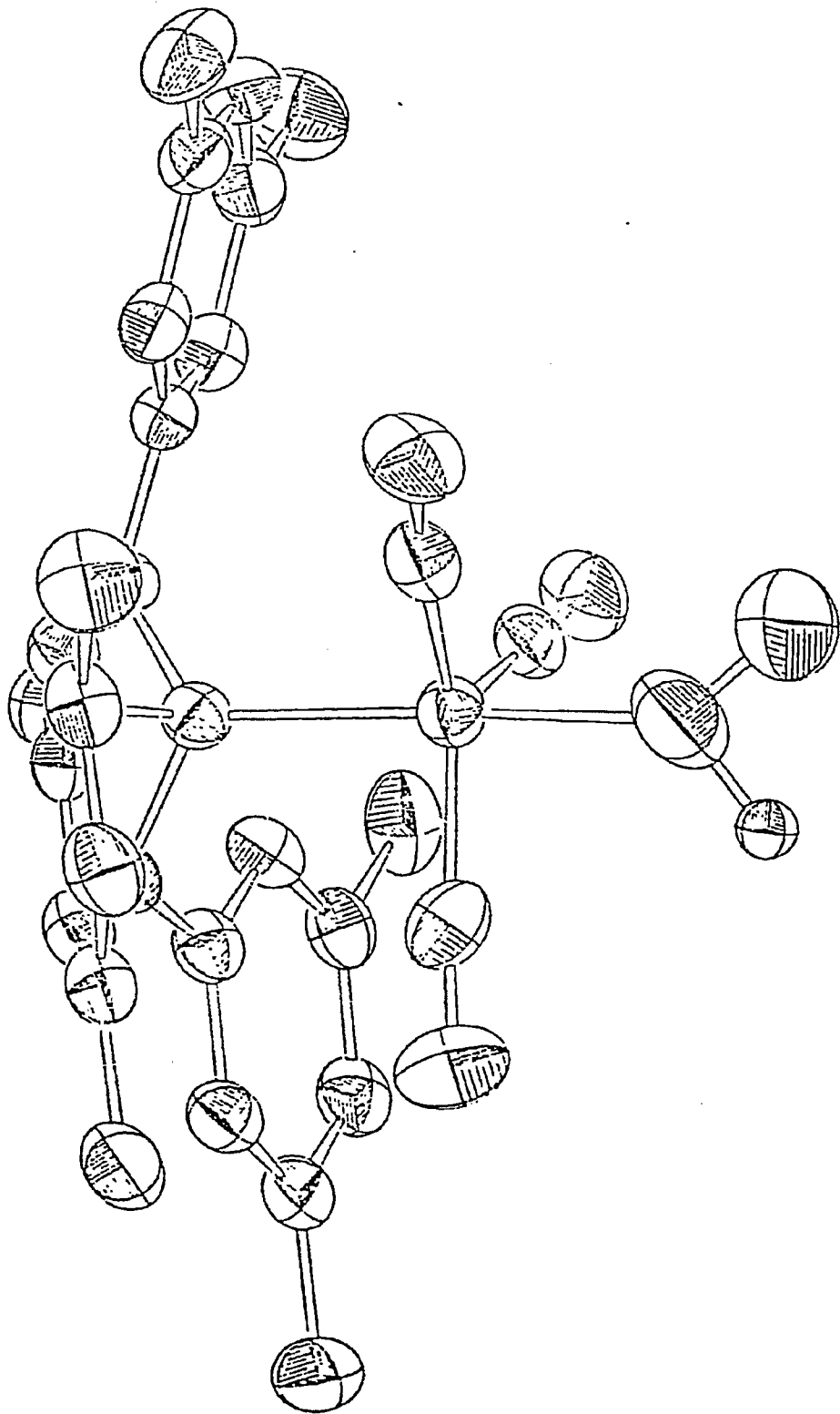


To ascertain the reasons for the failure to observe metal formyl complexes in the reactions of metal hydrides with CO, we have developed a new synthesis of metal formyl complexes and have studied their properties. During the past year our efforts have been concentrated along two lines. (1) We have attempted to compare the structure, kinetic stability, and thermodynamic stability of a metal formyl complex with an analogous metal acyl complex. These studies are aimed at discovering what if anything is unusual about metal formyl complexes. (2) We have studied the reactivity of metal formyl compounds.

A. Comparison of Metal Formyl and Metal Acyl Compounds

1. Structure. Our discovery⁴ that trialkoxyborohydrides react with metal carbonyl compounds to give stable metal formyl complexes has opened the way to the study of the properties of these important compounds. During the past year, we have completed an X-Ray Crystal structure of $\text{N}(\text{CH}_2\text{CH}_3)_4^+[(3,5-(\text{CH}_3)_2-\text{C}_6\text{H}_3\text{O})_3\text{P}](\text{CO})_3\text{FeCOH}^-$.⁵ The crystal structure is shown in Figure 1. The basic structure is a trigonal

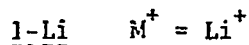
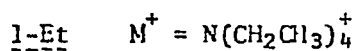
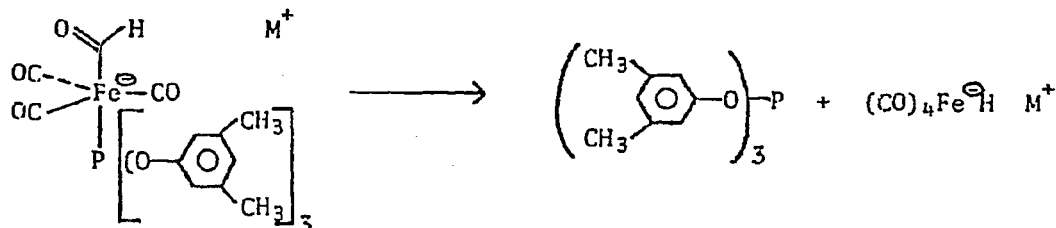
FIGURE 1.



bipyramid with three equatorial CO ligands and an axial phosphite and axial formyl ligand. We intend to determine the X-ray structure of the exactly analogous acetyl iron compound for a detailed comparison. However, it is already clear that there is nothing unusual about the structure of metal formyl compounds. For example, the Fe-COH bond length is 1.96 Å, the Fe-CO bond length is 1.77 Å, and the Fe-CH-O angle is 135°; for comparison the Mn-COCH₃ bond length is 2.04 Å, the Mn-CO bond length is 1.83 Å, and the Mn-C(CH₃)-O bond angle is 125° in the anionic bisacylmanganese compound $N(CH_2CH_3)_4^+(CO)_4Mn(COCH_3)(COC_6H_5)^-$.⁶ The wider Fe-CH-O angle may be related to the hydride donor ability of the formyl compound. To judge whether the Fe-CH-O angle is unusually wide, we will need to determine the structure of the corresponding acetyl compound.

2. Kinetic Stability of Metal Formyl and Metal Acetyl Compounds.

The kinetic stability of $[(3,5-(CH_3)_2-C_6H_3O)_3P](CO)_3FeCOH^-$ was determined and an effort was made to compare its stability with that of the corresponding acetyl iron compound.⁷ The decomposition of $N(CH_2CH_3)_4^+L(CO)_3FeCOH^-$, 1-Et, was studied over the temperature range 47-79°C. 1-Et decomposes cleanly by expulsion of phosphite to give $HFe(CO)_4^-$ and $(3,5-(CH_3)_2-C_6H_3O)_3P$. The kinetics of the reaction are cleanly first order; in particular, the rate of reaction is not inhibited by phosphite produced in the decomposition or by added phosphite. Activation parameters were found to be $\Delta H^\ddagger = 29 \pm 1.3$ kcal mole⁻¹, $\Delta S^\ddagger = 7.9 \pm 4.7$ eu, $\Delta G^\ddagger = 27 \pm 2$ kcal mole⁻¹ (336°K), $E_a = 30 \pm 2$ kcal mole⁻¹, and $\log A = 15 \pm 1$.

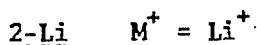
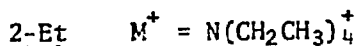
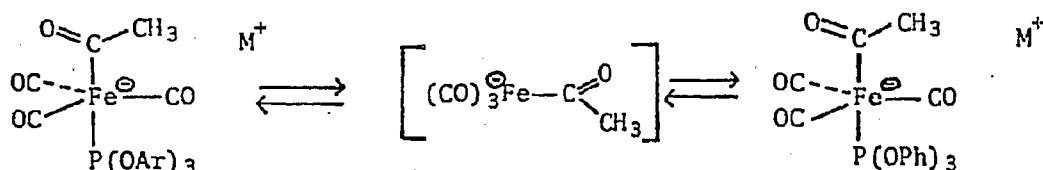


The decomposition of the lithium salt of the formyl complex was also studied to determine the effects of cations on the rate of decomposition. The lithium salt was found to decompose about 1.7 times slower than the tetraethylammonium salt.

Overall, the metal formyl complexes are kinetically quite stable and their kinetic stability is not unusual.

It was not possible to directly compare the kinetic stability of the formyl complexes with that of the corresponding acetyl iron compounds. In the case of the acetyl iron compounds, the equilibrium lies on the side of the carbonylated acetyl species instead of the decarbonylated methyl species. However, it was possible to measure the rate of phosphite exchange of the corresponding acetyl iron compound; this rate corresponds to the rate of phosphite dissociation from $L(CO)_3Fe-COCH_3$. Since the decomposition of the formyl compound may well involve rate determining dissociation of phosphite, a comparison of the rate of decomposition of metal formyl compounds with the rate of ligand exchange of metal acetyl compounds gives information on ligand labilization by formyl and acetyl ligands.

The rate of phosphite exchange with $N(CH_2CH_3)^+ [3,5-(CH_3)_2-C_6H_3O]_3P^-$ $(CO)_3FeCOCH_3^-$, $\underline{2-Et}$, was $1.26 \times 10^{-6} \text{sec}^{-1}$ at 62°C ; this is about 50 times slower than the rate of decomposition of $\underline{1-Et}$. On the other hand, the lithium salt $\underline{2-Li}$ underwent very rapid phosphite exchange at 26°C ($k = 1.62 \times 10^{-4} \text{sec}^{-1}$). The rate acceleration due to Li^+ ion was estimated to be about 20,000. Similar cation effects have been reported previously. For example, Na^+ ion is known to catalyze ^{13}CO exchange in $[(C_6H_5)_3P]_2N^+(CO)_4FeH^-$,⁸ and the rates of ligand exchange reactions of $Tl^+Co(CO)_4^-$ ⁹ and $Li^+[(C_6H_5)_3P](CO)_3FeC(O)C_6H_5^-$ ¹⁰ vary with solvent in a fashion suggestive of varying degrees of cation interaction with the anions.



The two unusual features of the decomposition of metal formyl complexes are (1) the absence of a strong cation effect and (2) the absence of phosphite inhibition. These features suggest that the mechanism of formyl complex decomposition may be different from that of metal acyl complexes which generally decompose by a two-step process of ligand dissociation followed by alkyl migration. Concerted ligand loss and hydride migration might explain the unusual features of formyl complex decomposition. Isotope effects will be used to probe this phenomenon in the future.

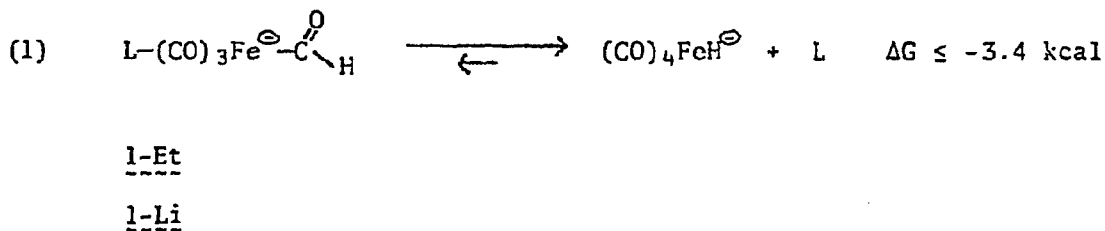
Estimated Relative Rates

	FORMYL → HYDRIDE		ACETYL LIGAND DISSOCIATION	
$N(CH_2CH_3)_4^+$	<u>1-Et</u>	1	<u>2-Et</u>	0.02
Li^{\oplus}	<u>1-Li</u>	0.58	<u>2-Li</u>	400

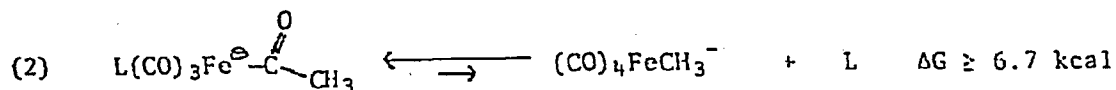
3. Relative Thermodynamic Stability of Metal Formyl and Metal Acetyl Compounds.

We have attempted to measure the relative thermodynamic stability of metal formyl and metal acetyl compounds relative to the corresponding decarbonylated metal-hydride and metal-alkyl compounds. Two techniques have been employed: (1) direct measurement of equilibria by NMR⁷ and (2) heats of reaction.¹¹

When 1-Et was heated to 90°C, loss of phosphite and formation of $(CO)_4FeH^-$ occurred; no metal formyl was observable and an NMR detection limit of 1 part in 450 was estimated. This establishes a maximum value for $K_{eq} \geq 1.25 \times 10^2 M$. Similarly, 1-Li has $K_{eq} \geq 1.22 \times 10^2 M$. These values correspond to $\Delta G \leq -3.4 \text{ kcal mole}^{-1}$.



In contrast, the corresponding methyl iron compound reacts with phosphite to give acetyl iron compounds 2-Li; no $FeCH_3$ compound was observed at equilibrium. The equilibrium constant was estimated to be $K_{eq} \leq 2.8 \times 10^{-5} M$ at 50°C. ($\Delta G \geq 6.7 \text{ kcal mole}^{-1}$)



2-Li

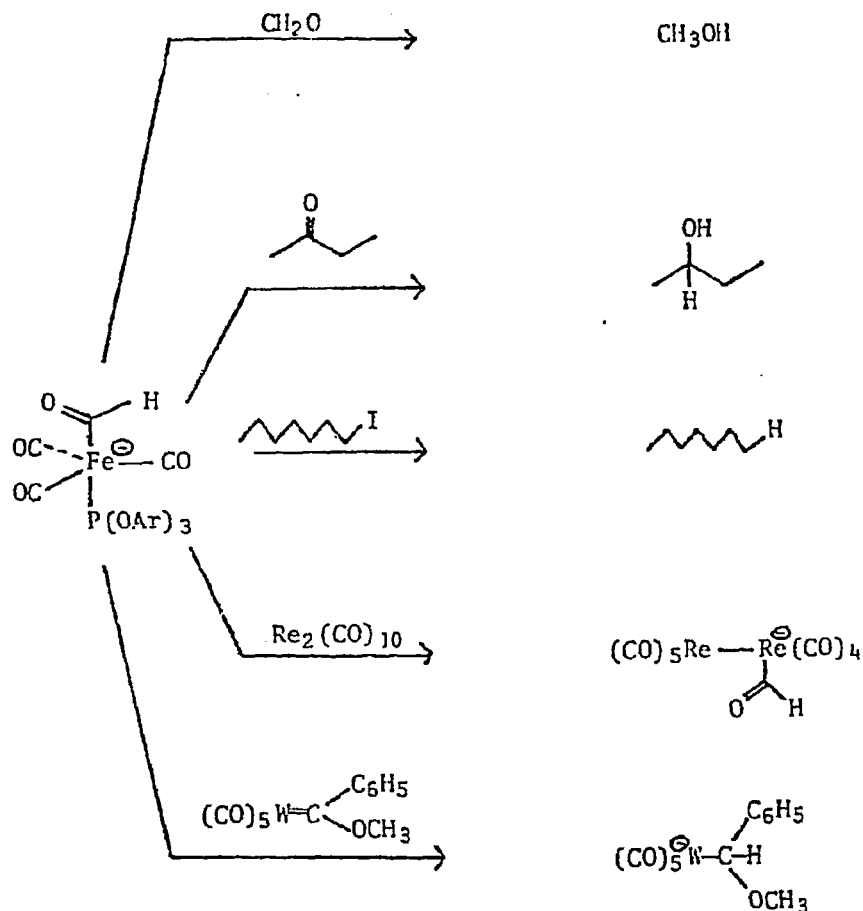
The free energy difference between carbonylation of methyl and of hydride compounds or iron is at least 10.1 kcal mole⁻¹. The major difference between metal formyl and metal acetyl compounds is the much lower thermodynamic stability of the metal formyl compounds. The lower thermodynamic stability is attributed mainly to the substantially higher M-H bond strength (- 50 kcal) compared with M-CH₃ bond strength (- 30 kcal).

Since only limits could be placed on the above free energy differences due to our inability to detect extremely small amounts of L(CO)₃FeCOH⁻ or (CO)₄FeCH₃⁻ at equilibrium, we are now attempting to measure heats of reaction for processes (1) and (2) shown above.¹¹ We will require a chemically clean system to get accurate values and we are looking for ways to minimize side reactions related to processes (1) and (2).

B. Chemical Reactivity of Metal Formyl Compounds

1. Hydride Donation Reactions.

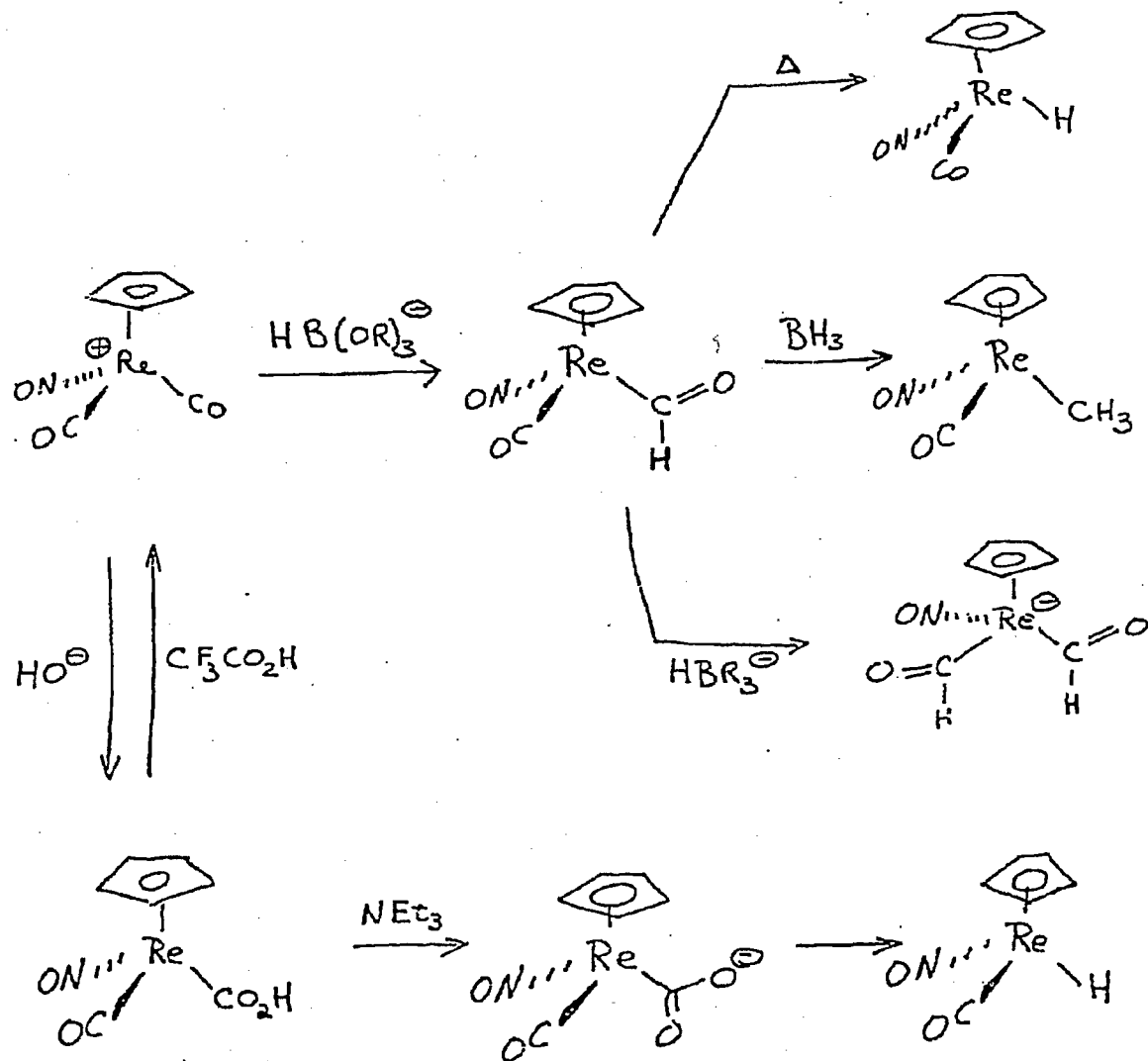
It is interesting that we have synthesized metal formyl compounds by hydride donation from borohydrides to metal carbonyls and that the metal formyls can in turn donate hydride to other substrates.¹² Some of the hydride donation reactions we discovered are outlined below.



2. Synthesis of a Neutral Metal Formyl Compound.

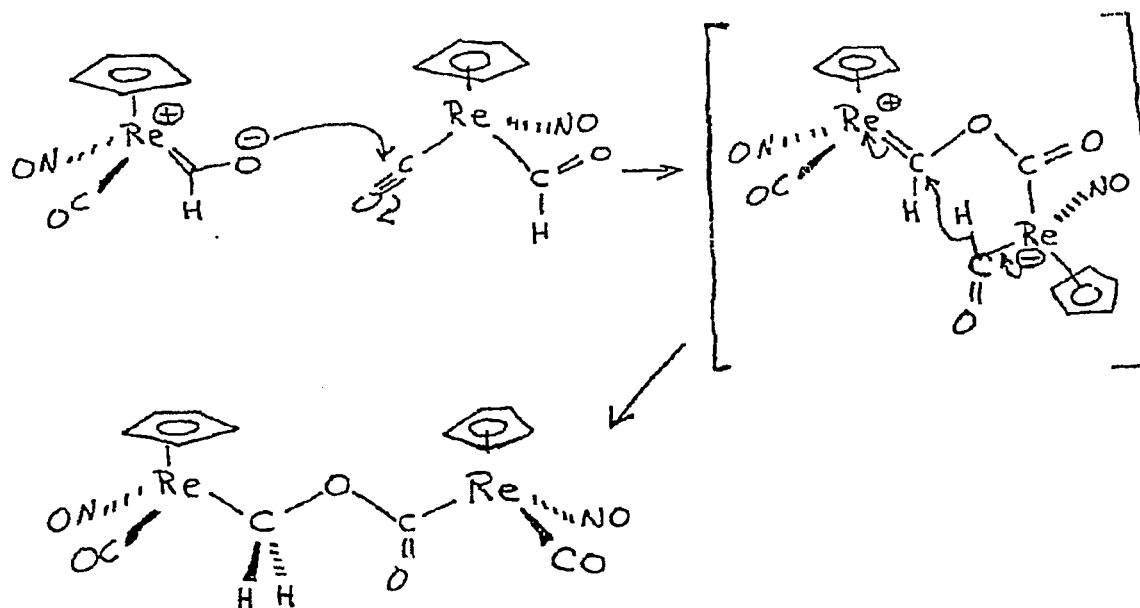
The moderate kinetic stability observed for anionic metal formyl compounds may be related to the delocalization of negative charge onto the formyl oxygen atom. We have now initiated studies of neutral metal formyl complexes to see if these compounds might also be stable. We have found that $(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{NO})^{\oplus}$ reacts with $\text{HB}(\text{OR})_3^-$ to produce a neutral metal formyl complex $(\text{C}_5\text{H}_5)\text{Re}(\text{CO})(\text{NO})(\text{CHO})$.¹³ In dilute solution, the neutral formyl complex is relatively stable and decomposes slowly to the corresponding metal hydride. The neutral formyl complex

is converted to the corresponding methyl compound on treatment with BH_3 . In contrast, $\text{HB}(\text{Et})_3^-$ reduces the neutral formyl compound to a bis formyl complex.



The most interesting reaction of the neutral formyl compound is its bimolecular disproportionation which occurs when the neat oil is allowed to sit at room temperature.¹¹ The dimeric product is a 1:1 mixture of two diastereomers (both Re atoms are chiral centers).

The NMR spectrum shows four C₅H₅ resonances for the two different rings in each of the two diastereomers; in addition, there are two AB quartets for the diastereotopic CH₂ protons of the two diastereomers. We believe the dimer arises via initial attack of the formyl oxygen of one compound on the free CO of another molecule of (C₅H₅)Re(CO)(CO)(CHO); it should be noted that the free CO was attacked by hydride to give a bis formyl compound. The resulting intermediate is set up for an intramolecular hydride donation from a formyl ligand to an oxycarbene group.



It should be noted that the dimer is the ester of a hydroxymethyl metal compound and hydrolysis might provide access to this proposed intermediate in CO reduction.

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