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

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Abstract

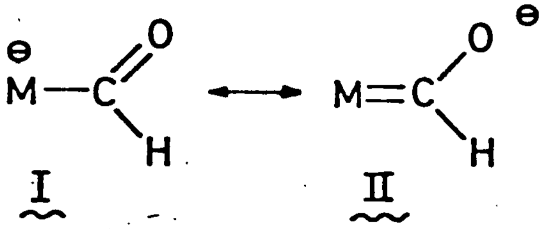
The stoichiometric reactions of metal complexes which parallel probable steps in the metal catalyzed reduction of CO are being investigated. It is hoped that the study of these model reactions will lead to an understanding of the structural factors influencing these individual reaction steps. The information 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 acetly 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.

We have prepared $(C_5H_5)Re(CO)(NO)(CH_2OH)$, the first authentic example of a hydroxymethyl metal compound and have begun studies of its reactions with acid, with base, with CO, and with H_2.

I. NEUTRAL METAL FORMYL COMPOUNDS

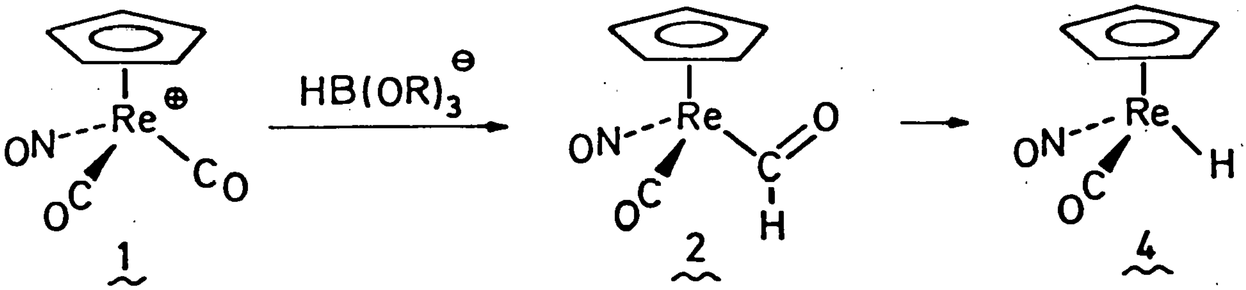
The low formyl CO stretching frequencies observed for these anionic species (for example, 1600 $cm^{-1}$for $(CO)_4FeCHO^-$) indicate a large contribution from carbenoid resonance structures such as II which place extensive negative charge on the formyl oxygen atom. The possibility that anionic metal formyl compounds might be anomalously stabilized by such resonance structures led us to investigate syntheses of neutral metal formyl complexes by hydride reduction of cationic metal carbonyl compounds.



A. Synthesis of Neutral Metal Formyl Compounds

At the time we began this work, $Os(CO)_2[P(C_6H_5)_3]_2Cl(CHO)$ was the only neutral metal formyl species which had been reported.[1] Neutral metal formyl species had been suggested as intermediates in the substitution reactions of metal carbonyl hydride complexes [2] and in the sodium borohydride reductions of the metal carbonyl cations $(C_5H_5)W(CO)_3[P(C_6H_5)_3]^+$ [3] and $(C_5H_5)Re(CO)_2NO^+$ to methyl [4] and hydroxymethyl metal complexes.[5]

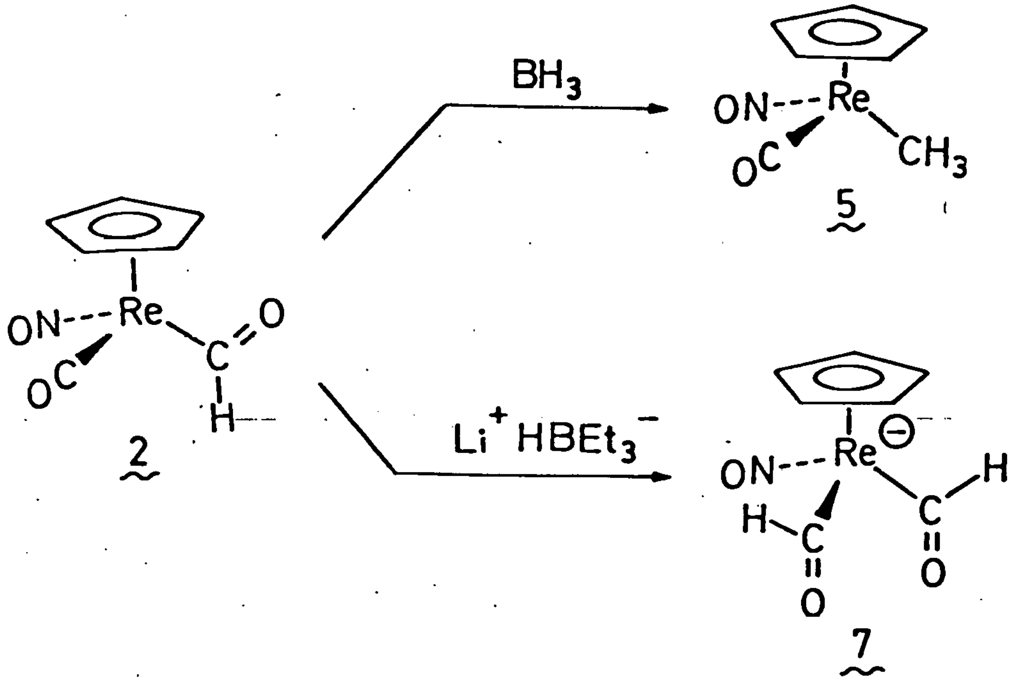
We found that $(C_5H_5)Re(CO)_2(NO)^+$ PF_6^-, 1, was reduced by K^+ $HB[OCH(CH_3)_2]_3^-$ in THF at -78°C to a deep orange solution of the neutral metal formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$, 2, which was characterized by IR and NMR.[6] The neutral formyl complex 2 could be isolated as an orange oil in 50% yield following hydrolytic workup at 0°C. Dilute solutions of 2 in THF or benzene undergo thermal decomposition over 10-20 hours at room temperature to give ~40% yield of the known metal hydride $(C_5H_5)Re(CO)(NO)H$, 4.[4] Gladysz[7] and Graham[8] have reported related syntheses of 2.



We found that Nesmeyanov's claim[5] that $(C_5H_5)Re(CO)_2(NO)^+$ could be reduced by $NaBH_4$ in benzene-water to the hydroxymethyl compound $(C_5H_5)Re(CO)(NO)(CH_2OH)$, 3, was inaccurate. Reduction under these conditions produced the neutral formyl compound 2 as the major product.

Treatment of formyl complex 2 with $BH_3 \cdot THF$ gives $(C_5H_5)Re(CO)(NO)(CH_3)$, 5, in ~50% yield. Earlier, Masters had found that $BH_3 \cdot THF$ efficiently reduced metal acyl complexes to metal alkyl complexes.[9] The reactivity of BH_3 towards α-oxygenated ligands is probably related to the fact that $BH_3 \cdot THF$ can act as a Lewis acid as well as a hydride donor.

In contrast to borane which reduces the formyl ligand of 2, lithium triethylborohydride attacks the carbonyl ligand of 2 to give the first diformyl complex $(C_5H_5)Re(NO)(CHO)_2^-$, 7.[6,7] Diformyl complex 7 is unstable in solution and decomposes over a period of 12-24 hrs at room temperature.

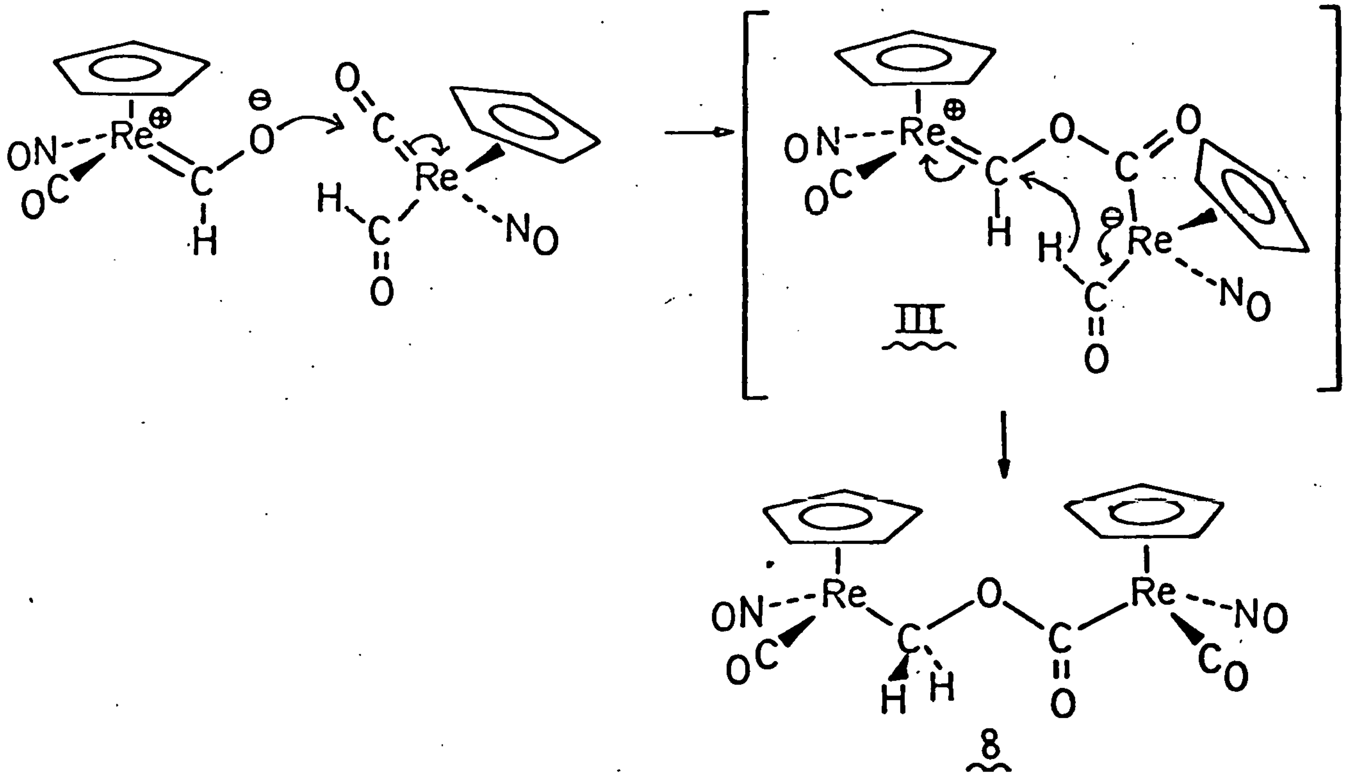


B. Disproportionation of $(C_5H_5)Re(CO)(NO)(CHO)$

Although dilute solutions of formyl complex 2 are relatively stable under nitrogen, when 2 is isolated as a neat orange oil at room temperature, it soon darkens and solidifies overnight to a dark red solid. Metal hydride 4, which is the major decomposition product of 2 in solution, is present only to a small extent in the red solid. Purification of the red solid gave a 50% yield of dimeric metallo ester $(C_5H_5)(CO)(NO)ReCO_2CH_2Re(CO)(NO)(C_5H_5)$, 8, as an air-stable red-orange powder, mp 105-115°C.[10] The disproportionation of formyl complex 2 to metallo ester 8 is only significant in very concentrated solutions (≥ 0.4 M).

Each rhenium atom of 8 is a chiral center and the isolated solid is a 1:1 mixture of the two possible diastereomers. The presence of two diastereomers of 8 is clearly evident in the 270 MHz ^{1}H NMR spectrum in benzene-d_6. Four cyclopentadienyl resonances - two from each diastereomer - are seen at δ 4.956, 4.958, 5.032, and 5.034. The diastereotopic methylene groups of each diastereomer give rise to two AB quartets at δ 5.89, 6.49 (J = 9.7 Hz) and at δ 5.99, 6.42 (J = 9.7 Hz).

The formation of 8 is suggested to proceed by the two step mechanism shown below. Initially, the formyl oxygen of one molecule of formyl complex 2 could attack the coordinated CO ligand of a second molecule of 2 to form intermediate III. The nucleophilicity of the formyl oxygen and the electrophilicity of the carbonyl carbon of 2 were noted above. Intermediate III is then ideally situated for internal hydride transfer from the formyl ligand attached to the negatively charged rhenium center to the carbene carbon attached to the positively charged rhenium center.



II. HYDROXYMETHYL METAL COMPOUNDS

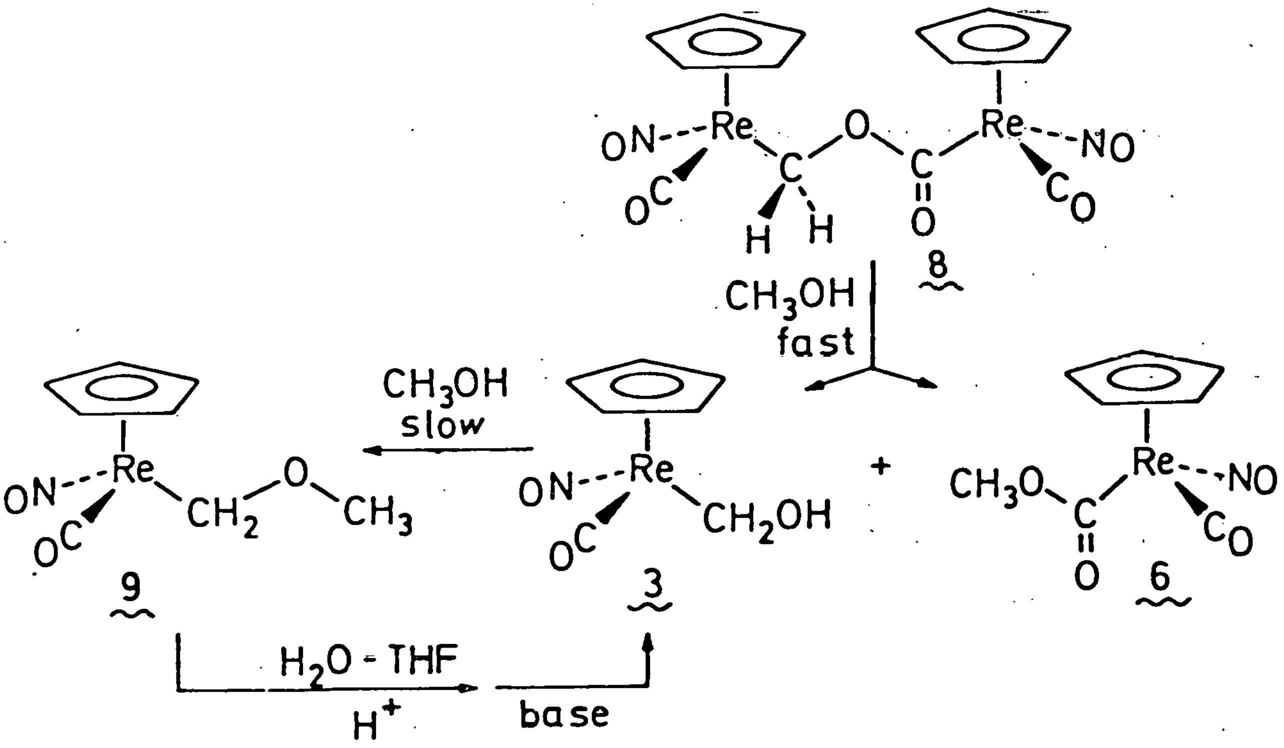
A. Synthesis of Hydroxymethyl Metal Compounds

1. Methanolysis of $(C_5H_5)(CO)(NO)ReCO_2CH_2Re(CO)(NO)(C_5H_5)$

Hydroxymethyl metal compounds have been proposed as important intermediates in metal catalyzed CO reduction but no authentic hydroxymethyl metal compounds had been synthesized. We initiated studies of the hydrolysis of metallo ester 8 in an effort to prepare an authentic sample of hydroxymethyl complex 3. In a model experiment, the methyl ester $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$, 6, was found to undergo rapid transesterification under very mild conditions. Methyl ester 6 was converted to the corresponding ethyl ester within 2 hrs upon treatment with ethanol in benzene-d_6 without added acid or base catalyst. It was encouraging that transesterification could be carried out under such mild conditions since there were suggestions in the literature that hydroxymethyl metal complexes might be quite labile.[11]

Methanolysis of metallo ester 8 was studied by NMR and proved to be complicated. Addition of two equivalents of CH_3OH to a benzene solution of metallo ester 8 led to the rapid appearance of the NMR spectra of methyl ester 6 and hydroxymethyl complex 3 (verified following its isolation). Then over a period of days, signals due to hydroxymethyl complex 3 disappear and are replaced by an AB quartet and methyl peak due to methoxymethyl complex 9 with a concurrent decrease in the signal due to methanol. Workup of the reaction mixture after several days led to the isolation of a mixture of methyl ester 6 and of methyl ether 9.

Although the desired hydroxymethyl metal complex 3 was shown by NMR to be present in large amounts in the early stages of the conversion of 8 to 6 and 9, the hydroxymethyl complex could not be isolated from the reaction mixtures. Brief solvolysis of metallo ester 8 in methanol, followed by evaporation of solvent gave only recovered 8 and small amounts of 6 and 9. This is the result of a rapid transesterification reaction which converts the hydroxymethyl complex 3 and methyl ester 6 back to dimeric metallo ester 8 upon removal of methanol. This approach to equilibrium was measured in both directions and found to have a half reaction time of less than 10 min at room temperature. The equilibrium constant for this transesterification was found to be approximately 1.



2. Hydrolysis of Methoxymethyl Complex $(C_5H_5)Re(NO)(CO)(CH_2OCH_3)$

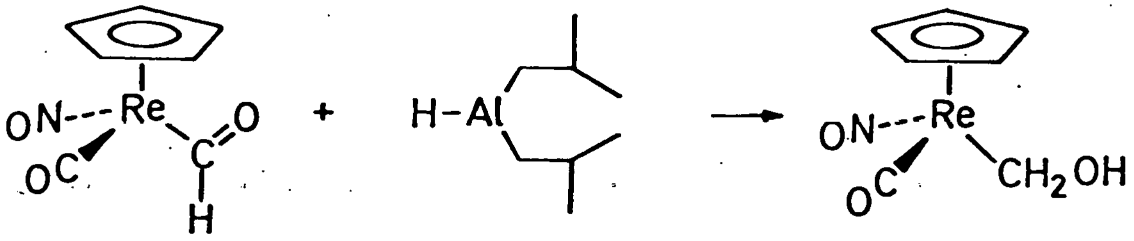
At this point, we turned our attention to the hydrolysis of isolated methoxymethyl complex 9 where reverse transesterification would not be a problem. Treatment of 9 with 0.1 equivalents of trifluoroacetic acid in

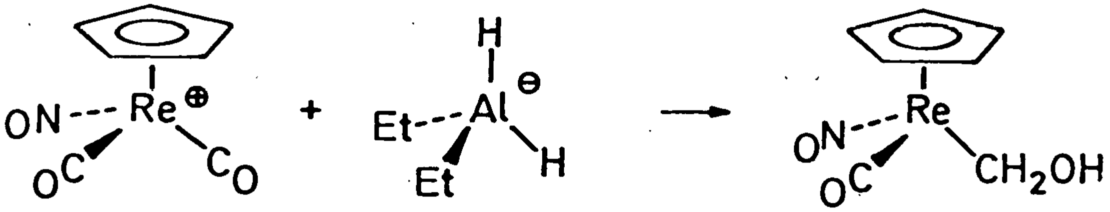
THF-water followed by workup gave dimer $[(C_5H_5)(CO)(NO)ReCH_2]_2O$ (10) and not the hydroxymethyl complex 3.

The desired hydroxymethyl complex was finally obtained when the acid-catalyzed hydrolysis of the methoxymethyl complex 9 was quenched with 0.15 equivalents of triethylamine prior to workup.[10] The hydroxymethyl complex 3 was isolated as a red-orange solid and identified spectroscopically. The ^1H NMR of 3 in benzene-$\underline{d}_6$ consists of a cyclopentadienyl resonance at δ 4.78, an AB quartet due to the diastereotopic methylene group at δ 5.83 and 5.11 (J = 10 Hz), and a singlet for the hydroxyl proton at δ 0.88. The signal at δ 0.88 disappears upon exchange with D_2O. The IR spectrum (toluene) shows ν_{CO} at 1967 cm^{-1} and ν_{NO} at 1699 cm^{-1} and (Fluorotube) ν_{OH} at 3215(br) cm^{-1} which is shifted to 2390(br) cm^{-1} in the D_2O exchanged material. While the IR and elemental analysis of 3 are similar to that reported by Nesmeyanov[5] for their "$(C_5H_5)Re(CO)(NO)(CH_2OH)$", the higher melting point (97-100°C with slow heating from 25°C, 105°C with heating from 95°C) and air stability of 3 clearly distinguish it from the material of Nesmeyanov (mp 69-71°C dec, rapidly oxidized). Based on our work, and Graham's work[8] it seems clear that Nesmeyanov may well have had a mixture which contained formyl complex 2, dimer 8, hydroxymethyl complex 3 and their decomposition products.

3. Alternate Syntheses of $(C_5H_5)Re(CO)(NO)(CH_2OH)$

Since we are very interested in studying the chemistry of hydroxymethyl metal compounds, it became essential to develop a more efficient synthetic route to the hydroxymethyl complex 3 than the above seven step sequence from $Re_2(CO)_{10}$ which gave a 7% overall yield. Since formyl complex 2 can be reduced to methyl complex 5 by the electrophilic hydride BH_3, we attempted its partial reduction with the electrophilic monohydridic reagent diisobutylaluminum hydride (DIBAL-H) in the hope of obtaining the hydroxymethyl complex 3. Indeed, reaction of formyl complex 2 with one equivalent of DIBAL-H gave some hydroxymethyl complex 3. However, since we were unable to accurately measure the amount of unstable starting formyl complex 2, over-reduction and under-reduction of 2 were problems.





We therefore examined the reaction of cation 1 with sodium diethylaluminum dihydride in the hope of initially forming formyl complex 2 and an equimolar amount of dialkylaluminum hydride which could convert 2 into the hydroxymethyl complex 3. Addition of a solution of sodium diethylaluminum hydride to a THF suspension of $(C_5H_5)Re(CO)_2NO^+PF_6^-$ at -78°C gave hydroxymethyl complex 3 in 45% isolated yield in a single step. The synthesis proceeds in 28% overall yield from $Re_2(CO)_{10}$ and provides a considerable savings in time and materials compared with our original preparation. Graham and Sweet have recently reported a similarly convenient synthesis of 3 from 1 with two equivalents of $NaBH_4$ in THF-water under carefully controlled conditions.[8]

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