MODEL STUDIES OF METAL CATALYZED CO REDUCTION

Charles P. Casey,[*] Stephen M. Neumann, Mark A. Andrews, and Donald R. McAlister

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

Abstract - Metal formyl anions are produced by reaction of borohydrides with metal carbonyls. The resulting metal formyl anions have moderate kinetic stability but are thermodynamically less stable than the corresponding metal hydrides. Anionic metal formyl compounds can react as hydride donors. Reaction of $(C_5H_5)Re(CO)_2(NO)^+$ with $HB(OR)_3^-$ produces the neutral metal formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$ which undergoes disproportionation as a neat oil to give the metallo ester $(C_5H_5)(CO)(NO)-ReCO_2CH_2Re(CO)(NO)(C_5H_5)$. Indirect hydrolysis of this metallo ester produced $(C_5H_5)Re(CO)(NO)(CH_2OH)$, the first authentic hydroxymethyl metal compound. Reduction of $(C_5H_5)Re(CO)_2(NO)^+$ with $H_2Al(CH_2CH_3)_2^-$ provides a more convenient synthesis of $(C_5H_5)Re(CO)(NO)(CH_2OH)$.

INTRODUCTION

The shortage of petroleum has caused increased interest in alternative sources of liquid fuels and petrochemical feedstocks. One such alternative that is now being widely investigated is the reduction of coal-derived carbon monoxide-hydrogen mixtures via the Fischer-Tropsch and related reactions (1). For the past several years, we have been studying some of the unusual intermediates and reactions which have been proposed to occur in CO reduction. We have studied the synthesis and reactions of metal formyl compounds, the hydrogenation of metal carbene complexes, and the synthesis of hydroxymethyl metal compounds.

SYNTHESIS OF METAL FORMYL COMPOUNDS

While transition metal formyl complexes may be important intermediates in the initiation step for the catalytic reduction of CO by H_2, the insertion of CO into a metal hydride to give a metal formyl compound has never been observed. In contrast, metal alkyl compounds undergo facile insertion of CO to give stable metal acyl compounds. To determine the key features which distinguish metal formyl compounds from metal acyl compounds, we have synthesized metal formyl compounds and studied their structure, their kinetic and thermodynamic stability, and their chemical reactivity.

The first metal formyl complex, $[(Ph_3P)_2N]^+ (CO)_4FeCHO^-$, was prepared in 1973 by Collman and Winter by the reaction of $Na_2Fe(CO)_4$ with acetic formic anhydride. Since we found that this was not a general route to metal formyl complexes, we investigated the reactions of metal carbonyl compounds with borohydrides. We found that reaction of either $Na^+ HB(OCH_3)_3^-$ or the more reactive $K^+ HB[OCH(CH_3)_2]_3^-$ with metal carbonyls produced metal formyl complexes (3). Two of the complexes which we were able to isolate and fully characterize were $(CH_3CH_2)_4N^+ [(3,5(CH_3)_2C_6H_3O)_3P](CO)_3 FeCHO^-$ and $(CH_3CH_2)_4N^+ (CO)_9Re_2CHO^-$ (4,5). In addition, we, Gladysz, and Winter have been able to observe many unstable metal formyl complexes formed by hydride reduction of metal carbonyls (3,5,6,7,8).
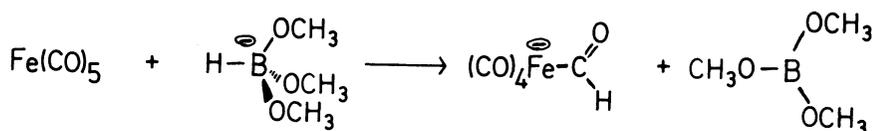
STRUCTURE OF METAL FORMYL COMPOUNDS

We have determined the X-ray crystal structure of $(CH_3CH_2)_4N^+{}_o[(3,5-(CH_3)_2C_6H_3O)_3P]$ $(CO)_3FeCHO^-$ and found that the Fe-formyl bond length of 1.95 Å and the Fe-C-O bond angle of the formyl ligand of 134° are quite normal compared with metal acyl species (9). Gladysz and Strouse have reported the X-ray crystal structure of $(C_5H_5)Re(PPh_3)(NO)(CHO)$ and have found a Re-formyl bond length of 2.05 Å and a Re-C-O bond angle of the formyl ligand of 128° (10). It is unfortunate that a crystal structure of the acetyl analog of either the iron or rhenium compounds is not available for comparison purposes.
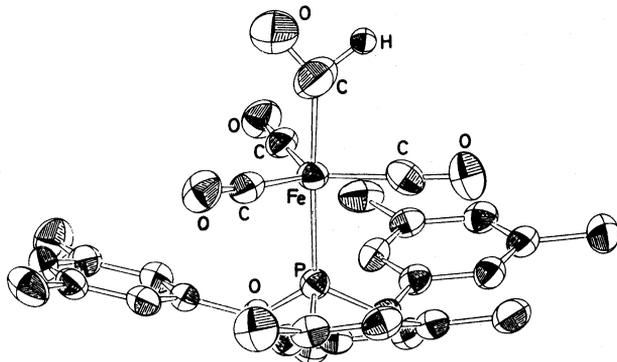
KINETIC AND THERMODYNAMIC STABILITY OF METAL FORMYL COMPLEXES

Anionic metal formyl compounds exhibit moderate kinetic stability. Thermal decomposition of $(CH_3CH_2)_4N^+[(C_6H_5O)_3P](CO)_3FeCHO^-$ in THF at 65°C gives a mixture of two metal hydrides in a 2.9:1 ratio: $(CO)_4FeH^-$, formed by loss of phosphite and hydride migration, and $[(C_6H_5O)_3P]-$ $(CO)_3FeH^-$, formed by loss of CO and hydride migration. The decarbonylation of the related tri-(3,5-dimethylphenyl)phosphite complex $(CH_3CH_2)_4N^+[(ArO)_3P](CO)_3FeCHO^-$ is cleaner and proceeded by exclusive loss of phosphite to give $(CO)_4FeCHO^-$ and $(ArO)_3P$ as the only observed products (11). The rate of formation of metal hydride from $(CH_3CH_2)_4N^+$ $[(ArO)_3P]-$ $(CO)_3FeCHO^-$ followed first order kinetics to greater than two half-lives and was unaffected by added phosphite. The half-life for the decomposition of $(CH_3CH_2)_4N^+$ $[(ArO)_3P](CO)_3FeCHO^-$ in THF at 67.3°C was 1.1 hr. Measurement of the rate of decomposition of the metal formyl complex over the temperature range 47°-79°C gave an activation energy for the process of 30 ± 2 kcal/mol. ($\Delta H^{\ddagger} = 29.0\pm1.3$ kcal, $\Delta S^{\ddagger} = 7.9\pm4.7$ eu at 63°C). The rate of decomposition of the related lithium salt, Li^+ $[(ArO)_3P](CO)_3FeCHO^-$, was 1.7 times slower than that of the tetraethylammonium salt.
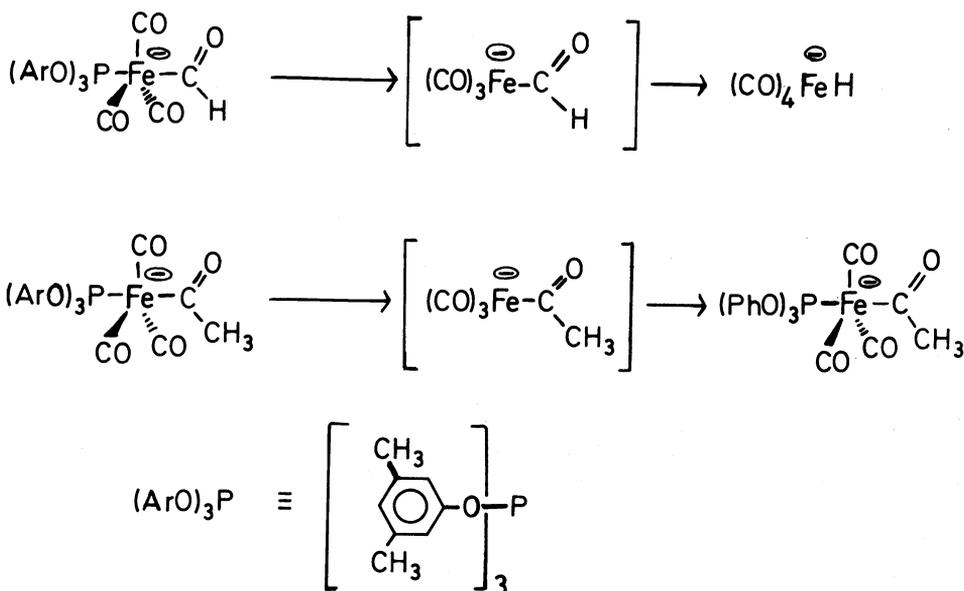
The decomposition of these iron formyl complexes is thought to proceed by rate determining phosphite dissociation followed by rapid hydride migration from the formyl carbon to iron. The fact that the rate of decomposition of the metal formyl complexes is independent of phosphite concentration would require that migration of hydride from the formyl group to the metal in the corrdinatively unsaturated intermediate be much faster than capture of the intermediate by phosphite. Our kinetic data is also in agreement with concerted loss of phosphite and hydride migration from the formyl group to iron.

We would like to have a direct comparison of the kinetic stability of a metal formyl compound with an analogous metal acetyl compound. However, the corresponding acetyl complex $(CH_3CH_2)_4N^+$ $[(ArO)_3P](CO)_3FeCOCH_3^-$ does not undergo loss of phosphite and formation of $(CO)_4FeCH_3^-$. In fact, $(CO)_4FeCH_3^-$ reacts with $(ArO)_3P$ to form the thermodynamically favored acetyl complex. The phosphite exchange reactions of the acetyl complex proceed via a coordinatively unsaturated intermediate very similar to the intermediate suggested to be formed in the rate determining step of the decomposition of the metal formyl complex. Thus, a comparison of the rate of decomposition of the formyl complex with the rate of phosphite exchange of the acetyl complex should provide a measure of the relative abilities of the formyl and acetyl ligands to labilize phosphite ligands in these closely related iron complexes. The rate of exchange of $(C_6H_5O)_3P$ with $[(ArO)_3P](CO)_3FeCHO^-$ was measured by ^{31}P NMR. The $(CH_3CH_2)_4N^+$ salt of the acetyl complex underwent phosphite exchange at 62°C with a first order rate constant of $1.26 \times 10^{-6} sec^{-1}$; this is 49 times slower than the decomposition of the $(CH_3CH_2)_4N^+$ salt of the formyl complex. The Li^+ salt of the acetyl compound underwent phosphite exchange greater than 10,000 times faster than did the $(CH_3CH_2)_4N^+$ salt; the first order rate constant for phosphite exchange of the Li^+ salt of the acetyl complex was $1.62 \times 10^{-4} sec^{-1}$ at 26°C. Previously, large cation and solvent effects were observed for the ^{13}CO exchange of $(CO)_4FeH^-$ (12) and ligand exchange of $[(C_6H_5)_3P](CO)_3FeCOC_6H_5^-$ (13). At present, we do not understand why the phosphite exchange of acetyl compounds is strongly catalyzed by Li^+ while the decomposition of formyl compounds is not catalyzed by Li^+.

Metal formyl compounds are much less thermodynamically stable than the corresponding metal acetyl compounds. The equilibrium between $(CH_3CH_2)_4N^+$ $[(ArO)_3P](CO)_3FeCHO^-$ and $(CH_3CH_2)_4N^+$ $(CO)_4FeH^-$ was studied by 270 MHz ^1H NMR. After $(CH_3CH_2)_4N^+$ $[(ArO)_3P](CO)_3FeCHO^-$ was heated to 75°C for 2 hours, only $(CO)_4FeH^-$ was observed. No metal formyl species was detectable under conditions where 0.2% could have been readily detected; this allowed an estimate to be made on the limit of $K_{eq} = [(ArO)_3P][FeH]/[FeCHO] \geq 125 M$. A similar limit on the value of K_{eq} was estimated in studies of the Li^+ salt of the formyl complex.

In contrast, the equilibrium between the acetyl iron compound and the corresponding methyl iron compound greatly favors the acetyl iron compound. None of the methyl iron compound was detectable by NMR at equilibrium. Estimates for the Li^+ salt were $K_{eq} = [(ArO)_3P]/[FeCH_3]-[FeCOCH_3] \geq 10^{-3}M$.
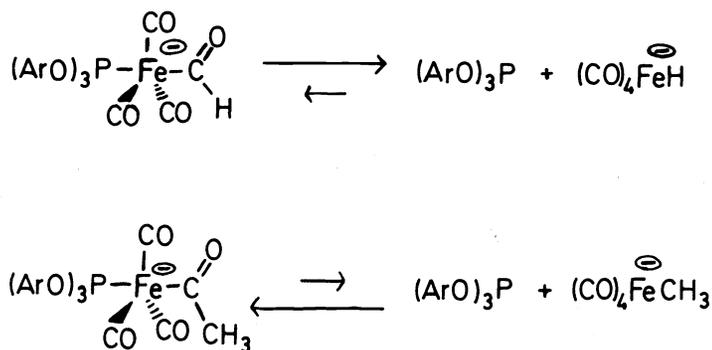
The difference in equilibrium constant for insertion of CO into a FeH and a Fe-CH$_3$ bond is therefore greater than 1.25×10^5 which corresponds to a free energy difference of at least 7.5 kcal mole^{-1}. The greatly different thermodynamic stabilities of metal acyl and metal formyl compounds is mainly attributable to the greater strength of M-H bonds (estimated 50-60 kcal mole^{-1}) compared with M-CH$_3$ bonds (estimated 30-40 kcal mole^{-1}). We are now attempting to obtain more sensitive measurements of metal formyl-metal hydride equilibrium constants by isotopic dilution techniques.

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.

HYDRIDE TRANSFER REACTIONS OF METAL FORMYL COMPOUNDS

Our group (4) and Gladysz's group (5) have discovered that metal formyl compounds can act as hydride donors to electrophiles such as ketones, alkyl halides, metal carbene complexes, and metal carbonyl compounds. $(CH_3CH_2)_4{}^+ [(C_6H_5O)_3P](CO)_3FeCHO^-$ reacts with 2-butanone to give a 95% yield of 2-butanol, with $n\text{-}C_7H_{15}I$ to give a 71% yield of heptane, and with $(CO)_5WC\text{-}(OCH_3)C_6H_5$ to give $(CO)_5WCH(OCH_3)C_6H_5{}^-$.

Reaction of $(CH_3CH_2)_4N^+ [(C_6H_5O)_3P](CO)_3FeCHO^-$ with 10 equivalents of CF_3CO_2H gave a 55% yield of methanol and a small amount (<5%) of formaldehyde. This reaction might proceed by initial cleavage of the iron-formyl bond to generate formaldehyde which is subsequently reduced by hydride donation from a second mole of formyl compound. Alternatively protonation of the formyl complex at oxygen could produce a hydroxycarbene complex of iron, Fe=CHOH, which could be reduced by hydride donation from a metal formyl complex to give a Fe-CH$_2$OH species which is subsequently cleaved by protonation to give methanol. We cannot distinguish between these two possible mechanisms.

Metal formyl complexes can transfer hydride to metal carbonyl compounds to produce new metal formyl complexes (4,5). These transformylation reactions can be used to determine the relative stability of a series of metal formyl complexes.

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.

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 (14). Neutral metal formyl species had been suggested as intermediates in the substitution reactions of metal carbonyl hydride complexes (15) and in the sodium borohydride reductions of the metal carbonyl cations $(C_5H_5)W(CO)_3[P(C_6H_5)_3]^+$ (16) and $(C_5H_5)Re(CO)_2NO^+$ to methyl (17) and hydroxymethyl metal complexes (18).

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° 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 (19). 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 (17). Gladysz (20) and Graham (21) have reported related syntheses of 2.
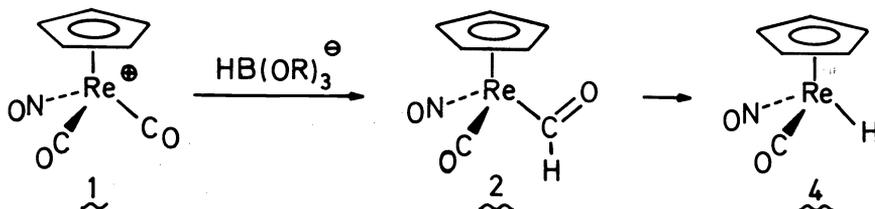
We found that Nesmeyanov's claim (18) that $(C_5H_5)Re(CO)_2(NO)^+$ could be reduced by $NaBH_4$ in benzene-water to the hydroxymethyl compound $(C_5H_5)Re(CO)(NO)(CH_2OH)$, 3, was inaccurate. Reduction under these conditions produced the neutral formyl compound 2 as the major product.

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 (22). 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 (19,20). Diformyl complex 7 is unstable in solution and decomposes over a period of 12-24 h at room temperature.
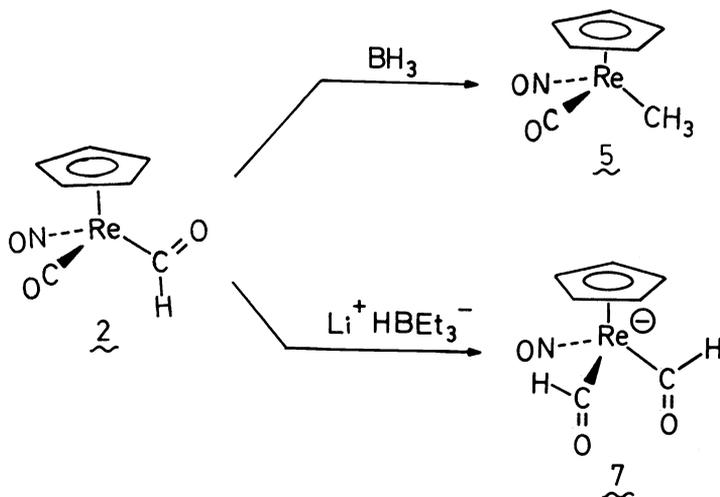
DISPROPORTIONATION OF $(C_5H_5)Re(CO)(NO)(CHO)$

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 (23). 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.
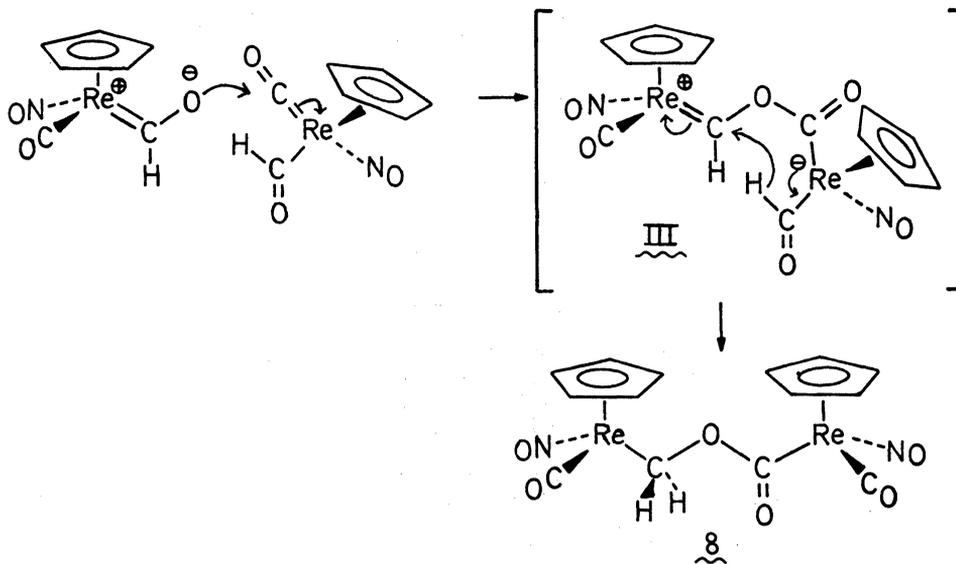
METHANOLYSIS OF $(C_5H_5)(CO)(NO)ReCO_2CH_2Re(CO)(NO)(C_5H_5)$

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 hours 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 (24).

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 minutes at room temperature. The equilibrium constant for this transesterification was found to be approximately 1.
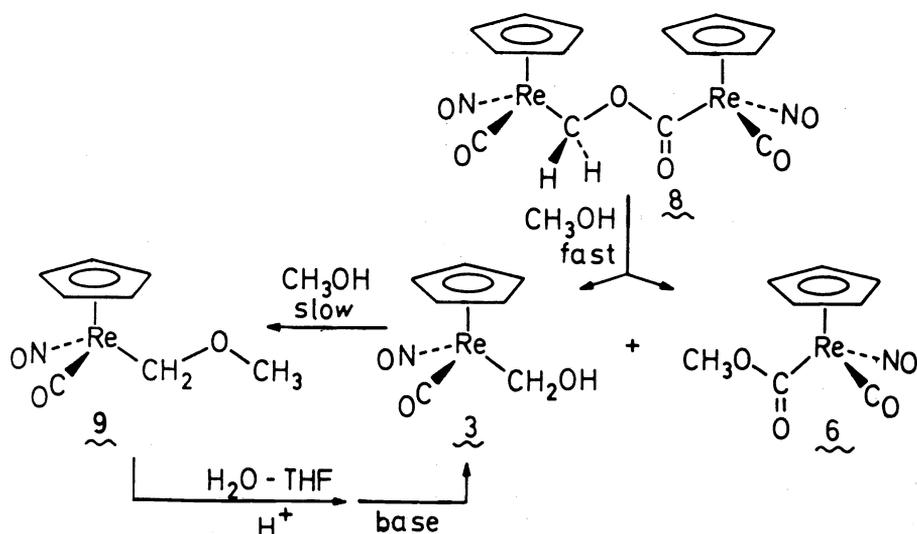
HYDROLYSIS OF METHOXYMETHYL COMPLEX $(C_5H_5)Re(NO)(CO)(CH_2OCH_3)$

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 (23). The hydroxymethyl complex 3 was isolated as a red-orange solid and identified spectroscopically. The ^1H NMR of 3 in benzene-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 (Fluorolube) 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 (18) 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 (21) 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.

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 diisobutyl-aluminum 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.
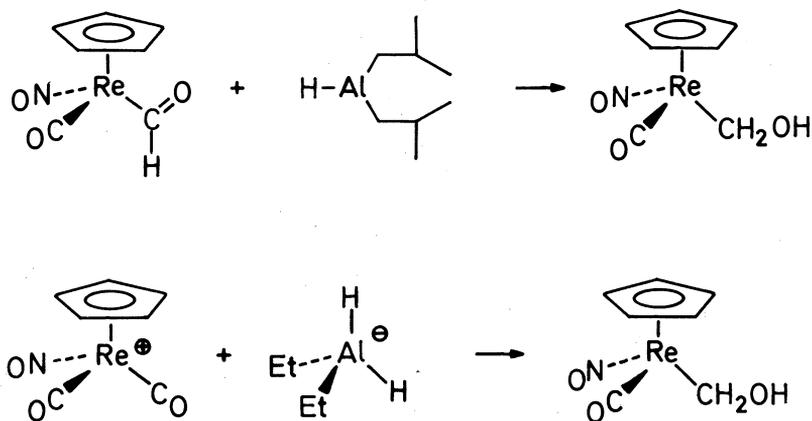
We therefore examined the reaction of cation 1 with sodium diethylaluminum dihydride in the hope of initially forming formyl complex 2 and an equimolar amount of dialkylaluminum hydride which could convert 2 into the hydroxymethyl complex 3. Addition of a solution of sodium diethylaluminum hydride to 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 (21).

The rhenium hydroxymethyl complex reported here is the first authentic example of a hydroxymethyl metal compound. Previously such complexes have been proposed as intermediates in many organometallic reactions but isolated hydroxymethyl complexes have been unavailable for study. The only other α-hydroxyalkyl metal compound reported was $(C_5H_5)Fe(CO)_2[C(CF_3)_2OH]$ which was synthesized by Stone from $(C_5H_5)Fe(CO)_2^-$ and hexafluoroacetone (25). Gladysz has attempted generation of $(CO)_5MnCH(OH)C_6H_5$ by two different routes but found that the presumed intermediate was not observable even at -50°C and only benzaldehyde and $HMn(CO)_5$ could be detected (24). Pruett proposed hydroxymethyl and 1,2-dihydroxyethyl rhodium intermediates in the rhodium cluster catalyzed conversion of CO/H_2 mixtures into ethylene glycol (26). Feder has suggested hydroxymethyl cobalt species as precursors of methanol in the cobalt carbonyl catalyzed reduction of CO by H_2 (27). Green has suggested hydroxymethyl tungsten intermediates in the photochemical reaction of $(C_5H_5)_2WH_2$ with CH_3OH to give $(C_5H_5)_2W(CH_3)(OCH_3)$ (28). α-Hydroxyalkyl metal complexes have been suggested as intermediates in the hydrogenation of aldehydes to alcohols by cobalt (29) and ruthenium complexes (30). Finally, α-hydroxyalkyl cobalt species have been suggested as intermediates in vitamin B_{12} chemistry (31).

We hope that study of hydroxymethyl complex 3 with acids, bases, CO, and H_2 will help to define the kind of chemistry to be expected from α-hydroxyalkyl metal compounds and will give greater insight into the mechanism of reactions for which α-hydroxyalkyl intermediates have been proposed.

REFERENCES

1. For reviews see C. Masters, Adv. Organomet. Chem. 17, 61-103 (1979); S. Olive, Angew. Chem., Int. Ed. Engl. 15, 136-141 (1976); I. Wender, Cat. Rev.-Sci. Eng. 14, 97-129 (1976); M. A. Vannice, ibid. 14, 153-191 (1976).
2. J. P. Collman, S. R. Winter, J. Am. Chem. Soc. 95, 4089-4090 (1973).
3. C. P. Casey and S. M. Neumann, J. Am. Chem. Soc. 98, 5395-5396 (1976).
4. C. P. Casey and S. M. Neumann, J. Am. Chem. Soc. 100, 2544-2545 (1978).
5. J. A. Gladysz and W. Tam, J. Am. Chem. Soc. 100, 2545-2547 (1978).
6. J. A. Gladysz and J. C. Selover, Tetrahedron Letters, 319-322 (1978).
7. J. A. Gladysz, G. M. Williams, W. Tam and D. L. Johnson, J. Organomet. Chem. 140, C1-C6 (1977).
8. S. R. Winter, G. W. Cornett and E. A. Thompson, J. Organomet. Chem. 133, 339-346 (1977).
9. C. P. Casey and D. R. McAlister, unpublished results.
10. W. K. Wong, W. Tam, C. E. Strouse and J. A. Gladysz, J. Chem. Soc., Chem. Commun, 530-532 (1979).

11. S. M. Neumann, Ph.D. Thesis, University of Wisconsin-Madison (1978).
12. M. Y. Darensbourg, D. J. Darensbourg and H. L. C. Barros, Inorg. Chem. 17, 297-301 (1978).
13. M. Y. Darensbourg and D. Burns, Inorg. Chem. 13, 2970-2973 (1974).
14. T. J. Collins and R. J. Roper, J. Chem. Soc., Chem. Commun., 1044-1045 (1976); T. J. Collins and R. J. Roper, J. Organomet. Chem. 159, 73-89 (1978).
15. A. Berry and T. L. Brown, J. Organomet. Chem. 33, C67-C68 (1971).
16. P. M. Treichel and R. L. Shubkin, Inorg. Chem. 6, 1328-1334 (1967).
17. R. P. Stewart, N. Okamota and W. A. G. Graham, J. Organomet. Chem. 42, C32-C34 (1972).
18. A. N. Nesmeyanov and L. L. Krasnoslobodskaya, Bull. Acad. Sci. USSR, 807-811 (1970).
19. C. P. Casey, M. A. Andrews and J. E. Rinz, J. Am. Chem. Soc. 101, 741-742 (1979).
20. W. Tam, W.-K. Wong and J. A. Gladysz, J. Am. Chem. Soc. 101, 1589-1591 (1979).
21. W. A. G. Graham and J. R. Sweet, J. Organomet. Chem. 173, C9-C12 (1979).
22. J. A. Van Doorn, C. Masters and H. C. Volger, J. Organomet. Chem. 105, 245-254 (1976).
23. C. P. Casey, M. A. Andrews and D. R. McAlister, J. Am. Chem. Soc. 101, 3371-3373 (1979).
24. J. A. Gladysz, J. C. Selover and C. E. Strouse, J. Am. Chem. Soc. 100, 6766-6768 (1978).
25. T. Blackmore, M. I. Bruce, P. J. Davidson, M. Z. Iqbal and F. G. A. Stone, J. Chem. Soc. A., 3153-3158 (1970).
26. R. L. Pruett, Ann. N.Y. Acad. Sci. 295, 239-248 (1977).
27. J. W. Rathke and H. M. Feder, J. Am. Chem. Soc. 100, 3623-3625 (1978).
28. L. Farrugia and M. L. H. Green, J. Chem. Soc., Chem. Commun., 416-417 (1975).
29. C. L. Aldridge and H. B. Jonassen, J. Am. Chem. Soc. 85, 886-891 (1963).
30. R. A. Sanchez-Delgado, J. S. Bradley and G. Wilkinson, J. Chem. Soc. (Dalton), 399-404 (1976).
31. R. H. Abeles and D. Dolphin, Acc. Chem. Res. 9, 114-120 (1976).