enables us to assign with some confidence an error limit of ±20 kJ mol^{-1}.

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(30) C. E. Housecroft, K. Wade, and B. C. Smith, *J. Chem. Soc., Chem. Commun.*, 765 (1978).

(31) Calculated from unit-cell parameters of H. E. Swanson and R. K. Fuyat, *Natl. Bur. Stand.* (*U.S.*), *Circ.*, No. 539, **2**, 13 (1953).

(32) Ignoring some of the objectionable assumptions of this application of the Birge–Sponer technique, one major objection which cannot be overlooked is the utilization of solid-state Raman frequencies. The Birge–Sponer technique is applicable to the determination of bond dissociation energies in the gas phase.[34] The fact that the solid-state values employed by these authors most certainly differ substantially from the free-ion values[35] makes meaningless the value of the bond energy determined by this procedure.

(33) C. D. Garner, G. Pilcher, K. J. Cavell, and S. Parkes, to be published; ref 23 quoted by Skinner in ref 7.

(34) The environmental perturbations which the solid state exerts on molecular vibrations is a complex problem which has long concerned spectroscopists. In some instances the "solvent effect" of the host crystal can be corrected by carrying out a parallel extrapolation of the observed frequencies of the molecule under investigation with that of a concurrently present ion whose free-ion stretching frequency is known (e.g., CN^-).[35] An alternative technique which in some cases seems to provide meaningful data is one in which the species of interest is generated and trapped as an isolated species in an inert gas matrix.[36]

(35) As an example of the magnitude of the influence which the solid state exerts on vibrational frequencies, consider the difference between the observed frequency for CN^- in a NaCl host lattice (2105 cm^{-1}) and that of the free ion (2038 cm^{-1}): G. R. Field and W. F. Sherman, *J. Chem. Phys.*, **47**, 2378 (1967).

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Reduction of Coordinated Carbon Monoxide. Synthesis of Neutral Metal Formyl and Hydroxymethyl Derivatives of the $(C_5H_5)Re(CO)_2(NO)^+$ Cation

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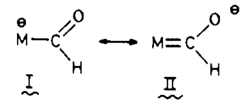
Abstract: The reaction of $(C_5H_5)Re(CO)_2(NO)^+PF_6^-$ (**1**) with potassium triisopropoxyborohydride in tetrahydrofuran at −78 °C gives the neutral formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$ (**2**) as an orange oil. Dilute solutions of **2** gradually decompose at room temperature to give $(C_5H_5)Re(CO)(NO)(H)$ (**4**). Reduction of **2** with $BH_3{\cdot}THF$ yields $(C_5H_5)Re(CO)(NO)(CH_3)$ (**5**), while reduction of **2** with lithium triethylborohydride gives the diformyl complex $(C_5H_5)Re(NO)(CHO)_2^-$ (**7**). Formyl complex **2** is unstable in neat oil form and disproportionates to give the dimeric metallo ester $(C_5H_5)(CO)(NO)ReCO_2CH_2Re(CO)(NO)(C_5H_5)$ (**8**) as a ~1:1 mixture of two diastereomers. Prolonged solvolysis of **8** in methanol yields the methyl ester $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$ (**6**) and the methoxymethyl complex $(C_5H_5)Re(CO)(NO)(CH_2OCH_3)$ (**9**). Ether **9** can be hydrolyzed with water-tetrahydrofuran under acid catalysis to give the first unsubstituted hydroxymethyl complex, $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**3**). Previous claims of the isolation of **3** are shown to be inaccurate. Complex **3** may also be more readily obtained by treatment of cation **1** with sodium diethylaluminum dihydride.

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. Many of our studies have centered around metal formyl species[2] which may be involved in the initiation step of CO reduction. The first formyl complex, $(CO)_4FeCHO^-$, was synthesized by Collman from $Fe(CO)_4^{2-}$ and acetic-formic anhydride.[3] Unfortunately, this route did not prove to be general and we[2] and others[4] have developed syntheses of a variety of anionic metal formyl complexes by treatment of neutral metal carbonyl compounds with borohydrides such as potassium triisopropoxyborohydride. The low formyl CO stretching frequencies observed for these anionic species (for example, 1600 cm^{-1} for $(CO)_4FeCHO^-$) indicated 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.



I II

At the time we began this work, only one neutral metal formyl species had been reported, the unstable and only partially characterized $Os(CO)_2[P(C_6H_5)_3]_2Cl(CHO)$.[5,14] Neutral metal formyl species had been suggested as intermediates in the substitution reactions of metal carbonyl hydride complexes,[6a] in the reaction of methoxide with $Ru[P(C_6H_5)_3]_3ClH$ to eventually give $Ru[P(C_6H_5)_3]_3(CO)H$,[6b] and in the sodium borohydride reductions of the metal carbonyl cations $(C_5H_5)W(CO)_3[P(C_6H_5)_3]^{+}$ [7] and $(C_5H_5)Re(CO)_2NO^{+}$ [8] to methyl and hydroxymethyl metal complexes.

In a preliminary communication, we reported that the reaction of $(C_5H_5)Re(CO)_2NO^+PF_6^-$ (**1**) with $K^+HB[OCH(CH_3)_2]_3^-$ gave the neutral metal formyl complex **2**.[9] In addition, we found that the claimed synthesis[10] of the only reported hydroxymethyl complex, $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**3**), was inaccurate and eventually succeeded in preparing authentic **3** by two alternate routes.[11] Here we

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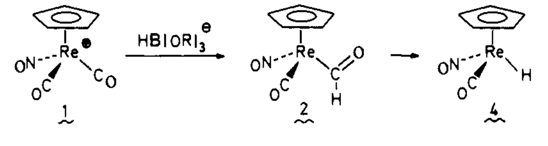
report our detailed findings concerning the synthesis of neutral formyl complex **2** and of hydroxymethyl complex **3**. Gladysz has now reported a related synthesis of **2** and other neutral formyl compounds.[12] Graham has reported a related preparation of hydroxymethyl complex **3**.[13] In addition, Roper has reported an unrelated synthesis of a stable neutral osmium formyl complex.[14]

Results

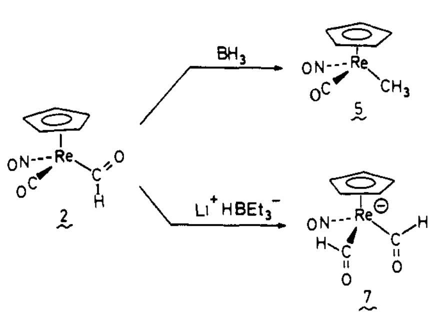
Synthesis and Characterization of $C_5H_5Re(CO)(NO)(CHO)$. Addition of a THF solution of potassium triisopropoxyborohydride to a suspension of $(C_5H_5)Re(CO)_2(NO)^+PF_6^-$ (**1**) in THF at −78 °C gives a deep orange solution. The ^1H NMR and IR spectra of the solution at room temperature clearly demonstrate the formation of $(C_5H_5)Re(CO)(NO)(CHO)$ (**2**). The NMR spectrum in THF-d_8 has a five-proton cyclopentadienyl resonance at δ 5.87 and a one-proton singlet at δ 16.29 assigned to the formyl proton. The far-downfield chemical shift of the formyl proton is extremely useful in characterizing these complexes. The infrared spectrum of formyl complex **2** has a strong CO stretching band at 1991 cm^{-1}, a strong NO stretching band at 1723 cm^{-1}, and a medium-intensity band at 1619 cm^{-1} which is assigned to the carbonyl stretch of the formyl ligand. Integration of the NMR spectrum using *p*-xylene as an internal standard indicated that **2** was formed in ~60% yield. Hydrolytic workup at 0 °C gave a ~50% yield of **2** as a slightly impure orange oil. Solutions of the orange oil gave spectra identical with those of in situ prepared **2**. In the NMR spectrum of **2** in benzene-d_6, the cyclopentadienyl resonance was shifted to δ 4.77, more than 1 ppm upfield from its position in THF, while the formyl resonance was relatively unshifted at δ 16.45. For all of the cyclopentadienylrhenium compounds reported here, benzene caused similar upfield chemical shifts of the cyclopentadienyl resonances. Attempts to purify **2** were unsuccessful in our hands owing to the high reactivity of concentrated solutions of **2** (vide infra). Graham and Sweet have reported the low-temperature isolation of **2** as an orange solid which decomposes when warmed above −10 °C.[13]

Solutions of formyl complex **2** are oxidized by air but none of the metal carboxylic acid $(C_5H_5)Re(CO)(NO)(CO_2H)$[9] was observed. Dilute solutions of **2** in THF or benzene undergo thermal decomposition with a time for half-decomposition of about 10 h at room temperature to give ~40% yield of the known metal hydride $(C_5H_5)Re(CO)(NO)H$ (**4**).[8]



Reductions of $(C_5H_5)Re(CO)(NO)(CHO)$. Treatment of formyl complex **2** with $BH_3{\cdot}THF$ gives the known methyl complex[8] $(C_5H_5)Re(CO)(NO)(CH_3)$ (**5**) in ~50% yield. Earlier Masters had found that $BH_3{\cdot}THF$ efficiently reduced metal acyl complexes to metal alkyl complexes.[15] $BH_3{\cdot}THF$ is a powerful reducing agent for α-oxygenated ligands in general: both the hydroxymethyl complex $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**3**) and the methyl ester complex $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$ (**6**)[10] are also reduced to methyl complex **5** by borane in THF. This reactivity toward 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**). Diformyl complex **7** is unstable in solution and decomposes over a period of 12–24 h at room temperature. The NMR spectra of toluene extracts of the decomposed diformyl reaction mixture show that some methyl complex **5** is present. Since complex **7** could not be isolated, it was characterized spectroscopically. The ^1H NMR in THF consisted of a five-proton cyclopentadienyl resonance at δ 5.57 and a two-proton formyl resonance at δ 14.66. The IR spectrum has a nitrosyl band at 1665 cm^{-1} and two formyl bands at 1540 and 1530 cm^{-1}.



An attempt to reduce formyl complex **2** with 1 atm of hydrogen at room temperature led to no reaction. This is not surprising in view of the high stability of related rhenium complexes toward thermal ligand substitution reactions.[16]

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 dilute solution, is present only to a small extent in the red solid. Extraction of the red solid with benzene gives a dark red oil which was recrystallized with difficulty from toluene–heptane to give 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. Each rhenium atom of **8** is a chiral center and the isolated solid is a 1:1 mixture of the two possible diastereomers **8a** and **8b**. The disproportionation of formyl complex **2** to metallo ester **8** is only significant in very concentrated solutions (≥0.4 M).

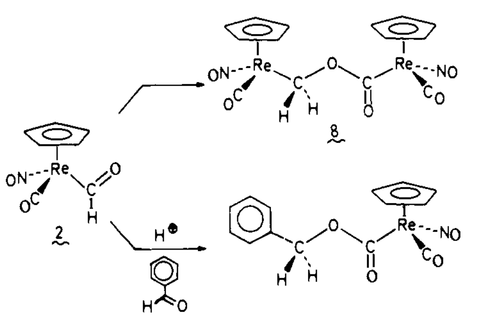
The IR spectrum of **8** in Nujol mull clearly indicates the presence of two chemically different rhenium centers: the CO and NO stretching bands at higher energy (1986 and 1722 cm^{-1}, respectively) are presumed to arise from the ligands of the more electron-poor rhenium bearing the carboxy end of the ester linkage, while the lower energy bands (1966 and 1702 cm^{-1}) are assigned to the stretching modes of the ligands on the more electron-rich rhenium at the alkoxy end. The ester functionality gives rise to bands at 1626 and 1010 cm^{-1}.

The presence of two diastereomers of **8** is clearly evident in the 270-MHz ^1H 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 5.99, 6.42 (J = 9.7 Hz) and were assigned on the basis of decoupling experiments. In solvents other than benzene-d_6, the ^1H NMR of **8** is complicated by overlap of cyclopentadienyl and methylene protons and the smaller chemical-shift differences observed for diastereotopic protons.

No parent ion was observed in the mass spectrum of **8**, but $(M - CO)^+$ and $(M - NO)^+$ are observed. The base peak in the spectrum due to $(C_5H_5)Re(CO)_2(NO)^+$ results from a typical ester fragmentation.

The reaction of formyl complex **2** with benzaldehyde was studied in an attempt to observe a "crossed" disproportionation reaction. A slow reaction between **2** and benzaldehyde to give $(C_5H_5)Re(CO)(NO)(CO_2CH_2C_6H_5)$ was observed at room temperature. This crossed disproportionation is apparently catalyzed by adventitious acid since the reaction is greatly accelerated by added acetic acid and strongly retarded by added triethylamine.

The possibility that the disproportionation of formyl com-



plex **2** to metallo ester **8** is also acid catalyzed was investigated. The effect of acids and bases on the rate of disproportionation of **2** was much less pronounced than in the reaction with benzaldehyde. Added acetic acid approximately doubled the rate of formation of **8** while added triethylamine halved the rate of formation of **8**. When attempts were made to remove adventitious acids by hydrolyzing the crude formyl complex reaction mixtures with 1 equiv of NaOH or by drying the ether solutions of **2** over K_2CO_3 instead of $MgSO_4$, ester dimer **8** still formed on evaporation of ether from solutions of **2**.

Methanolysis of Metallo Ester Dimer $(C_5H_5)(CO)(NO)ReCO_2CH_2Re(CO)(NO)(C_5H_5)$. Nesmeyanov reported that reduction of cation **1** by sodium borohydride in benzene-water produces an orange, air-sensitive solid, mp 69-71 °C dec.[10] The structure of the solid was assigned to be the hydroxymethyl complex $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**3**) on the basis of elemental analysis (C, H, N, Re) and IR spectra [3300-3200 (s), 3120 (s), 2935 (s), 1980 (s), 1660 (s), 1420 (m), 1350-1260 (w), 1070 (m), 1010 (m), and 825 cm^{-1} (m)]. An NMR spectrum was not reported. However, we[9] and two other groups[12,13] have found that formyl complex **2** is the major product of $NaBH_4$ reduction of **1** in benzene-water, not the hydroxymethyl complex **3**.

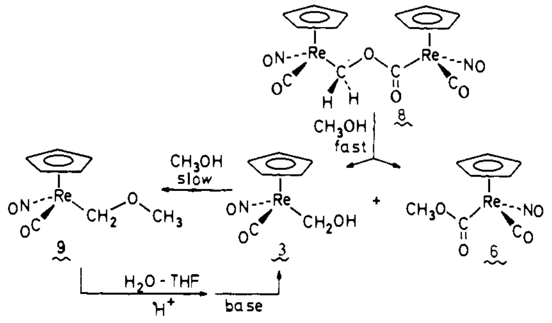
To obtain an authentic sample of hydroxymethyl complex **3**, we initiated studies of the hydrolysis of metallo ester **8**. In a model experiment, the methyl ester $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$ (**6**)[10] was found to undergo rapid transesterification under very mild conditions. Methyl ester **6** was converted to the corresponding ethyl ester within 2 h 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.[17]

Methanolysis of metallo ester **8** in benzene-d_6 resulted in a complicated sequence of changes in the ^1H NMR spectra which were initially difficult to decipher. The only obvious conclusion that could be drawn initially was that the rapid appearance of a new singlet at δ 3.60 indicated the formation of the expected methyl ester **6**. After several days, a second methyl singlet grew in at δ 3.24 which was subsequently found to be due to the methoxymethyl complex $(C_5H_5)Re(CO)(NO)(CH_2OCH_3)$ (**9**). The signal at δ 3.60 due to **6** remained essentially constant as the signal at δ 3.24 due to **9** grew.

In a larger scale reaction, solvolysis of metallo ester **8** in methanol for 5 days gave a mixture of methyl ester **6** and methoxymethyl complex **9**. The ^1H NMR of $(C_5H_5)Re(CO)(NO)(CH_2OCH_3)$ (**9**) in benzene-d_6 consisted of a methyl singlet at δ 3.24, a cyclopentadienyl singlet at δ 4.80, and an AB quartet for the diastereotopic methylene group at δ 5.14 and 5.30 (J = 9.5 Hz). Previously, methoxymethyl metal complexes have been obtained from reactions of organometallic anions with chloromethyl methyl ether.[18]

With detailed knowledge of the NMR spectra of **6** and **9** available, it now became possible to sort out the complex changes observed in the ^1H NMR during the methanolysis of dimer **8** in benzene-d_6 by using multiple-field NMR to distinguish between peak separations due to coupling constants and those due to chemical-shift differences and by measuring the effect of alcohol concentration on chemical shifts.

The spectrum of metallo ester **8** in benzene-d_6 taken immediately after addition of 2 equiv of methanol shows that the chemical shifts of all the dimer protons are altered—presumably by hydrogen bonding between methanol and the amide-like (ν_{CO} 1626 cm^{-1}) ester carbonyl group of **8**. Within minutes two new cyclopentadienyl peaks, a methyl ester peak, and a new methylene AB quartet appear, indicating the formation 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. In addition, the peaks due to residual dimer **8** revert to their benzene only positions as the methanol concentration drops. To further complicate matters, the cyclopentadienyl signals due to final products **6** and **9** are almost coincident at 100 MHz, as are some of the methylene signals. For example, the left and right halves of the two AB methylene quartets of **8** appear as pseudotriplets after the addition of methanol.



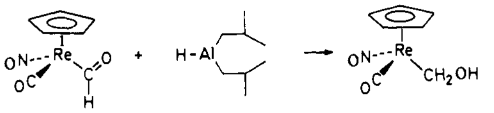
Although the desired hydroxymethyl metal complex **3** was shown by NMR to be present in large amounts in the early stages of the conversion of **8** to **6** and **9**, the hydroxymethyl complex could not be isolated from the reaction mixtures. Brief solvolysis of metallo ester **8** in methanol, followed 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.

$$\mathbf{8} + CH_3OH \rightleftarrows \mathbf{3} + \mathbf{6}$$

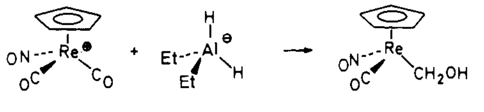
Hydrolysis of Methoxymethyl Complex $(C_5H_5)Re(NO)(CO)(CH_2OCH_3)$. At this point, we turned our attention to the hydrolysis of isolated methoxymethyl complex **9**, where reverse transesterification would not be a problem. Treatment of **9** with 0.1 equiv of trifluoroacetic acid in THF-water, concentration, and extraction with toluene gave an orange solid. Spectral data, however, indicated that it was not hydroxymethyl complex **3** but the ether dimer $[(C_5H_5)(CO)(NO)ReCH_2]_2O$ (**10**).[19]

The desired hydroxymethyl complex was finally obtained when the acid-catalyzed hydrolysis of the methoxymethyl complex **9** was quenched with 0.15 equiv of triethylamine prior to workup. 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[10] 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,[13] 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 diisobutylaluminum hydride (DIBAL-H) in the hope of obtaining the hydroxymethyl complex **3**. Indeed, reaction of formyl complex **2** with 1 equiv of DIBAL-H gave some hydroxymethyl complex **3**. However, since we were unable to accurately measure the amount of unstable starting formyl complex **2**, overreduction and underreduction 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 2 equiv of $NaBH_4$ in THF-water under carefully controlled conditions.[13]



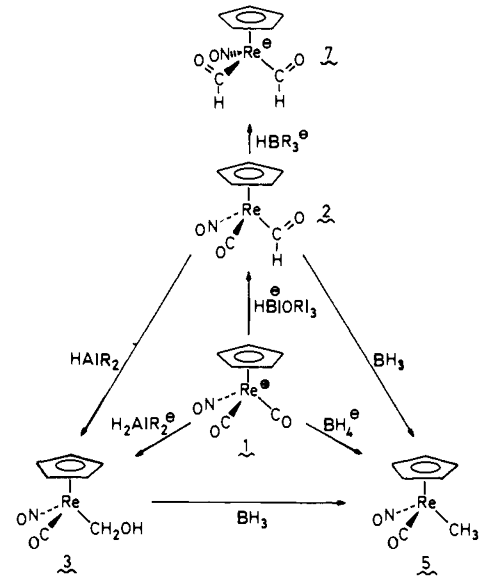
Discussion

Selective Reductions. Scheme I outlines the selective hydride reductions of coordinated CO and formyl ligands which can be achieved by variation of the hydride donor reagent. By simply altering the reducing agent, it is possible to partially reduce a CO ligand of cation **1** either to a formyl ligand or to a hydroxymethyl ligand or to completely reduce it to a methyl ligand. Similarly, selective reduction of formyl complex **2** to diformyl complex **7**, to hydroxymethyl complex **3**, or to methyl complex **5** can be achieved.

In complexes which contain both acyl and CO ligands, the site of nucleophilic attack is normally the CO ligand.[20] An exception to this pattern is the selective reduction of acyl groups to ethyl groups by the Lewis acid reducing agent borane observed by Masters.[15] In this work, we have similarly found that the nucleophilic hydride reducing agent $HBEt_3^-$ attacks the coordinated CO ligand of formyl complex **2** to produce diformyl complex **7** while the electrophilic reducing agents borane and DIBAL-H attack the formyl group of **2**.

The selectivity differences observed in these reductions can be explained in terms of the differing electronic structures of the CO and formyl ligands and in terms of Lewis acid catalysis. The coordinated CO ligand has a moderately electrophilic carbon atom and a weakly nucleophilic oxygen atom. In contrast, the formyl ligand has a weakly electrophilic carbon atom and a moderately nucleophilic oxygen atom; this is evidenced by the low-frequency formyl CO stretch of 1619 cm^{-1} for **2** which occurs at significantly lower frequency than the CO stretch of organic amides. Thus, in the absence of Lewis acid catalysts, the coordinated CO ligand is more reactive toward nucleophilic hydride donors than is the formyl ligand of **2**.

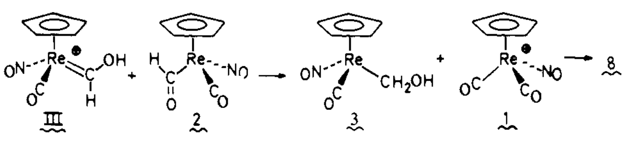
Scheme I



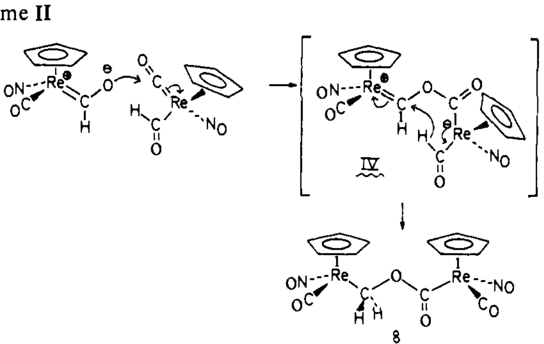
Interaction of a Lewis acid with formyl complex **3** should occur at the more nucleophilic oxygen atom of the formyl ligand. This interaction selectively enhances the reactivity of the formyl carbon atom toward nucleophiles. Either intra- or intermolecular reduction of the formyl ligand can now occur selectively. It should be pointed out that Lewis acids also can interact strongly with hydroxymethyl ligands and catalyze their reduction to alkyl groups.

Disproportionation of $(C_5H_5)Re(CO)(NO)(CHO)$. In contrast to anionic formyl complexes, which are strong hydride donors,[2,4] the neutral formyl complex **2** does not reduce acetone. This is similar to the reactivity difference between formate anion, which is a hydride donor, and neutral formate esters, which are not. Formyl complex **2** does, however, reduce benzaldehyde with the aid of acid catalysis and does undergo a disproportionation reaction. While dilute solutions of formyl complex **2** undergo unimolecular decomposition to metal hydride **4**, decomposition of **2** *as a neat oil* presumably occurs by a bimolecular process to give dimeric metallo ester **8**. This redox disproportionation of formyl complex **2** to ester **8** resembles the Cannizzaro and Tischenko reactions of aldehydes (for example, a commercial synthesis of ethyl acetate involves the aluminum alkoxide catalyzed disproportionation of acetaldehyde).[21]

Two mechanisms appear to be operative for the formation of metallo ester **8**—one which is acid catalyzed and one which is not. The acid-catalyzed reaction probably proceeds by protonation of the formyl oxygen of **2** to give cationic carbene complex III which is now a sufficiently good electrophile to be



Scheme II



reduced by a weak hydride donor such as the neutral formyl complex **2**.[22] Hydride transfer from **2** to III would initially give hydroxymethyl complex **3** and cation **1** which could then combine to give ester **8**. A similar mechanism would explain the cross disproportionation of **2** and benzaldehyde.

The non-acid-catalyzed formation of **8** is suggested to proceed by the two-step mechanism shown in Scheme II. 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 IV. The nucleophilicity of the formyl oxygen and the electrophilicity of the carbonyl carbon of **2** were noted above. Intermediate IV 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. The ability of anionic metal formyl complexes to act as hydride donors to metal carbene complexes has been observed.[22] Gladysz's report that the triphenylphosphine substituted formyl complex, $(C_5H_5)Re(NO)[P(C_6H_5)_3](CHO)$, is stable toward dimerization at room temperature[12] may be due to the absence of a CO ligand which would be required for the formation of an intermediate similar to IV.

Reactions of Metallo Esters and Metallo Ethers. The extremely rapid exchange reactions of alcohols with the rhenium-substituted esters and ethers are highly unusual.

$$(C_5H_5)Re(CO)(NO)(CO_2R) + R'OH \rightleftarrows (C_5H_5)Re(CO)(NO)(CO_2R') + ROH$$

$$(C_5H_5)Re(CO)(NO)(CH_2OR) + R'OH \rightleftarrows (C_5H_5)Re(CO)(NO)(CH_2OR') + ROH$$

The transesterifications were complete within 2 h in benzene-d_6 in the absence of added acid or base catalysts. The exchange reactions of metallo ethers were slower, requiring 5 days in benzene-d_6 in the absence of acid catalysts. Catalysis of the ether exchange reactions by trifluoroacetic acid led to essentially complete reaction within 2 h. These facile exchanges are in marked contrast to the transesterifications of ordinary organic esters, which require acid or base catalysis, and to ether formation and exchange reactions, which require acid catalysts.

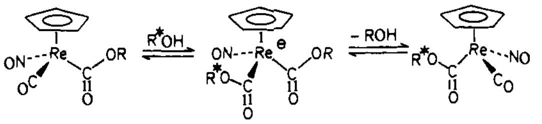
The enhanced exchange rates observed for the metallo esters and ethers are undoubtedly due to the strong electron-donating ability of the rhenium center which can stabilize cationic intermediates.

$$(C_5H_5)(CO)(NO)Re(CO_2R) \rightleftharpoons (C_5H_5)Re(CO)_2(NO)^+\ OR^- \xrightarrow{R'OH}$$

$$(C_5H_5)(CO)(NO)Re(CH_2OR) \rightleftharpoons (C_5H_5)(CO)(NO)Re^+{=}CH_2\ OR^- \xrightarrow{R'OH}$$

A similar mechanism has been postulated for reactions of iron metallo esters.[23]

The transesterification of $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$ might also proceed by attack of alcohol at a terminal carbonyl ligand to give a metallo diester which then can undergo loss of an alcohol unit to give the exchanged metallo ester. Such a mechanism has been proposed to explain the racemization



observed in methanolysis of $(C_5H_5)Fe[P(C_6H_5)_3](CO)(CO_2\text{-menthyl})$.[24] However, the fact that both $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$ and $(C_5H_5)Re[P(C_6H_5)_3](NO)(CO_2CH_3)$ undergo exchange with ethanol at nearly equal rates indicates that it is unlikely that **6** undergoes transesterification by an addition-elimination route.

The ether exchange reaction will be discussed in detail in a future paper dealing with the chemistry of the hydroxymethyl complex **3**.

Hydroxymethyl Complexes. The rhenium hydroxymethyl complex reported here is the first authentic example of a hydroxymethyl 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.[17] Pruett proposed hydroxymethyl- and 1,2-dihydroxyethylrhodium intermediates in the rhodium cluster catalyzed conversion of CO/H_2 mixtures into ethylene glycol.[26] Feder has suggested hydroxymethylcobalt species as precursors of methanol in the cobalt carbonyl catalyzed reduction of CO by H_2.[27] Green has suggested hydroxymethyltungsten 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-hydroxyalkylcobalt 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.

Experimental Section

General. The following compounds were purchased from the commercial sources indicated and used without further purification: $Re_2(CO)_{10}$ (Pressure Chemical Co. or Strem Chemicals Inc.), NO_2PF_6 (Alfa), $KHB(OCH(CH_3)_2)_3$ (1 M solution in THF, Aldrich), and diisobutylaluminum hydride (1 M solution in hexane, Aldrich).

All reactions were carried out under nitrogen unless otherwise indicated. Tetrahydrofuran (THF) was distilled under N_2 from sodium benzophenone ketyl prior to use.

$(C_5H_5)Re(CO)_3$. Using a procedure similar to that of Fischer,[32] $Re(CO)_5Br$ (10.2 g, 25.0 mmol) and sodium cyclopentadienide (~50 mmol) were refluxed in benzene (125 mL) for 18 h to give $(C_5H_5)Re(CO)_3$ (6.0 g, 70%) isolated by sublimation at 75 °C under high vacuum. Substitution of either THF or toluene as a solvent gave product contaminated with significant amounts of $Re_2(CO)_{10}$ which is difficult to separate.

$(C_5H_5)Re(CO)_2(NO)^+PF_6^-$ (1). Solid NO_2PF_6 was added in small portions to a stirred solution of $(C_5H_5)Re(CO)_3$ (3.21 g, 9.57 mmol) in CH_3CN (20 mL, dried over molecular sieves). Vigorous gas evolution took place immediately and the colorless solution became deep yellow-brown. Addition of NO_2PF_6 was terminated when no more gas evolution occurred (~2.5 g, 13 mmol). Diethyl ether (175 mL) was then added immediately, resulting in a voluminous, yellow precipitate which was collected, washed with ethanol and ether, and dried under vacuum to give moderately air-stable **1** (4.2 g, 90%).[10]

$(C_5H_5)Re(CO)(NO)(CHO)$ (2). Method A. A solution of potassium triisopropoxyborohydride (0.48 mL, 1.0 M in THF, 0.48 mmol) was added dropwise via syringe to a stirred suspension of $(C_5H_5)Re(CO)_2(NO)^+PF_6^-$ (**1**, 215 mg, 0.45 mmol) in THF (3 mL) at −78 °C. The mixture was stirred at −78 °C until a clear, deep orange-brown solution formed (15-60 min). ^1H NMR spectra of this reaction mixture at ambient temperature showed a 60% yield of formyl complex **2** (δ 16.29, 1 H; 5.87, 5 H vs. added *p*-xylene) with $(C_5H_5)Re(CO)(NO)(H)$ (5%) as the only other observable species. Similarly, IR spectra (2100-1500 cm^{-1}) showed only absorptions due to **2**. The −78 °C bath was replaced by an ice bath and the reaction quenched by the sequential addition of 0 °C water (20 mL) and 0 °C ether (15 mL). The orange ether layer was transferred via syringe to a Schlenk flask containing anhydrous $MgSO_4$ (3 g) and 5-10 mL of ether cooled to 0 °C. The reaction mixture was extracted with additional ether at 0 °C until the extracts were nearly colorless. The combined extracts were dried over $MgSO_4$ at 0 °C for 30-60 min, transferred by syringe, and concentrated under aspirator vacuum at 0 °C. The resulting orange oil was placed under oil-pump vacuum at 0 °C for 10-15 min to remove the last traces of solvent to give slightly impure $(C_5H_5)Re(CO)(NO)(CHO)$ (~80 mg, 50%). NMR (C_6D_6): δ 16.45 (1 H), 4.77 (5 H). IR (THF): 1991 (s), 1723 (s), 1619 (m) cm^{-1}. Typical impurities present were trace amounts of $(C_5H_5)Re(CO)(NO)(H)$, ester dimer **8**, 2-propanol, and THF. The formyl complex could not be further purified owing to its rapid dimerization in neat oil form and its rapid partial decomposition in concentrated solutions to give an insoluble precipitate.

Method B. Lithium triethylborohydride (1 M in THF) was used in place of potassium triisopropoxyborohydride in the above procedure with similar results except that cation **1** did not react at −78 °C and had to be warmed to −20 °C to obtain a reasonable reaction rate.

Method C. A freshly prepared solution of $NaBH_4$ (0.5 mL, 0.66 M, 0.33 mmol) in 0 °C water was added to a mixture of **1** (101 mg, 0.21 mmol), water (2.0 mL), and ether (10 mL) at 0 °C. Gas was rapidly evolved and the ether layer became orange. After 15 min the ether layer was transferred to another flask at 0 °C. Additional extracts were combined and evaporated at 0 °C to give an orange oil. The oil was dissolved in C_6D_6 and assayed by NMR vs. added *p*-xylene. The major product (~40%) was identified by IR and NMR as formyl complex **2**. Only small amounts (~10%) of hydroxymethyl complex **3** were present. Synthesis of **2** by this method has been detailed by Sweet and Graham.[13]

A similar experiment duplicating on a 10% scale as nearly as possible Nesmeyanov's published synthesis[10] of hydroxymethyl complex **3** gave similar results to the ether workup described above, except that the slow room temperature evaporation of solvent led to the formation of some ester dimer **8** and insoluble precipitates.

Thermal Decomposition of $(C_5H_5)Re(CO)(NO)(CHO)$ (2). A solution of **2** in C_6D_6 containing *p*-xylene as internal standard was maintained at about 22 °C and monitored periodically. After some initial rapid precipitation, the formyl complex decomposed by roughly first-order kinetics ($k \approx 2 \times 10^{-5}\ s^{-1}$, $t_{1/2} \approx 10$ h). The major product that could be observed by NMR was $(C_5H_5)Re(CO)(NO(H)$ (~25%) with a slight increase also seen in the peaks due to ester dimer **8**. Very similar decomposition kinetics were found for **2** prepared in situ in THF.

A sample of **2** prepared by method A from **1** (149 mg, 0.31 mmol) was dissolved in THF (60 mL) and allowed to stand at room temperature for 3 days. The solvent was then evaporated and the residue extracted with hexane. Evaporation gave an orange oil identified as $(C_5H_5)Re(CO)(NO)(H)$ (25% based on **1**, ~40% based on **2**) by comparison of IR and ^1H NMR spectra with those of an authentic sample.

Reaction of $(C_5H_5)Re(CO)(NO)(CHO)$ (2), with BH_3. **2** prepared by method A from **1** (202 mg, 0.42 mmol) was dissolved in THF (10 mL) and treated at 0 °C with a solution of BH_3 in THF (1.0 mL, 1.85 M, 1.85 mmol). The mixture was brought to room temperature and after 30 min the solvent was evaporated on an aspirator and the residue extracted with hexane in air. Evaporation gave a red-orange solid identified as $(C_5H_5)Re(CO)(NO)(CH_3)$ (**5**, 64 mg, 47%) by comparison of IR and ^1H NMR spectra with those of an authentic sample.[8]

The reduction of hydroxymethyl complex **3** and methyl ester **6** with BH_3 proceeded similarly.

Reaction of $(C_5H_5)Re(CO)(NO)(CHO)$ (2) with Diisobutylaluminum Hydride. **2** prepared by method A from **1** (262 mg, 0.54 mmol) was dissolved in THF (10 mL) and treated at 0 °C with a solution of diisobutylaluminum hydride in hexane (0.4 mL, 1.0 M, 0.40 mmol). The reaction mixture was warmed to room temperature for 1.5 h, quenched with saturated aqueous NH_4Cl (25 mL), and extracted with toluene. The toluene extract was concentrated on a rotary evaporator and the residue was dissolved in toluene, filtered and evaporated to give **3** as a gummy, orange solid (55 mg, ~45% from **2**). ^1H NMR spectra showed that **3** was contaminated with small, varying amounts of methyl complex **5**, hydride **4**, and ester dimer **8**.

$(C_5H_5)Re(NO)(CHO)_2^-$ (7). A solution of lithium triethylborohydride in THF (0.21 mL, 1.0 M, 0.21 mmol) was added to a suspension of **1** (50 mg, 0.10 mmol) in THF (0.3 mL) in an NMR tube at −78 °C. Mixing and warming to room temperature resulted in the formation of a deep orange-brown solution whose spectral properties are consistent with those expected for **7**. NMR (THF): δ 14.66 (2 H), 5.57 (5 H). IR (THF): 1665 (s, ν_{NO}), 1540 and 1530 cm^{-1} (m, ν_{CHO}). Attempts to isolate **7** by precipitation with aqueous tetramethylammonium chloride or bis(triphenylphosphiniminium) chloride in dichloromethane were unsuccessful. The in situ generated **7** decomposes over a period of hours to another species. IR (THF): 1960 (s), 1710 (s) cm^{-1}. NMR (THF): δ 5.68. Evaporation of solvent and extraction with toluene yields impure methyl complex **5** identified by ^1H NMR (acetone-d_6): δ 5.77, 0.85.

Complex **7** is also formed when **2** prepared in situ from **1** and 1 equiv of lithium triethylborohydride is treated with a second 1 equiv of hydride, demonstrating the intermediacy of formyl complex **2** in the synthesis of **7**. No ^1H NMR evidence could be obtained for the formation of **7** when potassium triisopropoxyborohydride was used in place of lithium triethylborohydride.

$(C_5H_5)(CO)(NO)ReCO_2CH_2Re(CO)(NO)(C_5H_5)$ (8). **2** (0.8-0.9 g, 2.4-2.7 mmol) prepared by method A from **1** (2.0 g, 4.2 mmol) was allowed to stand under vacuum at room temperature for 4-12 h and then under nitrogen for 2-4 days. During this time the orange oil rapidly darkened and then gradually solidified to a deep red solid. The solid was extracted with benzene and the extracts were exposed to air until no more precipitate formed (2-4 h). The mixture was filtered and the filtrate evaporated on a rotary evaporator to give a dark oil, which was recrystallized with difficulty from toluene-heptane at −30 °C to give **8** as air-stable, red-orange microcrystals (0.38-0.46 g, 45-55% based on **2**). The material is a 1:1 mixture of diastereomers (mp 105-115 °C, sealed capillary under nitrogen) which could not be separated. NMR and IR are given in the Results section.

Effect of Acid and Base on Disproportionation of $(C_5H_5)Re(CO)(NO)(CHO)$. **2** prepared by method A from **1** (0.405 g, 0.84 mmol) was dissolved in 1.2 mL of C_6D_6. The solution was divided into three 0.4-mL portions and added to NMR tubes under nitrogen. Acetic acid (2 μL, 36 μmol) was added to one tube and triethylamine (5 μL, 35 μmol) added to another. ^1H NMR spectra of each were taken at t = 15 min, 4 h, and 21 h. At t = 15 min, all three samples showed ester dimer **8**, hydroxymethyl complex **3**, formyl complex **2**, and hydride **4** in a ratio of 0.5:0.3:2.7:0.3, relative to residual C_6D_5H (1.0). After 4 h, the triethylamine-treated sample showed little change, a ratio of **8:3:2:4** of 0.5:0.3:2.0:0.4. The sample without additives showed some dimer formation, a ratio of **8:3:2:4** of 0.8:0.4:1.9:0.3. The acid-treated sample showed ester dimer formation twice as great as the control, a ratio of 1.5:0.4:1.1:0.3. After 21 h, the ratios of **8:3:2:4** were 0.5:0.3:0.7:0.5 (triethylamine sample), 1.0:0.5:1.0:0.3 (untreated), and 1.9:0.5:0.3:0.3 (acetic acid).

Reaction of $(C_5H_5)Re(CO)(NO)(CHO)$ with C_6H_5CHO. This experiment was carried out identically with the one just described, except that benzaldehyde (freshly purified by liberation from its sodium bisulfite addition complex with sodium carbonate, followed by vacuum transfer, 75 μL, 0.74 mmol) was added to the C_6D_6 solution of **2** prior to transfer to NMR tubes. Spectra taken after 3 h showed that the sample treated with acetic acid had been converted extensively (~30-40%) to $(C_5H_5)Re(CO)(NO)(CO_2CH_2Ph)$ (plus some ester dimer **8**) while the untreated and triethylamine-treated samples showed only minor changes. After 20 h, the untreated sample showed extensive conversion (~50%) to $(C_5H_5)Re(CO)(NO)(CO_2CH_2Ph)$ while the triethylamine-treated sample still showed only minor conversion (~20%) to $(C_5H_5)Re(CO)(NO)(CO_2CH_2Ph)$ (hydride **4**

being a more significant product).

The benzyl ester $(C_5H_5)Re(CO)(NO)(CO_2CH_2Ph)$ was identified by comparison of its NMR (C_6D_6) [δ 4.86 (s, 5 H), 5.22 (s, 2 H), 7.08 (m, 2 H and C_6D_5H), and 7.35 (m, 3 H)] with that of a sample prepared independently by treatment of **1** with excess benzyl alcohol in THF in the presence of 1 equiv of sodium carbonate. Further confirmation of its identity was made by its transesterification with methanol to give methyl ester **6** and benzyl alcohol (by NMR).

$(C_5H_5)Re(CO)(NO)(CH_2OCH_3)$ (9). A solution of ester dimer **8** (0.34 g, 0.50 mmol) in methanol (50 mL) was stirred at room temperature for 5 days. The solvent was then evaporated and the residue extracted with a minimal volume of heptane. The heptane-insoluble portion was shown to be nearly pure methyl ester **6** by IR and ^1H NMR. The heptane extracts were evaporated to give an orange oil which gradually solidified on further pumping to give **9** as air-stable, red-orange crystals (0.15 g, 85%) which may be recrystallized from heptane, mp (sealed capillary under nitrogen) 40.5-41.5 °C, NMR in Results section. IR (heptane): 1976 (s, ν_{CO}), 1715 cm^{-1} (s, ν_{NO}). MS $(M - CO)^+$: calcd for $C_7H_{10}NO_2{}^{187}Re$, 327.0242; found, 327.0242.

$(C_5H_5)Re(CO)(NO)(CH_2OH)$ (3). Method A. A solution of methyl ether **9** (45 mg, 127 μmol) in THF (6 mL)-water (12 mL) was treated with trifluoroacetic acid (1 μL, 13 μmol). The mixture was stirred for 2.5 h, treated with triethylamine (3 μL, 22 μmol), concentrated to ~8 mL, and extracted with toluene. The orange extracts were evaporated under vacuum to give nearly pure **3** as an orange powder (35 mg, 80%).

Method B. A solution of sodium diethylaluminum dihydride in toluene (1.5 mL, 2.16 M, 3.24 mmol) was added dropwise via syringe to a stirred suspension of **1** (1.516 g, 3.14 mmol) in THF (5 mL) at −78 °C. The resulting deep red solution was stirred at −78 °C for 30 min and at 0 °C for 30 min. The reaction mixture was quenched with saturated aqueous NH_4Cl (100 mL) and extracted thoroughly with toluene in a separatory funnel in air. There is a strong tendency for emulsions to form during the extraction. The orange toluene extracts were evaporated on a rotary evaporator, and the residue was dissolved in toluene, filtered, and reevaporated. The resulting dark orange solid was extracted with hexane to remove traces of methyl complex **5**, leaving pure **3** (0.48 g, 45%). Recrystallization from toluene-heptane gives **3** as an air-stable, orange powder, mp (sealed capillary under nitrogen) 97-100 °C with slow heating from 25 °C, 105 °C with heating from 95 °C. NMR (C_6D_6): δ 0.88 (s, 1 H, exchanges with D_2O), 4.78 (s, 5 H), 5.11 and 5.84 (AB quartet, J = 10 Hz, 2 H). IR (toluene): 1967 (s, ν_{CO}), 1699 cm^{-1} (s, ν_{NO}). IR (Fluorolube): 3215 cm^{-1} (s, br, ν_{OH}) shifted to 2390 (s, ν_{OD}) in $(C_5H_5)Re(CO)(NO)(CH_2OD)$. MS: calcd for $C_7H_8NO_3{}^{187}Re$, 341.0032; found, 341.0013.

Anal. Calcd for $C_7H_8NO_3Re$: C, 24.70; H, 2.37; N, 4.12; Re, 54.71. Found: C, 25.14; H, 2.39; N, 4.08; Re, 54.03.

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