

Stepwise Reduction of Coordinated Carbon Monoxide

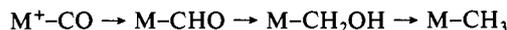
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Abstract: Reduction of $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2][\text{BF}_4]$ (**1**) by NaBH_4 in THF and THF/ H_2O mixtures afforded formyl $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CHO}]$ (**2**), hydroxymethyl $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_2\text{OH}]$ (**3**), and methyl $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_3]$ (**4**) derivatives selectively and in high yields depending upon stoichiometry and reaction conditions. Individual reduction steps among **1**–**4** have been investigated. Reduction of **2** to **4** and **3** to **4** by NaBH_4 in THF demonstrates the activation of formyl and hydroxymethyl functional groups in these complexes. Pentamethylcyclopentadienyl analogues of all compounds have been prepared; $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{CO})\text{CHO}$ (**6**) has enhanced stability and crystallinity relative to **2** and can be isolated in analytically pure form.

The recognition that petroleum reserves are finite has resulted in renewed interest in coal as an alternative source for petrochemical feedstocks and fuels. Many of the more promising processes for coal conversion such as the Fischer–Tropsch reaction involve hydrogenation of carbon monoxide in the presence of transition-metal catalysts. The search for new homogeneous catalysts and model compounds has focused attention on the hydric reduction of coordinated carbon monoxide in discrete metal carbonyls.¹

The stoichiometric reduction of a coordinated carbonyl to methyl was first demonstrated in 1967 by Treichel and Shubkin.² These authors found that treatment of $[(\eta\text{-C}_5\text{H}_5)\text{M}(\text{PPh}_3)(\text{CO})_3]^+$ ($\text{M} = \text{Mo}$ or W) with sodium borohydride in anhydrous tetrahydrofuran afforded $(\eta\text{-C}_5\text{H}_5)\text{M}(\text{PPh}_3)(\text{CO})_2\text{CH}_3$ in relatively high yield (69% for W and 27% for Mo) and suggested the methyl ligand arose from reduction of a carbonyl group. In 1972 a similar reaction was reported³ from these laboratories with $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2]^+$ to give the neutral methyl derivative, again in reasonable yield (50%). It was postulated that these reactions occurred with the intermediacy of formyl and hydroxymethyl complexes, although no such species were isolated:

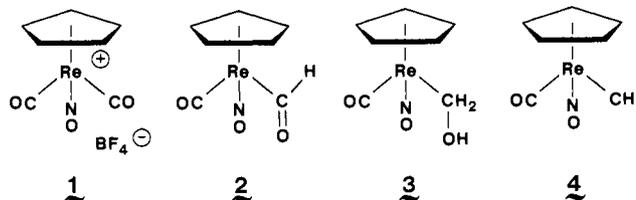


Transition-metal formyl complexes were subsequently prepared and isolated by indirect routes: $[(\text{OC})_4\text{FeCHO}]^-$ in 1973⁴ and $(\text{OC})_2(\text{PPh}_3)_2\text{Os}(\text{Cl})(\text{CHO})$ in 1976.⁵ The preparation of formyls by direct reduction of coordinated carbon monoxide was first accomplished in 1976 by Casey and Neuman⁶ using trialkoxyborohydrides. This route was soon established as a fairly general reaction of metal carbonyls.⁷

Hydroxymethyl complexes have proven more elusive. Prior to the beginning of this research, two substituted hydroxymethyls had been reported: $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}(\text{CF}_3)_2\text{OH}$,⁸ a stable compound, and $(\text{OC})_3\text{MnCH}(\text{C}_6\text{H}_5)\text{OH}$,⁹ a presumed reaction

intermediate that decomposed rapidly at -50°C . A reaction claimed¹⁰ in 1970 to lead to the compound $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_2\text{OH}$ appears to be erroneous, since attempts to reproduce the work in this¹¹ and other laboratories^{12,13} have been unsuccessful.

The present study was undertaken to demonstrate the existence of formyl (**2**) or hydroxymethyl (**3**) intermediates in the borohydride reduction³ of the carbonyl cation **1** to the methyl derivative **4**. Since the earlier work³ in this laboratory, such intermediates



had assumed great importance as possible stages in the Fischer–Tropsch process. Our preliminary results on the stepwise reduction of **1** to **2**, **3**, and **4** using a $\text{NaBH}_4\text{-H}_2\text{O-THF}$ system have been reported.¹¹ During the course of our investigation, other syntheses have been reported for **2**^{12,13} and **3**.^{14,15} In this paper, we present full details and discussion of our results on the cyclopentadienyl system, as well as a study of pentamethylcyclopentadienyl analogues of **1**–**4**. The $(\eta\text{-C}_5\text{Me}_5)$ analogue of **2** is of special interest in view of its enhanced stability. In addition, we have demonstrated all possible reduction steps in high yield among compounds **1**, **2**, **3**, and **4** with NaBH_4 in both $\text{H}_2\text{O/THF}$ and anhydrous THF. These reactions clearly delineate the stepwise nature of the hydric reduction of coordinated carbon monoxide and of formyl and hydroxymethyl ligands. Possible mechanisms and the synthetic implications of these NaBH_4 reactions will be discussed.

Results

Sodium Borohydride Reductions of $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2][\text{BF}_4]$ (1**).** Reaction of $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2]^+$ (**1**) with 1 mol of NaBH_4 in water led to the isolation of the neutral formyl complex $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CHO}$ (**2**) in 62% yield. Contrary

(1) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. Olivé, G. H.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136. Labinger, J. A. In "Transition Metal Hydrides"; Bau, R., Ed.; American Chemical Society: Washington, D.C., 1978; Adv. Chem. Ser. No. 167, p 149. Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

(2) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328.

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(4) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089.

(5) Collins, T. J.; Roper, R. J. *J. Chem. Soc., Chem. Commun.* **1976**, 1044; *J. Organomet. Chem.* **1978**, *159*, 73.

(6) Casey, C. P.; Neuman, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395.

(7) Winter, S. R.; Cornett, G. W.; Thompson, E. A. *J. Organomet. Chem.* **1977**, *133*, 339. Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1. Casey, C. P.; Neuman, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. Gladysz, J. A.; Merrifield, J. H. *Inorg. Chim. Acta* **1978**, *30*, 2317.

(8) Blackmore, T.; Bruce, M. I.; Davidson, P. J.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3153.

(9) Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6768.

(10) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Krasnoslobodskaya, L. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 860; *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* 807. The claimed synthesis of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_2\text{OH}$ involved reaction of 1.3 mol of NaBH_4 with 1.0 mol of $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2][\text{BF}_4]$ in benzene–water.

(11) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9.

(12) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741.

(13) Tam, W.; Wong, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

(14) Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 3371.

(15) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

vidually in both THF and THF/H₂O. Yields of these reactions were determined by an NMR method so that the stoichiometry would be revealed independently of product stability or ease of isolation. The results of this study are shown in Scheme III.

These reactions show a sharp contrast in the behavior of NaBH₄ under anhydrous and aqueous conditions. In anhydrous THF (eq 4, 6, and 8), 1 mol of NaBH₄ is capable of reducing coordinated CO, CHO, or CH₂OH ligands to a CH₃ group. In the presence of water (eq 5, 7, and 9), each of these reactions proceeds only to the next more reduced state.

Discussion

There are two aspects to the work described in this paper. The first involves synthesis (by reasonably efficient processes) and characterization of formyl, hydroxymethyl, and methyl complexes in both the (η-C₅H₅)Re(NO)(CO)- and (η-C₅Me₅)Re(NO)(CO)-series. These compounds are of great interest as models for proposed intermediates in Fischer-Tropsch processes¹ and are at the present time unique in their stability and ease of preparation.

The second aspect comprises a study of individual reduction steps in the (η-C₅H₅)Re(NO)(CO)-series. This raises interesting questions as to the mechanisms of the reactions with borohydride and shows rather clearly the way in which the organic ligands are being activated by the rhenium moiety. In the following discussion, we shall deal in turn with these two aspects.

Preparation of Formyl, Hydroxymethyl, and Methyl Complexes from [(η-C₅H₅)Re(NO)(CO)₂][BF₄]⁻ (1). Early evidence^{2,3} that CO coordinated to transition metals was readily reduced to CH₃ by NaBH₄ attracted little attention until the late seventies. At that time, an interest in intermediates in CO reduction prompted us¹¹ and others^{12,13} to reinvestigate reactions of [(η-C₅H₅)Re(NO)(CO)₂]⁺. Our study began with attempts to observe spectroscopically intermediates in the reaction of 1 with NaBH₄ in anhydrous THF. Infrared and NMR monitoring showed only loss of starting material with concurrent generation of 4 in virtually quantitative yields. Similar observations were obtained on reaction of 1 with a deficiency of NaBH₄. The latter result led to the realization that only 1 mol of NaBH₄ was necessary to reduce a coordinated CO to a CH₃ ligand (eq 3). Thus, in anhydrous THF, one BH₄⁻ unit is capable of donating three hydride equivalents.

At this point, we turned our attention to sodium borohydride-H₂O reductions. The use of water as a solvent had some practical advantages over the THF system. Both NaBH₄ and 1 are much more soluble in water than in THF, greatly enhancing the rate of reaction. When reduction is complete, the neutral rhenium product can be extracted into an organic solvent, leaving the sodium salt and boron byproducts in the aqueous phase. To maintain a homogenous reaction with starting materials or products insoluble in H₂O, we used THF-H₂O mixtures. The mixed solvent also allows reaction temperatures below 0 °C. Addition of a solvent such as hexane or CH₂Cl₂ to the THF-H₂O mixtures results in separation of an organic phase containing the rhenium product.

When the reaction of [(η-C₅H₅)Re(NO)(CO)₂]⁺ with 1 mol of NaBH₄ was repeated in H₂O, a different reduction product was obtained. The product was almost exclusively the formyl 2 (eq 1) with only traces of 4. The formyl must arise from a one-hydride reduction of the coordinated carbonyl, and we conclude that in aqueous solution BH₄⁻ becomes a one-hydride donor. The role of water in altering the reaction will be discussed later, but here we stress its convenience in permitting the none too thermally stable 2 to be extracted rapidly and in reasonable purity as a solid. Preparation of 2 has also been reported from the reaction of 1 with the monohydride reducing agents K[HB(O-*i*-Pr)₃]¹² and Li(HBEt₃).^{12,13}

The remaining presumed intermediate in carbonyl reduction is the hydroxymethyl complex 3. We found that it could be prepared conveniently and in high yield from 1 by using 2 mol of NaBH₄ in the presence of water (eq 2). The reaction probably occurs in two steps, with each of the required 2 mol of BH₄⁻ delivering one hydride. The first BH₄⁻ would convert 1 to 2, while

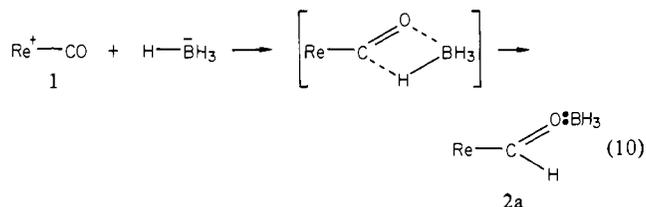
the second converts 2 to a species which on hydrolysis gives 3. It is of interest that 3 has recently been prepared from 1 by use of the dihydrido reducing agent Na(H₂AlEt₂) followed by hydrolysis.¹⁵

Preparation of Formyl, Hydroxymethyl, and Methyl Complexes from [(η-C₅Me₅)Re(NO)(CO)₂][PF₆]⁻ (5). With rational methods for the reduction of coordinated carbon monoxide to formyl, hydroxymethyl, and methyl ligands available, we sought to extend the new synthetic routes to other carbonyl cations. The low thermal stability of (η-C₅H₅)Re(NO)(CO)CHO (2) made it an unattractive model compound, and we turned to the analogous pentamethylcyclopentadienyl derivatives in the hope that stability and crystallinity would be enhanced.¹⁸ The necessary starting cation, [(η-C₅Me₅)Re(NO)(CO)₂][PF₆]⁻ (5), was prepared and reduced to the formyl (6), hydroxymethyl (7), and methyl (8) derivatives (Scheme II) in fair to good yields. General conditions and stoichiometries followed those of the η-C₅H₅ series, but with some changes. For example, in the THF-water synthesis of 7, the proportion of water had to be reduced to maintain solubility of the intermediate 6.

The η-C₅Me₅ group considerably enhanced the stability of the formyl compound. Orange crystals of 6 melted sharply at 69–70 °C, with darkening and vigorous gas evolution. However, crystalline 6 slowly darkens even at room temperature, and for intervals longer than a day or so should be stored in a freezer. The behavior of 6 in solution is reminiscent of 2 as described by Casey et al.¹⁵ In dilute solution, 6 goes mainly to (η-C₅Me₅)Re(NO)(CO)H with a half-life of about 12 h; decomposition of concentrated solutions leads to a complex mixture of products including the hydride. The significantly greater stability of 6 in solution compared to 2 can be attributed in part to a decreased lability of the terminal carbonyl as a result of greater electron release by the pentamethylcyclopentadienyl ligand (ν_{CO} = 1981 cm⁻¹ in 6, 1999 cm⁻¹ in 2). On the other hand, the stability of 6 in the crystalline state may result from enhanced van der Waals forces between molecules in a more favorable packing arrangement. The result in any case is a much more tractable compound that can readily be obtained in pure crystalline form.

Stepwise Reductions and Mechanisms. After completion of the preparative study in the η-C₅H₅ system, we were intrigued with the widely different reaction modes of NaBH₄ in anhydrous THF and in THF/H₂O. Further, the synthesis of (η-C₅H₅)Re(NO)(CO)CH₂OH (3) from the cation 1 suggested that borohydride was capable of reducing a coordinated formyl group. Thus, we investigated systematically the reduction of 1, 2, and 3 with 1 mol of NaBH₄ in both H₂O/THF and anhydrous THF, with the results summarized in Scheme III.

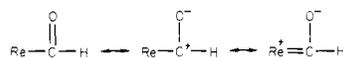
Reduction of Coordinated CO. In anhydrous THF (eq 4) 1 mol of NaBH₄ supplies the three hydrides required to reduce coordinated carbon monoxide to a methyl group. However, in aqueous solution (eq 5), 1 mol of NaBH₄ delivers only one hydride and reduction proceeds only to the formyl stage. The first step in both these reactions is presumed to be the same: transfer of one hydride via an intermediate with substantial boron-oxygen interaction to produce the formyl as a borane adduct 2a (eq 10).¹⁹ In aqueous



solution, 2a would undergo rapid hydrolysis to boric acid and

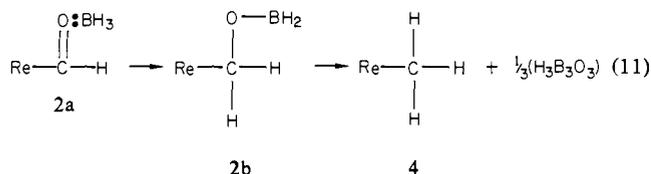
(18) Maitlis, P. M. *Acc. Chem. Res.* 1978, 11, 301.

(19) The canonical forms for 2 imply considerable negative charge on oxygen, so 2 should be a good Lewis base:



hydrogen;²⁰ the reduction process would stop and **2** would be isolated.

In anhydrous THF, the adduct **2a** must undergo further reactions in which two more hydrides are transferred to carbon, a process shown schematically in eq 11.²¹ This may well be an intermolecular process.



At this stage, it is important to compare and contrast the results on the rhenium complex **2** with the well-known borane reduction of organic aldehydes.²³ In the latter case, an initial carbonyl-borane adduct may form, but this goes on to various alkoxyboranes (eq 12). *The reaction does not proceed to the alkane R-CH₃.*



Hydrolysis of the alkoxyborane mixture is required, and the product is the alcohol RCH₂OH.

The foregoing reactions provide noteworthy examples of ligand activation upon coordination by a transition metal. Sodium borohydride will not reduce CO under ordinary conditions,²⁴ yet reduction of the CO ligand in $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2]^+$ occurs rapidly at room temperature. Activation in this instance is provided by the increased positive charge on the carbonyl carbon due to electron donation to rhenium, whereby nucleophilic attack is favored. The influence of a transition metal is equally clear in the borane reductions, in which the rhenium formyl goes to a methylrhenium complex, while the organic formyl (i.e., aldehyde) goes to the alcohol.

Reduction of Coordinated Formyl. As shown in Scheme III, 1 mol of NaBH₄ reduces the formyl ligand to hydroxymethyl in aqueous solution (eq 7) or to methyl (eq 6) in anhydrous THF. It is informative to compare these reactions with borohydride reduction of an organic aldehyde.

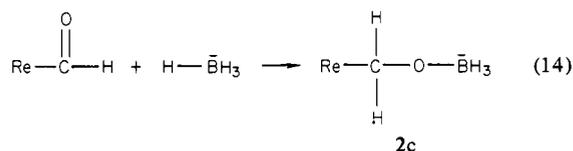
Sodium borohydride reacts²³ with 4 mol of aldehyde as shown in eq 13. This reaction occurs with four successive hydride



transfers, each faster than the one preceding. When this reaction is carried out under aqueous conditions the product NaB(OCH₂R)₄ is hydrolyzed to RCH₂OH and NaB(OH)₄.

In contrast to organic aldehydes, the formyl complex **2** consumes 1 mol of NaBH₄ under both aqueous and anhydrous conditions. The use of less than 1 mol of NaBH₄ results in incomplete reaction.²⁵ Obviously the NaBH₄ reductions of aldehydes and transition-metal formyls do not occur in the same manner.

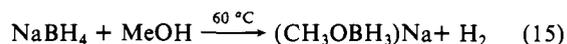
As suggested by its valence bond description,¹⁹ the formyl complex **2** should be susceptible to nucleophilic attack at the -CHO carbon. Thus, a reasonable first step in the reactions of both eq 6 and 7 is hydride attack at the formyl ligand as shown in eq 14.^{26a} In the presence of water the alkoxyborohydride **2c**



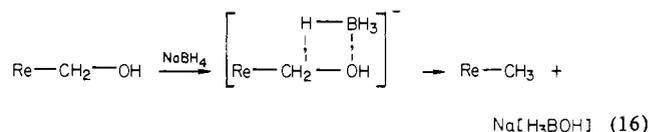
would hydrolyze to **3**, and this must occur at a rate faster than **2c** can reduce a second mole of formyl.

In anhydrous THF, **2c** is transformed into **4**,^{26b} a process which requires transfer of a hydride to carbon and loss, at least formally, of OBH₂⁻. The latter species is unprecedented; another pathway would involve loss of hydride by **2c** to form **2b**, which would ultimately give **4**, as in eq 11.

Reduction of Coordinated Hydroxymethyl. The reaction of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{NO})\text{CH}_2\text{OH}$ (**3**) with 1 mol of NaBH₄ gives under anhydrous or aqueous conditions the methyl complex **4** (Scheme III). Reactions 8 and 9 again show the contrast between organic functional group chemistry and organotransitional-metal chemistry. Alcohols are not generally reduced by sodium borohydride.²³ Certain acidic alcohols such as methanol²⁸ do react with NaBH₄ (eq 15), but these reactions occur with deprotonation, *not* reduction, of the alcohol.



Reduction of **3** probably involves nucleophilic displacement of OH⁻, assisted by coordination of BH₃ (eq 16). This remarkable



change in reactivity as compared with organic alcohols may be rationalized in terms of the canonical forms shown:



Indeed, a cationic carbene species, $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{PPh}_3)(\text{NO})\text{CH}_2]^+$, has been prepared and reacts with hydride sources, generating the methyl derivative.^{29a}

Conclusions

The two series of rhenium complexes described here are the first instances in which models for all presumed intermediates in carbon monoxide reduction have been prepared. Both hydroxymethyl derivatives **3** and **7** are thermally stable, tractable compounds that should serve to correct the notion that all transition-metal hydroxymethyl complexes have low stability. The formyl derivative in the pentamethyl series (**6**) is especially well suited to further study. It is likely that the synthetic procedures developed in this work, in particular NaBH₄ in THF/H₂O, will prove equally useful in reductions of other systems.

The investigation of individual reduction steps has shown how water controls the degree of reduction obtained with NaBH₄ and has shed light on possible mechanisms. It has also demonstrated

(20) This is consistent with the observation that the aqueous reactions (eq 5, 7, and 9) occur with gas evolution, presumably hydrogen.

(21) Consonant with this scheme, it has been reported that **2** reacts with THF·BH₃ to form **4**.^{12,13} Earlier work by Masters et al.²² on THF·BH₃ reduction of transition-metal acetyls to ethyl complexes was rationalized in a similar way except that a second mole of BH₃ was presumed to attack the alkoxyborane in the final stage of the reaction. Involvement of a second mole of BH₃, or of BH₄⁻, is of course ruled out in the present work by the stoichiometry of eq 4.

(22) Van Doorn, J. A.; Masters, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245.

(23) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972.

(24) Rathke, M. W.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 2606.

(25) This difference in stoichiometry is further emphasized by eq 7. If 4 mol of **2** had reacted with each NaBH₄, the resulting hydroxymethyl complex **3** would have been further reduced to **4** as shown by eq 9.

(26) (a) In contrast, **2** reacts with Li(HBEt₃) to form an anionic bisformyl complex, $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CHO})_2]^-$.^{12,13} Negative charge in the latter would be delocalized as it is in the acetylacetonate-like anions of Lukehart et al.²⁷ We suggest that the tautomeric alkoxy form, $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_2\text{O}^-$, is stabilized in **2c** by the strong acceptor BH₃. (b) Conversion of **2** to **4** in anhydrous THF cannot involve the intermediacy of **3** on the basis of the observed relative rates for reactions 6 and 8.

(27) Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *J. Am. Chem. Soc.* **1975**, *97*, 6903.

(28) Brown, H. C.; Mead, E. J.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1955**, *77*, 6209.

(29) (a) Wong, W. K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. (b) A referee has made the interesting point that amides R₂N-CHO are readily reduced by BH₃ to R₂N-CH₃ and suggested that the important thing in activation of X-CHO is to have a lone pair or the equivalent on X. The lone pair would lead to canonical forms of the type R₂N⁺=C(O⁻)H similar to Re⁺=C(O⁻)H invoked in ref 19.

the profoundly altered reactivity of formyl and hydroxymethyl functional groups when they are bonded to a transition metal, an aspect which has perhaps been neglected relative to the activation of CO.^{29b}

We are currently exploring the applicability of NaBH₄/H₂O/THF reductions to other metal carbonyl derivatives such as $[(\eta\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_3]^+^{17}$ and continuing an investigation of the reactions and properties of formyl and hydroxymethyl complexes.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Solvents were dried by using standard procedures and distilled immediately before use. Rhenium carbonyl was purchased from Strem Chemicals and sodium borohydride from Aldrich. $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ was prepared by the literature method³⁰ and $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ by a modification of the published procedure³¹ developed in this laboratory.³²

Mass spectra were determined at low ionizing voltages (typically 16 eV) because at the customary 70 eV the spectrum was too complex for easy identification of the fragmentation pattern. Infrared spectra were measured by using a Nicolet MX-1 Fourier transform instrument.

Preparation of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2[\text{BF}_4]$ (1). Nitrosium tetrafluoroborate (0.70 g, 6.00 mmol) in 30 mL of nitromethane was added dropwise to $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ (2.00 g, 5.96 mmol) in 30 mL of CH₃NO₂ at -15 °C over a period of 1 h. The solution gradually became light yellow. The reaction was warmed to room temperature and the solvent removed under reduced pressure. The residue was dissolved in the minimum volume of acetone, decolorized with charcoal, filtered, and precipitated with ether to give **1** as lemon yellow microcrystals (2.30 g, 91%): IR (cm⁻¹) (CH₂Cl₂) 2115 (s), 2060 (s), $\nu(\text{CO})$, 1813 (s) $\nu(\text{NO})$; ¹H NMR (CD₂Cl₂) δ 6.36. Anal. Calcd for C₇H₅ReO₃NBF₄: C, 19.82; H, 1.19; N, 3.30. Found: C, 19.85; H, 1.15; N, 3.37.

Preparation of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CHO}$ (2). A solution of NaBH₄ (0.045 g, 1.18 mmol) in 5 mL of H₂O was added dropwise to a stirred solution of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2[\text{BF}_4]$ (0.5 g, 1.18 mmol) in 5 mL of H₂O at 0 °C over the course of 0.5 h. The initial yellow solution turned orange and an orange precipitate appeared. After addition of the NaBH₄, the suspension was extracted with 3 × 20 mL of hexane, and these initial extracts were discarded.³³ The aqueous suspension was then extracted with additional hexane (7 × 20 mL), and the extracts were combined. Cooling the hexane solution to -78 °C afforded the formyl complex **2** as an orange, microcrystalline solid (0.25 g, 62%): IR (cm⁻¹) (hexane) 1999 (s), $\nu(\text{CO})$, 1731 (s), $\nu(\text{NO})$, 1630 (m) $\nu(\text{CHO})$; ¹H NMR (methylcyclohexane-*d*₁₄) δ 5.51 (5 H), 16.2 (1 H).

Preparation of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_2\text{OH}$ (3). A solution of NaBH₄ (0.090 g, 2.36 mmol) in 5 mL of H₂O was added dropwise to a stirred solution of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2[\text{BF}_4]$ (0.500 g, 1.18 mmol) in 5 mL of H₂O and 5 mL of tetrahydrofuran (THF) at 0 °C. The resulting orange solution was warmed to room temperature and extracted with 3 × 7 mL of CH₂Cl₂. Addition of hexane to the combined organic layers at -40 °C gave an orange solid. Recrystallization from CH₂Cl₂/hexane at -20 °C afforded **3** as orange crystals (0.279 g, 70%): mp 95–96 °C; IR (cm⁻¹) (THF) 3460 (s, br), $\nu(\text{OH})$, 1953 (s), $\nu(\text{CO})$, 1695 (s) $\nu(\text{NO})$; mass spectrum (70 °C, 16 eV) M⁺, (M - CO)⁺, (M - NO)⁺, (M - CO - NO)⁺; ¹H NMR (Me₂SO-*d*₆) δ 5.88 (5 H); lines of an ABX pattern (CH₄H₂OH_X) at 5.55 (1 H), 5.15 (1 H) and 3.94 (1 H); ³J_{AX} = 6.1 Hz, ³J_{BX} = 5.5 Hz, ²J_{AB} = 9.3 Hz. Anal. Calcd for C₇H₈ReO₃N: C, 24.85; H, 2.37; N, 4.12. Found: C, 24.85; H, 2.36; N, 3.91.

Preparation of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_3$ (4). A suspension of NaBH₄ (0.045 g, 1.18 mmol) and $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})_2[\text{BF}_4]$ (0.50 g, 1.18 mmol) in 25 mL of THF was stirred for 1.5 h at 25 °C. The resulting red solution was filtered and the THF removed under reduced pressure. The solid residue was extracted with hexane, filtered, and slowly cooled to -40 °C to give **4** as red crystals (0.336 g, 88%): mp 75–76 °C; IR (cm⁻¹) (hexane) 1970 (s), $\nu(\text{CO})$, 1715 (s) $\nu(\text{NO})$; mass spectrum (60 °C, 14 eV), M⁺, (M - CO)⁺, (M - CO - NO)⁺; ¹H NMR (CD₂Cl₂) δ 5.62 (5 H), 0.92 (3 H).

Preparation of $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{CO})_2[\text{PF}_6]$ (5). Nitrosium hexafluorophosphate (0.87 g, 4.97 mmol) in 30 mL of CH₃NO₂ was added dropwise to $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ (2.00 g, 4.93 mmol) in 30 mL of CH₃NO₂ at -15 °C over a period of 1 h. The solution gradually became

light yellow. After warming to room temperature, solvent was removed under reduced pressure. The residue was dissolved in the minimum volume of acetone, decolorized with charcoal, filtered, and precipitated with ether to give **5** as lemon yellow microcrystals (2.46 g, 90%): IR (cm⁻¹) (CH₂Cl₂) 2092 (s), 2036 (s), $\nu(\text{CO})$, 1794 (s) $\nu(\text{NO})$; ¹H NMR (CD₂Cl₂) δ 2.37. Anal. Calcd for C₁₂H₁₅ReO₃NPF₆: C, 26.09; H, 2.74; N, 2.54. Found: C, 26.18; H, 2.70; N, 2.64.

Preparation of $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{CO})\text{CHO}$ (6). A solution of NaBH₄ (0.034 g, 0.90 mmol) in 10 mL of H₂O was added dropwise to a vigorously stirred suspension of **5** (0.50 g, 0.90 mmol) in 20 mL of H₂O at 0 °C over the course of 0.5 h. The initial yellow suspension turned orange and an orange precipitate appeared. After the mixture was stirred for an additional 0.5 h, H₂O was syringed away and discarded. The precipitate was cooled to -15 °C to freeze any traces of H₂O and extracted at this temperature with 3 × 30 mL of hexane. The combined extracts were immediately cooled to -78 °C, and the orange precipitate collected and recrystallized from hexane to give **6** as orange crystals (0.245 g, 66%): mp 69–70 °C dec; IR (cm⁻¹) (hexane) 1981 (s), $\nu(\text{CO})$, 1707 (s), $\nu(\text{NO})$, 1615 (m) $\nu(\text{CHO})$; mass spectrum (45 °C, 17 eV) M⁺, (M - H)⁺, (M - H - CO)⁺; ¹H NMR (methylcyclohexane-*d*₁₄) δ 2.27 (15 H), 16.59 (1 H). Anal. Calcd for C₁₂H₁₆ReO₃N: C, 35.28; H, 3.95; N, 3.43. Found: C, 35.29; H, 4.01; N, 3.34.

Preparation of $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_2\text{OH}$ (7). Sodium borohydride (0.041 g, 1.08 mmol) was added to a solution of **5** (0.30 g, 0.54 mmol) in 10 mL of THF and 0.25 mL of H₂O at -5 °C. The initial yellow solution turned red with vigorous gas evolution and precipitation of a white solid (NaPF₆). After the mixture was stirred for 10 min, the reaction was warmed to room temperature and the solvent removed under reduced pressure. The residual solid was extracted with hexane, filtered, and slowly cooled to -78 °C to give **7** as reddish-orange crystals (0.155 g, 70%): mp 105–106 °C; IR (cm⁻¹) (hexane) 1954 (s), $\nu(\text{CO})$, 1688 (s) $\nu(\text{NO})$; mass spectrum (60 °C, 14 eV) M⁺, (M - OH)⁺, (M - OH - CO)⁺; ¹H NMR (Me₂SO-*d*₆) δ 2.02 (15 H); lines of an ABX pattern (CH₄H₂OH_X) at 5.51 (1 H), 4.45 (1 H) and 3.80 (1 H); ³J_{AX} = 3.8 Hz, ³J_{BX} = 6.3 Hz, ²J_{AB} = 9.5 Hz. Anal. Calcd for C₁₂H₁₈ReO₃N: C, 35.11; H, 4.42; N, 3.41. Found: C, 35.03; H, 4.39; N, 3.40.

Preparation of $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_3$ (8). A suspension of NaBH₄ (0.017 g, 0.45 mmol) and **5** (0.25 g, 0.45 mmol) in 20 mL of THF was stirred for 1.0 h at 25 °C. The resulting red solution was filtered and the THF removed under reduced pressure. The solid residue was extracted with hexane, filtered, and slowly cooled to -78 °C to give **8** as red crystals (0.151 g, 85%): mp 116–117 °C; IR (cm⁻¹) (hexane) 1949 (s), $\nu(\text{CO})$, 1692 (s) $\nu(\text{NO})$; mass spectrum (45 °C, 14 eV) M⁺, (M - CO)⁺, (M - CO - NO)⁺; ¹H NMR (CD₂Cl₂) δ 2.00 (15 H), 0.62 (3 H). Anal. Calcd for C₁₂H₁₈ReO₃N: C, 36.53; H, 4.60; N, 3.55. Found: C, 36.29; H, 4.45; N, 3.52.

Analytical Procedures in Stepwise Reductions. Reactions 4 and 8. Sodium borohydride (0.25 mmol) and the rhenium substrate (0.25 mmol) were stirred in 5 mL of THF at room temperature. When the reaction was complete, the entire solution was drawn into a calibrated syringe, its volume noted, and an aliquot transferred to a second Schlenk tube where THF was removed on the vacuum line. The residue was taken up in THF-*d*₈, the ¹H NMR obtained, and the yield determined by integration vs. added benzene.

Reactions 5 and 9. Sodium borohydride (0.25 mmol) in 3 mL of H₂O was added dropwise to the rhenium substrate (0.25 mmol) in 3 mL of H₂O and 3 mL of THF at the specified temperature. After the reaction was complete, the solution was extracted with CH₂Cl₂ and the total volume of the extracts determined by means of a calibrated syringe. An aliquot was transferred to a second vessel, and solvents were evaporated at -30 °C on the vacuum system. The residue was dissolved in THF-*d*₈, the ¹H NMR obtained, and the yield calculated vs. added benzene.

Reactions 6 and 7. In these reactions the thermal stability of the formyl complex, $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CHO}$, required that the quantity of this reagent first be determined by ¹H NMR spectroscopy. After calculation of the quantity of the formyl compound present, 1 equiv of NaBH₄ was added and the reactions and yield calculations were carried out as described above.

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