complex mixture: the products of the solid-state reaction could not be detected by the TLC analysis.

(5) D. Leibfritz and J. D. Roberts, *J. Am. Chem. Soc.*, **95**, 4996 (1973).
(6) The ^{13}C NMR spectrum of 4 was carried out in perdeuterated acetic acid, because of its low solubility in methanol. However differences in chemical shifts between the two solvents are not exceeding 0.1–0.6 ppm, except for C_3, C_{12}, and HOC(CH$_3$)$_2$ carbons (0.5–1.5 ppm). This could be demonstrated from comparative studies of 2 and 3 in both solvents.
(7) The dehydration was carried out according to the procedure of E. Keinan and Y. Mazur, private communication: 3% FeCl$_3$ supported on SiO$_2$ was suspended with 0.5% 2 and 3 in methanol and dried under vacuum for 1 h: this was followed by extraction of the steroid with methanol and precipitation of the FeCl$_3$ with Na$_2$HCO$_3$.
(8) The oxidation was performed as described by Donald G. Lee in "Oxidation", Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N.Y., 1969, p 17. The high resolution mass spectrometric analysis is consistent with structure 6. The two most characteristic fragments obtained in addition to the mo-

B, 121   C, 95
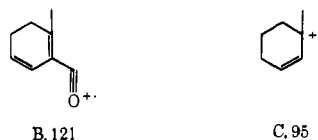
lecular peaks are B and C. See Z. V. Zaretskii in "Mass Spectrometry of Steroids". Wiley, New York, N.Y., 1976, p 11.
(10) The complex 1 (2C$_{24}$H$_{40}$O$_4$·C$_3$H$_6$O) crystallizes in space group $P2_12_12_1$: a = 25.809 (5), b = 13.610 (2), c = 7.233 (1) Å; Z = 4 molecules of 1 and 2 molecules of acetone: D_c = 1.102 g cm^{-3}. The crystal structure was determined with an R factor of 0.10 for 2505 reflections.
(11) P. B. M. Craven and G. T. DeTitta, *J. Chem. Soc., Chem. Commun.*, 530 (1972).
(12) S. C. De Sanctis, E. Giglio, V. Pavel, and C. Quagliata, *Acta Crystallogr., Sect. B*, **28**, 3656 (1972).
(13) Because of the change in hybridization and bond length of the carbonyl group upon excitation, a slight difference of the geometrical picture as described by the x-ray analysis in the ground state is expected. For a discussion, see J. C. D. Brand and D. G. Williams, *Adv. Phys. Org. Chem.*, **1**, 365 (1963).
(14) In the intramolecular hydrogen abstractions described in ref 3, the allylic abstractable hydrogens are in the plane of the keto group.
(15) The crystal structure of C$_{24}$H$_{38}$O$_4$·C$_3$H$_6$O was measured in a closed capillary saturated with acetone vapor. It crystallizes in a space group $P2_12_12_1$: a = 24.47, b = 14.26, c = 7.50 Å; Z = 4 molecules of 8 and 4 molecules of acetone: D_c = 1.129 g cm^{-3}. The crystal structure was determined with an R factor of 0.08 for 2579 reflections.
(16) For a discussion of the conditions on hydrogen abstractions in rigid cyclic systems, see F. D. Lewis, R. W. Johnson, and R. A. Ruden, *J. Am. Chem. Soc.*, **94**, 4292 (1972).

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Hydride Donation Reactions of Transition Metal Formyl Complexes

Sir:

We recently developed a new synthesis of metal formyl complexes,[1] which have been proposed as important intermediates in the metal catalyzed reduction of CO by H$_2$.[2] The availability of metal formyl complexes has allowed us to study their kinetic and thermodynamic stability and their chemical reactivity. Here we report that metal formyl complexes can act as hydride donors to electrophiles such as ketones, alkyl halides, and metal carbonyls.

Whereas Et$_4$N$^+$ *trans*-[(C$_6$H$_5$O)$_3$P](CO)$_3$FeCHO$^-$ (1) decomposes to Et$_4$N$^+$(CO)$_4$FeH$^-$ and (C$_6$H$_5$O)$_3$P with a half-life of ~1 h at 67 °C in tetrahydrofuran,[3] attempts to obtain a ^{1}H NMR spectrum of 1 in acetone-d_6 at ambient temperature led to disappearance of the formyl hydrogen resonance at δ 14.9 within 25 min and suggested that 1 had reacted with acetone. Reaction of 1 with 2-butanone overnight at ambient temperature followed by acid hydrolysis gave a 95% yield of 2-butanol, as determined by gas chromatography.[4] The

possibility that 2-butanone is reduced by (CO)$_4$FeH$^-$ formed in situ is excluded since 1 reacts with 2-butanone much faster than it decomposes to (CO)$_4$FeH$^-$ and since no reaction between (CO)$_4$FeH$^-$ and 2-butanone was observed by infrared spectroscopy.

Reaction of a THF solution of 1 (0.346 mmol) with CF$_3$CO$_2$H (10 equiv) led to the formation of CH$_3$OH (0.095 mmol, 27%) and no observable formaldehyde (<5%).[5,6] Methanol might arise from acid cleavage of 1 to give formaldehyde which is subsequently reduced to methanol by hydride donation from a second equivalent of 1.[8] Alternatively, methanol could arise via O protonation of 1 to give hydroxycarbene complex 2, which is subsequently reduced to hydroxymethyl complex 3 by a second equivalent of 1; cleavage of 3 by acid would give methanol. Either of the two routes leads to a maximum 50% yield of methanol.
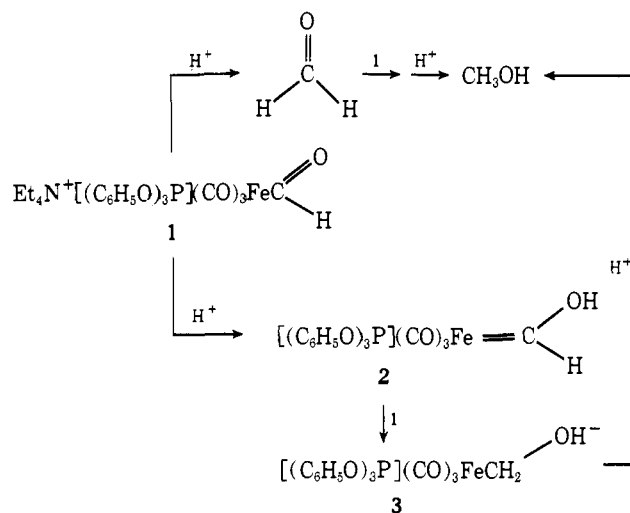
Collman and Winter have reported that [(C$_6$H$_5$)$_3$P]$_2$-N$^+$(CO)$_4$FeCHO$^-$ reacts with 1-iodooctane to give octane (75%) and a trace of nonanal; octane formation was attributed to decarbonylation of [(C$_8$H$_{17}$)(CHO)Fe(CO)$_4$], followed by hydride migration and reductive elimination of octane.[9] We have found that Et$_4$N$^+$ *trans*-[(ArO)$_3$P(CO)$_3$FeCHO$^-$ (Ar = 3,5-dimethylphenyl) reacts with n-C$_7$H$_{15}$I when stirred overnight at ambient temperature in THF to give n-C$_7$H$_{16}$ (71%) and (CO)$_4$FeP(OAr)$_3$; <0.2% n-C$_7$H$_{15}$CHO was observed.[10] Since formyl complexes appear to function as hydride donors, we propose that heptane is formed by nucleophilic displacement of iodide by the formyl hydrogen atom.
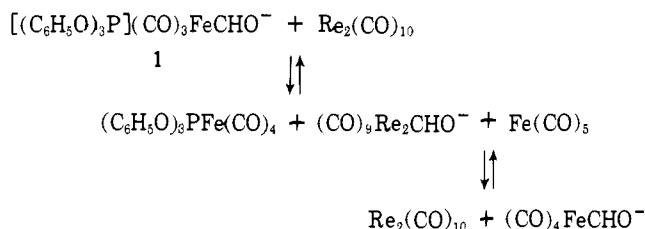
Metal formyl complexes can transfer hydride to metal carbonyl compounds to produce new metal formyl complexes.[11] These "transformylation" reactions can be used to determine the relative stability of a series of metal formyl complexes. The reaction of 1 with Re$_2$(CO)$_{10}$ in THF-d_8 was followed by ^{1}H NMR. The characteristic doublet at δ 14.9 due to 1 is rapidly replaced by a singlet at 16.04 attributed to Et$_4$N$^+$ *cis*-(CO)$_9$Re$_2$CHO$^-$ (4) formed in 82% yield as determined by NMR integration.[12] (CO)$_4$Fe[P(OC$_6$H$_5$)$_3$] was detected by IR as a co-product of the reaction.

4 was independently synthesized by reaction of K$^+$HB(O-i-Pr)$_3^-$ with Re$_2$(CO)$_{10}$ in THF at 0 °C, followed by aqueous basic workup and cation exchange with Et$_4$N$^+$Br$^-$. 4 was recrystallized from THF–hexane, and isolated in 32% yield as a yellow, air-stable solid.[13,14] 4 was characterized spectroscopically: ^{1}H NMR (THF-d_8) δ 1.32 (tt, J = 7.2, J_{NH} = 1.5 Hz, 12 H, NCH$_2$CH_3), 3.40 (q, J = 7.2 Hz, 8 H, NCH_2CH$_3$), 16.04 (s, 1 H, ReCHO); IR (THF) 2084 (w), 2066 (m), 2015 (s), 1979 (s), 1949 (w–m), 1899 (w–m, MCO), 1559 (w, MCH=O) cm^{-1}; IR (KBr) 2089 (vw), 2068 (m), 2009 (s), 1890 (s, sh), 1936 (w–m), 1884 (m), 1734 (m), 1602 (m), 1493

(m-s) cm^{-1}. The observation of four different MCO resonances in the low temperature ^{13}C NMR[15] of **4** establishes the cis geometry of the compound: ^{13}C NMR (THF-d_8, -53 °C, 0.07 M, Cr(acac)$_3$), δ 7.6 (NCH$_2$CH$_3$), 52.1 (NCH$_2$CH$_3$), 188.8, 194.4, 199.0, 203.2 (relative intensity: 0.9, 0.8, 4.7, 2.5 ReCO), 264.2 (ReCHO).[19]

Solutions of **4** as well as the solid were found to be sensitive to fluorescent laboratory lights. Photolysis of a THF solution of **4** in an NMR tube produces a metal hydride (δ -7.1) in 81% yield as determined by NMR. Preparative photolysis of **4** gave **5** in 38% yield after recrystallization. The dinuclear rhenium hydride,[16] Et$_4$N$^+$ cis-(CO)$_9$Re$_2$H$^-$ (**5**) was more conveniently prepared by reaction of K$^+$HB(O-i-Pr)$_3$$^-$ with Re$_2$(CO)$_{10}$ at 45-50 °C for 3 h under fluorescent laboratory lighting. Aqueous basic workup, cation exchange with Et$_4$N$^+$Br$^-$ and recrystallization from THF-hexane gave **5** in 33% yield.[13] Elemental analysis,[17] IR, and ^{1}H NMR established the gross structure of **5**: ^{1}H NMR (acetone-d_6) δ 1.40 (tt, $J = 7.2$, J_{NH} = 1.5 Hz, 12 H, NCH$_2$CH$_3$), 3.50 (q, $J = 7.2$ Hz, 8 H, NCH$_2$CH$_3$), -7.10 (s, 1 H, ReH); IR (THF) 2078 (vw), 2028 (m), 1972 (s), 1924 (w-m), 1888 (m) cm^{-1}; IR (KBr) 2082 (vw), 2028 (m), 2004 (m), 1968 (s), 1931 (m), 1912 (m), 1865 (ms), 1733 (w) cm^{-1}. The observation of five different MCO resonances in the low temperature ^{13}C NMR[18] of **5** establishes the cis geometry of the compound: ^{13}C NMR (THF-d_8, -70.6 °C, 0.07 M, Cr(acac)$_3$), δ 7.7 (NCH$_2$CH$_3$), 52.1 (NCH$_2$CH$_3$), 189.9, 195.4, 199.0, 201.1, 202.0 (relative intensity: 1.1, 0.9, 0.9, 3.8, 2.3 ReCO).

Transformylation reactions between various metal formyl and metal carbonyl compounds indicate the following order of stability of formyl complexes relative to their metal carbonyl precursors: [(C$_6$H$_5$)$_3$P]$_2$N$^+$(CO)$_4$FeCHO$^-$ > Et$_4$N$^+$ cis-(CO)$_9$Re$_2$CHO$^-$ > Et$_4$N$^+$ trans-[C$_6$H$_5$O$_3$P](CO)$_3$-FeCHO$^-$. The possibility that these transformylations proceed via decarbonylation to give a metal hydride which then transfers hydride to a metal carbonyl is excluded since the reaction of **1** with Re$_2$(CO)$_{10}$ or Fe(CO)$_5$ is faster than decomposition of **1** to (CO)$_4$FeH$^-$ and since Et$_4$N$^+$(CO)$_4$FeH$^-$ does not react with Re$_2$(CO)$_{10}$, Fe(CO)$_5$, or (CO)$_4$FeP-(OC$_6$H$_5$)$_3$ under the reaction conditions.

$$[(C_6H_5O)_3P](CO)_3FeCHO^- + Re_2(CO)_{10}$$

$$\mathbf{1} \quad \updownarrow$$

$$(C_6H_5O)_3PFe(CO)_4 + (CO)_9Re_2CHO^- + Fe(CO)_5$$

$$\updownarrow$$

$$Re_2(CO)_{10} + (CO)_4FeCHO^-$$

Supplementary Material Available: Preparation of **4** and **5** (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **98**, 5395 (1976); see also S. R. Winter, G. W. Cornett, and E. A. Thompson, *J. Organomet. Chem.*, **133**, 339 (1977).
(2) G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **15**, 136 (1976). For other reviews of the Fischer-Tropsch reaction, see (a) M. A. Vannice, *J. Catal.*, **37**, 449, 462 (1975); (b) H. H. Storch, N. Golumbic, and R. B. Anderson, "The Fischer-Tropsch and Related Synthesis", Wiley, New York, N.Y., 1951; (c) P. H. Emmett, Ed., "Catalysis", Vol. 4, Reinhold, New York, N.Y., 1956.
(3) C. P. Casey and S. M. Neumann, unpublished results.
(4) 1/8 in. × 20 ft 20% UCON 50 HB 280X on 60/80 Chrom P column at 85 °C.
(5) The formation of formaldehyde on acidification of (CO)$_4$FeCHO$^-$ solutions has been previously reported by Collman[9] and confirmed by us.[1]
(6) 1/4 in. × 15 ft 10% Ethofat 60/25 on 40/60 Fluoropak 80 column at 110

°C.[7] H$_2$ (6-10%) was also observed and attributed to the presence of a similar amount of Et$_4$N$^+$(CO)$_4$FeH$^-$ in the starting material.
(7) K. Bombauch and W. Bull, *Anal. Chem.*, **34**, 1237 (1962).
(8) **1** reacts with excess formaldehyde in THF to give a 73% yield of methanol.
(9) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973).
(10) Yields by gas chromatography on 1/8 in. × 30 ft 20% UCON 50 HB 280X on 60/80 Chrom P column at 70 °C (heptane) and 155 °C (octanal).
(11) Gladysz has observed that (CO)$_9$Mn$_2$CHO$^-$ (formed in situ from Mn$_2$(CO)$_{10}$ and Li(C$_2$H$_5$)$_3$BH) reacts with Fe(CO)$_5$ to give (CO)$_4$FeCHO$^-$: J. A. Gladysz, G. M. Williams, W. Tam, and D. L. Johnson, *J. Organomet. Chem.*, **140**, c1 (1977).
(12) Yield was determined by using the signal for the P(OC$_6$H$_5$)$_3$ group as an internal standard.
(13) Detailed procedures for these preparations are included as supplementary material. See paragraph at end of paper regarding supplementary material.
(14) Anal. Calcd for C$_{18}$H$_{21}$NO$_{10}$Re$_2$: C, 27.58; H, 2.70; N, 1.79; Re, 47.51. Found: C, 26.34; H, 2.49; N, 1.40; Re, 48.66.
(15) The thermal decoupling of nuclear quadrupole moments has been previously reported for metal carbonyl compounds: (a) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **60**, C31 (1974); (b) M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. K. LiShingMan, and J. Takats, *J. Am. Chem. Soc.*, **98**, 4810 (1976).
(16) For a survey of known hydridocarbonyl complexes of rhenium, see (a) D. Guisto, *Inorg. Chim. Acta Rev.*, **8**, 91 (1972); (b) M. Bennett, A. Graham, J. Hoyano, and W. Hutcheon, *J. Am. Chem. Soc.*, **94**, 6232 (1972).
(17) Anal. Calcd for C$_{17}$H$_{21}$NO$_9$Re$_2$: C, 27.02; H, 2.80; N, 1.85; Re, 49.28. Found: C, 27.11; H, 3.01; N, 1.73; Re, 48.98.
(18) At ambient probe temperatures, broadening by the Re quadrupole causes the three upfield carbonyl resonances to disappear and the two downfield resonances to broaden and merge to a broad singlet at δ 201.1.
(19) NOTE ADDED IN PROOF. In higher resolution ^{13}C NMR of **4**, the peak at 199.0 was resolved into two resonances seperated by 3.6 Hz. Five MCO resonances were also observed in the ^{13}C NMR Li$^+$ cis-(CO)$_9$Re$_2$CHO$^-$ (THF-d_8, -57 °C, 0.07 M, Cr(acac)$_3$: δ 189.1, 194.5, 199.4, 200.1, 203.6 (relative intensity: 0.9, 1.4, 3.5, 1.2, 1.9 ReCO), 284.3 (ReCHO).
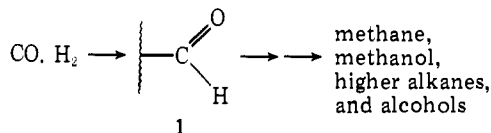
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Binuclear and Mixed Metal Formyl Complexes: Isolation, Characterization, and Chemistry

Sir:

Carbon monoxide-hydrogen gas mixtures can be transformed by heterogeneous catalysts at high temperatures and pressures to methane, alcohols, and gasoline (Fischer-Tropsch process).[1-3] The initially formed intermediate in these reactions is believed to be the surface-bound formyl **1**.[3,4]

$$CO, H_2 \longrightarrow \text{—}C\overset{O}{\underset{H}{\diagdown}} \longrightarrow \longrightarrow \begin{array}{l} \text{methane,} \\ \text{methanol,} \\ \text{higher alkanes,} \\ \text{and alcohols} \end{array}$$

$$\mathbf{1}$$

The rational development of milder, homogeneous, and more selective Fischer-Tropsch-type processes[5] requires the study of homogeneous homologues of **1** and other surface-bound intermediates on the reaction coordinate between CO and alkanes and alcohols. In this communication, we report (a) the synthesis of the first isolable *binuclear* formyl complex (**2**) by reaction of Li(C$_2$H$_5$)$_3$BH with Re$_2$(CO)$_{10}$, (b) the availability of the kinetically less stable mixed metal formyl complex **3** by reaction of Li(C$_2$H$_5$)$_3$BH with ReMn(CO)$_{10}$, (c) reactions which establish **2** and **3** as potent hydride donors, and (d) the formation of formaldehyde and methanol from K$^+$-**2**.

$$Li^+(CO)_5Re\overset{-}{Re}(CO)_4(\overset{O}{\overset{\|}{C}H}) \qquad Li^+(CO)_5M'\overset{-}{M}(CO)_4(\overset{O}{\overset{\|}{C}H})$$

$$\mathbf{2} \qquad\qquad \mathbf{3}, \text{ M, M}' = \text{Re, Mn}$$

$$Li^+(CO)_5Mn\overset{-}{Mn}(CO)_4(\overset{O}{\overset{\|}{C}H})$$

$$\mathbf{4}$$