chloride (20 mL). A white solid precipitated within 1 min. The suspension was filtered and the solid washed with methylene chloride (20 mL) to give the bis(mercuric chloride) adduct of ethyl 2-phenyl-2-propenyl sulfide as a white solid (110 mg, 0.152 mmol, 90.9%): mp 123–124 °C; ^{1}H NMR (Me_2SO-d_6, 60 MHz) δ 7.13–7.62 (m, 5 H, C_6H_5), 5.43 (s, 1 H, $=CH_2$ hydrogen cis to phenyl group), 5.21 (s, 1 H, $=CH_2$ hydrogen trans to phenyl group), 3.65 (s, 2 H, $CH_2SCH_2CH_3$), 2.52 (q, J = 7 Hz, 2 H, $CH_2SCH_2CH_3$), 1.12 (t, J = 7 Hz, 3 H, $CH_2SCH_2CH_3$).

Anal. Calcd for $C_{11}H_{14}Cl_4Hg_2S$: C, 18.31; H, 1.94; Cl, 19.67. Found: C, 18.05; H, 1.62; Cl, 17.15.[15]

Reaction of (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate with Equimolar Cyanide Ion. (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt tetrafluoroborate (Ib) (175 mg, 0.468 mmol) was dissolved in dry, degassed acetonitrile (15 mL). Tetraethylammonium cyanide (73 mg, 0.468 mmol) was added, and the reaction mixture was stirred at room temperature for 30 min. During this time the solution became light red. The solvent was removed under reduced pressure (water aspirator). The resulting brown oil was chromatographed (silica gel, ether, acetone). A red oil (200 mg eluted with acetone) was obtained after solvent removal. The red oil is believed to be an impure monocyano adduct of Ib: IR (thin film) 3400 (s, br, H_2O), 2970 (s), 2940 (m), 2890 (m), 2090 (m, CN), 1685 (s), 1670 (s), 1660 (s), 1650 (s), 1635 (s), 1615 (s), 1450 (m), 1430 (m), 1415 (m), 1360 (s), 1340 (m), 1300 (m), 1215 (m), 1165 (m), 1135 (s), 1015 (s), 1000 (m), 945 (m), 905 (m), 890 (m), 820 (m), 780 (m), 750 (m) cm^{-1}; UV max (CH_3CN)[16] 544 nm (ϵ 28), 408 (144), 253 (3070); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.52–7.13 (m, 30 H, C_6H_5), 7.32 (s), 5.05 (s, 5 H, C_5H_5), 3.36 (s), 2.62 (s), 2.40 (s), 2.17 (s), 1.42 (s), 1.35 (s), 1.24 (s), 0.85 (s).

Reaction of (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate with Thiocyanate Ion. (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt tetrafluoroborate (Ib) (100 mg, 0.268 mmol) was dissolved in dry, degassed acetone (40 mL). Potassium thiocyanate (156 mg, 1.60 mmol) was added, and the solution was stirred for 30 min at room temperature. During this time the solution turned blue-green. The solvent was removed under reduced pressure (water aspirator) to give a green solid. The solid was chromatographed (silica gel, ether, acetone). A brown oil was obtained from the ether fraction after solvent removal. The acetone fraction yielded a blue solid, [$K_2Co(NCS)_4$]. The brown oil was rechromatographed (silica gel, pentane, ether). Pentane elution and solvent removal gave a yellow oil. A brown oil was obtained from the ether fraction. Yellow oil: IR (thin film) 3070 (m), 3050 (m), 3030 (m), 2950 (s), 2920 (s), 2860 (m), 1720 (s), 1680 (w, C=C), 1585 (m), 1615 (w, $C{=}CC_6H_5$) 1485 (m), 1435 (s), 1420 (m, $C{=}CH_2$), 1350 (w, C=CHR), 1310 (m), 1270 (s), 1115 (m), 1060 (m), 890 (m, $C{=}CH_2$), 815 (w, C=CHR), 800 (w, C=CHR), 740 (s) cm^{-1}, ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.13–7.43 (m), 6.39 (s), 6.20 (s), 5.48 (s), 4.73 (s), 4.30 (s), 4.22 (s), 3.07 (s), 2.77 (s), 2.38 (s), 2.30–1.97 (m). Brown oil: IR (thin film) 3400 (m, br, H_2O), 3070 (w), 3050 (m), 3030 (m), 2950 (s), 2910 (s), 2860 (m), 1710 (m), 1690–1640 (s, C=C), 1620 (w, $C{=}CC_6H_5$), 1590 (w), 1480 (w), 1430 (m), 1410 (m), 1250 (s), 1080 (m), 1060 (m), 1035 (m), 1010 (m), 790 (s), 770 (s), 740 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.87–7.23 (m), 4.40 (s), 4.32 (s), 2.90–2.07 (m), 1.73–1.27 (m). $K_2Co(NCS)_4$: IR (KBr) 3400 (s, br, H_2O), 2060 (s, SCN), 720 (m, br) cm^{-1}; visible (acetone), 620, 584 (sh) nm. Similar results were obtained with tetraethylammonium thiocyanate.

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Registry No. Ib, 79991-97-2; Ib′, 79991-99-4; II, R = CH_3, 79992-70-4; II, R = C_2H_5, 51876-02-9; III, R = CH_3, 25650-53-7; V, 79991-92-7; [$K_2Co(NCS)_4$], 19543-13-5; tetraethylammonium (π-cyclopentadienyl)tricyanocobaltate(III), 79991-93-8; α-bromomethylstyrene, 3360-54-1; ethanethiol, 75-08-1.

(15) Mercury often interferes with analysis for chlorine: C. Ayers in "Comprehensive Analytical Chemistry", C. L. Wilson and D. W. Wilson, Eds., Vol. 1B, Elsevier, New York, 1960, p 230.

(16) Molar absorptivities are low because of the presence of impurities.

Syntheses of Kinetically Unstable Neutral Formyl Complexes via $Li(C_2H_5)_3BH$ and "Transformylation" Reactions of Metal Carbonyl Cations

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Low-temperature syntheses of the kinetically unstable formyls (η-C_5H_5)Re(NO)(CO)(CHO) (**9**), (η-C_5H_5)Mn(NO)(CO)(CHO) (**10**), $Re(PPh_3)(CO)_4(CHO)$ (**11**), $Mn(PPh_3)_2(CO)_3(CHO)$ (**12**), $Ir(PPh_3)_2(CO)_2(CHO)$ (**13**), and (η-C_5H_5)$Mo(PPh_3)(CO)_2(CHO)$ (**14**) by reaction of $Li(C_2H_5)_3BH$ with the corresponding metal carbonyl cations are described. Formyls **9**, **10**, and **11** can also be synthesized by hydride transfer from the stable neutral formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO) (**1**) to the appropriate metal carbonyl cation precursor ("transformylation"); this procedure avoids formation of byproduct $(C_2H_5)_3B$. Whereas **9** (in dilute solution) and **13** decarbonylate to detectable metal hydrides upon warming, the decomposition chemistry of the other formyls is more complex and sometimes involves the dichloromethane cosolvent.

Introduction

Several simple neutral metal carbonyl complexes ($Co_2(CO)_8$, $Mn_2(CO)_{10}$, $Ru(CO)_5$) have been found to be catalyst precursors for the homogeneous reduction of CO/H_2 gas mixtures to oxygen-containing organic molecules.[2] For such transformations, a plausible initial step is the formation of a catalyst bound formyl (–CHO). Hence the synthesis of neutral, homogeneous transition metal formyl complexes has been an extremely active research area.[3]

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(2) (a) Feder, H. M.; Rathke, J. W. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 45 and references therein. (b) Pruett, R. L *Ibid.* **1977**, *295*, 239. (c) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419. (d) Dombek, B. D. *Ibid.* **1980**, *102*, 6855. (e) Fahey, D. R. *Ibid.*, **1981**, *103*, 136. (f) Keim, W.; Berger, M.; Schlupp, J. *J. Catal.* **1980**, *61*, 359. (g) Knifton, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 188.

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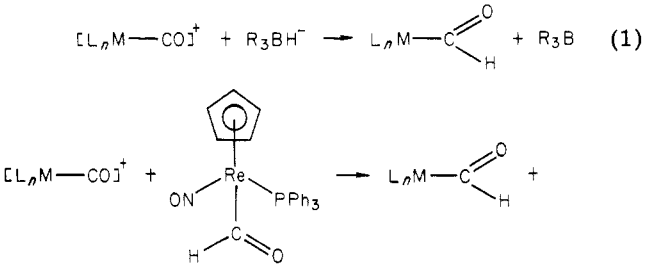
To date, three types of neutral formyl complexes, (η-C_5H_5)Re(NO)(PPh_3)(CHO) (1),[4,5] Os(Cl)(CO)(CN-*p*-$C_6H_4CH_3$)(PPh_3)$_2$(CHO),[6] and Ir(X)(H)(PMe_3)$_3$(CHO) (X = H, CH_3),[7] have proved isolable in pure form. The formyl ligands in these compounds are in general reducible with BH_3 and related hydride donors.[4,5,7] However, no well-defined reactions have yet been observed with H_2 or transition-metal hydrides, which are plausible reducing agents for catalyst-bound formyls. Thus, it appears that it will not be possible to precisely model the individual steps of the foremention CO reduction reactions with neutral formyl complexes which are stable at room temperature.

Consequently, we have focused our attention on the synthesis of *unstable* formyl complexes—certain of which may be close relatives of catalytic intermediates in homogeneous CO reduction. In this paper, we report (a)[8] that the reaction of $Li(C_2H_5)_3BH$ with metal carbonyl cations (eq 1) provides an entry of considerable generality into



(1)

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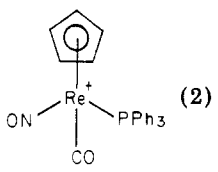

(2)

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unstable neutral formyl complexes, (b) that (η-C_5H_5)Re(NO)(PPh_3)(CHO) (1) reacts cleanly with certain metal carbonyl cations to generate new formyl complexes via "transformylation" (eq 2),[9,10] and (c) selected decomposition data on the formyl complexes thus prepared.

Results

The metal carbonyl cations listed in Table I were dissolved or suspended in the indicated solvents and treated with 1.0–1.1 equiv of $Li(C_2H_5)_3BH$ in THF. In all cases, good NMR evidence[3] for the formation of the corresponding neutral formyl complexes was obtained. With the exception of the formyl (η-C_5H_5)Re(NO)(CO)(CHO) (9) derived from cation 3, all formyl complexes decomposed

Table I. Data on Neutral Metal Formyl Complexes Prepared from Metal Carbonyl Cations and $Li(C_2H_5)_3BH$ [a]

starting metal carbonyl cation		solvent: temp, °C	metal formyl product		yield of formyl,[b] %	^{1}H NMR,[c] δ	^{13}C NMR,[c,d] δ	thermal stability
[(η-C_5H_5)Re(NO)(CO)$_2$]$^+BF_4^-$	(3)	THF; −23	(η-C_5H_5)Re(NO)(CO)(CHO)	(9)	100	15.77[e]	265.9 (s)	several h 25 °C
[(η-C_5H_5)Mn(NO)(CO)$_2$]$^+PF_6^-$	(4)	THF; −23	(η-C_5H_5)Mn(NO)(CO)(CHO)	(10)	100	13.45 (s)	303.7 (s)	rapid decomp 10 °C
[Re(PPh_3)(CO)$_5$]$^+BF_4^-$	(5)	CH_2Cl_2; −23	Re(PPh_3)(CO)$_4$(CHO)	(11)	90	13.98 (s)	275.6 (d, 9)	rapid decomp 20 °C
[Mn(PPh_3)$_2$(CO)$_4$]$^+PF_6^-$	(6)	CH_2Cl_2; −22	Mn(PPh_3)$_2$(CO)$_3$(CHO)	(12)	71	13.23 (t, 4)	301.2 (br s)[f]	rapid decomp 0 °C
[Ir(PPh_3)$_2$(CO)$_3$]$^+PF_6^-$	(7)	CH_2Cl_2; −60	Ir(PPh_3)$_2$(CO)$_2$(CHO)	(13)	80	12.85 (t, 17)		rapid decomp −30 °C
[(η-C_5H_5)Mo(PPh_3)(CO)$_3$]$^+PF_6^-$	(8)	CH_2Cl_2; −41	(η-C_5H_5)Mo(PPh_3)(CO)$_2$(CHO)	(14)	41	14.70 (d, 4)		rapid decomp −41 °C

[a] By reaction with 1.0-1.1 equiv of $Li(C_2H_5)_3BH$ in THF with the metal cation dissolved or suspended in the given solvent at −78 °C, followed by warming to the given temperature. [b] Determined by ^{1}H NMR relative to *p*-di-*tert*-butylbenzene standard or total phenyl protons (PPh_3) in the homogeneous sample; accuracy is considered to be within ±10%. [c] Multiplicity and *J* (Hz) in parentheses. [d] ^{1}H NMR Chemical Shifts were obtained by reference to *p*-di-*tert*-butylbenzene or CH_2Cl_2 solvent peak (δ 5.30) at the indicated temperature unless noted; values are temperature dependent. [e] Samples were 0.03 M in Cr(acac)$_3$ and spectra recorded at −60 °C unless noted; THF-d_8 or CD_2Cl_2 were used as solvents. [f] Recorded at ambient probe temperature.

(3) For a review of transition-metal formyl complexes, see: Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

(4) (a) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589. (b) Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530. (c) Wong, W.-K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. (d) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *Ibid.*, **1982**, 104, 141.

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(7) Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7109.

(8) A portion of this study has been communicated.[4a]

(9) (a) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1. (b) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545.

(10) (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. (b) *Adv. Chem. Ser.* **1979**, *No. 173*, 132.

rapidly at or below room temperature.

Formyl **9** exhibited a half-life of several hours at room temperature and was additionally characterized by an in situ IR spectrum (cm^{-1}, THF): $\nu_{C\equiv O}$ 1985 (s); $\nu_{N\equiv O}$ 1709 (s); $\nu_{C=O}$ 1614 (m). However, efforts to isolate **9** in pure form were unsuccessful. Formyl **9** has been prepared via related routes by Casey[5a] and Graham (who obtained **9** as orange microcrystals),[5b] but analytically pure material has not yet been reported. A dilute solution of **9** (0.001 M, prepared in situ) decomposed principally to $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$ (57% isolated). Similar observations have been previously reported by Casey.[5a]

The decomposition products of formyls **10–14** were also briefly examined. When $Ir(PPh_3)_2(CO)_2(CHO)$ (**13**) was warmed to −40 °C, quantitative decomposition to $Ir(PPh_3)_2(CO)_2H$ occurred, as evidenced by a new ^1H NMR resonance at δ −10.60 (t, $J_{^1H-^{31}P}$ = 3 Hz) (lit.[11] δ −10.97 (J = 3 Hz)). At room temperature, the IR spectrum ((cm^{-1}, CH_2Cl_2/THF): 2084 (w), 1985 (m), 1972 (sh), 1923 (s)) agreed well with that reported for $Ir(PPh_3)_2(CO)_2H$ ((cm^{-1}, CH_2Cl_2 (two isomers)): A, 2085 (w), 1984 (s), 1930 (m, sh); B, 2050 (sh), 1972 (m), 1920 (s)).[11]

Samples of $Re(PPh_3)(CO)_4(CHO)$ (**11**) which were allowed to stand at room temperature gave complex IR spectra ((cm^{-1}, CH_2Cl_2/THF): 2109 (m), 2082 (m), 1999 (s), 1988 (s), 1968 (s), 1948 (s), 1859 (w)). No rhenium hydrides were detected by ^1H NMR, but some IR bands matched absorptions reported for $Re(PPh_3)(CO)_4(H)$ (cm^{-1}, C_6H_{12}: 2081 (m), 1993 (s), 1978 (vs), 1966 (s)).[12] Chromatography of the reaction residue remaining after solvent evaporation gave $Re(PPh_3)(CO)_4(Cl)$ (**IR** (cm^{-1}, CCl_4): 2106 (m), 2018 (m), 2003 (s), 1941 (s))[13] in 44% yield.

Similarly, decomposed samples of $(\eta\text{-}C_5H_5)Mo(PPh_3)(CO)_2(CHO)$ (**14**) did not exhibit any metal hydride resonances in the ^1H NMR. However, addition of CCl_4 to the reaction mixture gave $(\eta\text{-}C_5H_5)Mo(CO)_3Cl$ in 78% yield. Decomposed samples of $(\eta\text{-}C_5H_5)Mn(NO)(CO)(CHO)$ (**10**) contained IR bands (cm^{-1}): 1967 (s), 1792 (s), 1715 (s), 1503 (s)) similar to those reported for the known dimer $[(\eta\text{-}C_5H_5)Mn(NO)(CO)]_2$ (cm^{-1}, halocarbon oil mull): 1956 (s), 1781 (s), 1707 (s), 1509 (s)).[14] When $Mn(PPh_3)_2(CO)_3(CHO)$ (**12**) was allowed to decompose, we did not observe ^1H NMR or IR evidence for known manganese hydrides, halides, or dimers.

Equation 1 clearly provides a general entry into neutral formyl complexes, but to date we have been unable to devise satisfactory means for removing the trialkylborane and ionic byproducts. Since formyl complexes have often been observed to act as hydride donors,[3,4c,d,5a,9,10] we sought to determine whether a neutral formyl complex might transfer hydride to a metal carbonyl cation ("transformylation"),[9,10] as exemplified in eq 2. By proper manipulation of solvents it seemed possible that the carbonyl cation byproduct (eq 2) might be precipitated, leaving a pure solution of neutral formyl. We selected $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (**1**) for initial study.

Formyl **1** and cation $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ (**3**) were mixed in CD_2Cl_2 at −78 °C. ^1H NMR monitoring at −73 °C revealed that some hydride transfer had occurred, but the reaction stopped at partial conversion, apparently due to the incomplete solubility of **3**. A similar reaction was attempted between **1** and cation $[Re(PPh_3)(CO)_5]^+BF_4^-$ (**5**) at −40 °C in CD_3CN. Under these conditions, **5** was completely soluble, but only a small amount of **1** dissolved. Again, reaction proceeded only to a very small conversion. Slow warming of either of these reactions did not improve product yields.

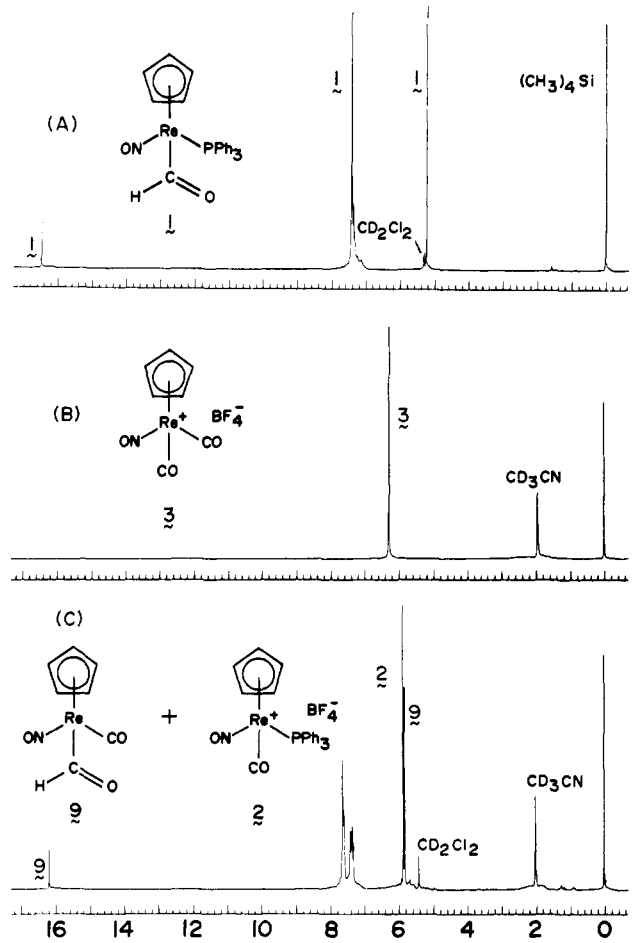

Figure 1. (A) **1** in CD_2Cl_2 at ambient probe temperature. (B) **3** in CD_3CN at ambient probe temperature. (C) Spectrum recorded at −40 °C 3 min after mixing samples A and B at −40 °C. For exact quantities employed, see Experimental Section.

"Transformylations" were next attempted in mixed CD_2Cl_2/CD_3CN solvent to solubilize both reactants. In a typical reaction, **3** in CD_3CN (see spectrum B, Figure 1) was added to **1** in CD_2Cl_2 (see spectrum A, Figure 1) at −40 °C. As shown in spectrum C (Figure 1), quantitative hydride transfer rapidly occurred to give $(\eta\text{-}C_5H_5)Re(NO)(CO)(CHO)$ (**9**) and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**2**). Subsequent addition of toluene-d_8 (−40 °C) precipitated most of the carbonyl cation **2** and shifted the C_5H_5 resonance of **9** upfield (Casey has observed an upfield shift in C_6D_6)[5a] to δ 5.49. A similar reaction of $[(\eta\text{-}C_5H_5)Mn(NO)(CO)_2]^+PF_6^-$ (**4**; in CD_3CN) with **1** (in CD_2Cl_2) at −40 °C cleanly gave $(\eta\text{-}C_5H_5)Mn(NO)(CO)(CHO)$ (**10**) and **2**.

Reaction of **1** (in CD_2Cl_2) with **5** (in CD_3CN) was very slow at −40 °C; complete hydride transfer took place only upon warming to 20 °C. Surprisingly, **1** and $[Mn(PPh_3)_2(CO)_4]^+PF_6^-$ (**6**) did not react at all. When **1** was similarly treated with $[Mn(CO)_6]^+CF_3SO_3^-$ at −50 °C, immediate formation of **2** (δ 5.99) was evident. However, ^1H NMR resonances were somewhat broadened, and no new formyl species or $(CO)_5MnH$ could be detected. The reaction mixture was warmed to room temperature; IR absorptions of **2** (2000 (s), 1764 (s) cm^{-1}) and $Mn_2(CO)_{10}$ (2044 (m), 2014 (s), 1981 (m) cm^{-1}) were present.

The above "transformylation" synthesis of **9** from **1** and **3** was conducted on a larger scale. The reaction was warmed to 0 °C, after which C_6H_6 was added to precipitate

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2. The mixture was allowed to stand at 15 °C for 1 h, after which **2** was isolated by Schlenk filtration (83%). Solvent was then removed from the filtrate at 10 °C to give an oily orange solid, which was shown by ^{1}H NMR in C_6D_6 to be a ca. 75:25 mixture of **9** and the bimetallic "ester" [(η-C_5H_5)Re(NO)(CO)](μ-CO_2CH_2–)[(CO)(NO)Re(η-C_5H_5)] (**15**) previously isolated and characterized by Casey.[5a] No (η-C_5H_5)Re(NO)(CO)(H) was present.

Discussion

The syntheses of unstable neutral formyl complexes described in this paper fill important gaps in preparative methodology but are not without limitations. An obvious requirement for the purification of kinetically labile formyl complexes is that all byproducts be easily removed at low temperature. Formyl synthesis utilizing $Li(C_2H_5)_3BH$ (eq 1) is complicated by the formation of $(C_2H_5)_3B$ (bp >60 °C) and Li^+ salts. Use of $Li(CH_3)_3BH$ would afford the more volatile by-product $(CH_3)_3B$ (bp −20 °C), but $Li(CH_3)_3BH$ is a significantly weaker hydride donor toward metal carbonyls.[15]

"Transformylation" reactions similar to eq 2 have been previously used in our laboratory[9] and Casey's[10] to generate anionic formyl complexes from neutral metal carbonyl precursors. Formyl complexes of third row metals and/or with good donor ligands are generally stronger hydride transfer agents; thus **1**, which has a very low $\nu_{C=O}$ (1559–1565 cm^{-1}), is an obvious choice for use in eq 2. Since the metal carbonyl cation byproduct in eq 2 can be precipitated by addition of a hydrocarbon solvent, quite pure solutions of labile formyl complexes can in principle be prepared by this route. The ^{1}H NMR chemical shifts of formyls synthesized via eq 2 (Figure 1 and Experimental Section) differ from those in Table I. This effect, which has been previously noted, is principally due to the presence of $(C_2H_5)_3B$ in the latter samples (which also imparts a temperature dependence);[3] solvent dependeces have also been observed.[5]

The mixed solvent systems generally utilized for eq 1 and 2 present some difficulties. Smooth "transformylation" requires a polar but inert cosolvent to dissolve the reactant cation. Acetonitrile (mp −46 °C) serves well, but reactions cannot be run significantly below −50 °C without some solvent freezing. One of our most highly sought synthetic targets, $Mn(CO)_5(CHO)$, does not appear to be stable at these temperatures. Also, the dichloromethane cosolvent can complicate analysis of the formyl decomposition chemistry; formyl complexes often thermally decarbonylate to metal hydrides,[3] which are in turn susceptible to free radical chlorination in halocarbon solvents.[16]

We were disappointed to find that samples of (η-C_5H_5)Re(NO)(CO)(CHO) (**9**) prepared via "transformylation" afforded, upon concentration, significant quantities of byproduct [(η-C_5H_5)Re(NO)(CO)](μ-CO_2CH_2)[(CO)(NO)Re(η-C_5H_5)] (**15**). Casey has previously shown that concentrated solutions of **9** (as opposed to dilute solutions, which decarbonylate as described above) decompose to **15** by both acid-catalyzed and non-acid-catalyzed mechanisms.[5a] Graham has reported carefully controlled conditions which lead to **9** free of **15**.[5b]

Of the remaining neutral formyl complexes synthesized, only $Ir(PPh_3)_2(CO)_2(CHO)$ (**13**) undergoes a straight-forward thermal decarbonylation to a metal hydride. However, in view of the above-mentioned tendency of transition-metal hydrides to abstract halogen from solvents, the isolation of $Re(PPh_3)(CO)_4(Cl)$ following the decomposition of $Re(PPh_3)(CO)_4(CHO)$ (**11**) constitutes (together with IR data) reasonable evidence for the intermediacy of $Re(PPh_3)(CO)_4H$. The formation of metal hydrides from (η-C_5H_5)Mo(PPh_3)$(CO)_2$(CHO) (**14**) and (η-C_5H_5)Mn(NO)(CO)(CHO) (**10**) is less certain. Although high-field metal hydride ^{1}H NMR resonances could not be detected, formation of a molybdenum chloride (subsequent to CCl_4 addition) and a manganese dimer, respectively, is consistent with metal hydride intermediates.

Our observation of $Mn_2(CO)_{10}$ following the attempted generation of $Mn(CO)_5(CHO)$ from **1** and $[Mn(CO)_6]^+$ $CF_3SO_3^-$ is relevant to an earlier experiment by Fiato, Vidal, and Pruett.[17] These authors noted that reaction of $(CO)_5Mn^-$ with ^{13}C-formic acetic anhydride at 0 °C gave varying quantities of $HMn(CO)_5$ and $Mn_2(CO)_{10}$; label distributions were consistent with the intermediacy of $Mn(CO)_5(CHO)$. Together with our data, it is clear that preparative methods which operate at yet lower temperatures will be required if neutral formyl complexes which are plausible intermediates in homogeneous catalytic CO reduction are to be directly observed.

Experimental Section

General Data. General procedures employed for this study were identical with those given in a previous paper.[4d] Starting materials were prepared as described in the following references: **1**,[4a,d] **3**,[4a,d] **4**,[14] **5** (analogously to the $PPhMe_2$-substituted cation using $NO^+BF_4^-$ instead of $NO^+PF_6^-$),[18] **6**,[19] **7**,[20] **8**,[21] $[Mn(CO)_6]^+$-$CF_3SO_3^-$.[22]

Preparations of (η-C_5H_5)Re(NO)(CO)(CHO) (9). A. Reaction of $Li(C_2H_5)_3BH$ with [(η-C_5H_5)Re(NO)$(CO)_2$]$^+BF_4^-$ (3). To 0.0336 g (0.0792 mmol) of **3** suspended in 0.3 mL of THF (containing 0.0047 g (0.0250 mmol) of *p*-di-*tert*-butylbenzene) in a septum capped 5-mm NMR tube at −78 °C was added 0.080 mL (0.080 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The homogeneous sample was transferred to a −23 °C (60-MHz) ^{1}H NMR probe. Data: see Table I.

B. Reaction of (η-C_5H_5)Re(NO)(PPh_3)(CHO) (1) with 3. Samples of **1** (0.010 g, 0.017 mmol) in CD_2Cl_2 (0.300 mL) and **3** (0.008 g, 0.019 mmol) in CD_3CN (0.100 mL) were prepared in separate septum-capped 5-mm NMR tubes and cooled to −40 °C (CH_3CN/CO_2 bath). The latter was then added to the former, giving a homogeneous solution which was quickly transferred to an NMR probe precooled to −40 °C. A ^{1}H NMR spectrum (200 MHz, C in Figure 1) was immediately recorded, which showed complete conversion to [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$ (**2**) (δ 5.87)[4] and **9** (δ 16.20 (1 H), 5.83 (5 H)).[4,5] Toluene-d_8 (0.300 mL) was then added. Formyl **9** remained in solution (δ 16.20, 5.49), and **2** precipitated.

Isolation of **9** was attempted from a larger scale reaction. To 0.040 g (0.070 mmol) of **1** in 3 mL of CH_2Cl_2 at −40 °C was added 0.030 g (0.071 mmol) of **3** in 1 mL of CH_3CN. The reaction was stirred at −40 °C for 10 min and then at 0 °C for 10 min. Benzene (20 mL) was added, and the reaction was kept at 15 °C for 1 h. During this time, **2** precipitated, which was isolated by Schlenk filtration (0.038 g, 0.058 mmol, 83%; IR (cm^{-1}, CH_2Cl_2) $\nu_{C=O}$ 2009 (s), $\nu_{N=O}$ 1765 (s)). Solvent was removed from the filtrate at 10 °C to give an oily orange solid, which a ^{1}H NMR spectrum (200 MHz) in C_6D_6 indicated to be a ca. 75:25 mixture of **9** and [(η-

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C_5H_5)Re(NO)(CO)](μ-CO_2CH_2–)[(CO)(NO)Re(η-C_5H_5)] (**15**) (C_5H_5 resonances, δ (vs. internal $(CH_3)_4Si$): 4.920, 4.922, 5.002, 5.004 (mixture of diastereomers) (lit.[5a] 4.956, 4.958, 5.032, 5.034)).

Decomposition of 9 in Dilute Solution. A solution of **9** was prepared by adding 0.270 mL (0.270 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF to 0.1136 g (0.268 mmol) of **3** in 15 mL of THF at −22 °C. After the resulting homogeneous yellow solution was warmed to room temperature, 250 mL of THF was added and the mixture stirred for 67 h. The solvent was then removed by rotary evaporation and the residue extracted with hexane until the hexane was colorless. The solvent was removed and the extraction repeated to give 0.0472 g (0.152 mmol, 57%) of a red-orange liquid, which a ^1H NMR spectrum indicated to be pure (η-C_5H_5)Re(NO)(CO)(H) (δ, C_6D_6): 4.66 (s, 5 H), −8.00 (s, 1 H).[23]

Preparations of (η-C_5H_5)Mn(NO)(CO)(CHO) (10). A. Reaction of $Li(C_2H_5)_3BH$ with [(η-C_5H_5)Mn(NO)(CO)$_2$]$^+PF_6^-$ (4). To 0.0645 g (0.184 mmol) of **4** suspended in 0.3 mL of THF (containing 0.0108 g (0.0567 mmol) of *p*-di-*tert*-butylbenzene) in a septum-capped 5-mm NMR tube at −78 °C was added 0.190 mL (0.190 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The homogeneous sample was transferred to a −23 °C (60-MHz) ^1H NMR probe. Data: see Table I.

B. Reaction of 1 with 4. A reaction similar to preparation B of **9** was conducted by using **1** (0.008 g, 0.014 mmol) in CD_2Cl_2 (0.300 mL) and **4** (0.007 g, 0.020 mmol) in CD_3CN (0.100 mL). A ^1H NMR spectrum (200 MHz) obtained in an indentical fashion at −40 °C showed complete conversion to [(η-C_5H_5)Re(NO)(PPh$_3$)(CO)]$^+PF_6^-$ (δ 5.86) and (η-C_5H_5)Mn(NO)(CO)(CHO) (**10**) (δ 14.77 (1 H), 5.28 (5 H)). The sample was warmed, and marked decomposition of **10** began between 0 and 20 °C.

Preparations and Decompositon of Re(PPh$_3$)(CO)$_4$(CHO) (11). A. Reaction of $Li(C_2H_5)_3BH$ with [Re(PPh$_3$)(CO)$_5$]$^+$-BF_4^- (5). To 0.0198 g (0.0293 mmol) of **5** in 0.3 mL of CH_2Cl_2 in a septum-capped 5-mm NMR tube at −78 °C was added 0.030 mL (0.030 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The homogeneous sample was transferred to a −23 °C (60-MHz) ^1H NMR probe. Data: see Table I.

B. Reaction of 1 with 5. A reaction similar to preparation B of **9** was conducted by using **1** (0.010 g, 0.017 mmol) in CD_2Cl_2 (0.300 mL) and **5** (0.012 g, 0.018 mmol) in CD_3CN (0.100 mL). A ^1H NMR spectrum (200 MHz) obtained in an identical fashion showed only a trace of reaction at −40 °C, but as the sample was warmed to 20 °C, conversion to [(η-C_5H_5)Re(NO)(PPh$_3$)(CO)]$^+$-BF_4^- (δ 5.86) and Re(PPh$_3$)(CO)$_4$(CHO) (**11**, δ 14.99) became complete.

A larger sample of **11** was prepared by adding 0.610 mL (0.610 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF to 0.4115 g of **4** in 50 mL of CH_2Cl_2. The reaction was warmed to room temperature (IR data: see Results), the solvent removed on a rotovap, and the residue chromatographed on silica gel with 5:95 (v/v) ethyl acetate/hexane. Thus obtained was 0.158 g (0.265 mmol, 44%) of Re(PPh$_3$)(CO)$_4$(Cl), which recrystallized from THF/hexane: mp 150–156 °C; IR, see Results. Anal. Calcd for $C_{22}H_{15}ClPO_4Re$: C, 44.34; H, 2.54; P, 5.20. Found: C, 44.68; H, 2.63; P, 5.26.

Preparation of Mn(PPh$_3$)$_2$(CO)$_3$(CHO) (12). To 0.457 g (0.0546 mmol) of [Mn(PPh$_3$)$_2$(CO)$_4$]$^+PF_6^-$ (**6**) in 0.3 mL of CH_2Cl_2 in a septum-capped 5-mm NMR tube at −78 °C was added 0.060 mL (0.060 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The homogeneous sample was transferred to a −22 °C (60-MHz) ^1H NMR probe. Data: see Table I.

Preparation and Decomposition of Ir(PPh$_3$)$_2$(CO)$_2$(CHO) (13). To 0.0647 g (0.0683 mmol) of [Ir(PPh$_3$)$_2$(CO)$_3$]$^+PF_6^-$ (**7**) in 0.3 mL of CH_2Cl_2 in a septum-capped 5-mm NMR tube at −78 °C was added 0.070 mL (0.070 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The sample was transferred to a −60 °C (60-MHz) ^1H NMR probe. Data: see Table I. The probe was warmed to −40 °C (^1H NMR: see Results) and an IR spectrum (Results) recorded after the solution was warmed to room temperature.

Preparation and Decomposition of (η-C_5H_5)Mo(PPh$_3$)-(CO)$_2$(CHO) (14). To 0.0257 g (0.0394 mmol) of [(η-C_5H_5)Mo-(PPh$_3$)(CO)$_3$]$^+PF_6^-$ (**8**) in 0.3 mL of CH_2Cl_2 in a septum-capped 5-mm NMR tube at −78 °C was added 0.040 mL (0.040 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The homogeneous sample was transferred to a −41 °C (60-MHz) ^1H NMR probe. Data: see Table I.

A larger sample was similarly prepared by adding 0.350 mL (0.350 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF to 0.2156 g (0.3307 mmol) of **8** in 20mL of CH_2Cl_2. The mixture was slowly warmed to room temperature (IR (cm^{-1}) 1935 and 1900 (br)), after which 2 mL (20 mmol) of CCl_4 was added. The yellow solution immediately turned red. The solvent was removed and the residue chromatographed on silica gel with CH_2Cl_2. A red band was collected, from which 0.0724 g (0.258 mmol, 78%) of (η-C_5H_5)-Mo(CO)$_3$Cl, identical with an authentic sample,[24] was obtained. IR (cm^{-1}, CH_2Cl_2): 2059 (m), 1969 (s).

Reaction of 1 with [Mn(CO)$_6$]$^+CF_3SO_3^-$. Samples of **1** (0.011 g, 0.019 mmol) in CD_2Cl_2 (0.300 mL) and [Mn(CO)$_6$]$^+$ $CF_3SO_3^-$ (0.008 g, 0.022 mmol) in CD_3CN (0.150 mL) were prepared in separate septum-capped ^1H NMR tubes. The former solution was cooled to −50 °C (CH_3CN/CO_2 slush), and the latter solution was slowly added. The homogeneous reaction mixture was rapidly transferred to a −50 °C ^1H NMR probe. A spectrum recorded immediately showed the complete conversion of **1** to **2** (δ 5.99 (br)), but no other new resonances between δ −10 and 25. IR: see Results.

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