$$\mathrm{MoCl_5} \xrightarrow{\mathrm{CH_3CN}} \underset{80\%}{\mathrm{MoCl_4(CH_3CN)_2}} \xrightarrow{\mathrm{THF}} \underset{70\%}{\mathrm{MoCl_4(THF)_2}} \xrightarrow[\substack{4\mathrm{L} \\ \mathrm{THF}}]{\mathrm{LiEt_3BH}} \mathrm{MoH_4L_4} \quad (4)$$

dation after a month; this compound is best stored in an inert atmosphere.

Acknowledgment. We thank the U.S. Department of the Army for support of this work and the Alfred P. Sloan Foundation for a fellowship (to R.H.C.).

Registry No. $MoH_4(PMePh_2)_4$, 32109-07-2; $WH_4(PMePh_2)_4$, 36351-36-7; $MoH_4(dppe)_2$, 32109-09-4; $WH_4(PEtPh_2)_4$, 41627-13-8; $LiEt_3BH$, 22560-16-3; $MoCl_4(THF)_2$, 16998-75-7; WCl_6, 13283-01-7.

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Homogeneous Reduction of Ligated Carbon Dioxide and Carbon Monoxide to Alkoxymethyl Ligands

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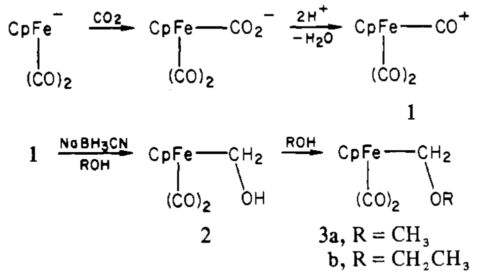
Studies on the stoichiometric reduction of ligated carbon monoxide to C_1 formyl, hydroxy- or alkoxymethyl, and methyl ligands are pertinent to the rational design of homogeneous catalysts that convert synthesis gas—CO/H_2 mixtures—to organic products.[1] Borohydride reagents (BH_4^-, HBR_3^-, $HB(OR)_3^-$) reduce, for example, neutral metal carbonyl systems to anionic formyl complexes,[2a–d] cationic metal carbonyls to neutral formyls,[2c,d] $CpRe(CO)_2NO^+$ to hydroxymethyl (also with $Et_2AlH_2^-$) and methyl compounds,[2d,e] $CpM(CO)_3PPh_3^+$ (M = Mo, W) into $CpM(CO)_2PPh_3(CH_3)$,[2f] and CO ligated to BH_3 or BEt_3.[2g] Transition-metal hydride complexes also have been used in fixing CO ligands.[3]

Our interest lies in probing reaction pathways for converting ligated CO to hydroxymethyl functionalities and then to C_2 or higher coordinated ligands. Alkoxymethyl complexes represent convenient products of CO fixation during stoichiometric studies since the anticipated instability of the analogous hydroxymethyl compounds is eliminated.[2d,e,4] Others have contemplated the intermediacy of hydroxymethyl complexes in homogeneous catalysis and have modeled facets of this chemistry with alkoxymethyl or acyloxymethyl derivatives.[5] We recently reported the selective conversion of $CpFe(CO)_2CH_2OCH_3$ to the phosphine-substituted complexes and their respective C_2 organic molecules: $CpFe(CO)L(CH_2CH_3)/CH_2{=}CH_2$, $CpFe(CO)L(CH_2CO_2CH_3)/CH_3CO_2CH_3$, and $CpFe(CO)L(CH_2CHO)/CH_3CHO$.[6]

This paper reports two observations on the fixation of CO and CO_2 ligands appended to $CpFe(CO)_2$. First, sodium cyanoborohydride in methanol or ethanol efficiently reduces a carbonyl on $CpFe(CO)_3^+$ (**1**), via a hydroxymethyl intermediate, to an alkoxymethyl ligand. Second, CO_2 is incorporated into this sequence by generating **1** from the reaction of $CpFe(CO)_2^-Na^+$ and CO_2 and then adding acid. Together both sequences constitute novel conversion of ligated CO_2 to an alkoxymethyl ligand.



Experimental Section

General Manipulations and Physical Measurements. All synthetic manipulations were performed under a nitrogen atmosphere with standard Schlenk techniques and glassware suitably modified for inert-atmosphere work.[7] A nitrogen atmosphere was routinely provided for the following four operations: (a) carrying out reactions, (b) handling all solutions of metal complexes, (c) column chromatography, and (d) breaking the vacuum to evacuated vessels, including the Buchi rotovaporator. Solvents for synthetic work and recording of spectral data were deoxygenated by bubbling dinitrogen through for 20 min. Camag alumina (neutral, activity 3) was used in column chromatography.

Infrared spectra were taken of CH_2Cl_2 solutions (0.10 M) with NaCl amalgam-spaced (1.0-mm) solution cells and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The ν(CO) frequencies (2200–1500 cm^{-1}) were calibrated against the polystyrene 1601-cm^{-1} absorption. ^1H NMR spectra were taken of concentrated $CDCl_3$ solutions, after centrifugation off of insoluble residues. Varian models EM-360 and XL-200 NMR spectrometers supplied the NMR spectra, which are reported as δ values downfield from internal Me_4Si. Combustion microanalyses were performed by Baron Consulting Co., Orange, CT.

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Materials. $CpFe(CO)_3{}^+BF_4{}^-$ (**1**)[8] and $CpFe(CO)_2CH_2OR$ (**3a**, R = Me; **3b**, R = Et)[9] were prepared according to literature procedures. Alkoxymethyl complexes **3a,b** are readily purified by trap-to-trap distillation (10^{-2} mm); overall, 17-g quantities (ca. 75% yields) were routinely procured from alkylation of $NaFe(CO)_2Cp$ with the chloromethyl methyl and ethyl ethers. (*Caution*: chloromethyl alkyl ethers are potential carcinogens.[26]) Reagent grade solvents, $NaBH_3CN$, phenyl- and ethyl isocyanates, and $HBF_4{\cdot}OEt_2$ were obtained commercially and used as received. Tetrahydrofuran (THF) and CH_2Cl_2 were distilled under nitrogen from sodium benzophenone ketyl and P_2O_5, respectively.

Synthesis. $CpFe(CO)_2CH_2OR$ (3a, R = Me; 3b, R = Et) from $CpFe(CO)_3{}^+BF_4{}^-$ (1). A suspension of $CpFe(CO)_3{}^+BF_4{}^-$ (**1**) (0.584 g, 2.0 mmol) in 30 mL of methanol was treated with $NaBH_3CN$ (0.126 g, 2.0 mmol) at room temperature. The initially insoluble organometallic salt gave a clear yellow solution within 0.5 h that turned red after an additional 3.5 h. Solvent was removed under reduced pressure (0.1 mm, 0 °C), and the red residue was evacuated for an additional hour. This latter operation distilled the volatile $CpFe(CO)_2H$ (**5**) into the vacuum traps.[10] The residue was extracted with ether (90 mL), filtered, concentrated, and then chromatographed on 75 g of alumina with 1:4 ether–pentane. Elution with the ether–pentane cleanly removed a yellow band, which produced $CpFe(CO)_2CH_2OCH_3$ (**3a**) as an amber fluid: 0.179 g (40%); IR (CH_2Cl_2) 2005, 1948 cm^{-1}; NMR ($CDCl_3$) δ 4.83 (s, 2, CH_2), 4.77 (s, 5, Cp), 3.21 (s, 3, CH_3); NMR (C_6H_6) δ 4.80 (s, 2, CH_2), 4.24 (s, 5, Cp), 3.16 (s, CH_3).

A second broad, brown band was eluted with CH_2Cl_2; this afforded $[CpFe(CO)_2]_2$ in 6% (21 mg) yield.

Substitution of ethanol for methanol gave $CpFe(CO)_2CH_2OCH_2CH_3$ (**3b**) (134 mg, 28%) after workup and chromatography, but a reaction time of 12 h at room temperature was required. $CpFe(CO)_2CH_2OCH_2CH_3$: IR (CH_2Cl_2) 2000, 1940 cm^{-1}; NMR ($CDCl_3$) δ 4.84 (s, 2, $FeCH_2$), 4.75 (s, 5, Cp), 3.34 (q, J = 7.0 Hz, 2, OCH_2), 1.13 (t, J = 7.0 Hz, 3, CH_3); NMR (C_6H_6) δ 4.83 (s, 2, $FeCH_2$), 4.33 (s, 5, Cp), 3.32 (q, J = 7.0 Hz, OCH_2), 1.11 (t, J = 7.0 Hz, CH_3).

$CpFe(CO)_2CH_2OCONHR$ (4a, R = Et; 4b, R = Ph). To a stirred suspension of $CpFe(CO)_3{}^+BF_4{}^-$ (**1**) (0.584 g, 2.0 mmol) in methanol (30 mL) at 0 °C was added $NaBH_3CN$ (0.126 g, 2.0 mmol). After 2 h of stirring at 0 °C, the resulting yellow mixture was evaporated to dryness (0 °C, 10^{-1} mm, 0.75 h), and then it was extracted with cold toluene (80 mL, 0 °C). Excess phenyl or ethyl isocyanate (3 mL) was added prior to storage at room temperature for 6 h. The corresponding orange solution was then concentrated (0.10 mm, 2 h) to an oily residue and was added in a minimum volume of ether to a 25 × 2 cm alumina chromatography column made up in pentane. Pentane elution brought down a brown band that contained $[CpFe(CO)_2]_2$ as the only organometallic. Et_2O elution then cleanly removed a broad yellow band of the urethane.[11]

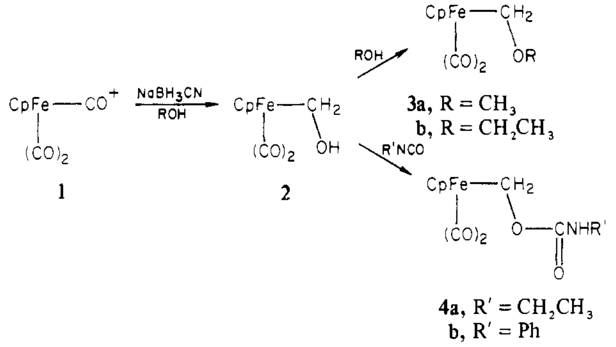
$CpFe(CO)_2CH_2OCONHCH_2CH_3$ (**4a**): yellow gum (0.071 g, 14% yield); IR (CH_2Cl_2) 2016, 1958 ($C{\equiv}O$), 1704 ($C{=}O$) cm^{-1}; NMR ($CDCl_3$) δ 5.24 (s, 2, $FeCH_2$), 4.80 (s, 5, Cp), 4.50 (m, 1, NH), 3.15 (dq, J = 7.0 Hz, 2, NCH_2), 1.09 (t, J = 7.0 Hz, 3, CH_3). The assignment of the five-line NCH_2 multiplet as an overlapping doublet of quartets was verified by spin decoupling experiments. Anal. Calcd for $C_{11}H_{13}NO_4Fe$: C, 47.34; H, 4.70. Found: C, 47.59; H, 4.89.

$CpFe(CO)_2CH_2OCONHC_6H_5$ (**4b**): yellow-tan gummy solid after precipitation with pentane (0.208 g, 32% yield); IR (CH_2Cl_2) 2018, 1961 ($C{\equiv}O$), 1722 ($C{=}O$) cm^{-1}; NMR ($CDCl_3$) δ 7.24 (br m, 5, Ph), 5.33 (s, 2, $FeCH_2$), 4.76 (s, 5, Cp). Anal. Calcd for $C_{15}H_{13}NO_4Fe$: C, 55.08; H, 4.01. Found: C, 54.91; H, 4.22.

$CpFe(CO)_3{}^+BF_4{}^-$ (1) from $CpFe(CO)_2{}^-Na^+$ and CO_2. $[CpFe(CO)_2]_2$ (4.0 g, 11.3 mmol) in 60 mL of THF was reductively cleaved with Na sand[12] (1.0 g, 43.5 mmol): agitation in an ultrasonic cleaning bath[13] for 3 h at room temperature afforded quantitative conversion to an orange solution of $CpFe(CO)_2Na$. Bubbling CO_2 into the cold (−80 °C) filtered solution of $CpFe(CO)_2Na$ for 20 min produced a dark green suspension. Addition of $HBF_4{\cdot}OEt_2$ (9.0 mL, 70 mmol) gave a dark pink suspension that was stirred without further change (except for CO_2 effervescence) at −55 °C (1 h) and then at room temperature (1 h). Solvent was removed (30 °C, 20 mm), and CH_3NO_2 extracts (100 mL) of the residue were filtered through a Celite pad. Treatment with ether (350 mL) produced a light yellow precipitate of $CpFe(CO)_3{}^+BF_4{}^-$ (**1**) that was collected, reprecipitated from CH_3NO_2–ether (50 mL:350 mL), and vacuum-dried: 5.89 g, 89% yield. Quantitative IR studies in CH_3NO_2 solution [$\nu(C{\equiv}O)$ 2123, 2074 cm^{-1}] and the NMR spectrum [CF_3CO_2H δ 5.89 (Cp)] established the absence of impurities.

Results and Discussion

One might have expected $CpFe(CO)_3{}^+$ to represent a terrible choice for CO fixation studies since its reduction to $CpFe(CO)_2H$ (**5**)[14] (with $NaBH_4$ in THF) and to $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (**6**)[15] (with $NaBH_3CN$ in THF) had been previously demonstrated. We confirmed these results and further demonstrated that 1 equiv of $NaBH_4$ in CH_3OH (0 °C) converts **1** to **5** exclusively. Also, 1 equiv of $NaBH_3CN$ in CH_3NO_2 or of $Ph_3PCH_3{}^+BH_3CN^-$ in CH_3NO_2 or CH_2Cl_2 likewise converts **1** to **6**. $NaBH_3CN$ in either CH_3OH or CH_3CH_2OH, however, reduces **1** to the corresponding alkoxymethyl complexes **3a,b** in moderate yields.



1

2

3a, R = CH_3
b, R = CH_2CH_3

4a, R′ = CH_2CH_3
b, R′ = Ph

Transience of a thermally unstable hydroxymethyl complex $CpFe(CO)_2CH_2OH$ (**2**), which subsequently undergoes solvolysis to **3a**,**b**, is consistent with the results of trapping experments. Adding ethyl or phenyl isocyanate to crude reaction mixtures of **1** and $NaBH_3CN$ (after the alcohol is replaced with toluene) derivatized **2** as the urethanes **4a,b**.[11] We could not unambiguously assign NMR absorptions to **2** in the above toluene extracts because variable amounts of $[CpFe(CO)_2]_2$, **5**, **3a**, and other impurities interfered. The fully characterized hydroxymethyl complex $CpRe(CO)NO(CH_2OH)$[2d,4a] also converts to its methoxymethyl derivative in methanol.

$NaBH_3CN$ chemoselectively reduces **1** in alcohol since neither $CpFe(CO)_2CH_3$ (**7**) nor $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (**6**) were detected. The absence of **7** was established through NMR examination of the reaction mixture under conditions where 5% **7** would have been detected; and **6** would have been easily detected by IR [ν(CO) 2045, 1968 cm^{-1} in THF] and isolated. Substantial amounts of $CpFe(CO)_2H$ (**5**) however did accumulate as the primary byproduct;[10] it thermally decomposed to $[CpFe(CO)_2]_2$.[14] Either CO deinsertion from an ephemeral

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(10) $CpFe(CO)_2H$ (**5**) was identified by IR ($\nu(C{\equiv}O)$ in CH_2Cl_2 2016, 1952 cm^{-1}), its facile decomposition (in the absence of solvent) to $[CpFe(CO)_2]_2$ at room temperature, and quantitative conversion to $CpFe(CO)_2Cl$ in CCl_4. This latter operation established at least a 25% conversion of **1** to **5**.

(11) $CpFe(CO)_2CH_2OCH_3$ (**3a**) is recovered quantitatively after treatment with excess ethyl or phenyl isocyanate in toluene for 12 h.

(12) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. "Vogel's Textbook of Practical Organic Chemistry", 4th ed.; Longmans, Green and Co.: New York, 1978; p 313.

(13) Luche, J.-L.; Damiano, J.-C. *J. Am. Chem. Soc.* **1980**, *102*, 7926. We find that ultrasonic agitation in the presence of Na pellets serves as a convenient means of generating $CpFe(CO)_2{}^-Na^+$ on a 10-mmol scale. Other procedures could be substituted: Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284 and references cited.

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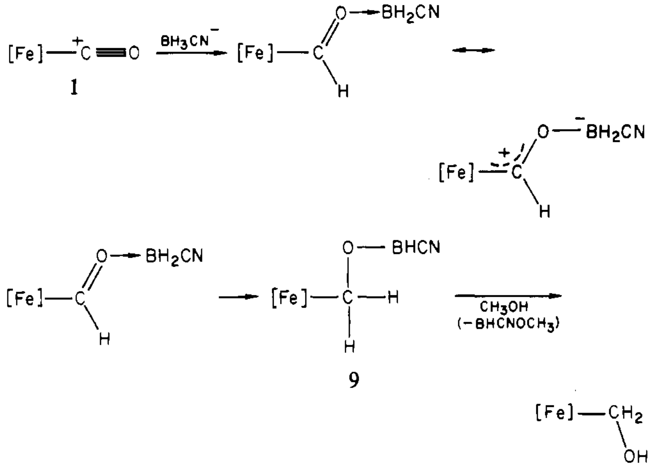
formyl complex[2a-d] $CpFe(CO)_2CHO$ (**8**)[16] or CH_2O deinsertion from **2** would account for **5**.

So why does the alcoholic $NaBH_3CN$ medium selectively reduce **1**[17] to **2** and **3a,b**? $NaBH_3CN$ serves as an excellent reducing agent for Lewis acids[18a] and is both milder and more selective than BH_4^- or Et_3BH^- toward coordinated ligands.[18b] A plausible reaction scheme for reduction of **1** thus incorporates Lewis acid stabilization and subsequent reduction of the formyl complex **8**[16] by BH_2CN,[19] giving **9**. A similar scheme was proposed for the BH_3 reduction of $CpFe(CO)_2COCH_3$ to $CpFe(CO)_2CH_2CH_3$ via a more reactive alkoxyborane intermediate $CpFe(CO)_2CH(OBH_2)CH_3$.[20] Transesterification of **9** by methanol then affords **2**.



One of the CO ligands on $CpFe(CO)_3^+$ (**1**) can be incorporated by treating the appropriate $CpFe(CO)_2$ reagent with CO or CO_2. Carbonylation of halide complexes $CpFe(CO)_2X$,[14,21a] labile salts $CpFe(CO)_2L^+$ (L = acetone,[21b] isobutylene,[21c] H_2O[21d]), or even ferrocene[21e] accordingly represent established preparative procedures of **1**. We now report that protonation of the CO_2 adduct of $CpFe(CO)_2^-Na^+$ [22] gives **1** in high yield; presumably an acid labile $CpFe(CO)_2CO_2H$[23] precursor is involved. (Alkoxycarbonyl complexes, e.g., $CpFe(CO)_2CO_2Et$, exhibit similar acid lability.[8]) The exact nature of the CO_2 adduct of $CpFe(CO)_2^-$ remains obscure (studies are in progress), but the formulation $CpFe(CO)_2C(O)OCO_2^-$ is consonant with facile generation of Na_2CO_3 in the absence of acid.[22] A similar $(CO_2)_2$ adduct of $W(CO)_5^{2-}$ also decomposes to CO_3^{2-} and $W(CO)_6$;[24] and other examples exist for both alkylation of ligated CO_2, giving an alkoxycarbonyl complex,[25a] and reduction to CO complexes.[25b] This study documents the first example of ligated CO_2 fixation, via a CO complex, to a transition-metal alkyl complex.

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged. An NSF departmental instrumentation grant partially paid for the FT NMR spectrometer employed.

Registry No. **1**, 31781-41-6; **3a**, 12108-35-9; **3b**, 12244-98-3; **4a**, 80293-89-6; **4b**, 80288-46-6; **5**, 35913-82-7; $CpFe(CO)_2^-Na^+$, 12152-20-4; $[CpFe(CO)_2]_2$, 12154-95-9; $NaBH_3CN$, 25895-60-7; methanol, 67-56-1; ethanol, 64-17-5; CO_2, 124-38-9; phenyl isocyanate, 103-71-9; ethyl isocyanate, 109-90-0.

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(17) (a) Our results with the $NaBH_3CN$ reduction of **1** are not prototypal for other cationic metal carbonyl complexes. Both $CpFe(CO)_2PPh_3^+$ and $CpMo(CO)_3PPh_3^+$ undergo no reaction with $NaBH_3CN$ in CH_3OH (12 h), but refluxing the solutions for 12 h provided cyano complexes: $CpFe(CO)PPh_3(CN)$[17b] (42% conversion, 41% $CpFe(CO)_2PPh_3^+BF_4^-$ recovered) and $CpMo(CO)_2PPh_3(CN)$[17c] (18% yield, 44% $CpMo(CO)_2PPh_3(H)$ also obtained). $CpMo(CO)_4^+$, $Mn(CO)_6^+$, and $Mn(CO)_5PPh_3^+$ (all PF_6^-) reacted with 1 equiv of $NaBH_3CN$ in CH_3OH (0 °C, 1 h) and exclusively gave the corresponding neutral hydride complexes in 80–95% yields. $Co(CO)_4PPh_3^+PF_6^-$ converted to $[Co(CO)_3PPh_3]_2$ quantitatively under the same conditions. (b) Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660. Faller, J. W. *J. Organomet. Chem.* **1975**, *96*, 99. (c) Beach, D. L.; Dattilo, M.; Barnett, K. W. *Ibid.* **1977**, *140*, 47.

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Convenient Route to Monocyclopentadienylzirconium(IV) Complexes

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Monocyclopentadienyl complexes have substantially contributed to the diversity of features of organometallic transition-metal compounds. However, surprisingly few such substrates have been described for group 4B metals. A major cause for the rare occurrence of $CpMR_3$ examples for at least the elements Zr and Hf appears to be the lack of easily available precursors rather than an extraordinarily low stability.[1] We and others[2a] have noticed that a suitable starting material such as $CpZrCl_3$ (**3**) for a synthesis of previously undisclosed substrates $CpZr(aryl)_3$ (**5**) is difficult to obtain by the usual *nucleophilic* routes via substitution of halide by cyclopentadienyl anion from various sources.[3] Sufficiently pure samples of **3** have recently been obtained in small quantities by two different *radical* pathways.[2] We here report an easily performable new synthesis of **3** which, in our opinion, appears to be superior to the tedious procedures reported yielding this versatile starting material in large amounts and high purity.

The photoinduced chlorination of zirconocene dichloride **1** leads to the selective removal of only one cyclopentadienyl ligand when carried out at ambient temperature.[4] Presumably

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