Acknowledgment. The work at Oklahoma was supported by Grant 04-7-158-44067 from the Office of Sea Grant, NOAA, department of Commerce. We thank Dr. R. E. Schroeder, Summerland Key, FL, and Ms. Lin Craft for assistance in collecting *H. melanodocia*, Dr. K. Ruetzler, Smithsonian Institution, for sponge identification, and Dr. P. Schmidt, Oklahoma Medical Research Foundation, Oklahoma City, OK, for use of a 270-MHz NMR spectrometer. Field desorption mass spectra were provided by the mass spectrometry facility at Massachusetts Institute of Technology, supported by a grant (principal investigator, Professor K. Biemann) from the Biotechnology Research Branch, Division of Research Resources. We gratefully acknowledge grants from the Phillips Petroleum Company, Bartlesville, OK, and the NSF (GP 38410) which aided in the purchase of NMR spectrometers. The Hawaii group thanks Drs. J. Dallas and J. Matson (UC, Davis), Dr. E. Kho (Stanford), and Mr. R. Okuda for ^{1}H NMR spectra and the National Science Foundation and the U.S. Food and Drug Administration for financial support. Crystallographic work was supported by NIH through a training grant to D.V.E. and CA 24487 to J.C.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, and bond angles (8 pages). Ordering information is given on any current masthead page.

Aspects of Homogeneous Carbon Monoxide Fixation: Selective Conversion of Two Carbonyl Ligands on (η^5-C_5H_5)Fe(CO)$_3^+$ to C_2 Organic Compounds

Thomas Bodnar, Gene Coman, Stephen LaCroce,
Carol Lambert, Kevin Menard, and Alan Cutler*

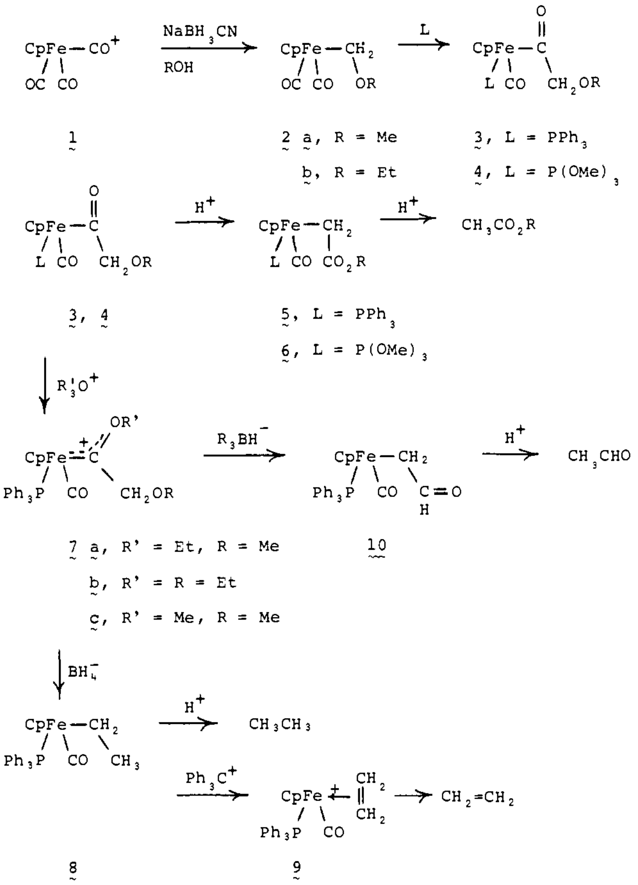
Department of Chemistry, Wesleyan University
Middletown, Connecticut 06457

Received December 22, 1980

The conversion of synthesis gas—CO and H_2 mixtures derived from coal—into organic compounds will provide an alternative source of C_2–C_4 organic feedstocks heretofore obtained from petroleum.[1] Such conversions using heterogeneous catalysts in the Fischer–Tropsch synthesis and related processes are limited by the complex organic mixtures produced. Switching to homogeneous catalysts, however, should engender potentially high and manipulative product selectivity.[2] Soluble transition organometallic complexes that catalytically change synthesis gas into ethylene glycol[3a] or ethanol[3b] and stoichiometrically reform CO ligands into the C_2 compounds ethane or ethylene,[4a] acetaldehyde,[4b] methyl acetate,[4c] or a coordinated enediolate of glycolaldehyde[4d] have been reported. Rational design of homogeneous catalysts for the selective transformation of synthesis gas into organic feedstocks requires further mechanistic details on reduction of CO ligands, subsequent synthesis reactions (i.e., chain growth of the C_1 ligand), and elimination of the desired organic molecule.

We now report viable reaction pathways for the stoichiometric transformation of two CO ligands on CpFe(CO)$_3^+$ (**1**) (Cp = η^5-C_5H_5) selectively to the C_2 organic compounds ethane, ethylene, methyl (or ethyl) acetate, or acetaldehyde. The first step requires fixation of a CO ligand: 1 equiv of $NaBH_3CN$ in methanol or ethanol reduces CpFe(CO)$_3^+$$BF_4^-$ (**1**) to the known η^1-alkoxymethyl complexes CpFe(CO)$_2$CH$_2$OR [**2a**, R = Me; **b**, R = Et].[5] After vacuum removal of solvent and CpFe(CO)$_2$H, **2a** (55%) and **2b** (33%) were isolated by column chromatography.[6] Alkoxyacetyl complexes CpFe(CO)L(COCH$_2$OR) [**3**, L = PPh$_3$; **4**, L = P(OMe)$_3$; **a**, R = Me; **b**, R = Et], which are derived from **2a,b**, then serve as key intermediates in the C_2-coordinated ligand reactions (Scheme I).[7]

Scheme I



Refluxing CH_3CN solutions of **2** and 100% excess of PPh$_3$ or P(OMe)$_3$ for 4 and 10 days, respectively, gave the alkoxyacetyl complexes **3** and **4**. After recrystallization from CH_2Cl_2–heptane, **3** and **4** were obtained in 30–50% yields as air-stable yellow solids.[8] These vigorous reaction conditions exemplify the difficulty with which alkoxymethyl ligands undergo alkyl–acyl migratory insertion;[9] comparable treatment of CpFe(CO)$_2$CH$_3$ affords 80%

---

[1] St-Pierre, L. E.; Brown, G. R., Eds. "Future Sources of Organic Raw Materials—CHEMRAWN I"; Pergamon Press: New York, 1980, pp 167–210. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; Chapter 12.

[2] (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (c) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136–141.

[3] (a) Pruett, R. L. *Ann. New York Acad. Sci.* **1977**, *295*, 239–248. Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466–6468; **1980**, *102*, 6855–6857. (b) Daroda, R. J.; Blackborow; J. R.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1098–1100.

[4] (a) Wong, K. S.; Labinger, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3652–3653. Wong, A.; Harris, M.; Atwood, J. D. *Ibid.* **1980**, *102*, 4529–4531. Masters, C.; van der Woude, C.; van Doorn, J. A. *Ibid.* **1979**, *101*, 1633–1644. Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 77–78. (b) Summer, C. E.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752–1754. (c) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *Ibid.* **1979**, *101*, 7417–7419. (d) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *Ibid.* **1978**, *100*, 2716–2724.

[5] Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044–5045. Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508–1515.

[6] (a) Further details on the reactions of $NaBH_3CN$ with cationic metal carbonyl complexes will be published separately: Coman, G.; Menard, K.; Cutler, A. manuscript submitted. (b) Precedent exists for this reductive step: NaH_2AlEt_2 in THF[c] or $NaBH_4$ in aqueous THF[d] convert CpReNO(CO)$_2^+$ to CpReNO(CO)CH$_2$OH. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rint, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927–1933. (d) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9–C12.

[7] (a) The only C_2 organic molecules previously derived from alkoxy- or hydroxyacetyl organometallic complexes are ethylene glycol[3] and glycolaldehyde.[3,7b] (b) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *172*, C27–C28.

[8] All new compounds gave satisfactory C, H elemental analyses, IR, and NMR data in accord with the proposed structures.

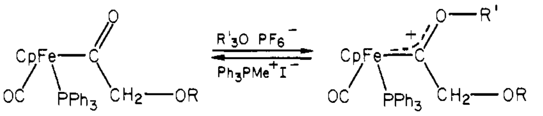
[9] Cawse, J. N.; Fiatto, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405–413. Other examples of migratory insertion involving CO and α-oxyalkyl ligands include:[3a] Heck, R. F.; Breslow, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 2499–2502. Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *Ibid.* **1978**, *100*, 6766–6768.

0002-7863/81/1503-2471$01.25/0 © 1981 American Chemical Society

yields of CpFe(CO)L($COCH_3$) [L = PPh_3, $P(OMe)_3$] in less than 1 day of refluxing.

Both series of alkoxyacetyl complexes [L = PPh_3 and $P(OMe)_3$] serve as precursors to free methyl or ethyl acetate. Facile acidic isomerization of **3** and **4** to the corresponding carboalkoxymethyl complexes CpFe(CO)L(CH_2CO_2R) [**5**, L = PPh_3; **6**, L = $P(OMe)_3$][10] followed by protic cleavage of the Fe–C bond generates the free alkyl acetate. Compounds **5** and **6** were intercepted in 60–77% yields after reaction of **3** and **4** with 1 equiv of trifluoromethanesulfonic acid in CH_2Cl_2, neutralization with triethylamine, and then isolation by column chromatography.[8,11] Excess acid (10-fold), furthermore, consumes **3** and **4** (or **5** and **6**) over 24 h at room temperature and eliminates the acetate. The methyl or ethyl acetate, identified by IR and NMR, was measured (53–58%) by quantitative IR analyses using the acetate ν_{CO} at 1735 cm^{-1}.

Phosphine substituted alkoxyacetyl complexes **3a,b** also serve as precursors to ethylene and acetaldehyde, but first the acyl ligand is activated as the cationic α,β-dialkoxyethylidene compounds CpFe(CO)PPh_3[C(OR′)CH_2OR]$^+$ [**7a**, R′ = Et, R = Me; **7b**, R′ = R = Et; **7c**, R′ = Me, R = Me].[12] This activation renders the α carbon of **7** sufficiently electrophilic for hydride addition from nucleophilic hydride donors.[13] We prepared **7a–c** by alkylation of **3** with $R'_3O^+PF_6^-$ in CH_2Cl_2; recrystallization from CH_2Cl_2–ether gave 70% yields of **7a–c** as air-stable yellow salts.



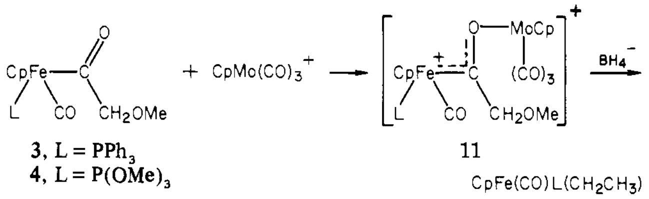
3 **7**

In accordance with the α-alkoxyalkylidene structures depicted,[15a,17b] excess iodide effects quantitative dealkylation of **7a–c** back to **3**. Use of the appropriate borohydride reagent, however, leads to selective addition of 1 or 2 hydride equiv at the activated α carbon of **7a–c**.

Treatment of **7a–c** with 1 equiv of $Ph_3PMe^+BH_4^-$ in CH_2Cl_2 and recrystallization from CH_2Cl_2–heptane affords the ethyl complex CpFe(CO)PPh_3(CH_2CH_3) (**8**) in 69% yield. No other organometallic products were detected. Absence of CpFe(CO)PPh_3(CH_2CH_2OR) stems from the susceptibility of the β-alkoxyethyl ligand to Lewis acid (e.g., BH_3) induced reduction to the ethyl ligand.[17] Others established that **8** produces either ethane upon protonation[11a] or ethylene upon heating above 60 °C.[18] We additionally obtained ethylene by converting **8** into CpFe(CO)PPh_3(η^2-$CH_2{=}CH_2$)$^+$ (**9**) with Ph_3C^+[19] and then either warming **9** to 40 °C or treating it with excess iodide.

Two carbonyl ligands on $CpFe(CO)_3^+$ (**1**) were also converted to acetaldehyde. One equivalent of $LiHBEt_3$ or LiHB(*sec*-Bu)$_3$ in THF (−80 °C) transforms **7** into the formylmethyl complex CpFe(CO)PPh_3(CH_2CHO) (**10**)[20] as the only organometallic product[21]—isolated in 63% yield after extraction with ether and precipitation with pentane. We released acetaldehyde from CH_2Cl_2 solutions of **10** by adding 1 equiv of trifluoromethanesulfonic acid. Acetaldehyde was identified by its 2,4-dinitrophenylhydrazone (isolated in 42% yield) and was determined directly (48%) by quantitative analysis of its IR ν_{CO} 1716-cm^{-1} absorption.

Now that stoichiometric conversion of two CO ligands selectively to the aforementioned C_2 organic compounds has been realized, our efforts have been directed toward replacing the borohydride and carbocation reagents used in Scheme I with transition-metal analogues. We recently reported that transition organometallic hydride complexes effect intermolecular hydride transfer to α-alkoxyethylidene ligands.[16] Carbocation reagents also can be replaced: $CpMo(CO)_3^+$[23] coordinates the acyl ligand of **3** and **4** and gives cationic μ_2-acyl complexes **11** that are activated to reduction by nucleophilic hydride donors. The reaction of **3** or **4** with $CpMo(CO)_3^+$ in CH_2Cl_2 at −40 °C and addition of $PPh_3Me^+BH_4^-$ at 0 °C thus gives the ethyl complexes CpFe(CO)L(CH_2CH_3) [**8**, L = PPh_3; $P(OMe)_3$] in 33–38% yield after column chromatography.[24] We would ultimately like to develop an organometallic system in which metal reagents activates CO and subsequent ligands (including bimetallic activation of acyl ligands) to intermolecular reduction by transition-metal complexes.[25]



3, L = PPh_3
4, L = $P(OMe)_3$
11

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged.

---

[10] The analogous rearrangement of $CpFe(CO)_2COCH_2OMe$ to a ketene–acetal complex $CpFe(CO)_2CH_2C(OH)OMe^+$ has been reported: Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 381–391.

[11] **5a**: Flood, T. C.; Miles, D. L. *J. Organomet. Chem.* **1977**, *127*, 33–44.

[12] **7a**: IR (CH_2Cl_2) 1987 (C≡O) cm^{-1}; NMR (acetone-d_6) δ 7.57 (br s, 15, PPh_3), 5.04 (s, 5, Cp), 4.37 (m, 2, OCH_2CH_3), 3.96 (br s, 2, CH_2OMe), 3.48 (s, 3, OCH_3), 1.43 (t, J = 7.0 Hz, 3, OCH_2CH_3). **7b**: IR (CH_2Cl_2) 1988 (C≡O) cm^{-1}; NMR (acetone-d_6) δ 7.57 (br s, 15, PPh_3), 5.04 (s, 5, Cp), 4.36 (quartet, J = 7.0 Hz, 2, $FeCOCH_2CH_3$), 4.06 (br s, 2, CH_2OEt), 3.68 (quartet, J = 7.0 Hz, 2, $CH_2OCH_2CH_3$), 1.40 (t, J = 7.0 Hz, 3, $FeCOCH_2CH_3$), 1.32 (t, J = 7.0 Hz, 3, $CH_2OCH_2CH_3$). Anal. Calcd for $C_{30}H_{32}O_3P_2FeF_6$: C, 53.55; H, 4.80. Found: C, 53.23; H, 5.03. **7c**: IR (CH_2Cl_2) 1985 (C≡O) cm^{-1}; NMR (acetone-d_6) δ 7.55 (br s, 15, PPh_3), 5.06 (s, 5, Cp), 4.17 (s, 3, $FeCOCH_3$), 3.91 (br s, 2, CH_2), 3.48 (s, 3, CH_2OCH_3).

[13] Nucleophilic hydride-donating reagents generally do not add hydride to the acyl ligand.[14] CpFe(CO)PPh_3($COCH_3$), for example, is inert to CH_2Cl_2 solutions of $Ph_3PMe^+BH_4^-$ at room temperature. Alkylation of the acetyl group—giving α-alkoxyethylidene complexes CpFe(CO)PPh_3[C(OR)CH_3]$^+$ (**12**)—according activates the α carbon to reaction with borohydride reagents.[15,16,17b] We found that 1 equiv of $Ph_3PMe^+BH_4^-$ in CH_2Cl_2 selectively reduces **12** to the ethyl complex **8** (77% yield after recrystallization from CH_2Cl_2–heptane), whereas $LiHBEt_3$ in THF gives exclusively CpFe(CO)PPh_3[CH(OR)CH_3] (70% yields after similar purification).[16]

[14] Van Doorn, J. A.; Masters, C.: Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245–254. Gladysz, J. A.; Selover, J. C. *Tetrahedron Lett.* 1978, 319–322. Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1979**, *171*, 65–71.

[15] (a) Davison, A.; Reger, D. *J. Am. Chem. Soc.* **1972**, *94*, 9237–9238. (b) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794–797. (c) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.*, in press.

[16] Bodnar, T.; LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 3292–3294.

[17] (a) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93–109. (b) BH_3 reagents also reduce α-alkoxymethyl complexes CpFe(CO)PPh_3(CH_2OR) to CpFe(CO)PPh_3(CH_3): Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604–606. Thus both α- and β-alkoxyethyl complexes should react with the BH_3 byproduct and give **8**.

[18] Su, S.; Wojcicki, A. *J. Organomet. Chem.* **1971**, *27*, 231–240. Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2769–2794.

[19] Chow, C.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271–7278.

[20] Formylmethyl complex **10** was independently synthesized in 56% yield by photolytic replacement of CO by PPh_3 on $CpFe(CO)_2CH_2CH(OMe)_2$ and chromatography on alumina. **10**: IR (CH_2Cl_2) 1926 (C≡O), 1635 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 9.18 (m, 1, CHO), 7.31 (br s, 15, PPh_3) 4.27 (s, 5, Cp), 1.75 (m, 1, $FeCH_2$), 1.01 (m, 1, $FeCH_2$). anal. Calcd for $C_{26}H_{23}O_2FeP$: C, 68.74; H, 5.10. Found: C, 68.59; H, 5.26.

[21] Exclusive formation of **10** requires monohydridic reduction of **7** to an α,β-dialkoxyethyl complex CpFe(CO)PPh_3[CH(OR′)CH_2OR],[22] which then suffers electrophile (e.g., BEt_3) induced ionization to a η^2-vinyl ether compound CpFe(CO)PPh_3[$CH_2{=}CHOR$]$^+$. Solvolysis then provides **10**. A similar set of reactions accounts for transformation of $CpFe(CO)_2CH_2CH(OMe)_2$ to $CpFe(CO)_2CH_2CHO$.[10]

[22] Monhydridic reduction has been established for $CpFe(CO)_2$[C(OEt)CH_2OMe]$^+$: 1 equiv of $LiHBEt_3$ in THF (−80 °C) provides $CpFe(CO)_2$[CH(OEt)CH_2OMe] in about 40% yield after reprecipitating twice from cold ether–pentane. The resulting brown oil has not been further purified; its spectral data are in accord with impure α,β-dialkoxyethyl complex as the only organometallic product. Work is continuing with (η^5-C_5Me_5)$Fe(CO)_2$ analogues in an attempt to obtain crystalline samples: Bodnar, T.; Cutler, A., work in progress.

[23] Beck, W.; Schloter, K. *Z. Naturforsch. B* **1978**, *33B*, 1214–1222.

[24] Bimetallic acyl complexes **11** were not isolated. However, the four analogous compounds Cp(CO)LFe{CO[M(CO)$_n$Cp]CH_3}$^+$ [L = CO, PPh_3; M = Fe (n = 2), Mo (n = 3)] have been characterized. Their preparation from the interaction of $CpM(CO)_n^+$ with the requisite acetyl complex, and their subsequent reactivity toward nucleophiles will be reported: LaCroce, S.; Cutler, A., manuscript in preparation.

[25] A preliminary account is appearing in: ACS *Symp. Ser.*, in press.