especially grateful to Dr. Donald J. Daigle of the USDA Southern Regional Research Center (New Orleans, LA) for the generous sample of 1. The assistance of Matthew Holtcamp and Nicole White is gratefully acknowledged.

Supplementary Material Available: Tables giving details of catalyzed hydrogenation processes using **4a** as catalyst, an ORTEP drawing of **2b**, and X-ray crystallographic tables for compounds **2a**, **2b**, and **4b**, including the atomic coordinates, anisotropic thermal parameters, bond angles, and bond distances (14 pages). Ordering information is given on any current masthead page.

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Bimetallic Iron Complexes with Carboxyethylene Bridges

Dorothy H. Gibson,* Jaime O. Franco, Michael T. Harris, and Tek-Sing Ong

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

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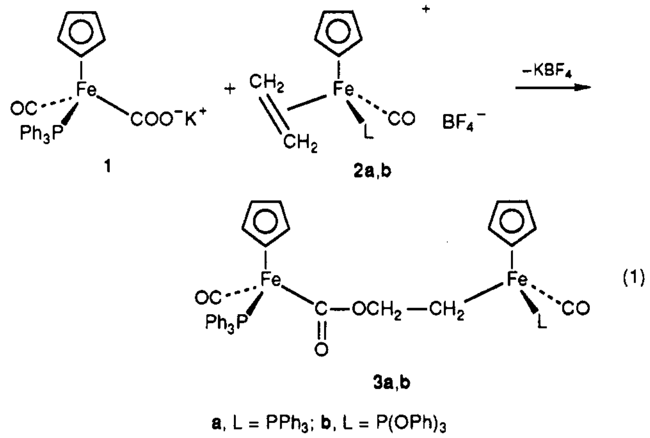
Summary: Reactions of the iron metallocarboxylate anion $CpFe(CO)(PPh_3)COO^-K^+$ (**1**) with ethylene-coordinated cations $CpFe(CO)(L)(C_2H_4)^+BF_4^-$ ($L = PPh_3, P(OPh)_3$) yield bimetallic complexes with a carboxyethylene bridge (**3a,b**); a pair of diastereomers, formed in nearly equal amounts, is produced in each case. Reactions of the bimetallic compounds with excess HBF_4 yield $CpFe(CO)_2(PPh_3)^+BF_4^-$ and $CpFe(CO)(L)(C_2H_4)^+BF_4^-$. Methanolysis of the carboxyethylene complexes yields $CpFe(CO)(PPh_3)COOCH_3$ and $CpFe(CO)(L)CH_2CH_2OCH_3$ (**7a,b**). Solvolysis of the latter compounds in ethanol gives the corresponding ethoxyethyl complexes **8a,b**. All new compounds have been fully characterized.

One of the ways being sought to utilize CO_2 as a building block for organic compounds involves its catalytic combination with alkenes, including ethylene. Several model stoichiometric reactions have been reported in which metal-bound ethylene has combined with CO_2 to generate new compounds, usually metallacycles;[1] in each product, the newly added carboxylate group is bound through oxygen to a transition-metal center. Also, bimetallic complexes with two acrylate bridging groups have been formed by insertion of CO_2 into carbon-hydrogen bonds in coordinated ethylene ligands.[2] Both catalytic and stoichiometric reactions have been initiated through C–C bond formation; new C–O bonds resulted from subsequent chemical degradations and afforded carboxylic acids or their derivatives (e.g., esters and lactones). The oxophilicity of the metal center does not seem to be critical, since early and late transition metals yield the same types of products. It has been often assumed that binding of CO_2 to the metal center precedes the reaction with a coordinated ethylene (or diene) ligand, but tangible evidence for this assumption is sparse.[3]

As noted previously, the binding of an alkene to a transition metal renders the alkene more susceptible to nucleophilic attack, particularly when the metal complex is cationic.[4] The increased reactivity has been attributed to "slippage" of the alkene to resemble an η^1 complex. Examples of the addition of nitrogen, phosphorus, and oxygen nucleophiles, as well as some carbon nucleophiles, are known.

We have examined the behavior of the carbon dioxide complex $CpFe(CO)(PPh_3)COO^-K^+$ (1)[5] toward ethylene-coordinated cations to determine whether the CO_2 ligand would be activated toward a metal-bound alkene. Our previous work with compound 1 demonstrated its weakly nucleophilic characteristics through its reactions with strong alkylating agents and with triphenyltin chloride.[5] With the two ethylene complexes[6] we have studied thus far, reactions with 1 lead to bimetallic complexes with bridging carboxyethylene groups:



The compounds are obtained in very good yields (75–83%) as a pair of diastereomers (nearly equal amounts) in each case; separation of the isomers has not yet been accomplished. To our knowledge, this type of coupling of CO_2 to ethylene has not been observed before. The new compounds provide models for catalytic intermediates in

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[1] Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747.

[2] Alvarez, R.; Carmona, E.; Galindo, A.; Gutierrez, E.; Marin, J. M.; Monge, A.; Poveda, M. L.; Ruiz, C.; Savariault, J. M. *Organometallics* **1989**, *8*, 2430.

[3] Braunstein, P.; Matt, D.; Nobel, D. *J. Am. Chem. Soc.* **1988**, *110*, 3207.

[4] (a) Busetto, L.; Palazzi, A.; Ros, R.; Belluco, U. *J. Organomet. Chem.* **1970**, *25*, 207. (b) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (c) Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660. (d) Knoth, W. H. *Inorg. Chem.* **1975**, *14*, 4566. (e) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426. (f) Kegley, S. E.; Bergstrom, D. T.; Crocker, L. S.; Weiss, E. P.; Berndt, W. G.; Rheingold, A. L. *Organometallics* **1991**, *10*, 567. (g) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (h) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.

[5] Gibson, D. H.; Ong, T.-S.; Ye, M. *Organometallics* **1991**, *10*, 1811.

[6] (a) Compound **2a**: Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Compound **2b**: Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155.

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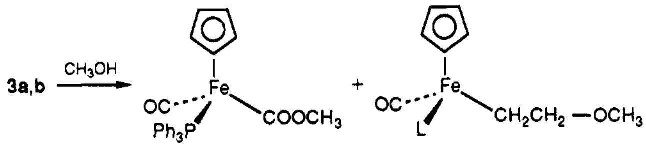
processes which could lead to the synthesis of formate derivatives from alkenes and CO_2.

Compounds **3a,b** have been characterized by elemental analysis and ^1H and ^{13}C NMR and infrared DRIFTS spectroscopy.[7] The DRIFTS spectra show the two bands at 1400–1500 cm^{-1} characteristic of CpFe(CO)(L)X complexes; the band near 1500 cm^{-1} is enhanced in **3b** because of the phosphite ligand. Absorptions at approximately 1000 and 1600 cm^{-1} are assigned to the carboxyl group and are similar to those of metallocarboxylate esters in this series.[5] ^1H NMR spectra show the sets of diastereotopic methylene protons as complex multiplets in **3a,b**. H,H-COSY experiments were required in order to identify the methylene protons of each diastereomer; these experiments also demonstrated the geminal coupling of the low-field methylene protons and vicinal coupling of all methylene protons in each diasteromer. Resonances in the region δ 210–214 of the ^{13}C NMR spectra are assigned to the carboxyl carbons in **3a,b** on the basis of comparisons with other compounds in the present study and with metallocarboxylate esters in this series.[5]

Reactions of **3a,b** with excess $HBF_4 \cdot Et_2O$ result in cleavage of the bimetallics; thus, **3a** yields $CpFe(CO)_2(PPh_3)^+BF_4^-$ (**4**, 93%)[5] and ethylene cation **2a** (74%) while **3b** yields **4** (89%) and **2b** (74%). Acid cleavages of metallocarboxylate esters are known to generate metal carbonyl cations and, presumably, the corresponding alcohols.[8] Therefore, the immediate precursors to **2a,b** in these reactions should be $CpFe(CO)(L)CH_2CH_2OH$ (**5a,b**; L = PPh_3 and $P(OPh)_3$, respectively); reactions of related compounds bearing a β-hydroxyethyl group with acids have been shown to generate ethylene cation complexes.[4d] Hydrolysis reactions of **3a,b** resulted in cleavage but did not afford the β-hydroxyethyl complexes; similarly, reactions of the ethylene cations **2a,b** with aqueous base did not produce **5a,b**.

Solvolysis reactions of **3a,b** with methanol also result in cleavage of the bimetallic compounds:



6

7a, L = PPh_3
b, L = $P(OPh)_3$

Compound **3a** provides **6**[5] (91%) and **7a** (58%); compound **3b** provides **6** (80%) and **7b** (83%). Compounds **7a,b** have been characterized by elemental analysis and by spectral data.[9] ^1H NMR spectra of each of these show four distinct multiplets for the diastereotopic methylene protons. H,H-COSY experiments show that each methylene proton is coupled to all others in each pair of enantiomers. Independently, samples of **7a,b** have been prepared by sodium methoxide addition to the ethylene cations **2a,b**; spectral properties of these compounds are identical with those of the products of the reactions shown above.

The results of the methanolysis reactions are similar to those of a carboxymethylene complex, $[CpRe(NO)(CO)C(O)OCH_2ReCp(NO)(CO)]$, studied by Casey et al.[10] which afforded $CpRe(NO)(CO)C(O)OCH_3$ and $CpRe(NO)(CO)CH_2OCH_3$. The latter product was shown to result from slow (5 days, room temperature) methanolysis of an intermediate hydroxymethyl complex. The solvolysis reactions of **3a,b** are more facile (**3a** requires 2 h at −10 °C; **3b** requires 10 min at room temperature), and we have not been able to observe any intermediate compounds. Solvolyses of **7a,b** in ethanol proceed more slowly: **7a** requires 8 h at −10 °C while **7b** requires 2 days at room temperature to give ethoxyethyl complexes **8a** and **8b**,[11] respectively. Efforts are in progress to establish other characteristic reactions of the bimetallic compounds.

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[7] Procedure for **3a**: In a glovebox under an atmosphere of dry nitrogen, compound **2a** (0.25 g, 0.48 mmol) was slurried in 15 mL of dry THF and the mixture was maintained at −40 °C. Compound **1** (0.24 g, 0.48 mmol) was then added and the mixture stirred 5 min and then warmed to −10 °C and stirred for 2h. The mixture was then cooled to −40 °C again and filtered. The product was precipitated from the filtrate by adding 100 mL of cold (−40 °C) pentane. The product was collected, washed with 2 × 25 mL of cold pentane, and then dried under vacuum (outside the glovebox) to give 0.35 g (83%) of **3a** as a yellow powder. Anal. Calcd for $C_{51}H_{44}Fe_2O_4P_2$: C, 68.48; H, 4.96. Found: C, 68.19; H, 5.08. IR ν_{CO} (Nujol): 1932 (s), 1900 (s), 1595 (m) cm^{-1}. DRIFTS (neat): 1602 (m), 1481 (m), 1434 (s), 1007 (s) cm^{-1}. ^1H NMR spectra showed the two isomers in a 59:41 ratio. ^1H NMR (THF-d_8, −50 °C): major isomer, δ 7.30 (m), 4.52 (m), 4.25 (s), 4.11 (s), 3.90 (m), 1.79 (m), 1.63 (m); minor isomer, δ 7.30 (m), 4.40 (m), 4.28 (m), 4.23 (s), 4.07 (s), 1.77 (m), 1.59 (m). ^{13}C NMR (THF-d_8, −40 °C): major isomer, δ 223.19 (d, J_{PC} = 33.3 Hz), 220.37 (d, J_{PC} = 30.6 Hz), 210.55 (d, J_{PC} = 34.4 Hz), 139.00–128.00 (multiple, overlapping peaks, phenyl carbons), 86.66 (s), 80.81 (s), 72.78 (s), 3.45 (d, J_{PC} = 17.5 Hz); minor isomer, δ 223.19 (d, J_{PC} = 33.3 Hz), 220.58 (d, J_{PC} = 30.8 Hz), 210.23 (d, J_{PC} = 34.4 Hz), 139.00–128.00 (multiple, overlapping peaks, phenyl carbons), 86.60 (s), 80.91 (s), 72.97 (s), 2.98 (d, J_{PC} = 18.7 Hz). Mp: 60–68 °C dec. Procedure for **3b**: In a Schlenk flask under nitrogen, compound **2b** (0.69 g, 1.20 mmol) was added to 20 mL of dry THF and the mixture cooled to −35 °C. Compound **1** (0.59 g, 1.19 mmol) was then added, and the mixture was stirred for 1 h at −10 °C. The mixture was cooled to −60 °C and filtered through a Schlenk vessel. The filtrate was concentrated to 10 mL under vacuum, and then 50 mL of cold (−60 °C) pentane was added to precipitate the product. The solid was collected by filtration, washed with 2 × 50 mL of cold pentane, and then dried under vacuum to give 0.84 g (75%) of the product. Anal. Calcd for $C_{51}H_{44}Fe_2O_7P_2$: C, 64.99; H, 4.70. Found: C, 64.17; H, 4.65. IR ν_{CO} (Nujol): 1925 (vs, br), 1580 (m, br) cm^{-1}. DRIFTS (neat): 1591 (m), 1487 (s), 1456 (m), 1006 cm^{-1}. ^1H NMR spectra showed the two isomers in a 55:45 ratio. ^1H NMR (toluene-d_8, −67 °C): major isomer, δ 4.37 (s), 4.46 (m), 3.95 (m), 3.73 (s), 1.77 (m), 1.64 (m); minor isomer, δ 4.37 (m), 4.32 (s), 3.82 (m), 3.75 (s), 1.79 (m), 1.64 (m). ^{13}C NMR (CD_2Cl_2, −50 °C): δ 220.13 (d, J_{PC} = 31.6 Hz), 220.08 (d, J_{PC} = 30.6 Hz), 219.56 (d, J_{PC} = 48.5 Hz), 213.25 (d, J_{PC} = 33.4 Hz), 213.04 (d, J_{PC} = 33.3 Hz), 151.38 (d, J_{PC} = 6.6 Hz), 136.17 (d, J_{PC} = 45.2 Hz), 133.22 (s), 129.81 (d, J_{PC} = 4.3 Hz), 129.65 (s), 127.97 (d, J_{PC} = 9.2 Hz), 124.78 (s), 121.42 (d, J_{PC} = 3.6 Hz). Cyclopentadienyl and methylene carbon resonances in the ^{13}C NMR spectrum are distinct: major isomer, δ 84.65 (s), 82.36 (s), 72.30 (s), −1.54 (d, J_{PC} = 28.9 Hz); minor isomer, δ 84.60 (s), 82.25 (s), 72.00 (s), −1.32 (d, J_{PC} = 28.2 Hz). Mp: 63–67 °C dec.

[8] Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

[9] Compound **7a**: Anal. Calcd for $C_{27}H_{27}FeO_2P$: C, 68.95; H, 5.79. Found: C, 68.61; H, 5.83. IR ν_{CO} (CH_2Cl_2): 1900 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.40 (s), 4.27 (s), 3.40 (m), 3.17 (s), 1.54 (m), 0.53 (m). ^{13}C NMR (CD_2Cl_2, 18 °C): δ 223.25 (d, J_{PC} = 32.7 Hz), 137.03 (d, J_{PC} = 40.2 Hz), 133.41 (d, J_{PC} = 10.1 Hz), 129.86 (s), 128.42 (d, J_{PC} = 8.8 Hz), 84.59 (s), 81.39 (s), 56.94 (s), 1.13 (d, J_{PC} = 18.5 Hz). The solid melted with decomposition at 120–121 °C. Compound **7b**: Anal. Calcd for $C_{27}H_{27}FeO_5P$: C, 62.57; H, 5.25. Found: C, 62.91; H, 5.26. IR ν_{CO} (pentane): 1940 cm^{-1}. ^1H NMR (C_6D_6, 50 °C): δ 7.05 (m), 3.94 (s), 3.84 (m), 3.65 (m), 3.42 (s), 1.86 (m), 1.68 (m). ^{13}C NMR (acetone-d_6): δ 220.71 (d, 45.8 Hz), 152.54 (d, 7.7 Hz), 130.48 (s), 125.53 (s), 122.25 (d, 4.5 Hz), 83.30 (s), 81.06 (s), 57.01 (s), −0.92 (d, 29.4 Hz). The solid melted with decomposition at 86–88 °C.

[10] Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

[11] Compound **8a**: Anal. Calcd for $C_{28}H_{29}FeO_2P$: C, 69.43; H, 6.04. Found: C, 69.36; H, 6.17. IR ν_{CO} (CH_2Cl_2): 1900 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 7.49 (m), 6.97 (s), 4.09 (s), 3.92 (m), 3.73 (m), 3.49 (q), 1.93 (m), 1.20 (t), 1.14 (m). ^{13}C NMR (C_6D_6): δ 223.17 (d, J_{PC} = 32.7 Hz), 130.17 (d, J_{PC} = 40.2 Hz), 133.13 (d, J_{PC} = 8.8 Hz), 129.30 (d, J_{PC} = 1.3 Hz), 128.02 (d, J_{PC} = 10.1 Hz), 84.20 (s), 79.40 (s), 64.40 (s), 15.80 (s), 1.90 (s). The solid melted with decomposition at 105–107 °C. Compound **8b**: Anal. Calcd for $C_{28}H_{29}FeO_5P$: C, 63.17; H, 5.49. Found: C, 63.49; H, 5.71. IR ν_{CO} (pentane): 1950 cm^{-1}. ^1H NMR (nitrobenzene-d_5, 50 °C): δ 7.44 (m), 4.15 (s), 3.77 (m), 3.68 (m), 3.60 (q), 1.77 (m), 1.51 (m), 1.26 (t). ^{13}C NMR ($CDCl_3$): δ 219.72 (d, J_{PC} = 46.2 Hz), 151.71 (d, J_{PC} = 7.5 Hz), 129.51 (s), 124.58 (s), 121.49 (d, J_{PC} = 5.0 Hz), 82.48 (d, J_{PC} = 1.0 Hz), 78.70 (s), 64.98 (s), 15.64 (s), −1.85 (d, J_{PC} = 29.4 Hz). The solid melted with decomposition at 73–76 °C.