Transition Organometallic Mediated Synthesis of a Malonic Ester from Carbon Monoxide

T. W. Bodnar, E. J. Crawford, and A. R. Cutler*

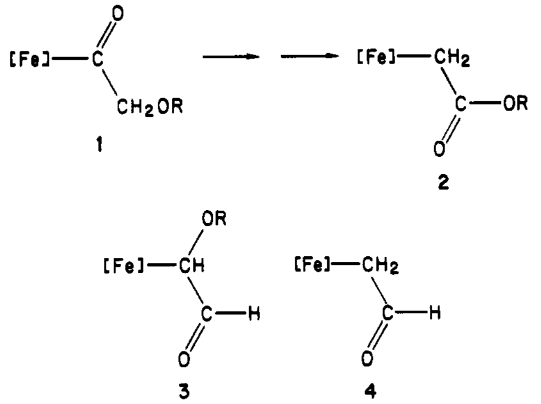
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Received May 20, 1985

Coordinated ligand reactions using the Fp ≡ (η-C_5H_5)$(CO)_2$Fe system as a template for converting three CO groups into the C_3 skeleton of dimethyl malonate, $CH_2(CO_2Me)_2$, are reported. The first CO originates in the previously reported reduction of $FpCO^+$ to $FpCH_2OMe$, which is the precursor to $Fp{=}CH_2^+$. Carbonylation of $Fp{=}CH_2^+$, followed by methanolysis, incorporates the second CO (which was exogenous, not ligated) as the ester carbonyl on the carbomethoxymethyl complex $FpCH_2CO_2Me$ (**2a**). Oxidation-promoted carbomethoxylation of **2a** (using Ce(IV) in methanol) then releases the free malonic ester—the third CO arriving via oxidation-induced alkyl–CO migratory insertion on **2a**. Attempts at independently synthesizing $FpCOCH_2CO_2CH_2CH_3$ by acylating Fp^{1-} with ethyl malonyl chloride are also reported.

Introduction

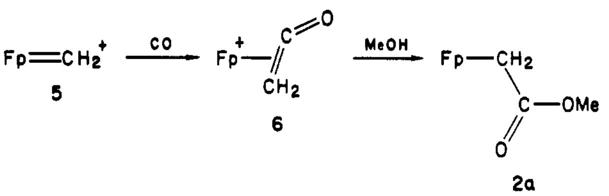
The (η^5-C_5H_5)$(CO)_2$Fe (or Fp) organometallic system and its phosphine- or phosphite-substituted derivatives have been used in synthetic studies for converting ligated carbon monoxide into oxygenated organic molecules.[1,2] Alkoxyacetyl iron complexes 1, with their C_2 ligand originating from two CO groups on $CpFe(CO)_3^+$, accordingly have been transformed selectively into carbalkoxymethyl 2, alkoxyformylmethyl 3, and formylmethyl 4 complexes (eq 1). These complexes, in turn, upon protonolysis afford acetic acid ester, glycoaldehyde ether, and acetaldehyde, respectively.[3]



(1)

[Fe] = Cp(CO)(L)Fe; L = CO, PPh_3, $P(OMe)_3$

Carbalkoxymethyl complexes 2 merit special attention for two reasons. First, the carbalkoxymethyl ligand selectively transforms to other C_2 ligands and hence to other organic products. Electrophilic activation and then reduction at the β-carbon of 2 [L = $P(OCH_3)_3$], for example, afford either the corresponding formylmethyl 4 or ethyl complexes.[3b] Second, this C_2 ligand can be assembled from carbon monoxide by using two different synthetic approaches, the aforementioned isomerization of the alkoxyacetyl system 1 representing one option.[4] Carbonylating Fp methylidene$^+$ **5**[5] and trapping the resulting ketene compound **6** with methanol (eq 2) illustrates the other approach.[6,7] Our present interest is in using carbalkoxymethyl complexes 2 after carbonyl insertion to generate CO-derived C_3-organic molecules.



(2)

Fp = $Cp(CO)_2Fe$

---

(1) Reviews concerned with the stoichiometric reduction of ligated CO: (a) Keim, W. In "Catalysis in C_1 Chemistry"; Keim, W., Ed.; D. Reidel Publishing Co.: Boston, 1983; Chapter 1. (b) Herrman, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (c) Sneedon, R. P. A. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Chapter 50.2. (d) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

(2) The C_1 manifold of coordinated ligands and their reactions extant in converting CO in $Cp(L_1)(L_2)FeCO^+$ (and related Fe or Ru complexes, L_1 and L_2 = phosphine or CO) into an alkoxymethyl or methyl ligand have been extensively documented: (a) Cutler, A. R. *J. Chem. Soc.* **1979**, *101*, 604. Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275. Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 121. (b) Casey, C. P.; Tukada, H.; Miles, W. H. *Organometallics* **1982**, *1*, 1083. Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134. Casey, C. P.; Fagan, P. J.; Day, V. W. *Ibid.* **1982**, *104*, 7360. Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43. (c) May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *234*, C49. (d) Gibson, D. H.; Ong, T.-S. *Organometallics* **1984**, *3*, 1911. (e) Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* **1981**, *215*, C30. See also: Knox, S. A. R. *Pure. Appl. Chem.* **1984**, *56*, 81. (f) Jorswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1049. (g) Kao, S. C.; Thiel, C. H.; Pettit, R. *Organometallics* **1983**, *2*, 914. Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Ibid*, **1982**, *1*, 911. Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *103*, 1627. (h) Davies, S. G.; Hibberd, J.; Simpson, S. J.; Thomas, S. E.; Watts, O. *J. Chem. Soc., Dalton Trans.* **1984**, 701. Davies, S. G.; Moon, S. D. *Nouv. J. Chem.* **1984**, *8*, 139. Davies, S. G.; Simpson, S. J.; Thomas, S. E. *J. Organomet. Chem.* **1983**, *254*, C29. (i) Wright, M. E.; Nelson, G. O. *J. Organomet. Chem.* **1984**, *263*, 371. Sumner, C. E.; Nelson, G. O. *J. Am. Chem. Soc.* **1984**, *106*, 432. Nelson, G. O. *Organometallics* **1983**, *2*, 1474. (j) Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics*, **1983**; *2*, 1461. Lin, Y. C.; Calbrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, 105 1679. (k) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 817. Lapinte, C.; Astruc, D. *J. Organomet. Chem.* **1984**, *260*, C13; J. *Chem. Soc., Chem. Commun.* **1983**, 340. (l) Dawkins, G. W.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41. (m) Brown, D. A.; Glass, W. K.; Turkiubeid, M. *Inorg. Chim. Acta* **1984**, *89*, L47.

(3) (a) Bodner, T.; Coman, G.; LaCroce, S. J.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* **1981**, *103*, 2571. Cutler, A.; Bodnar, T.; Coman, G.; LaCroce, S.; Lambert, C.; Menard, K. In "Catalytic Activation of Carbon Monoxide"; Ford, P., Ed.; American Chemical Society: Washington, D.C., 1981; *ACS Symp. Ser. No. 152*, Chapter 19. (b) Crawford, E.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* **1985**, *107*, 3130. (c) Bodnar, T.; Crawford, E.; Cutler, A., manuscript submitted.

(4) Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 381.

(5) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. Green, M. L. H.; Ishag, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508. (b) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (c) Theoretical studies: Schilling, B. E. R.; Hoffman, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. Kostic, N. M.; Fenske, R. F. *Organometallics*, **1982**, *1*, 974. (d) Bodnar, T. W.; Cutler, A. R. *Organometallics* **1985**, *4*, 1558.

(6) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926.

(7) Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247.

0276-7333/86/2305-0947$01.50/0

We would have preferred adding the third carbonyl directly to $\mathrm{FpCH_2CO_2CH_3}$ (**2a**), obtaining the $\mathrm{C_3}$-carbomethoxyacetyl complex $\mathrm{FpCOCH_2CO_2CH_3}$ (**7a**), but previous attempts at carbonylating **2** (L = CO, $\mathrm{PPh_3}$), even using acid catalysis, instead returned starting material.[7] Complex **2a**, however, upon oxidation-promoted carbonylation in methanol (a net carbalkoxylation reaction[8]) produced dimethyl malonate. In this paper, experimental procedures are presented for (1) converting the methylidene salt **5** to $\mathrm{FpCH_2CO_2CH_3}$ (**2a**) and (2) converting the carbomethoxymethyl ligand (plus CO) into malonic ester.

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere using standard syringe/septum and Schlenk-type bench-top techniques for handling moderately air-sensitive organometallics.[9]

Infrared spectra were taken of $\mathrm{CH_2Cl_2}$ solutions (0.10 mmol/1.5 mL) in a NaCl amalgam-spaced (0.10-mm) solution cell and were recorded on a Perkin-Elmer Model No. 297 spectrophotometer. Varian Models T-60 and XL-200 NMR spectrometers supplied the NMR spectra, which are reported in δ values downfield from $\mathrm{(CH_3)_4Si}$. GLC analyses were performed by using a Gow-Mac Model No. 505 instrument, equipped with 4 ft. by $^1/_4$ in. Cu columns packed with Carbowax-20 M (20%) or DC-200 (20%) on Chromosorb P (80/100 mesh), both kept at 128 °C. Quantitative GLC analyses were done by using an internal standard.

The $\mathrm{AgPF_6}$ was used as received (as a free-flowing white powder) from Ozark Mahoning, but being very hygroscopic it must be stored under nitrogen. Further vacuum drying of this salt at 100 °C did not improve the yields in subsequent synthetic chemistry. Metal carbonyl complexes $\mathrm{Cp(CO)_2Fe^-Na^+}$,[9d] $\mathrm{Cp(CO)_2Fe^-K^+}$,[10] $\mathrm{Cp(CO)_2FeCH_2OCH_3}$,[2a,5a] $\mathrm{Cp(CO)_2FeCH_2Cl}$,[5a] and $\mathrm{Cp(CO)_2FeCH_2CH_3}$[11] were prepared by literature procedures and judged pure by IR and NMR spectroscopy. Authentic samples or spectra of $\mathrm{Cp(CO)_2FeH}$,[2a,12] $\mathrm{Cp(CO)_2FeCl}$,[13] $\mathrm{Cp(CO)_2FeCO^+PF_6^-}$,[2a] $\mathrm{Cp(CO)_2Fe(CH_2{=}CH_2)^+PF_6^-}$,[11b,14] $\mathrm{Cp(CO)_2FeCH_2CO_2CH_3}$ (**2a**),[15] and $\mathrm{[Cp(CO)_2Fe]_2}$[9d] were available from previous studies for direct spectroscopic comparison.

Conversion of $\mathbf{(C_5H_5)(CO)_2FeCH_2Cl}$ to $\mathbf{(C_5H_5)(CO)_2FeCH_2CO_2CH_3}$ (2a). A Fischer-Porter bottle (total volume = 90 mL) containing a Teflon-coated magnetic stirring bar was heated in 150 °C oven for 30 min and cooled to room temperature, while being flushed with nitrogen. The bottle was then purged briefly with carbon monoxide [Caution! An efficient hood must be used.], as a CO-saturated $\mathrm{CH_2Cl_2}$ solution (15 mL) of $\mathrm{AgPF_6}$ (220 mg, 0.87 mmol) was prepared and cooled to −78 °C. This solution was treated with light orange $\mathrm{Cp(CO)_2FeCH_2Cl}$ (196 mg, 0.87 mmol) and immediately pressurized with CO (80 psig). This pressure was maintained as the vigorously stirred suspension (light yellow precipitate) was warmed to room temperature (20 min). The CO pressure then was released, and excess methanol (1.5 mL) was added, with no apparent change in appearance of the light orange suspension. The resulting mixture was filtered through a 0.5-cm pad of Celite, which was washed with $\mathrm{CH_2Cl_2}$ (2 × 10 mL) and then with acetone (3 × 8 mL).

The combined $\mathrm{CH_2Cl_2}$ filtrates were treated with triethylamine (0.3 mL, 2.15 mmol), and the basic solution was passed through a 3 × 3 cm column of alumina. Washing the column with $\mathrm{CH_2Cl_2}$ (35 mL) removed all the yellow organometallics that, after distillation of solvent, left a dark yellow oil. This was extracted with ether (4 × 10 mL) until the extracts were colorless; ether was evaporated to give a dark yellow gum of spectroscopically pure $\mathrm{Cp(CO)_2FeCH_2CO_2CH_3}$ (**2a**) (202 mg, 93% yield): IR ($\mathrm{CH_2Cl_2}$) 2021, 1968 ($\mathrm{C{\equiv}O}$), 1685 ($\mathrm{C{=}O}$) $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$) δ 4.80 (s, 5 H, Cp), 3.56 (3, 3 H, $\mathrm{OCH_3}$), 1.51 (s, 2 H, $\mathrm{FeCH_2}$). The light yellow, ether-insoluble residue (113 mg) corresponded to $\mathrm{(CH_3CH_2)_3NH^+PF_6^-}$.

The combined acetone filtrates were evaporated to leave as light yellow solid (18 mg) a 1:1 mixture of $\mathrm{Cp(CO)_2FeCO^+PF_6^-}$ and $\mathrm{Cp(CO)_2Fe(CH_2{=}CH_2)^+PF_6^-}$ (3% yield each).

When the reaction was repeated, but maintaining 1 atm CO throughout the reaction sequence, the yield of $\mathrm{Cp(CO)_2FeCH_2CO_2CH_3}$ (**2a**) dropped to 81%, after an otherwise identical workup. The yields of $\mathrm{Cp(CO)_2Fe(CH_2{=}CH_2)^+}$ and $\mathrm{Cp(CO)_2FeCO^+PF_6^-}$ were 6% and 3%, respectively. Alternatively, the reaction also was conducted by not supplying the CO until after the $\mathrm{Cp(CO)_2FeCH_2Cl}$ was added (at −78 °C). (The $\mathrm{AgPF_6}$ solution in $\mathrm{CH_2Cl_2}$ was not purged with CO initially.) Introduction of CO (1 atm) immediately into the resulting purple suspension gave an orange mixture, as it warmed to 0 °C (20 min). After addition of methanol and workup, **2a** was obtained in 34% yield, along with $\mathrm{Cp(CO)_2Fe(CH_2{=}CH_2)^+PF_6^-}$ (18%) and $\mathrm{Cp(CO)_2FeCO^+PF_6^-}$ (8%). In other experiments, the purple suspension obtained after adding $\mathrm{Cp(CO)_2FeCH_2Cl}$ to the $\mathrm{AgPF_6}$–$\mathrm{CH_2Cl_2}$ solution (−78 °C) was pressurized with CO (80 psig) immediately and worked up as reported: yields **2a** (44%), $\mathrm{Cp(CO)_2Fe(CH_2{=}CH_2)^+PF_6^-}$ (20%), $\mathrm{Cp(CO)_2FeCO^+PF_6^-}$ (18%).

Conversion of $\mathbf{(C_5H_5)(CO)_2FeCH_2OCH_3}$ to $\mathbf{(C_5H_5)(CO)_2FeCH_2CO_2CH_3}$ (2a). A methylene chloride solution (15 mL) of $\mathrm{Cp(CO)_2FeCH_2OCH_3}$ (195 mg, 0.88 mmol) was cooled (−78 °C), and a stream of CO was bubbled through the clear yellow solution as excess $\mathrm{HBF_4{\cdot}O(CH_2CH_3)_2}$ (0.40 mL, 3.2 mmol) was added. The resulting light orange solution was warmed to room temperature (15 min), the flow of CO was stopped, and the resulting hemiacetal complex $\mathrm{Cp(CO)_2FeCH_2C(OH)(OCH_3)^+PF_6^-}$[4] [IR ($\mathrm{CH_2Cl_2}$) 2041, 1990 $\mathrm{cm^{-1}}$] was neutralized with triethylamine (0.30 mL, 2.14 mmol). This produced an orange solution that was evaporated, vacuum dried briefly (10^{-2} mm, 0.5 h), and chromatographed on alumina. An orange band was eluted cleanly with $\mathrm{CH_2Cl_2}$; it was evaporated to an orange oil that was extracted with ether (30 mL) and evaporated. An orange-yellow gum remained (144 mg after vacuum drying at 10^{-2} mm, 2 h) of spectroscopically pure $\mathrm{Cp(CO)_2FeCH_2CO_2CH_3}$ (**2a**) (55% yield).

Further development of the chromatography column with ether removed $\mathrm{[Cp(CO)_2Fe]_2}$ as a red band and, after removal of solvent, a reddish-black solid [yield 34 mg (24%)].

Carbalkoxylation of $\mathbf{(C_5H_5)(CO)_2FeCH_2CO_2CH_3}$ (2a). An orange-brown solution of $\mathrm{Cp(CO)_2FeCH_2CO_2CH_3}$ (**2a**) (160 mg, 0.64 mmol) in 10 mL of methanol was purged with CO as it was cooled to −78 °C. Carbon monoxide was bubbled vigorously through the solution as $\mathrm{(NH_4)_2Ce(NO_3)_6}$ (1.75 g, 3.19 mmol) was added in one portion. The ceric salt slowly dissolved as the reaction was warmed to −30 °C and held at this temperature for 0.5 h (1 atm of CO). This dark green supernatant afforded a dark green solution as the reaction mixture then approached room temperature (0.5 h). The reaction was added to 30 mL of water and extracted with $\mathrm{CH_2Cl_2}$ until the extracts were colorless (7 × 2 mL). This pale yellow solution was passed through alumina (10 g), which was washed with ether, and the combined effluents were evaporated. This product was identified as dimethyl malonate by comparing its IR and ^{1}H NMR spectra and its GLC

---

(8) Daub, G. W. *Prog. Inorg. Chem.* **1977**, *22*, 409. Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57. Kochi, J. K. In "Organometallic Mechanisms in Catalysis" Academic Press: New York, 1978; Chapter 18. Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

(9) (a) Eisch, J. J. "Organometallic Synthesis"; Academic Press: New York, 1981; Vol. 2. (b) Brown, H. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975. (c) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill, New York, 1969. (d) King, R. B. "Organometallic Synthesis"; Academic Press: New York, 1965; Vol. 1.

(10) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263. Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284.

(11) (a) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104. (b) Green, M. L. H.; Nagy, P. *J. Organomet. Chem.* **1963**, *1*, 58.

(12) Fergusson, S. B.; Sanderson, L. J.; Shackleton, T. A.; Baird, M. C. *Inorg. Chim. Acta* **1984**, *83*, L45.

(13) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 68. Fischer, E. O.; Moser, E. *Inorg. Synth.* **1970**, *12*, 35.

(14) Knoth, W. H. *Inorg. Chem.* **1975**, *14*, 1566. Cutler, A.; Entholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

(15) (a) King, R. B.; Bisnette, M.; Fronzaglia, A. *J. Organomet. Chem.* **1966**, *5*, 341. (b) Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* **1969**, 1309. (c) Aumann, R.; Wörmann, H. *Chem. Ber.* **1979**, *112*, 1233. Also ref 3a, 4, and 6.

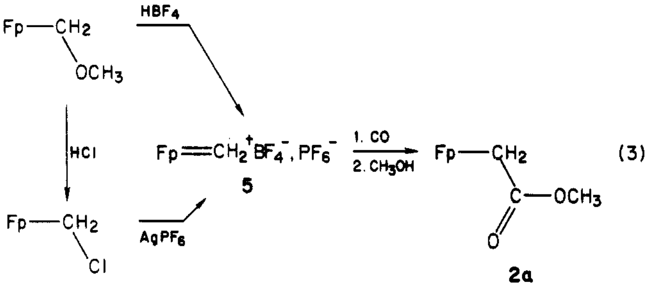
(16) (a) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. King, R. B. *Ibid.* **1975**, *100*, 111. (b) Siegl, W. O.; Collman, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 2516. Engelbrecht, J.; Greiser, T.; Weiss, E. *J. Organomet. Chem.* **1981**, *204*, 79. (c) Galamb, V.; Pâlyi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Y. T. *Ibid.* **1981**, *209*, 183.

traces on both columns with those of an authentic sample. By these procedures, neither methyl acetate nor methyl methoxyacetate were detected. Quantitative GLC analyses on the DC 200 column, using ethyl propionate as the internal standard, established a 53% yield of $CH_2(CO_2CH_3)_2$.

The same carbalkoxylation reaction, but using $Cp(CO)_2FeCH_2CH_3$ and ethanol, was carried out as a control. Workup and evaporation of the solvent (0 °C) left a light brown oil that was identified by IR and ^1H NMR spectroscopy and by GLC on both columns as chemically pure ethyl propionate. Quantitative GLC analysis on the DC 200 column, using dimethyl malonate as the internal standard, determined a 71% yield of $CH_3CH_2CO_2CH_2CH_3$.

Results and Discussion

The Fp carbomethoxymethyl complex (**2a**)[15] was synthesized by carbonylating the extremely reactive Fp methylidene salt, **5**, and then treating the reaction mixture with methanol (eq 3). Although both the Fp chloromethyl and methoxymethyl complexes serve as precursors to **5** (after chloride abstraction with $AgPF_6$ and protonation with HBF_4, respectively), the former proved more convenient. Once generated, $Fp{=}CH_2^+$ (**5**) must be used immediately at −80 °C, or otherwise it degrades to $Fp(CH_2{=}CH_2)^+$ and Fp^+ (hence $FpCO^+$ by disproportionation).[5] But in the presence of carbon monoxide, **5** affords the stable η^2-(*C*,*C*)-ketene compound **6** (eq 2) in essentially quantitative yield.[6] In this study, however, we intercepted the in situ generated **6** with methanol as the (carbomethoxymethyl)Fp complex (**2a**), (eq 3).



5

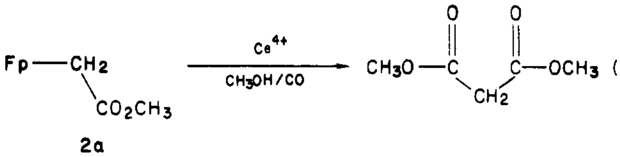
2a

(3)

The isolated yields of **2** after chromatography depended on the procedure adopted in generating $Fp{=}CH_2^+$. With the $FpCH_2Cl/AgPF_6$ procedure, the yield of **2a** varied from 82% (1 atm of CO used) to 93% (5.4 atm of CO), whereas with $FpCH_2OCH_3/HBF_4$ (1 atm of CO) only a 55% yield of **2a** was obtained. Both procedures, as detailed in the Experimental Section, are straightforward; the most important experimental variable is that the reaction mixture must be saturated with CO as **5** is generated. Otherwise greatly diminished yields of **2a** result. The final triethylamine quench engendered in both procedures deprotonates the ketene acetal intermediate[4] $FpCH_2C(OCH_3)(OH)^+PF_6^-$ to **2a**.

Many examples of transition organometallic carbalkoxymethyl complexes have been reported, although nearly all were prepared by reacting an organometallic nucleophile with chloro- or bromomethylacetate.[1b,15a] This route unfortunately provides only very low yields of **2a**.[4,15a,b] Protic isomerization of alkoxyacetyl complexes **1**, in contrast, readily affords organoiron carbalkoxymethyl complexes (eq 1) in good yields.[3a,b,4] We have already presented arguments favoring the intermediacy of ketene complexes (e.g., **6**) during this isomerization, and, in fact, both $FpCOCH_2OCH_3$ and $FpCH_2CO_2CH_3$ (**2a**) afford **6**[3b] in strong acids. A final carbomethoxymethyl complex, $(CO)_4FeCH_2CO_2CH_3^{1-}$, resulted from the reaction of methoxide and the diferracyclopropane complex $Fe_2(\mu\text{-}CH_2)(CO)_8$, presumably via coupling of the CH_2 bridge and methoxycarbonyl ligand.[17]

Oxidation-induced carboalkoxylation of $FpCH_2CO_2Me$ (**2a**) affords the C_3 dimethyl malonate from the carbomethoxymethyl ligand (eq 4). Under standard carbalkoxylation conditions—5 equiv of $Ce(NH_4)_2(NO_3)_6$ in methanol at −30 °C (1 atm of CO)—**2a** afforded its malonic ester in 53% yield. The product was identified by its IR and ^1H NMR spectral data and its GLC retention time. As a control, the same reaction with Fp ethyl (eq 5) afforded ethyl propionate in 71% yield.

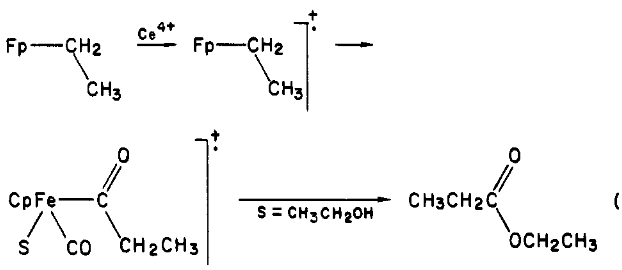


2a

(4)

We cannot account for the lower yield of malonic ester vs. the control reaction giving ethyl propionate. Certainly the starting **2a** is consumed, and, further, no other organometallics are detected. Neither were methyl acetate nor methyl methoxyacetate, potential degradation products of $Cp(CO)FeCOCH_2CO_2CH_3^{+\cdot}$ in methanol, detected by GLC or by IR and NMR spectroscopy. It must be noted, however, that very little information is available concerning carbalkoxylation of alkyl complexes bearing heteroatom substituents.[18]

The one-electron oxidation of **2a**, as with other Fp alkyl complexes, nevertheless, greatly facilitates the alkyl–CO migratory insertion reaction, as recently adduced by Giering,[19] Kochi,[20] Bly,[21] and their respective co-workers. This enhanced migration in fact had been assumed for a number of years in the oxidatively induced carbalkoxylation of transition organometallic alkyl complexes (eq 5).[8,22] In this reaction, it is assumed that solvent alcohol attacks the acyl ligand in the resulting 15- or 17-electron acyl complex. Two salient points, however, must be noted.



(5)

---

[17] (a) Keim, W.; Röper, M.; Strutz, H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 432. (b) Metal-surface bound carbalkoxymethyl ligands have been implicated via labeling studies in the synthesis of alcohols during Fischer–Tropsch processes. Hackenbruch, J.; Keim, W.; Röper, M.; Strutz, H. *J. Mol. Catal.* **1984**, *26*, 129.

[18] Oxidative carbalkoxylation of Fp-β-aminoalkyl complexes extrudes β-lactams: Wong, P. K.; Madhavarao, M.; Marten, D. F.; Rosenblum, M. *Ibid.* **1977**, *99*, 2823. Berryhill, S. R.; Rosenblum, M. *J. Org. Chem.* **1980**, *45*, 1984. Berryhill, S. R.; Price, T.; Rosenblum, M. *Ibid.* **1983**, *48*, 158. Javaherl, S.; Giering, W. P. *Organometallics* **1984**, *3*, 1928. Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441.

[19] Magnuson, R. H.; Zulu, S.; T'sai, W.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887. Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *Ibid.* **1982**, *104*, 5790; *Organometallics* **1983**, *2*, 460.

[20] Klinger, R. J.; Kochi, J. K. *J. Organomet. Chem.* **1980**, *202*, 49.

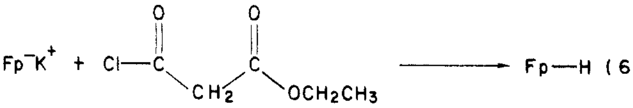
[21] Bly, R. S.; Silverman, G. S.; Hossain, M. M.; Bly, R. K. *Organometallics* **1984**, *3*, 642. Bly, R. S.; Silverman, G. S.; Bly, R. K. *Ibid.* **1985**, *4*, 374.

[22] For examples of oxidative alkoxycarbonylation of Fp alkyl complexes: Anderson, S.; Fong, C.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1973**, *163*. Nicholas, K. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 4449. Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *Ibid.* **1974**, *96*, 2814. Lennon, P.; Rosan, A. M.; Rosenblum, M. *Ibid.* **1977**, *99*, 8426. Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521. Reger, D. L.; Mintz, E. *Organometallics* **1984**, *3*, 1759. Wright, M. E.; Hoover, J. F.; Nelson, G. O.; Scott, C. P.; Glass, R. S. *J. Org. Chem.* **1984**, *49*, 3059. Wright, M. E. *Organometallics* **1983**, *2*, 558.

First, the CO incorporated into the organic ester originates from within the complex, even though somewhat higher yields of this ester result in the presence of exogenous CO. Second, acyl ligands (at least on neutral Fp complexes) are not otherwise susceptible to nucleophilic attack (e.g., alcoholysis)[23] unless they are activated as their 17-electron cation radical compound.

Clearly one or more carbomethoxyacetyl complexes, as 18-electron (**7a**)[24] and/or 17-electron (as in eq 5) species, must intervene during carbalkoxylation of **2a**. Only two examples of carbalkoxyacetyl complexes, $(NO)(CO)_2(PPh_3)FeCOCH_2CO_2CH_2CH_3$[25] and $(PPh_3)(CO)_3CoCOCH_2CO_2CH_3$,[26] have been previously characterized, the latter extruding CO at room temperature and leaving $(PPh_3)(CO)_3CoCH_2CO_2CH_3$.[16c,26] Of particular revelance to this study are the results of a recent study by Pályi and co-workers on the carbalkoxylation of $Co(CO)_4CH_2CO_2CH_2CH_3$.[27] Using this carbethoxymethyl complex (which was procured from $Co(CO)_4^-Na^+$ and ethyl bromoacetate) and I_2 in methanol, under 1 atm of CO, they obtained methyl ethyl malonate in up to 70% yield. Other malonate esters recently have been prepared by Rudler and co-workers[28] through "double carbonylation" of $(CO)_8Fe_2(\mu\text{-}CH_2)$ in the requisite alcohol.

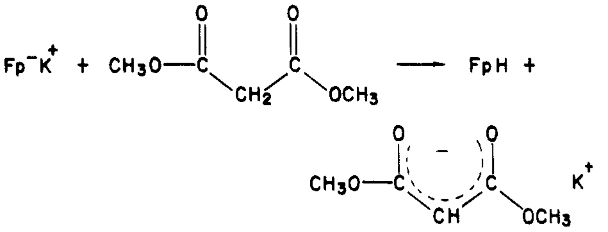
In an attempt to independently synthesize a Fp carbalkoxyacetyl complex, $FpCOCH_2CO_2CH_2CH_3$ (**7b**), Fp^- (Na^+ and K^+ salts) were reacted with ethyl malonyl chloride in tetrahydrofuran (−78 to 20 °C) (eq 6). Certainly this projected acylation reaction (to give **7b**) represents a general procedure for generating transition organometallic acyl complexes.[16] FpH, instead, formed in 85% yield, with the remaining organometallic fraction corresponding (by IR spectroscopy) to Fp_2 and FpCl. Excess CCl_4 derivatized the FpH as FpCl (90%).[2a,12]



(6)

The organic residue from the Fp^- reaction with ethyl malonyl chloride was not identified. The IR spectrum within the 1760–1600 cm^{-1} organic carbonyl ν(CO) region exhibited a very broad absorption centered at 1745 cm^{-1}, which was independently reproduced after treating ethyl malonyl chloride (in THF) with excess triethylamine. This latter dehydrochlorination reaction should generate ethoxycarbonylketene dimer.[29]

That simple proton transfer from the ethyl malonyl chloride to Fp^- occurs initially is consistent with the results of treating Fp^-K^+ (in THF) with dimethyl malonate. Essentially quantitative protonation of Fp^- occurred (eq 7). (The FpH also was derivatized as FpCl by adding CCl_4.) In this reaction, however, the enolate was detected by IR spectroscopy [ν(CO) 1685, 1661 cm^{-1}], and acid treatment (HCl) immediately regenerated the malonic ester. The same enolate results upon deprotonating dimethyl malonate in THF solution with KH.[29]



(7)

In summary, we have converted three CO groups to the C_3 skeleton of a malonic ester. The first CO originated in the reduction of $FpCO^+$ to $FpCH_2OCH_3$ (the methoxyl group deriving from solvent), followed by transformation to $Fp{=}CH_2^+$. The second CO, exogenous, added to this methylidene ligand and formed the ester carbonyl (after methanolysis) of $FpCH_2CO_2CH_3$ (**2a**). The third CO arrived via oxidation-induced alkyl–CO migratory insertion on **2a** and then methanolysis (i.e., net carbalkoxylation) to eliminate dimethyl malonate.

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

Registry No. **2a**, 12214-69-6; $Cp(CO)_2Fe(CH_2{=}CH_2)^+PF_6^-$, 12082-28-9; $Cp(CO)_2FeCO^+PF_6^-$, 38834-26-3; $Cp(CO)_2FeCH_2C(OH)(OCH_3)^+PF_6^-$, 55337-36-5; $[Cp(CO)_2Fe]_2$, 12154-95-9; CO, 630-08-0; $Cp(CO)_2FeCH_2Cl$, 12107-38-9; $Cp(CO)_2FeCH_2OCH_3$, 12108-35-9; dimethyl malonate, 108-59-8.

---

[23] Johnson, R. W.; Pearson, R. G. *Inorg. Chem.* **1971**, *10*, 2091. Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436. Selover, J. C.; Marsi, M.; Parker, D. W.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *206*, 317.

[24] $Cp(CO)(PPh_3)FeCOCH_2CO_2CH_3$ (**7b**) [prepared by alkylating $Cp(CO)(PPh_3)FeCOCH_2^-Li^+$ with $ClCO_2CH_3$] immediately degrades to $Cp(CO)(PPh_3)FeCO^+$ and $LiCH_2CO_2CH_3$. Alktogu, N.; Felkin, H.; Baird, G. J.; Davies, S. G.; Watts, O. *J. Organomet. Chem.* **1984**, *262*, 49.

[25] Chaudhari, F. M.; Knox, G. R.; Pauson, P. L. *J. Chem. Soc. C* **1967**, 2255.

[26] (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499. (b) Hoff, C. D.; Ungváry, F.; King, R. B.; Marko, L. *J. Am. Chem. Soc.* **1985**, *107*, 666.

[27] Tasi, M.; Galamb, V.; Pályi, G. *J. Organomet. Chem.* **1982**, *238*, C31.

[28] Navarre, D.; Rose-Munch, F.; Rudler, H. *J. Organomet. Chem.* **1985**, *284*, C15.

[29] (a) Lutknitskii, F. I.; Vovsi, B. A. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 487. Ward, R. S. In "The Chemistry of Ketenes, Allenes, and Related Compounds", Part 1; Patai, S., Ed.; Wiley: New York, 1980; Chapter 7. Staudinger, H.; Becker, H. *Chem. Ber.* **1917**, *50*, 1016. (b) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; Chapter 9.