$$Mn(CO)_5CHF^+ + Mn(CO)_5Bz \rightarrow Mn(CO)_5CHPh^+ + Mn(CO)_5CH_2F \quad (8)$$

Mixtures of $Mn(CO)_5Bz$ and D_2 did not show evidence for H/D exchange in any of the fragment ions. Only the deuterated species $Mn(CO)_n(Bz)(D)^+$ were observed (n = 0–4). The proton affinity of the complex was not measured.

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Registry No. $Mn(CO)_5Bz$, 14049-86-6; $[(CO)_5Mn-Mn(CO)_5]$, 10170-69-1.

Preparative and Reaction Chemistry of the Bimetallic μ-Formate and μ-Acetate Complexes $[(\eta\text{-}C_5H_5)(CO)_2Fe]_2O_2CR^+PF_6^-$

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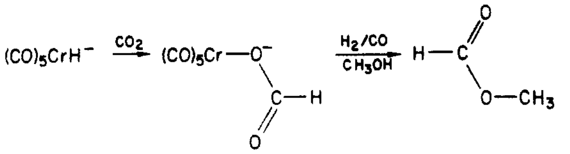
Unidentate η^1-*O* Fp–O_2CR and bimetallic μ-(η^1-*O,O'*) $Fp_2(O_2CR)^+PF_6^-$ carboxylate complexes (R = H, CH_3) have been synthesized and characterized [Fp = (η^5-C_5H_5)$(CO)_2Fe$]. Even though only a formate or acetate ligand bridges the Fp centers, these Fp_2 μ-carboxylate salts do not dissociate in even polar solvents. Nucleophilic hydride donors and other nucleophiles (I^-, PPh_3) cleave these bimetallic salts via direct displacement at an iron center. No evidence was found, using labeling studies, for hydride addition to the μ-(η^1-*O,O'*)-formate bridge and transience of a μ-(η^1-*O,O'*)-methylenedioxy ligand, Fp–OCH_2O–Fp.

Introduction

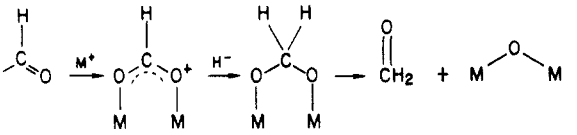
The reduction of carbon dioxide that is suitably ligated to a transition organometallic complex offers an alternative and potentially unique source of C_1 ligands. Most studies to date have elaborated on transforming a metal hydride complex plus CO_2 into coordinated formate.[1] In one set of studies by Darensbourg and co-workers, anionic group 6 metal pentacarbonyl formates—prepared by this procedure—further functioned as catalysts in converting CO_2 (in methanol) to methyl formate (eq 1).[2] Examples



(1)

also abound in the heterogeneous catalysis literature for hydrogenating carbon dioxide (as opposed to CO_2-derived CO) to methanol or to methane—possibly involving formate intermediates.[1] Given these developments it is surprising that information on reducing formate ligated to transition organometallic complexes is generally lacking.

We are interested in establishing coordinated ligand transformations and reaction conditions for reducing ligated formate to formaldehyde (or to methanol). Equation 2 illustrates, as a working hypothesis, one such set of reactions that uses a bimetallic μ-(η^1-*O,O'*)-formate complex 1 as the C_1-template. Its reduction could afford a μ-methylenedioxy system 2[3,4] that subsequently either extrudes formaldehyde or eliminates the starting formate complex $M(O_2CH)$ and metal hydride MH. As possible precedent for the former pathway (eq 2) the reaction between



(2)

1 2

Cp_2ClZrH and CO_2 has been reported by Floriani and co-workers[5] to give $(Cp_2ClZr)_2O$ and formaldehyde. The general problem, however, remains: Carboxylate ligands even as their μ-carboxylate complexes 1 are well established,[6] but their reductive chemistry remains to be developed. With this impetus we now report (1) preparation of examples of symmetrical, bridging μ-(η^1-*O,O'*)-carboxylate compounds 1 from the known Cp-

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(3) A methylenedioxy complex results when formaldehyde forms its μ-(η^1-*O,O'*) acetyl molybdate on polyoxomolybdate. Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Liu, R.-S. *J. Am. Chem. Soc.* **1979**, *101*, 491. Examples of complexes containing methylenedithio ligands are more common; and in a future publication we will present the reaction chemistry of the fully characterized $FpSCH_2SFp$. Menard, K.; Cutler, A. manuscript in preparation.

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$(CO)_2Fe$–(η^1-*O*)-formate (3)[7] and corresponding acetate (4) complexes[8] and (2) reactions of the μ-carboxylate compounds 1 with reducing agents.

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere by using standard syringe/septum and Schlenk-type bench-top techniques for handling moderately air-sensitive organometallics.[9] Solvents for synthetic work and for recording spectral data were deoxygenated by bubbling nitrogen through for ca. 20 min.

Infrared spectra were taken of CH_2Cl_2 solutions (0.10 mmol/1.5 mL—or 3.0 mL for bimetallics) in a NaCl amalgam-spaced (0.10 mm) solution cell and were recorded on a Perkin-Elmer Model No. 927 spectrophotometer. The ν(CO) frequencies (2200–1450 cm^{-1}) were calibrated against the polystyrene 1601 cm^{-1} absorption; they are believed accurate to ±2 cm^{-1} below and ±5 cm^{-1} above 2000 cm^{-1}. Organoiron complexes used in this study exhibit straight-line Beer's law behavior in the IR spectra of their CH_2Cl_2 solutions, which facilitated quantitative monitoring of their reactions through analysis of absorptivity changes in the terminal carbonyl ν(CO) and especially in the carboxylate $\nu_{asym}(CO_2)$ region. By this procedure and using the intense $\nu_{asym}(CO_2)$ absorptions at least 2% of the carboxylate complexes 3, 4, 6, and 7 can be quantified. ^1H NMR spectra were taken of concentrated $CDCl_3$, CD_3NO_2, or $(CD_3)_2CO$ solutions after trace amounts of insoluble residues were centrifuged. $^{13}C\{^1H\}$ NMR spectra were recorded by using $CDCl_3$ or CH_2Cl_2 solutions; coupling constants $^1J_{CH}$ (in Hz) were measured by using the gated-decoupling procedure. Varian Models T-60 and XL-200 NMR spectrometers supplied the NMR spectra, which were reported as δ values in parts per million downfield from internal $(CH_3)_4Si$. Combustion microanalyses were performed by Baron Consulting Co., Orange, CT, and by Mic Anal, Tucson, Az.

Organic reagents were procured commercially and used as received. Methylene chloride was additionally distilled under nitrogen from P_2O_5; the anhydrous ether used either was taken from a freshly opened can or was distilled under nitrogen from sodium benzophenone ketyl. The reagents $Ph_3C^+PF_6^-$[10] and $Ph_3PCH_3^+BH_4^-$[11] were prepared by modifications of published procedures. The titer of the substituted borohydride reagents $LiHB(CH_2CH_3)_3$, $LiDB(CH_2CH_3)_3$, and $KHB[OCH(CH_3)_2]_3$ (as THF solutions from Aldrich Chemical Co.) was assayed by spectral monitoring (IR and NMR) of their reactions with $Cp(CO)(PPh_3)FeC(CH_3)OCH_3^+PF_6^-$.[12] $Fp(THF)^+PF_6^-$[13] was prepared by modification of published procedures,[14] and $Fp(NCCH_3)^+PF_6^-$[13b,15,20] was obtained through treating $Fp(THF)^+PF_6^-$ with acetonitrile and reprecipitating from CH_2Cl_2/ether. Metal carbonyl complexes, $FpCH_3$,[9d] and $Cp(CO)(PPh_3)FeH$[16] also were prepared by literature procedures and judged pure by IR and NMR spectroscopy. Authentic samples and/or spectral data of FpH,[17] FpCl,[18] FpI,[9d] $FpFBF_3$,[14,19] $FpPPh_3^+PF_6^-$,[20] and Fp_2[9d] were available from previous studies for direct comparison.

Preparation of Fp–(η^1-*O*)-Formate: $(\eta^5\text{-}C_5H_5)(CO)_2FeOC(O)H$ (3). To a yellow-brown methylene chloride solution (20 mL) of $FpCH_3$ (0.991 g, 5.16 mmol) was added first 88% formic acid (0.35 mL, 7.74 mmol) and then, with efficient stirring, excess (1.0 mL) $HBF_4{\cdot}O(CH_3)_2$. Gas evolution ensued during this dropwise addition of tetrafluoroboric acid. Immediately after gas evolution ceased (5 min), the resulting dark red solution was neutralized by adding excess anhydrous potassium carbonate (10 g) in portions. The mixture was filtered, and all color was extracted from the potassium carbonate by washing with CH_2Cl_2. IR spectra of the combined orange-brown CH_2Cl_2 filtrates indicate the presence of FpO_2CH (3) and up to 10% Fp_2 as the only organometallic products. This solution was diluted by half with heptane before being concentrated on a Büchi rotovaporator (22 °C, 30 mm). The initial gum that coated the flask during solvent evaporation was discarded, and continued concentration of the supernatant produced red-orange to orange crystals of 3 that were collected, washed with pentane, and vacuum dried: yield 0.602 g (53%); IR (CH_2Cl_2) 2005, 2049 cm^{-1} ($\eta{\equiv}O$), 1617 cm^{-1} (CO_2); IR (KBr) 2003, 2040 cm^{-1} ($C{\equiv}O$), 1609 cm^{-1} ($\nu_{asym}(CO_2)$), 1300 cm^{-1} ($\nu_{asym}(CO_2)$); ^1H NMR ($CDCl_3$) δ 5.06 (s, 5 H, Cp), 7.61 (s, 1 H, O_2CH); ^{13}C NMR ($CDCl_3$) δ 212.01 (CO), 169.6 (d, J_{CH} = 202.9 Hz, O_2CH), 84.82 (Cp).

Anal. Calcd for $C_8H_6O_4Fe$: C, 43.27; H, 2.70. Found: C, 43.30; H, 2.42.

Preparation of Fp–(η^1-*O*)-Acetate: $(\eta^5\text{-}C_5H_5)(CO)_2FeOC(O)CH_3$ (4). A CH_2Cl_2 solution (20 mL) of $FpCH_3$ (0.992 g, 5.16 mmol) was protonated by adding glacial acetic acid (0.35 mL, 5.68 mmol) and then $HBF_4{\cdot}O(CH_3)_2$ (0.85 mL, 10.3 mmol). Workup procedure and observations parallel those for isolating Fp formate 3. Fractional crystallization from CH_2Cl_2–heptane left FpO_2CCH_3 (4) as red-orange crystals: 0.684 g (56%); IR (CH_2Cl_2) 2001, 2052 cm^{-1} ($C{\equiv}O$), 1617, 1601 (CO_2); ^1H NMR ($CDCl_3$) δ 5.03 (Cp), 1.86 (O_2CCH_3); ^{13}C NMR ($CDCl_3$) δ 212.37 (CO), 179.55 (O_2CCH_3), 84.73 (Cp), 22.89 (quart, J_{CH} = 132.9 Hz, O_2CCH_3).

Anal. Calcd for $C_9H_8O_4Fe$: C, 45.79; H, 3.39. Found: C, 45.98; H, 3.17.

Preparation of Fp_2–μ-(η^1-*O*,*O*′)-Formate(1+) (6): $(\eta^5\text{-}C_5H_5)(CO)_2FeOC(H)OFe(CO)_2(\eta^5\text{-}C_5H_5)^+PF_6^-$. A dark red methylene chloride solution (45 mL) containing FpO_2CH (3) (0.678 q, 3.06 mmol) and $Fp(THF)^+PF_6^-$ (1.205 g, 3.06 mmol) turned cloudy over 5 h, and an IR spectrum of this supernatant indicated complete consumption of starting 3. The intense formate $\nu_{asym}(CO_2)$ thus had shifted from 1617 to 1577 cm^{-1}. The combined filtrates, after filtering through Celite (1 cm) and extracting the filter bed with more CH_2Cl_2, were added dropwise to excess ether (200 mL). A light orange to orange-red powder settled immediately. This was filtered, washed with ether, and then freed of remaining solvent first with a stream of nitrogen and then under vacuum (10^{-2} mm, 1 h). The precipitate was redissolved in CH_2Cl_2 (15 mL), layered with ether (40 mL), and stored at +5 °C for 8 h. Dark red crystals that deposited were collected, washed with ether, and vacuum dried. 6: yield 1.17 g (70%); IR (CH_2Cl_2) 2063, 2015 cm^{-1} ($C{\equiv}O$), 1577 cm^{-1} (CO_2); IR (KBr) 2009, 2073 cm^{-1} ($C{\equiv}O$), 1573 cm^{-1} ($\nu_{asym}(CO_2)$), 1361 cm^{-1} ($\nu_{asym}(CO_2)$); ^1H NMR (acetone-d_6) δ 5.45 (s, 10 H, Cp), 7.17 (s, 1 H, HCO_2); ^{13}C NMR (CH_2Cl_2) δ 210.39 (CO), 180.14 (d, J_{CH} = 210.9 Hz, HCO_2), 85.49 (Cp).

Anal. Calcd for $C_{15}H_{11}O_6Fe_2PF_6$: C, 33.10; H, 2.02. Found: C, 32.53; H, 2.13.

Preparation of Fp_2–μ-(η^1-*O*,*O*′)-Acetate(1+) (7): $(\eta^5\text{-}C_5H_5)(CO)_2FeOC(CH_3)OFe(CO)_2(\eta^5\text{-}C_5H_5)^+PF_6^-$. FpO_2CCH_3 (4) (0.401 g, 1.71 mmol) and $Fp(THF)^+PF_6^-$ (0.672 g, 1.70 mmol) were dissolved in CH_2Cl_2 (25 mL), and the reaction was carried out and worked up as described for preparing the μ-formate analogue 6. Dark red crystals of $FpOC(CH_3)OFp^+PF_6^-$ (7) were

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[8] Abbreviations and descriptors: Cp = $\eta^5\text{-}C_5H_5$; THF = tetrahydrofuran; Fp = $Cp(CO)_2Fe$ fragment.

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thus obtained (0.631 g) in 66% yield. Alternatively, the product can be isolated in similar yield by reprecipitating from CH_2Cl_2/excess ether: IR (CH_2Cl_2) 2060, 2010 cm^{-1} (CO), 1545 cm^{-1} (CO_2); ^1H NMR (CD_3NO_2) δ 5.29 (s, 10 H, Cp), 1.88 (s, 3 H, O_2CCH_3); ^{13}C NMR (CH_2Cl_2) δ 211.39 (CO), 188.76 (O_2CCH_3), 85.97 (Cp), 23.65 (quart, *J* = 138.2 Hz, O_2CCH_3).

Anal. Calcd for $C_{16}H_{13}O_6Fe_2PF_6$: C, 34.42; H, 2.33. Found: C, 33.33; H, 2.37.

Reactions of (η^5-C_5H_5)(CO)$_2$Fe(OCOH) (3) and (η^5-C_5H_5)(CO)$_2$Fe(OCOCH$_3$) (4) with $Ph_3C^+PF_6^-$. FpO_2CH (**3**) (249 mg, 1.12 mmol) and $Ph_3C^+PF_6^-$ (217 mg, 0.56 mmol) were dissolved in 16.8 mL of CH_2Cl_2. Neither gas evolution nor other physical changes were detected for this red-orange solution; an IR spectrum after 10 min indicated 95% consumption of starting **3**, concomitant with near quantitative buildup of the μ-formate $Fp_2(O_2CH)^+PF_6^-$ (**6**). This IR spectral monitoring procedure is especially definitive since the formate $\nu_{asym}(CO_2)$ for **3** and **6**, separated by 40 cm^{-1}, are as intense as the metal carbonyl terminal ν(CO). The product μ-formate **6** was isolated by adding the reaction solution to excess ether (80 mL), filtering the red-orange precipitate, washing with ether, and vacuum drying the resulting 212 mg (69%) of spectroscopically pure **6**. Triethyloxonium hexafluorophosphate can be substituted for $Ph_3C^+PF_6^-$ in the above procedure: Results of IR spectral studies were consistent with quantitative conversion of **3** to **6**. The same reaction but using FpO_2CCH_3 (**4**) in place of **3** afforded the same results. Essentially quantitative conversion of **4** to its bimetallic μ-acetate **7** obtained, as ascertained by IR spectroscopy.

Attempted Bridging Carboxylate Ligand Redistribution Reactions. $Fp_2(O_2CH)^+PF_6^-$ (**6**) (22 mg, 0.4 mmol) and FpO_2CCH_3 (**4**) (9 mg, 0.4 mmol) were dissolved in 0.4 mL of CD_3NO_2, and ^1H NMR spectra of the red-orange solution were recorded over 5 h. No change was noted in the spectra: **6**: δ 7.03 (O_2CH) and 5.36 (Cp); **4** δ 5.15 (Cp) and 1.69 (O_2CCH_3). In particular, $Fp_2(O_2CCH_3)^+$ (**7**) was not detected. Aliquots from a CH_2Cl_2 solution (3.3 mL) containing $Fp_2(O_2CCH_3)^+$ (**7**) (61 mg, 0.11 mmol) and FpO_2CH (**3**) (24 mg, 0.11 mmol) were removed over 3 h and were examined by IR spectroscopy. No change in the spectra of this red-orange solution were noted, and $Fp_2(O_2CH)^+$ (**6**) was not observed [$\nu(CO_2)$ 1577 cm^{-1} vs. 1545 cm^{-1} for **7**].

Reaction of (η^5-C_5H_5)(CO)$_2$FeOC(H)OFe(CO)$_2$(η^5-C_5H_5)$^+$-PF_6^- (6) with LiHB(CH_2CH_3)$_3$ and with LiDB(CH_2CH_3)$_3$. In a typical reaction a CH_2Cl_2 solution (2.8 mL) of $Fp_2(O_2CH)^+$ (**6**) (50 mg, 0.09 mmol) was treated with 0.10 mL of a THF solution containing $LiHBEt_3$ (0.09 mmol). The resulting brown solution was assayed by IR spectroscopy as containing 0.038 mmol of FpO_2CH (**3**) (85% yield). In addition, spectra recorded immediately after the borohydride reagent was added FpH [ν(CO) 2016, 1952 cm^{-1}] as the only other organometallic product, approximately equimolar with respect to the concentration of **3**. Solutions quickly degraded, however, as the FpH smoothly converted into Fp_2 [ν(CO) 1998, 1955 cm^{-1}, ν(C=O) 1774 cm^{-1}]. Identity of FpH was confirmed by treating the solution with CCl_4 (0.1 mL): immediate conversion of FpCl [ν(CO) 2057, 2009 cm^{-1}] was effected. During these IR spectral studies the concentration of FpO_2CH (**3**) did not change. Similar results obtained when the reaction was carried out at −80 °C and the IR spectral observations were made at room temperature.

Identical results were obtained by using THF solution of $KHB(OCH(CH_3)_2)_3$ in place of $LiHB(CH_2CH_3)_3$. Reactions between $Fp_2(O_2CCH_3)^+PF_6^-$ (**7**) and $LiHB(CH_2CH_3)_3$ proceeded as reported for **6**, except that the Fp acetate complex **4** was formed.

Attempts at recovering the formate **3** or acetate **4** complexes from these hydride-transfer reactions, however, were thwarted by our inability to get these carboxylate products as solids. The resulting gummy residues, even after column chromatography on Florisil, resisted all attempts at crystallization. IR and NMR spectral studies of these products, however, indicated that only **3** or **4**, Fp_2, and traces of borane residues were present. Continued handling attempts at purifying these residues inevitably yielded insoluble decomposition products.

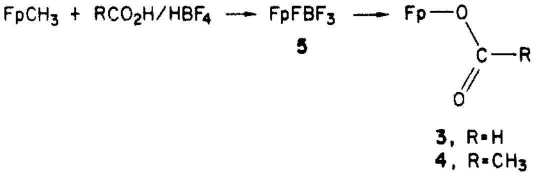
To a dark red solution of $Fp_2(O_2CH)^+PF_6^-$ (**5**) (304 mg, 0.56 mmol) in CH_2Cl_2 (7.6 mL) was added dropwise in THF solution containing $LiDB(CH_2CH_3)_3$ (0.56 mL, 0.56 mmol). The resulting red-brown solution (containing a trace amount of suspension) was left at room temperature for 8 h. Chromatography of the reaction product on Florisil (8 × 1 cm in column) with CH_2Cl_2 cleanly eluted a brown band, which was identified as spectroscopically pure Fp_2 (99 mg, 100%). Further development of the column with acetone cleanly removed an orange-red band that contained FpO_2CH (3) and small amounts of borane residues. As further attempts to purify this orange residue were unsuccessful, it was analyzed by ^1H NMR spectroscopy in $CDCl_3$. Integration of the formate absorption (δ 7.62) vs. the Cp resonance (δ 5.08) provided a 1.0/5.0 ratio.

IR Spectral Observations: Attempted Reduction of (η^5-C_5H_5)(CO)$_2$FeOC(H)OFe(CO)$_2$(η^5-C_5H_5)$^+PF_6^-$ (5) and (η^5-C_5H_5)(CO)$_2$FeO$_2$CH (3). A CH_2Cl_2 solution (5.3 mL) containing $Fp_2(O_2CH)^+PF_6^-$ (*6*) (96 mg, 0.18 mmol) was treated with $Ph_3PCH_3^+BH_4^-$ (52 mg, 0.18 mmol). The red-orange solution, unchanged in appearance, contained FpH as the only organometallic material—in quantitative yield as judged by IR spectroscopy. The FpH converted to FpCl with CCl_4 and transformed to Fp_2 upon sitting at room temperature.

Reaction of FpO_2CH (**3**) (52 mg, 0.23 mmol) in CH_2Cl_2 solution (3.2 mL) with 1 equiv of $BH_3{\cdot}S(CH_3)_2$ in CH_2Cl_2 solution (0.24 mL) effected an immediate color change from red-orange to light orange. An IR spectrum indicated clean conversion of **3** to FpH, which was assayed as above.

Results and Discussion

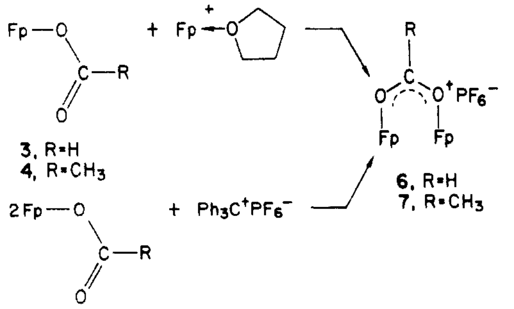
Preparation and Characterization of Bridging Formate and Acetate Complexes. The formate and acetate complexes **3** and **4** required as starting materials were conveniently prepared by protonating $FpCH_3$ (eq 3)



(3)

with mixtures of formic or acetic acids and $HBF_4{\cdot}O(CH_3)_2$ in methylene chloride. Tetrafluoroboric acid cleaves CH_4 from $FpCH_3$ and generates the labile $FpFBF_3$ (**5**),[19] which then reacts with the carboxylic acid. Neither carboxylic acid, in contrast to CF_3CO_2H,[21] cleaves methane from $FpCH_3$ under ambient conditions. Both carboxylate complexes are routinely prepared in over 50% yields as air-stable, red-orange crystalline solids. Alternative preparations of FpO_2CH (**4**), entailing reactions of aqueous sodium formate with $Fp(THF)^+$[7b] or with $Fp(OH_2)^+$,[7a] in our hands proved unreliable.

Two synthetic routes to the bridging carboxylate compounds **6** and **7** were developed. In the first route (eq 4)



(4)

(5)

the labile $Fp(THF)^+PF_6^-$[13] metalated **3** or **4**. IR spectral monitoring of the progress of the reaction was greatly facilitated by the intense carboxylate $\nu_{asym}(CO_2)$ shifting 40 cm^{-1} to lower energy η^1-*O* (**3** and **4**) as transformed to μ-(η^1-*O*,*O*′) (**6** and **7**). In the second synthetic route (eq 5) trityl carbocation abstracted carboxylate from **3** or **4**,

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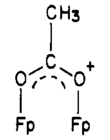
[21] (a) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653. (b) DeLuca, N.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *193*, 359.

and the resulting in situ generated $Cp(CO)_2Fe^+$ Lewis acid ligated the remaining **3** or **4**. Either procedure provides **6** and **7** in good yields as air-stable, red crystals or orange-red precipitates from CH_2Cl_2/ether; these reprecipitate intact from methylene chloride, nitromethane, acetone, or acetonitrile solution and excess ether. We prefer the first synthetic route, however, as it conserves the starting carboxylate complex.

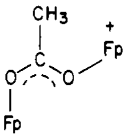
The synthetic procedures for the μ-carboxylate compounds **6** and **7** resemble that used for preparing the μ-halide salts $Fp\text{–}X\text{–}Fp^+$.[15a,22] Graham and Mattson,[19] for example, demonstrated that $FpFBF_3$ (**5**) generated from FpI (eq 6) readily coordinates another FpI as the stable μ-iodide salt.

$$\text{Fp-I} + \text{AgBF}_4 \rightarrow \underset{\mathbf{5}}{\text{FpFBF}_3} \xrightarrow{\text{FpI}} \text{Fp-I-Fp}^+\text{BF}_4^- \quad (6)$$

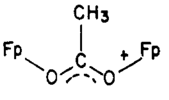
Structures assigned to the Fp_2 μ-carboxylate salts **6** and **7** rest on interpretation of their spectral data. Both Fp groups on each bimetallic compound thus appear spectroscopically (IR and ^1H and ^{13}C NMR) equivalent and have considerable partial positive charge residues on the Fe centers. With $Fp_2(O_2CH)^+$ (**6**), for example, the Cp resonance in the ^1H NMR spectrum (δ 5.36, CD_3NO_2) and the IR terminal carbonyl $\nu(CO)$ (2068, 2022 cm^{-1}, CH_2Cl_2)—both indicators of partial charge at the metal[23]—lie rather close to similar data for $Fp(THF)^+$ [δ 5.43; $\nu(CO)$ 2075, 2028 cm^{-1}]. Appearance of single Cp resonances in the ^1H and ^{13}C NMR spectra of **6** and **7**, however, signifies rapid interconversion (on the NMR time scale) of the syn-syn, syn-anti, and anti-anti isomers. We in fact observed that the ^1H NMR spectrum of **7** in acetone-d_6 was temperature dependent. Upon cooling this solution to –60 °C both Cp and methyl singlets broadened from 3 to 10 Hz (half-height width). Since we have no further information on this solution behavior, the more commonly occurring syn-syn structure will be assumed for **6** and **7**.



syn-syn-**7**

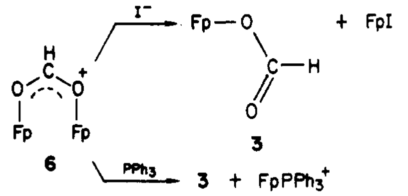


syn-anti-**7**



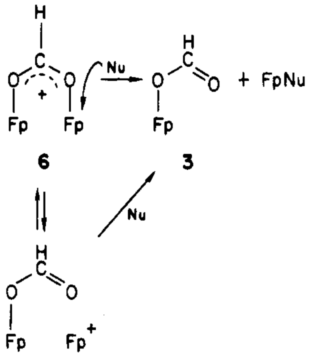
anti-anti-**7**

That the formate ligand transforms from unidentate η^1-*O* (on **3**) to bridging η^1-*O,O′* (on **6**) is especially evident upon examining their IR spectra as KBr pellets. With **3** the difference in the intense carboxylate stretching frequencies, $\Delta\nu = \nu_a(CO_2) - \nu_s(CO_2)$, is 309 cm^{-1}. This rather large value exceeds that for ionic formate ($\Delta\nu$ = 238 cm^{-1} for $K^+O_2CH^-$ as KBr pellet) and is consistent with the unidentate (η^1-*O*) bonding for FpO_2CH (**3**).[24] The corresponding lower $\Delta\nu$ = 212 cm^{-1} value for $Fp_2(O_2CH)^+$ (**6**), in contrast, supports the bridging formate structure.[24,25]



(7)

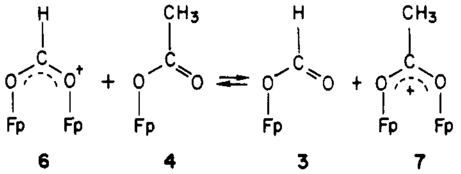
The Fp_2 formate salt **6** undergoes facile bridge cleavage reactions with a variety of nucleophiles. Both iodide and PPh_3 thus cleave **6** to FpO_2CH (**3**) and either FpI[9d] or $FpPPh_3^+$[20] (eq 7), as deduced from IR and ^1H NMR spectral studies. Reactions between $(n\text{-butyl})_4N^+I^-$ or PPh_3 (0.10-mmol each) and 1 equiv of **6** in 3.0 mL of CH_2Cl_2 accordingly proceeded to 85% conversion within 2.0 and 0.5 h, respectively.



(8)

(9)

Two obvious pathways exist for these bridge cleavage reactions. Either the nucleophile (Nu) displaces on the iron center, with FpO_2CH (**3**) as the leaving group (eq 8) or the bimetallic **6** dissociates into **3** and the Lewis acid Fp^+, which the nucleophile then intercepts (eq 9). In the former pathway an interchange mechanism involving either an associative or dissociative transition state (as observed in the CO substitution reactions of metal carbonyls with nucleophiles)[26] accounts for the observed products. Transience of the second pathway, involving initial dissociation of **6**, requires that **6** in solution ionizes into FpO_2CH (**3**)/Fp^+ (eq 8 and 9).



(10)

We looked for redistribution of carboxylate ligands between Fp_2 formate **6** and Fp acetate **4** (eq 10) that would indicate formate bridge dissociation on **6**.[27] If **6** did ionize into **3**/Fp^+, then coordination of **4** with Fp^+ should gradually afford measurable amounts of **7**. NMR spectral monitoring of a CD_3NO_2 solution containing equimolar amounts of **6** and **4** for 5 h, however, established the presence of only starting materials, under conditions that all possible components **1**–**4** would have been discerned. The reverse direction to the postulated equilibrium (eq 10) was also approached by mixing equimolar amounts of **3** and **7** in CH_2Cl_2. IR spectral monitoring (3 h) likewise

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(22) Cotton, F. A.; Frenz, B. A.; White, A. J. *J. Organomet. Chem.* **1973**, *60*, 147.

(23) (a) King, R. B. *Inorg. Chim. Acta* **1968**, *2*, 454. (b) Heberhold, M.; Jablonski, C. R. *Chem. Ber.* **1969**, *102*, 788. Heberhold, M.; Widersatz, G. O.; Kreiter, C. G. *J. Organomet. Chem.* **1976**, *104*, 209. (c) Cutler, A.; Raghu, S.; Rosenblum, M. *Ibid.* **1974**, *77*, 381.

(24) (a) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227. (b) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed; Wiley: New York, 1978, p 232.

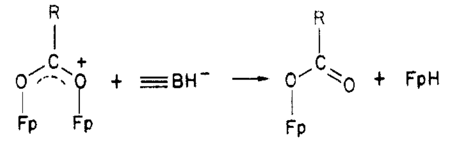
(25) Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295.

(26) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113. Atwood, J. D.; Wovkulich, M. J.; Sonnenberger, D. C. *Acc. Chem. Res.* **1983**, *16*, 350.

(27) Solution stability of **6** in acetonitrile further demonstrates that it does not dissociate into FpO_2CH (**3**)/Fp^+ [eq 8 and 9), since solvent would have intercepted Fp^+ as the nonlabile $Fp(NCCH_3)^+$[15] derivative. Bridged **6** accordingly remains intact for at least 5 h in CH_3CN—neither $Fp(NCCH_3)^+$ nor **3** being detected by NMR spectroscopy. [For $Fp(NCCH_3)^+PF_6^-$, the ^1H NMR spectrum (CD_3NO_2) has its Cp resonance at δ 5.47 vs. δ 5.36 and 5.18 for **6** and **3**, respectively.] Nonlability of $Fp(NCCH_3)^+$ was confirmed by its inability to convert FpO_2CH (**3**) to **6**. IR spectral monitoring of a CH_2Cl_2 solution containing equivalent amounts of $Fp(NCCH_3)^+PF_6^-$ and **3** (0.10 mmol/1.5 mL) established that no reaction occurred after 5 h.

indicated the absence of carboxylate exchange. Therefore, nucleophile-induced bridge-splitting reactions of Fp_2 μ-carboxylates **6** and **7** cannot entail prior dissociation of the carboxylate bridge.[28]

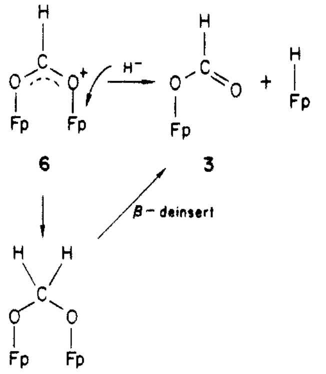
Attempted Reduction of Bridging Formate and Acetate Complexes. Bridging carboxylate compounds $Fp_2(O_2CH)^+$ (**6**) and $Fp_2(O_2CCH_3)^+$ (**7**) upon treating with 1 equiv of monohydride donors $LiHB(CH_2CH_3)_3$ or $KHB[OCH(CH_3)_2]_3$ cleanly suffer carboxylate bridge cleavage (eq 11). Quantitative yields of the corresponding η^1-*O*-carboxylate **3** or **4** and FpH immediately result (as ascertained by IR spectral monitoring), although the FpH subsequently degrades to the iron dimer Fp_2.[29] Identity of FpH was substantiated through its facile conversion to FpCl in the presence of CCl_4.[17] Overall, the stoichiometry of the above reactions between hydride donors[30] and the μ-carboxylate salt **6** or **7** follows the pattern set by reactions of other nucleophiles.



(11)

6, R = H
7, R = CH₃
3
4

Two plausible mechanisms for hydride donors reacting with the Fp_2 carboxylates, e.g., **6**, merit consideration. Hydride could displace at an iron center of **6** (eq 12)—analogous to other nucleophiles—and eliminate FpO_2CH (**3**) as the leaving group; or hydride could add to the μ-carboxylate at its central carbon (eq 13). In the latter pathway the resulting μ-(η^1-*O*,*O*′)-methylenedioxy **8**, an alkoxide complex, should β-deinsert[32] FpH and generate the observed FpO_2CH (**3**).

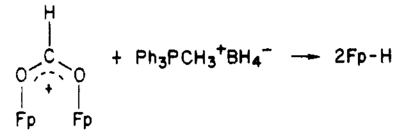


(12)
(13)

6 **3** **8**

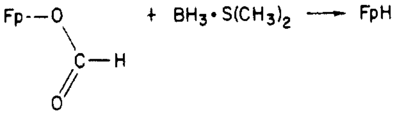
We used the reaction of the Fp_2 μ-formate salt **6** with Super-Deuteride, $LiDB(CH_2CH_3)_3$, as a probe into the intermediacy of the methylenedioxy **8**. If deuteride addition to **6** takes place at the carboxylate ligand, then the resulting FpOCHDOFp should fragment into approximately equal amounts of labeled FpO_2CD and unlabeled FpO_2CH (**3**). When this reaction was carried out, however, only unlabeled formate complex **3** was recovered after column chromatography, thus precluding hydride (deuteride) addition from these trialkylborohydride reagents to the central carboxylate carbon.

Borohydride (BH_4^-) also reduces the μ-formate complex, although reaction of **6** with 1 equiv of $Ph_3PCH_3^+BH_4^-$ in methylene chloride proved unusual in that complete conversion to FpH occurred (eq 14). No IR spectral evidence for any organometallic or carboxylate-containing species (2200–1500 cm^{-1}) was evident. In a relevant reaction, a methylene chloride solution of $BH_3 \cdot S(CH_3)_2$ converted Fp formate **3** to FpH (eq 15)—again a clean transformation as evidenced by IR spectral monitoring. No further studies were carried out other than noting that the FpH formed during the reactions depicted in eq 14 and 15 formed in 85–93% yield and that it converted quantitatively to Fp_2. We infer that borohydride reacts directly with **6** to give FpO_2CH (**3**) (eq 14), BH_3,[33] and the first equivalent of FpH; then BH_3 and **3** affords the second equivalent of FpH.[34]



(14)

6



(15)

3

Conclusions

Fp_2-μ-(η^1-*O*,*O*′)-carboxylate complexes have been prepared and characterized. Even though only a formate or acetate ligand bridges the Fp centers, these compound do not dissociate in even polar solvents. Nucleophilic hydride donors and other nucleophiles evidently react with these bimetallic salts through direct displacement at the iron center. We found no evidence, using labeling studies, for hydride addition to the carboxylate (i.e., formate) bridge

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[28] A number of bimetallic and cluster systems containing μ-(η^1-*O*,*O*′)-formate exhibit facile CO_2 deinsertion (reversibly under some conditions). Presumably these reactions entail formate bridge opening to a labile unidentate formate ligand that subsequently ejects CO_2. Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119. Fisher, J. R.; Mills, A. J.; Sumner, S.; Brown, M. P.; Thompson, M. A.; Puddephatt, R. J.; Frew, A. A.; Manojlovic-Muir, L.; Muir, K. W. *Organometallics* **1982**, *1*, 1421. Darensbourg, D. J.; Pola, M.; Waller, J. *Ibid.* **1983**, *2*, 1285.

[29] Under the conditions of our experiments the FpH produced slowly decomposes to Fp_2 in solution. This metastable behavior, probably analogous to the autocatalytic decomposition of other metal carbonyl hydrides,[29a] has been noted previously when FpH is generated by reactions[17a,29b] other than protonation of Fp^{-1}. Solutions containing FpH that has been prepared by protonating Fp^-,[17b,29c] on the other hand, are more stable. (a) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494. (b) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627. (c) Whitesides, T. H.; Shelly, J. *J. Organomet. Chem.* **1975**, *92*, 215. Wong, A.; Harris, M.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 4529. Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 121.

[30] The reaction between **6** and the organoiron hydride complex Cp(CO)(PPh$_3$)FeH was examined by IR spectroscopy in 1:1 CH_2Cl_2/acetonitrile. This relatively weak hydride donor—it does not reduce acetone—has proved to be an effective reduing agent for alkenes or alkoxycarbenes ligated to Fp^+.[31] Under the above reaction conditions, however, **6** afforded 90% conversion (4 h) to FpH/FpO_2CH (**3**) and $Cp(CO)(PPh_3)Fe(NCCH_3)^+$.

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

[32] (a) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (b) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231. Geoffroy, G. L.; Lehman, J. R. *Adv. Inorg. Radiochem.* **1977**, *20*, 189. (b) Wilczewski, T.; Bochênska, M.; Biernat, J. F. *J. Organomet. Chem.* **1981**, *215*, 87.

[33] Reaction of $Ph_3PCH_3^+RH_4^-$ and CH_3I, for example, gives $Ph_3PCH_3^+I^-$ and liberates CH_4 and BH_3.

[34] (a) It is worth recalling that BH_3 reduces organic carboxylic acids and esters, but not their carboxylate salts. House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 78. Lane, C. F. *Chem. Rev.* **1976**, *76*, 773. (b) In a possibly related reaction, BH_3 upon reacting with acetyl complexes Cp(CO)(L)FeCOCH$_3$ forms significant amounts of the hydride Cp(CO)(L)FeH (in addition to the corresponding ethyl compound). Van Dorn, J. A.; Masters, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245.

and transience of a μ-(η^1-*O,O'*)-methylenedioxy ligand. This report represents our initial venture into synthesizing and attempting to reduce complexes bearing bridging formate ligands; studies in progress are extending this work to analogous bimetallic complexes using early transition-metal centers.

Acknowledgment. Support from the National Science Foundation, Grant CHE-8305484, is gratefully acknowledged.

Registry No. **3**, 42870-99-5; **4**, 53323-73-2; **5**, 76391-69-0; **6**, 96364-03-3; **7**, 96364-05-5; $\mathrm{FpCH_3}$, 12080-06-7; $\mathrm{Fp_2}$, 38117-54-3; $\mathrm{Fp(THF)^+PF_6^-}$, 72303-22-1; FpH, 35913-82-7; FpPCl, 12107-04-9; FpPI, 12078-28-3; $\mathrm{FpPPh_3}$, 32626-58-7; $\mathrm{Cp(CO)(PPh_3)Fe(NCCH_3)^+}$, 47636-90-8; $\mathrm{Cp(CO)(PPh_3)FeH}$, 32660-22-3; $\mathrm{Ph_3PCH_3^+BH_4^-}$, 40001-26-1; $\mathrm{HCO_2H}$, 64-18-6; $\mathrm{CH_3CO_2H}$, 64-19-7.

Studies on Carbonylating Organoiron Alkyl Complexes (η-C_5H_5)(CO)(L)FeR

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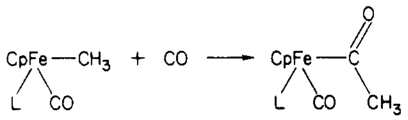
Optimal reaction conditions and ancillary ligand configurations on the (η^5-C_5H_5)$(CO)_2FeCH_3$ "system" are described in order to promote their carbonylation to their corresponding acetyl complexes. Three procedures now are available for promoting CO insertion on this system using 1–6.3 atm of CO. (1) Incorporating an η^5-indenyl (In) and/or PPh_3 ligand in place of Cp and/or CO fine tunes the iron center so that the acetyl compound readily forms. The most reactive methyl complex $\mathrm{In(CO)(PPh_3)FeCH_3}$ in CH_2Cl_2 incorporates CO at 1 atm and gives its acetyl derivative. In contrast, switching from $\mathrm{Cp(CO)_2FeCH_3}$ to (η^5-$C_5(CH_3)_5$)$(CO)_2FeCH_3$ has essentially no effect on the facility of the carbonylation chemistry, whereas $\mathrm{Cp(CO)_2RuCH_3}$ is much less reactive. (2) Choosing the appropriate solvent often proves critical. Most organic solvents (including Me_2SO and DMF) do not support CO insertion (80 psig of CO) on $\mathrm{Cp(CO)(PPh_3)FeCH_3}$; however, acetonitrile, nitromethane, and trifluoroethanol are perfectly adequate solvents for carbonylation. Trifluoroethanol, in particular, appears promising, probably because it could function as a hydrogen bond donor (i.e., acid catalyst) to an incipient acetyl ligand. IR spectral evidence is available for hydrogen bond complexation of the acetyl ligand on $\mathrm{Cp(CO)_2Fe}$ and $\mathrm{Cp(CO)(PPh_3)Fe}$ complexes. (3) Adding an acid catalyst (protonic) permits carbonylation of either $\mathrm{Cp(CO)_2FeCH_3}$ or $\mathrm{Cp(CO)(PPh_3)FeCH_3}$ under exceedingly mild conditions. With HBF_4 (1% stiochiometrically) both methyl complexes in CH_2Cl_2 add CO at 1 atm. Other useful catalysts include $\mathrm{Ph_2NH_2^+BF_4^-}$ for the former and *p*-nitrophenol or pyridinium ($\mathrm{C_5H_5NH^+BF_4^-}$) for the latter. None of the above procedures, however, are successful for carbonylating the substituted methyl complexes $\mathrm{Cp(CO)(PPh_3)FeCH_2X}$ (X = OCH_3, Ph, CO_2CH_3) or even $\mathrm{In(CO)(PPh_3)FeCH_2OCH_3}$.

Introduction

Relatively little is known about carbonylating Cp(CO)(L)Fe methyl and other alkyl complexes (eq 1).[1] This rather surprising development contravenes both the importance of these organoiron complexes in mechanistic and synthetic organometallic chemistry, and the importance of CO insertion into metal–carbon (alkyl) bonds as a key step in catalytic chemistry.[2]



$$\mathrm{CpFe(L)(CO)}\text{—}\mathrm{CH_3} + \mathrm{CO} \longrightarrow \mathrm{CpFe(L)(CO)}\text{—}\mathrm{C(=O)CH_3} \qquad (1)$$

1, L = CO **2**
3, L = PPh_3 **4**
5, L = $P(OCH_3)_3$ **6**

The parent methyl complex $\mathrm{Cp(CO)_2FeCH_3}$ (**1**) reportedly gives its acetyl derivative **2** only at higher CO pressures and temperatures (325 atm, approaching 97 °C) in tetradecane.[3] In contrast, the phosphine-substituted alkyl complexes $\mathrm{Cp(CO)(PPh_3)FeR}$ apparently add CO under considerably milder conditions. Treichel and co-workers[4] thus observed $\mathrm{Cp(CO)(PPh_3)FeCH_3}$ (**3**) providing its acetyl $\mathrm{Cp(CO)(PPh_3)FeCOCH_3}$ (**4**) with 1 atm of CO in heptane (90–100 °C, 25% yield of **4**), Wojcicki and Reich-Rohwig[5] noted an analogous 2-phenylpropyl complex adding CO (4 atm) in acetonitrile (25 °C, 24 h, 25% yield), and Flood's group[6] reported inserting CO (1–4 atm) onto the ethyl complex in nitroethane (22 °C, 18 h, 82% at 50 psig of CO) and in several other dipolar aprotic solvents. Brunner[7] observed, in contrast to the above results, that **3** in toluene carbonylates very slowly even at 400 atm of CO (7% yield **4** after 24 h, 30 °C).[8] The question we pose is: for a given

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(1) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. Kuhlman, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195.

(2) (a) Collman, J. P.; Hegdus, L. S. "Principles and Applications of Organo-transition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

(3) King, R. B.; King, A. D., Jr.; Igbal, M. Z.; Frazier, C. C. *J. Am. Chem. Soc.* **1978**, *100*, 1687.

(4) Treichel, P.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177.

(5) Reich-Rohwig, P.; Wojcicki, A. *Inorg. Chem.* **1974**, *13*, 2457.

(6) Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 2853. Flood, T. C.; Campbell, K. D.; Downs, H. H.; Nakanishi, S. *Organometallics* **1983**, *2*, 1590.

(7) Brunner, H.; Vogt, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 405. Brunner, H.; Hammer, B.; Bernal, I.; Draux, M. *Organometallics* **1983**, *2*, 1595.

(8) Flood[6] and Brunner[7] have investigated the stereochemistry engendered in carbonylating optically active $\mathrm{Cp(CO)(PPh_3)Fe}$ alkyl complexes. Their results substantiate the alkyl-to-ligated CO migratory insertion mechanism,[8] with incoming CO occupying the terminal CO position. It should be noted that although these CO insertion processes can be highly stereospecific; the stereochemistry observed depends on the solvent used and possibly on the presence/absence of Lewis acids. (a) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. (b) Flood, T. C.; Jensen, J. E.; Stalter, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410. (c) Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37 and references cited.

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