$CpYbL_2$, and the former is more intense than the latter. The fragmentation of these molecular ions are characterized by their loss of the Cp ligand. The β-diketonato ligand, however, is difficult to fragment as a unit, and frequently the substituent R or R′ at either end cleaves first. The extent of cleavage depends on the properties of R or R′. Although the thermal stability of 12 Cp_2YbL- and $CpYbL_2$-type compounds are different, disproportionation reaction may take place, resulting in the creation of Cp_3Yb and YbL_3, when these compounds reach a certain evaporation temperature. The disproportionation products $Cp_3Yb^{\bullet+}$ and $YbL_3^{\bullet+}$ have a fragmentation mechanism that is different from that of the corresponding molecular ions.

Registry No. 1, 72105-01-2; 2, 106043-08-7; 3, 72105-02-3; 4, 113753-81-4; 5, 113753-76-7; 6, 113753-94-9; 7, 113753-97-2; 8, 113753-82-5; 9, 106018-28-4; 10, 106018-29-5; 11, 113753-95-0; 12, 113753-96-1.

Carbonylation of (η^5-Indenyl)$(CO)_2$Fe-α-Alkoxyalkyl Complexes Using Bimetallic α-Alkoxyacyl Intermediates

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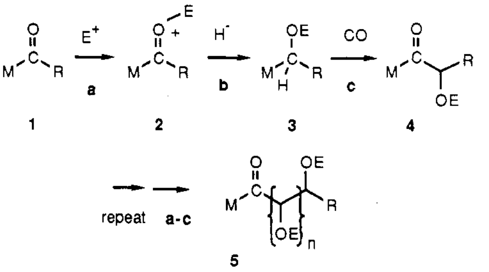
Treatment of alkoxymethyl complexes $In(CO)_2Fe{-}CH_2OR$ (In = η^5-indenyl; R = Me, Et) with the metalate $In(CO)_2Fe^-Na^+$ in THF solution affords bimetallic alkoxyacetyl intermediates $In(CO)Fe(\mu\text{-}CO)_2Fe(In)(COCH_2OR)^-Na^+$ (**13a,b**). IR spectra of these intermediates closely resemble the data for the fully characterized $In_2(CO)_3Fe_2(COCH_3)^-$ and $CpIn(CO)_3Fe_2(COCH_3)^-$ salts. Alkoxyacetyl dimers **13a,b** react with MeI and CO (1 atm) to give (3 h) the mononuclear alkoxyacetyl compounds $In(CO)_2Fe{-}COCH_2OR$ in 50–60% yields. The acetyl complex $In(CO)_2Fe{-}COCH_3$ upon activating ($Et_3O^+PF_6^-$) and reducing ($NaBH_4$) gives $In(CO)_2Fe{-}CH(OEt)CH_3$ (**12**). Subjecting **12** to the same two-step carbonylation procedure—treatment with $In(CO)_2Fe^-Na^+$ and then MeI/CO (1 atm)—produces $In(CO)_2Fe{-}COCH(OEt)CH_3$ (59% yield). This procedure thus is used in carbonylating α-alkoxyalkyl complexes that otherwise are inert toward CO (100 atm). A mechanism involving reversible η^5–η^3 indenyl ring slippage during both formation and cleavage of bimetallic acyl complexes (e.g., **13**) is advanced.

Introduction

Poly(alkoxymethylene) acyl ligands (**5**) that retain an oxygen functionality at each carbon center and derive from carbon monoxide are attractive synthetic objectives.[1-3] In one synthetic approach these transition organometallic acyl complexes result from repeating a three-step sequence of ligand reactions (eq 1): (a) electrophilic activation of an acyl ligand, (b) hydride transfer to its oxycarbenoid derivative **2**, and (c) carbonylation of the resulting alkoxyalkyl group on **3**. Selecting the organometallic template for supporting these ligand construction reactions, however, is complicated by their antithetical requirements. The first two ligand reactions a and b, resulting in net reduction of the acyl ligand, require a coordinatively saturated, nonlabile metal center in order to contain the chemistry at the acyl ligand.[4] The carbonylation reaction, in contrast, requires a relatively labile metal center for the alkyl–CO migratory-insertion step.[5] We recently demonstrated that using the (dppe)$(CO)_2$Co system as the organometallic template balances these contradictory requirements.[6,7]



(1)

Cp$(CO)_2$Fe or Fp complexes and their phosphine- or phosphite-substituted derivatives Cp(CO)(L)Fe are desirable systems for supporting the ligand reactions depicted in eq 1.[2,8] The corresponding acyl ligand reduction steps

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[3] A limited number of complexes bearing such highly oxygenated alkyl ligands (having two or more alkoxy groups) have been reported.[2,3a–c] These include glycosylmetalate complexes (and their acyl derivatives) derived from glycoside halides.[3d] (a) Rosenblum, M.; Turnbull, M. M.; Foxman, B. M. *Organometallics* **1986**, *5*, 1062. (b) Finke, R. G.; McKenna, W. P.; Schiraldi, D. A.; Smith, B. L.; Pierpont, C. *J. Am. Chem. Soc.* **1983**, *105*, 7592, 7605. (c) Schubert, U.; Fischer, E. O. *Justus Liebigs Ann. Chem.* **1975**, 393. Fischer, E. O.; Schubert, U.; Kalbfus, W.; Kreiter, C. G. *Z. Anorg. Allg. Chem.* **1975**, *416*, 135. Doetz, K. H.; Kuhn, W.; Thewalt, U. *Chem. Ber.* **1985**, *118*, 1126. (d) Rosenthal, A.; Koch, H. *J. Tetrahedron Lett.* **1967**, 871. Deshong, P.; Slough, G. A.; Elango, V.; Trainor, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7788. Trainor, G. L.; Swart, B. E. *J. Org. Chem.* **1983**, *48*, 2447. Trainor, G. L. *J. Organomet. Chem.* **1985**, *282*, C43.

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[5] Alexander, J. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds; Wiley: New York, 1985; Vol. 2, Chapter 5.

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[7] In related studies, Stimson and Shriver obtained C_1–C_4 alkenes by reacting $(CO)_5Mn{-}CH_3$ with CO plus diborane. Chain growth apparently entails BH_3 reduction of an acyl to its homologus saturated alkyl ligand, which then inserts CO. Stimson, R. E.; Shriver, D. F. *Organometallics* **1982**, *1*, 787. Brown, S. L.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 84.

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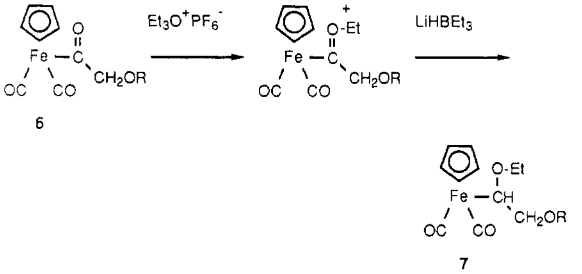
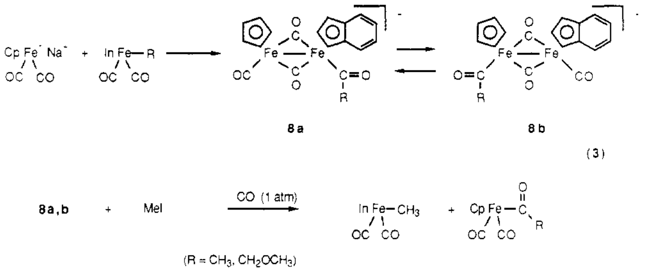
a and b have been thoroughly documented,[5] and high diastereoselectivity has been observed during the synthesis of Cp(CO)(L)Fe alkoxyalkyl complexes **4**.[9] In related work, we procured the α,β-dialkoxyethyl complexes **7** (R = Me, Et) from the Fp alkoxyacetyl compounds **6** (eq 2).[2]



(2)

The CpFe–α-alkoxyalkyl compounds unfortunately do not carbonylate under conditions that their corresponding hydrocarbyl complexes readily add CO and afford acyl derivatives.[10,11] We have been unsuccessful in directly carbonylating examples of Cp(CO)(L)Fe–CH_2OR to their alkoxyacetyl products Cp(CO)(L)Fe–C(O)CH_2OR, which nevertheless are independently available via other synthetic routes.[12]

(Alkoxymethyl)iron complexes do carbonylate after replacing the η^5-Cp ligand by the η^5-indenyl ligand (In) and adopting a two-step, metalate-promoted CO insertion procedure.[15] This procedure involves (i) a stable bimetallic acyl intermediate **8** resulting from metalate-induced alkyl–CO migration, (ii) the presence of at least one η^5-In ligand on this intermediate, and (iii) its regioselective cleavage to mononuclear acyl compounds (eq 3). The structure of the bimetallic acetyl intermediate **8** (R = CH_3), which crystallizes as **8b** PPN$^+$,[16] has been determined, and the **8a**–**8b** tautomeric equilibrium or acetyl ligand shuttle has been demonstrated by ^1H NMR magnetization transfer experiments. The salient point is that carbonylating an iron alkoxymethyl group using 1 atm of CO is now possible.



(3)

In the present report, we extend this In(CO)$_2$Fe carbonylation chemistry to the ligand synthesis reactions noted in eq 1. Two questions are addressed. First, will In(CO)$_2$Fe$^-$ interact with InFe(CO)$_2$–α-alkoxyalkyl complexes under conditions analogous to those summarized by eq 3 to give homologous acyl compounds? Both In ligands in the bimetallic acyl intermediate are required for subsequent chain extension reactions. We also would prefer to generate and use (i.e., carbonylate) this intermediate with its Na$^+$ counterion, thus skipping the PPN$^+$ metathesis step. The second question is will coupling the acyl reduction (steps a and b) and the carbonylation chemistry (step c) summarized in eq 1 be possible by using In(CO)$_2$Fe complexes in place of their Fp congeners?

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere by using standard syringe/septum and Schlenk techniques.[17] Infrared spectra were taken by using CH_2Cl_2 of THF solutions and were recorded on a Perkin-Elmer Model 297 spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded by using a Varian XL-200 spectrometer; spectra are reported as δ values downfield after internal Me_4Si. Results of homonuclear spin–spin decoupling experiments (^1H NMR spectra) and APT sequences ($^{13}C\{^1H\}$ NMR spectra) were used in structural assignments.

Organic reagents were purchased and used as received. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl; methylene chloride was distilled from P_2O_5. Anhydrous ether was taken from a freshly opened can or was distilled from sodium benzophenone ketyl. The purification of commercially available $Et_3O^+PF_6^-$ [2] and the preparation of In(CO)$_2$Fe-containing starting materials have been documented.[18] Combustion microanalyses were performed by Desert Analytics, Tucson, AZ.

In(CO)$_2$Fe–CH$_2$OR (9a, R = CH$_3$; 9b, R = Et). THF solutions of In(CO)$_2$Fe$^-$Na$^+$ were prepared as needed by Na(Hg) cleavage of (In(CO)$_2$Fe)$_2$ (4.0 mmol/150 mL). These solutions were cooled (−78 °C) and treated with 1.0 equiv of a chloromethyl ether (*Caution*: potential carcinogen). After being warmed to room temperature (1 h), the yellow-brown solutions were evaporated. The resulting brown oil was extracted with pentane, and the combined extracts were filtered through a column of activity 2 alumina (2 × 6 cm), leaving brown decomposition products at the top of the column. Evaporating the filtrates (10^{-2} mm, 2 h, 25 °C) left crude **9a,b** as yellow-brown oils (33–50% yields), which were not purified further due to their instability. As these compounds rapidly decomposed upon attempted storage (−20 °C), they were generated as required and used immediately. **9a**: IR (CH_2Cl_2) 1998, 1940 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40, 7.15 (A_2B_2 multiplets, 4 H, In: benzo), 5.32 (d, J = 3 Hz, In: $H_{1,3}$), 4.98 (t, J = 3 Hz, In: H_2), 4.37 (s, Fe–CH_2), 3.24 (s, OCH_3). **9b**: IR (CH_2Cl_2) 1995, 1940 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (m, 4 H, In: benzo), 5.32 (d, J = 2.9 Hz, In: $H_{1,3}$), 4.88 (t, J = 2.9 Hz, In: H_2), 4.32 (s, Fe–CH_2), 3.26 (q, J = 7.0 Hz, OCH_2), 1.08 (t, J = 7.0 Hz, OCH_2CH_3).

In(CO)$_2$Fe=C(OEt)CH$_3^+$PF$_6^-$ (11). To a CH_2Cl_2 solution (40 mL) containing In(CO)$_2$Fe–COCH$_3$ (**10**) (1.40 g, 5.2 mmol) was added triethyloxonium hexafluorophosphate (1.26 g, 5.1 mmol). The clear, dark yellow-brown solution remaining after 7 h was added dropwise to ether (400 mL). This produced a lemon yellow precipitate that was filtered, washed with ether (3 × 30 mL), and vacuum dried. Spectroscopically pure In(CO)$_2$Fe=C(OEt)CH$_3^+$PF$_6^-$ (**11**) was obtained as a moisture-sensitive bright yellow powder (2.01 g, 87% yield), which was reprecipitated analytically

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(8) (a) Bodnar, T. W.; Crawford, E. J.; Cutler, A. R. *Organometallics* **1986**, *5*, 947. (b) Crawford, E. J.; Lambert, C.; Menard, K. P.; Cutler, A. R. *J. Am. Chem. Soc.* **1985**, *107*, 3130.

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(11) It is of course possible to homologate functionalized alkyl complexes (but only once) using phosphine-promoted alkyl–CO migratory insertion [e.g., Cp(CO)$_2$Fe–CH$_2$OR to Cp(CO)(PPh$_3$)Fe–COCH$_2$OR]. Bodnar, 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. *ACS Symp. Ser.* **1981**, *No. 152*, 279.

(12) Attempts to promote carbonylation of Cp(CO)(L)Fe–CH$_2$OR by adding Lewis acids,[13] by protonating,[10] by incorporating oxidative electron-transfer chain catalysis,[14] and by substituting η^5-indenyl for Cp and PPh$_3$ for ligated CO[10] proved unsuccessful.

(13) Markham, J.; Tolman, W.; Menard, K.; Cutler, A. *J. Organomet. Chem.* **1985**, *294*, 45.

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(15) Forschner, T. C.; Cutler, A. R.; Kullnig, R. K. *J. Oganomet. Chem.* **1988**, *356*, C12.

(16) PPN is an acronym for Ph$_3$P=N=PPh$_3$.

(17) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(18) Forschner, T. C.; Cutler, A. R. *Inorg. Chim. Acta* **1985**, *102*, 113.

pure from a mixture of dichloromethane and ether (1:5): IR ($\mathrm{CH_2Cl_2}$) 2061, 2020 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CD_3NO_2}$) δ 7.74, 7.55 (AA′BB′, In: benzo), 6.09 (d, J = 2.8 Hz, In: $\mathrm{H_{1,3}}$), 5.54 (t, J = 2.8 Hz, In: $\mathrm{H_2}$), 4.85 (q, J = 7.0 Hz, $\mathrm{OC\mathit{H}_2CH_3}$), 3.12 (s, Fe–C–$\mathrm{C\mathit{H}_3}$), 1.66 (t, J = 7.0 Hz, $\mathrm{OCH_2C\mathit{H}_3}$); $^{13}\mathrm{C\{^1H\}}$ NMR ($\mathrm{CD_3NO_2}$) δ 334.2 (Fe=C), 210.8 (C≡O), 132.6 and 126.4 (In: benzo), 107.6 (In: 3a,7a), 98.0 (In: $\mathrm{C_2}$), 81.4 ($\mathrm{OCH_2}$), 77.5 (In: $\mathrm{C_{1,3}}$), 46.8 (Fe–C–$\mathrm{\mathit{C}H_3}$), 14.6 ($\mathrm{OCH_2\mathit{C}H_3}$). Anal. Calcd for $\mathrm{C_{15}H_{15}O_3PFeF_6}$: C, 40.57; H, 3.41. Found: C, 40.29; H, 3.54.

Upon treating $\mathrm{CH_2Cl_2}$ solutions of **11** with $(n\text{-Bu})_4\mathrm{N^+I^-}$ (2-fold excess) for 1 h, $\mathrm{In(CO)_2Fe{-}COCH_3}$ (**10**) was regenerated quantitatively, as judged by IR spectral monitoring. The IR spectrum for **10** ($\mathrm{CH_2Cl_2}$) has ν(CO) absorptions at 2020, 1961, and 1651 $\mathrm{cm^{-1}}$.

Reduction of $\mathrm{In(CO)_2Fe{=}C(OEt)CH_3{}^+PF_6{}^-}$ (11). Procedure 1. A $\mathrm{CH_2Cl_2}$ solution (26 mL) containing $\mathrm{In(CO)_2Fe{=}C(OEt)CH_3{}^+PF_6{}^-}$ (**11**) was generated by alkylating $\mathrm{In(CO)_2Fe{-}C\text{-}OCH_3}$ (**10**) (0.457 g, 1.70 mmol) with $\mathrm{Et_3O^+PF_6{}^-}$ (0.467 g, 1.66 mmol). IR spectral monitoring indicated that the reaction was complete within 6 h. The resulting yellow-brown solution was cooled (−78 °C) and was treated with a THF solution of $\mathrm{LiHBEt_3}$ (1.7 mL, 1.7 mmol). The resulting yellow-orange solution after being warmed to room temperature was evaporated, and the orange oil was redissolved in ether (5 mL)–pentane (1 mL). A light tan solid precipitated as the solution was cooled (−78 °C); the supernatant liquid was chromatographed on activity 3 alumina with pentane–ether. The yellow band that eluted with pentane was precipitated from pentane (−78 °C), filtered, and vacuum dried. This yielded 0.341 g (67%) of spectroscopically pure $\mathrm{In(CO)_2Fe{-}CH(OEt)CH_3}$ (**12**) as a gummy yellow solid. Trace amounts of residual borane impurities were evident by ^{1}H NMR spectroscopy: ($\mathrm{CDCl_3}$) δ 0.9, 1.4, 3.5.

Procedure 2. A yellow $\mathrm{CH_2Cl_2}$ solution (20 mL) of $\mathrm{In(CO)_2Fe{=}C(OEt)CH_3{}^+PF_6{}^-}$ (**11**) (0.745 g, 1.68 mmol) was added dropwise to a stirred, cold (−78 °C) methanolic solution (40 mL) of sodium metal (0.801 g, 35 mmol) and $\mathrm{NaBH_4}$ (0.621 g, 16.3 mmol). The resulting yellow-orange solution was warmed to room temperature and then was transferred to a seperatory funnel containing 400 mL of water. This was extracted with $\mathrm{CH_2Cl_2}$ (3 × 25 mL). The combined $\mathrm{CH_2Cl_2}$ extracts were washed with water, dried ($\mathrm{MgSO_4}$), and evaporated. A yellow-orange oil remained that was redissolved in ether (10 mL), concentrated to 2 mL, and cooled to −78 °C after 1 mL of pentane was added. This afforded analytically pure $\mathrm{In(CO)_2Fe{-}CH(OEt)CH_3}$ (**12**) as a waxy yellow solid: yield 0.463 g (92%); IR ($\mathrm{CH_2Cl_2}$) 1995, 1934 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.37, 7.05 (AA′BB′, In: Benzo), 5.43 (br s, 1 H, In: $\mathrm{H_{1or3}}$), 5.24 (br s, 1 H, In: $\mathrm{H_{3or1}}$), 4.90 (t, J = 3.0 Hz, 1 H, In: $\mathrm{H_2}$), 4.56 (q, J = 5.9 Hz, 1 H, Fe–CH), 3.54 (dq, J = 7.0, 9.3 Hz, 1 H, $\mathrm{OC\mathit{H}_AH_B}$), 3.21 (dq, J = 7.0, 9.3 Hz, 1 H, $\mathrm{OCH_A\mathit{H}_B}$), 1.60 (d, J = 5.9 Hz, 3 H, Fe–C–$\mathrm{CH_3}$), 1.13 (t, J = 7.0 Hz, 3 H, $\mathrm{OCH_2C\mathit{H}_3}$); $^{13}\mathrm{C\{^1H\}}$ NMR ($\mathrm{CDCl_3}$) δ 217.8, 216.5 (C≡O), 127.0, 126.1 and 125.4, 124.2 (In: benzo C's), 106.2 and 105.5 (In: $\mathrm{C_{3a,7a}}$), 103.4 (In: $\mathrm{C_2}$), 78.8 (Fe–CH), 73.1 and 72.8 (In: $\mathrm{C_{1,3}}$), 65.0 ($\mathrm{O\mathit{C}H_2CH_3}$), 32.1 (Fe–C–$\mathrm{\mathit{C}H_3}$), 15.0 ($\mathrm{OCH_2\mathit{C}H_3}$). Anal. Calcd for $\mathrm{C_{15}H_{16}O_3Fe}$: C, 60.03; H, 5.37. Found: C, 59.45; H, 5.36.

Preparation of $\mathrm{In(CO)_2Fe{-}COCH_2OCH_3}$ (15a). A THF solution (150 mL) containing $\mathrm{In(CO)_2Fe^-Na^+}$ was generated by Na(Hg) cleavage of $\mathrm{[In(CO_2)Fe]_2}$ (2.00 g, 0.44 mmol) and was treated (−80 °C) with methoxyacetyl chloride. After being warmed to room temperature (1 h), the resulting yellow-brown solution was evaporated. Methylene chloride extracts (total 25 mL) of the brown gum were filtered through a 2 × 6 cm column of alumina; the yellow brown eluate was concentrated (to 10 mL) and diluted with heptane (5 mL). Yellow-brown crystals of $\mathrm{In(CO)_2Fe{-}COCH_2OCH_3}$ (**15a**) were deposited at −75 °C. These were collected and vacuum dried, giving 1.09 g (41% yield): IR ($\mathrm{CH_2Cl_2}$) 2021, 1961, 1655 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.46, 7.20 (AA′BB′, In: benzo), 5.60 (d, J = 2.9 Hz, In: $\mathrm{H_{1,3}}$), 4.98 (t, J = 2.9 Hz, In: $\mathrm{H_2}$), 3.96 (s, $\mathrm{Fe{-}COCH_2}$), 3.36 (s, $\mathrm{OCH_3}$); $^{13}\mathrm{C\{^1H\}}$ NMR ($\mathrm{CH_2Cl_2}$) δ 252.2 (C=O), 213.6 (C≡O), 123.7, 127.1 (In: benzo), 106.2 (In: $\mathrm{C_{3a,7a}}$), 100.5 (In: $\mathrm{C_2}$), 88.9 ($\mathrm{Fe{-}CO\mathit{C}H_2}$), 7.27 (In: $\mathrm{C_{1,3}}$), 58.6 ($\mathrm{OCH_3}$). Anal. Calcd for $\mathrm{C_{14}H_{12}O_4Fe}$: C, 56.03; H, 4.04. Found: C, 56.20; H, 4.11.

Carbonylation of $\mathrm{In(CO)_2Fe{-}CH_2OCH_3}$ (9a). A reddish brown THF solution (30 mL) containing $\mathrm{[In(CO)_2Fe]_2}$ (0.522 g, 1.15 mmol) was vigorously stirred with excess 1% Na(Hg) for 1 h. After sediment was allowed to settle (0.5 h), a yellow-brown solution corresponding to quantitative reduction of starting dimer [IR ν(CO) 1989, 1948, 1790 $\mathrm{cm^{-1}}$] to $\mathrm{In(CO)_2Fe^-Na^+}$ [IR ν(CO) 1883, 1866, 1816, 1779 $\mathrm{cm^{-1}}$] was obtained. A 16.0-mL aliquot of this anion solution (1.23 mmol) was treated with $\mathrm{In(CO)_2Fe{-}CH_2OMe}$ (**9a**) (0.259 g, 0.95 mmol) in 5 mL of THF. IR spectral monitoring of the yellow-brown solution after being left sitting for 2 h was consistent with conversion of **9a** to $\mathrm{In(CO)Fe(\mu\text{-}CO)_2Fe(In)(COCH_2OCH_3)^-Na^+}$ (**13a**): ν(CO) 1920, 1708, 1531 $\mathrm{cm^{-1}}$.

The reaction mixture was diluted with THF (30 mL) before MeI (0.40 mL, 6.42 mmol) and carbon monoxide (2.5 h) were added. Then the mixture was evaporated, and the brown residue was transferred with 7 mL of $\mathrm{CH_2Cl_2}$ to a chromatography column containing 2 × 25 cm of activity 3 alumina/pentane. Three fractions were separated and eluted. Fraction 1, $\mathrm{In(CO_2)Fe{-}CH_3}$, was recovered from the yellow band that was removed with pentane and identified by its ^{1}H NMR spectrum, 106 mg (0.44 mmol). Fraction 2, $\mathrm{[In(CO)_2Fe]_2}$, next was eluted as a brown band using 1:3 $\mathrm{CH_2Cl_2}$–pentane and was identified spectroscopically, 176 mg (0.39 mmol). Fraction 3, a yellow band, was removed with $\mathrm{CH_2Cl_2}$. This fraction was concentrated to 4 mL, diluted with 2 mL of pentane, and cooled (−78 °C). The resulting yellow crystals (176 mg) were filtered, vacuum dried, and identified as spectroscopically pure $\mathrm{In(CO)_2Fe{-}COCH_2OCH_3}$ (**15a**) (62% yield).

Carbonylation of $\mathrm{In(CO)_2Fe{-}CH_2OCH_2CH_3}$ (9b). A THF solution (17 mL) initially containing $\mathrm{In(CO)_2Fe{-}CH_2OCH_2CH_3}$ (**9b**) (0.235 g, 0.82 mmol) and $\mathrm{In(CO)_2Fe^-Na^+}$ (0.86 mmol) was stirred 2 h. IR spectral monitoring confirmed conversion of **9b** to the proposed intermediate $\mathrm{In(CO)Fe(\mu\text{-}CO)_2Fe(In)\text{-}COCH_2OCH_2CH_3{}^-Na^+}$ (**13b**): ν(CO) 1920, 1705, 1528 $\mathrm{cm^{-1}}$. The reaction mixture was diluted with 30 mL of THF and was treated with $\mathrm{CH_3I}$ (0.60 mL, 0.96 mmol) and CO (1 atm, 3 h). Chromatographic workup afforded $\mathrm{In(CO)_2Fe{-}CH_3}$ (fraction 1: 92 mg, 0.38 mmol) and $\mathrm{(In(CO)_2Fe)_2}$ (fraction 2: 86 mg, 0.19 mmol). The last fraction, a yellow band, was eluted with ether; bright yellow crystals (149 mg) of $\mathrm{In(CO)_2Fe{-}COCH_2OCH_2CH_3}$ (**15b**) (58% yield) were obtained: IR ($\mathrm{CH_2Cl_2}$) 2020, 1960, 1655 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.45, 7.20 (AA′BB′, In: benzo), 5.59 (d, J = 3.1 Hz, In: $\mathrm{H_{1,3}}$), 4.99 (t, J = 3.1 Hz, In: $\mathrm{H_2}$), 3.92 (s, $\mathrm{COCH_2}$), 3.48 (q, J = 7.0 Hz, $\mathrm{OC\mathit{H}_2CH_3}$), 1.19 (t, J = 7.0 Hz, $\mathrm{OCH_2C\mathit{H}_3}$); $^{13}\mathrm{C\{^1H\}}$ NMR ($\mathrm{CDCl_3}$) δ 253.8 (C=O), 213.3 (C≡O), 123.7, 127.0 (In: benzo), 105.9 (In: $\mathrm{C_{3a,7a}}$), 101.1 (In: $\mathrm{C_2}$), 87.3 ($\mathrm{Fe{-}C(O){-}\mathit{C}H_2}$), 72.6 (In: $\mathrm{C_{1,3}}$), 66.4 ($\mathrm{O\mathit{C}H_2CH_3}$), 14.6 ($\mathrm{OCH_2\mathit{C}H_3}$). Anal. Calcd for $\mathrm{C_{15}H_{14}O_4Fe}$: C, 57.36; H, 4.49. Found: C, 57.63; H, 4.55.

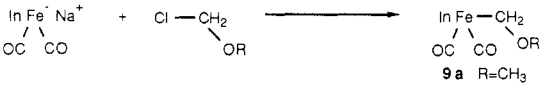
Carbonylation of $\mathrm{In(CO)_2Fe{-}CH(OEt)CH_3}$ (12). A THF solution (30 mL) of $\mathrm{In(CO)_2Fe^-Na^+}$ (1.77 mmol) was treated with $\mathrm{In(CO)_2Fe{-}CH(OEt)CH_3}$ (**12**) (0.344 g, 1.15 mmol) in 5 mL of THF. The resulting yellow-brown solution was stirred at room temperature until IR spectral monitoring showed complete conversion of **12** to $\mathrm{In(CO)Fe(\mu\text{-}CO)_2Fe(In)COCH(OEt)CH_3{}^-Na^+}$ (**14**): ν(CO) 1921, 1702 $\mathrm{cm^{-1}}$. This reaction was over within 2 h. Additional THF (30 mL) and MeI (0.60 mL, 9.6 mmol) were added before vigorously stirring with 1 atm of CO (3 h). After column chromatographic workup on alumina, the following three fractions were obtained: (1) $\mathrm{In(CO)_2Fe{-}CH_3}$ (0.133 g, 0.55 mmol), (2) $\mathrm{(In(CO)_2Fe)_2}$ (0.190 g, 0.42 mmol), and (3) a yellow band removed with ether. This latter eluate was diluted with pentane and cooled (−78 °C). The resulting light red-orange powder was filtered, washed with pentane at −78 °C, and vacuum dried. $\mathrm{In(CO)_2Fe{-}COCH(OCH_2CH_3)CH_3}$ (**16**): 0.221 g (59% yield); IR ($\mathrm{CH_2Cl_2}$) 2020, 1961, 1637 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.45, 7.18 (AA′BB′, In: benzo), 5.59 (m, 1 H, In: $\mathrm{H_{1or3}}$), 5.56 (m, 1 H, In: $\mathrm{H_{3or1}}$), 4.98 (t, J = 3.0 Hz, In: $\mathrm{H_2}$), 3.51 (q, J = 6.6 Hz, 1 H, $\mathrm{Fe{-}COC\mathit{H}}$), 3.45 (dq, J = 7.1, 2.4 Hz, 1 H, $\mathrm{OC\mathit{H}HCH_3}$), 3.38 (dq, J = 7.1, 2.4 Hz, 1 H, $\mathrm{OCH\mathit{H}CH_3}$), 1.15 (t, J = 7.0 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 1.04 (d, J = 6.6 Hz, $\mathrm{Fe{-}COCC\mathit{H}_3}$); $^{13}\mathrm{C\{^1H\}}$ NMR ($\mathrm{CDCl_3}$) δ 261.9 (C=O), 214.2 and 213.8 (C≡O), 126.8 and 123.7 (In: benzo C's), 106.1 and 105.4 (In: $\mathrm{C_{3a,7a}}$), 90.8 (Fe–COCH), 72.7 and 72.5 (In: $\mathrm{C_{1,3}}$), 64.4 ($\mathrm{OCH_2CH_3}$), 16.0 ($\mathrm{Fe{-}COCCH_3}$), 14.6 ($\mathrm{OCH_2CH_3}$). Anal. Calcd for $\mathrm{C_{16}H_{16}O_4Fe}$: C, 58.56; H, 4.92. Found: C, 58.70; H, 4.99.

Results and Discussion

I. (η^5-Indenyl)$\mathrm{(CO)_2Fe}$–α-Alkoxyalkyl Complexes.

Alkoxymethyl complexes $\mathrm{In(CO)_2Fe{-}CH_2OR}$ (**9a**, R = $\mathrm{CH_3}$;

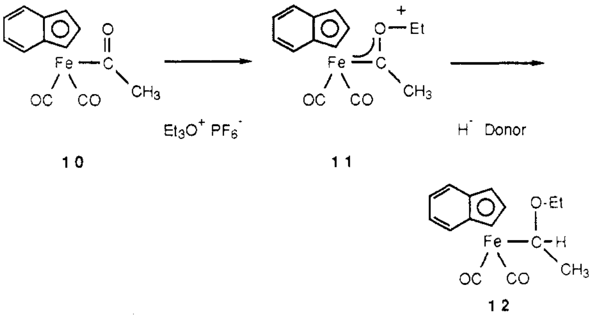
9b, R = CH_2CH_3) are available by metalating an α-chloro ether with $In(CO)_2Fe^-Na^+$ (eq 4).[18] Sodium amalgam cleavage of dimeric $[In(CO)_2Fe]_2$ provides this metalate; reaction conditions and workup procedures used in alkylating $In(CO)_2Fe^-Na^+$ resemble those used in synthesizing analogous CpFe-alkyl compounds $Fp–CH_2OR$.[19] The major difference is that **9a** and **9b** are considerably less stable than the corresponding Fp compounds. Both **9a,b** form as amber oils after column chromatography (33–50% yields) that decompose upon storage at -10 °C. Increased handling during attempted purification by high-vacuum distillation, low-temperature crystallization, or chromatography further encourages their decomposition. These compounds, however, are characterized unambiguously by IR and ^1H NMR spectroscopy and by converting to their more stable alkoxyacetyl derivatives $In(CO)_2Fe–COCH_2OR$ (**15a,b**).



(4)

9a R=CH_3
9b R=CH_2CH_3

The α-ethoxyethyl complex **12** results from straightforward alkylation (activation) and then hydride transfer[4a,b] to the parent acetyl compound **10** (eq 5). We isolate the ethoxycarbene compound **11** (87% yield) after treating **10** with $Et_3O^+PF_6^-$ for 6–8 h and reprecipitating the product from CH_2Cl_2–ether. The resulting dark yellow solid, obtained analytically pure, has IR and ^1H and ^{13}C NMR spectra in accord with its proposed structure. Reacting **11** in CH_2Cl_2 solution with iodide quantitatively regenerates the acetyl starting material **10**, as expected.[2,20] Ethoxycarbene complex **11**, although susceptible to atmospheric hydrolysis, is a stable product possessing solubility and handling properties similar to its Fp analogue.[21]



10 **11** (5) **12**

Two procedures were used in converting **11** to the α-ethoxyethyl complex **12**. Lithium triethylborohydride rapidly reduces **11** in CH_2Cl_2 solution (-80 °C) and produces **12** in over 60% yield after column chromatography. We note that this indenyl-containing alkyl complex is more stable toward column chromatography than is the analogous Fp complex. Trace amounts of unidentified borane residues remained, and these hinder the subsequent carbonylation reaction. Brookhart's procedure[22] using excess $NaBH_4$ in methanolic NaOMe as the reductant (-80 °C) therefore was adopted for reducing **11**. This procedure affords analytically pure **12** in over 90% yield after a workup procedure involving aqueous extraction versus CH_2Cl_2 and column chromatography. Both reductive procedures are carried out in a one-pot operation by starting with the acetyl complex **10**, activating it with $Et_3O^+PF_6^-$, and mixing the CH_2Cl_2 solution of the ethoxycarbene compound **11** with the reductant.

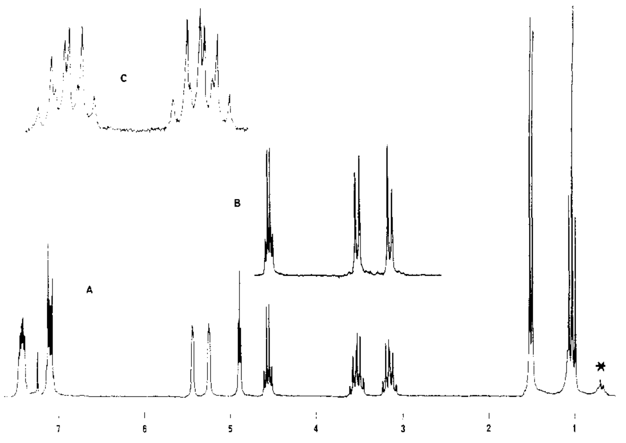
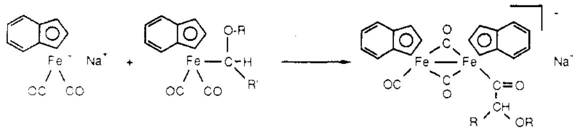


Figure 1. ^1H NMR spectrum of $In(CO)_2Fe–CH(OCH_2CH_3)CH_3$ (**12**) in $CDCl_3$ (200 MHz): A, normal scan, δ 0.5–7.7 (the asterisk denotes impurity); B, homonuclear spin decoupling at δ 1.6; C, normal scan, enlargement of δ 3.1–3.7 region.

Both ^1H and ^{13}C NMR spectra of **12** are significantly perturbed by the presence of the chiral center. Ring positions 1/3 and ipso 3a/7a on the η^5-indenyl ligand are diastereotopic and now represent magnetically and chemical shift nonequivalent sites.[23] In the ^1H NMR spectrum (Figure 1), the usual doublet–triplet pattern of the η^5-indenyl hydrogens $H_{1,3}$ and H_2 for achiral $In(CO)_2Fe$–alkyl and –acyl complexes (cf. data for **10a,b**) are replaced by two broad singlets for H_1 and H_3 plus the triplet (J = 3.0 Hz) for H_2.[24] Diastereotopic methylene hydrogens on the ethoxy group likewise are magnetically nonequivalent and give two doublets of quartets. In the $^{13}C\{^1H\}$ NMR spectrum, the diastereotopic carbonyls produce two signals, as do the pairs of nonequivalent carbon centers C_1/C_3, ipso C_{3a}/C_{7a}, C_4/C_7, and C_5/C_6.

II. Carbonylation of α-Alkoxyalkyl Complexes. The carbonylation procedure is carried out in two stages that entail forming the bimetallic acyl anions **13a,b** and **14** and then cleaving these dimers with MeI and CO (1 atm). Treating an alkoxymethyl complex **9a** or **9b** in THF solution with 1 equiv (or more) of the metalate $In(CO)_2Fe^-Na^+$ affords the bimetallic acyl anions **13a** and **13b** (eq 6). These were characterized only by their solution IR spectra: ν(CO) 1920, 1705, and 1530 cm^{-1}. The appearance of this three-band pattern closely resembles that observed for analogous mixed $InCp(CO)_3Fe_2$–acetyl anions **8** (R = CH_3), which have the depicted binuclear structure possessing a cis array of In/Cp ligands and a



(6)

9a (R' = H R = Me) **13a**
9b (R' = H, R = Et) **13b**
12 (R' = CH_3, R = Et) **14**

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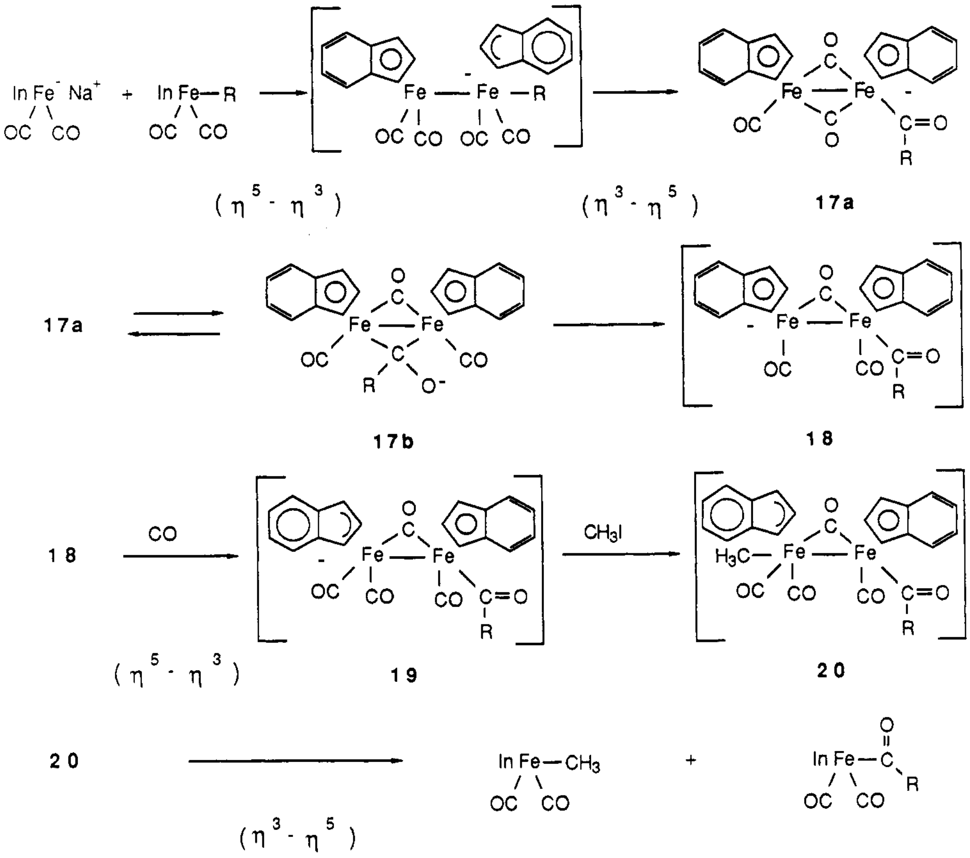
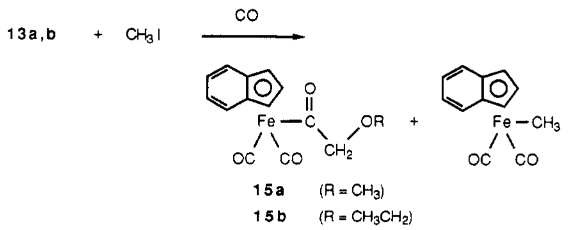


Figure 2.

terminal acetyl ligand.[15] The IR spectra of **13a,b** differ slightly from that of the fully characterized acetyl analogue $In_2(CO)_3Fe_2COCH_3^-Na^+$ [ν(CO) 1921, 1710, and 1553 cm^{-1}][15] by the position of the lowest energy acyl ν(CO). We attribute this 23 cm^{-1} decrease for **13a,b** to chelation and hence tighter binding of the Na^+ counterion.

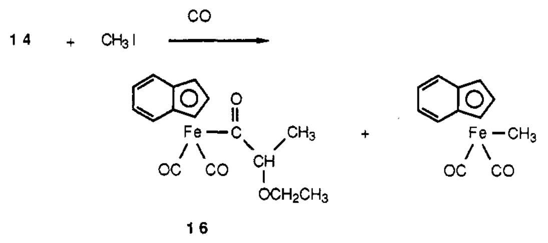
In some reactions, using excess metalate $In(CO)_2Fe^-Na^+$ more rapidly gave the desired bimetallic alkoxyacetyl compounds **13a,b**. We found no evidence for revesible formation of **13a,b**; unreacted alkoxymethyl compounds **9a,b** were not detected, for example. The presence of excess metalate did not interfere with the overall carbonylation sequence, since the methyl iodide reaction in the second stage converted excess metal anion to easily separated $In(CO)_2Fe-CH_3$.

Methyl iodide treatment of in situ generated **13a,b** in the presence of 1 atm of CO (3 h) produces the alkoxyacetyl complexes **15a,b** (eq 7) in 60% yield after column chromatography. The organometallic byproducts $In(CO)_2Fe-CH_3$ and $[In(CO)_2Fe]_2$ elute before **15a,b** and thus are easily separated. The new alkoxyacetyl complexes **15a,b**, which are much more stable than the corresponding alkoxymethyl starting materials **9a,b**, are fully characterized. Their ^1H and ^{13}C NMR spectra are consistent with the indicated structures for $In(CO)_2Fe$–acyl compounds not having a chiral center. The methoxyacetyl complex **15a** also is available (41% yield) by metalating methoxyacetyl chloride with $In(CO)_2Fe^-Na^+$.



(7)

Carbonylating the α-ethoxyethyl complex **12** by treating it first with $In(CO)_2Fe^-Na^+$ (eq 6) and then with CH_3I/1 atm CO (eq 8) affords the acyl compound $In(CO)_2Fe-COCH(OEt)CH_3$ (**16**). Column chromatography of the crude reaction mixture gave **16** in 59% yield as a stable, light red-orange powder. ^1H and ^{13}C NMR spectra of this fully characterized material also indicate the presence of a chiral center, although chemical shift differences between diastereotopic protons (indenyl H_1 and H_3 and the ethoxy methylene doublets of quartets) are much less pronounced than with **12**.



(8)

Adopting $In(CO)_2Fe$ complexes versus their Fp congeners in synthetic transition organometallic chemistry clearly offers significant advantages. The synthetic versatility associated with the more established Fp system is retained, yet the presence of the η^5-indenyl ligand offers enhanced reactivity. Synthetic procedures for making $In(CO)_2Fe$–alkyl and –acyl starting materials and for performing subsequent coordinated ligand reactions certainly follow from those used with analogous Fp compounds. We additionally have demonstrated several cases where enhanced reactivity of $In(CO)_2Fe$ complexes evidently derives from reversible η^5–η^3 indenyl ligand ring slippage.[25]

These examples include (1) carbonylation of In(CO)(L)FeCH_3 (L = CO, PPh_3) to corresponding acetyl complexes under unusually mild conditions,[10] (2) irreversible carbonylation of $\text{In(CO)}_2\text{Fe}^-\text{Na}^+$ to $(\eta^3\text{-In})(\text{CO})_3\text{Fe}^-\text{Na}^+$ (which was characterized by X-ray crystallography) and its subsequent alkylation,[26] (3) interchange of acetyl and terminal carbonyl groups on $\text{In(CO)}_2\text{Fe}{-}^{13}\text{C(O)CH}_3$ in the presence of catalytic amounts of $\text{In(CO)}_2\text{Fe}^-\text{Na}^+$ or Fp^-Na^+,[27] and (4) formation and subsequent carbonylation of bimetallic acyl complexes **8** (eq 3) and **13** and **14** (eq 6–8).[15] In each example the enhanced or unique reactivity is attributed to readily accessible $(\eta^3\text{-In})\text{Fe}$ intermediates.

Mechanistic studies in progress further address the unusual binuclear carbonylation sequence (eq 6–8). In Figure 2 we outline a plausible pathway for first forming a bimetallic acyl compound, **17**, and then degrading it to the desired mononuclear acyl compound in the presence of carbon monoxide.

Reversible η^5–η^3 indenyl ligand ring slippage,[25] although speculative, does account for the regioselectivity observed in carbonylating the mixed CpInFe_2 system (eq 3).[15] Forming the bimetallic acyl complexes **8** (eq 3), **13a,b** and **14** (eq 6), and **17** (Figure 2) presumably involves metalate-induced alkyl–CO insertion[28] concomitant with reversible η^5–η^3 In ring slippage. Nucleophilic attack of the metalate $\text{In(CO)}_2\text{Fe}^-\text{Na}^+$ at the iron center of the alkyl complex thus affords $\text{In(CO)}_2\text{Fe–Fe(CO)}_2(\text{R})(\eta^3\text{-In})^-\text{Na}^+$ as a logical intermediate or transition state.[29] Carbonylation of the resulting binuclear acyl complex **18** then produces the $(\eta^3\text{-In})\text{Fe–CO}$ adduct **19**, analogous to $(\eta^3\text{-In})\text{Fe(CO)}_3^-$, that methylates at iron and gives **20**. Degradation of **20** produces the observed mononuclear products.

Conclusions

Two major conclusions emerge from this study. First, the (alkoxymethyl)iron complexes **9a,b** do carbonylate under mild conditions (1 atm of CO) and give their mononuclear alkoxyacetyl derivatives **13a,b** when the two-stage carbonylation procedure is adopted. Treating the in situ generated bimetallic compounds **13a,b** (eq 6 and 7) containing terminal alkoxyacetyl ligands with CO/CH_3I—literally a one-pot operation—conveniently produces **15a,b** in good yields. In contrast, direct carbonylation of **9a,b** or of related Cp- or In-containing iron alkoxymethyl complexes does not occur up to 100 atm of CO.

Successful coupling of acetyl ligand reduction and subsequent carbonylation steps is the second outcome of this work. Initial activation and reduction of the acetyl ligand on **10** to the α-ethoxyethyl compound **12** (eq 5)—corresponding to the first two steps (a and b) in eq 1—used methodology established with Fp complexes. Carbonylation of **12**—as in step c in eq 1—using the in situ generated bimetallic intermediate **14** (eq 6 and 8) produced the mononuclear α-ethoxypropionyl complex **16**. Previous examples of homologating acyl complexes of related CpFe systems, in contrast, entailed fully reducing the acyl functional group to its methylene–alkyl derivative before carbonylating.[7]

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

Registry No. **9a**, 96412-74-7; **9b**, 119566-80-2; **10**, 96412-64-5; **11**, 119566-82-4; **12**, 119566-83-5; **13a**, 119566-89-1; **13b**, 119566-86-8; **14**, 119566-87-9; **15a**, 119566-84-6; **15b**, 119566-85-7; **16**, 119566-88-0; $\text{In(CO)}_2\text{Fe}^-\text{Na}^+$, 52326-30-4; $(\text{In(CO)}_2\text{Fe})_2$, 36632-68-5; $\text{In(CO)}_2\text{FeCH}_3$, 71498-19-6; chloromethyl ether, 542-88-1; methoxyacetyl chloride, 38870-89-2.

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(29) Analogous Fp complexes lack this reactivity. No reaction occurs between Fp^-Na^+ and $\text{Fp–CH}_2\text{OMe}$ in THF solution (6 h), as deduced by IR spectral monitoring. We favor carbonylation of **18** preceding the alkylation step. Alternative pathways requiring initial alkylation or oxidative addition of CH_3I to **18** appear less likely. Examples of **17** do react with CH_3I in the absence of exogenous CO, but binuclear μ-vinylidene products derived from **17a** are the ultimate products.[15]