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; $FpCH_3$, 12080-06-7; Fp_2, 38117-54-3; $Fp(THF)^+PF_6^-$, 72303-22-1; FpH, 35913-82-7; FpPCl, 12107-04-9; FpPI, 12078-28-3; $FpPPh_3$, 32626-58-7; $Cp(CO)(PPh_3)Fe(NCCH_3)^+$, 47636-90-8; $Cp(CO)(PPh_3)FeH$, 32660-22-3; $Ph_3PCH_3^+BH_4^-$, 40001-26-1; HCO_2H, 64-18-6; CH_3CO_2H, 64-19-7.

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

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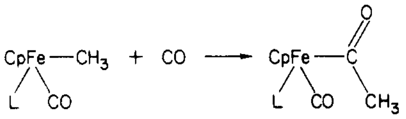
Optimal reaction conditions and ancillary ligand configurations on the (η^5-C_5H_5)$(CO)_2FeCH_3$ "system" are described in order to promote their carbonylation to their corresponding acetyl complexes. Three procedures now are available for promoting CO insertion on this system using 1–6.3 atm of CO. (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 $In(CO)(PPh_3)FeCH_3$ in CH_2Cl_2 incorporates CO at 1 atm and gives its acetyl derivative. In contrast, switching from $Cp(CO)_2FeCH_3$ to (η^5-$C_5(CH_3)_5$)$(CO)_2FeCH_3$ has essentially no effect on the facility of the carbonylation chemistry, whereas $Cp(CO)_2RuCH_3$ 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 $Cp(CO)(PPh_3)FeCH_3$; 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 $Cp(CO)_2Fe$ and $Cp(CO)(PPh_3)Fe$ complexes. (3) Adding an acid catalyst (protonic) permits carbonylation of either $Cp(CO)_2FeCH_3$ or $Cp(CO)(PPh_3)FeCH_3$ under exceedingly mild conditions. With HBF_4 (1% stoichiometrically) both methyl complexes in CH_2Cl_2 add CO at 1 atm. Other useful catalysts include $Ph_2NH_2^+BF_4^-$ for the former and *p*-nitrophenol or pyridinium ($C_5H_5NH^+BF_4^-$) for the latter. None of the above procedures, however, are successful for carbonylating the substituted methyl complexes $Cp(CO)(PPh_3)FeCH_2X$ (X = OCH_3, Ph, CO_2CH_3) or even $In(CO)(PPh_3)FeCH_2OCH_3$.

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]



(1)

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

The parent methyl complex $Cp(CO)_2FeCH_3$ (**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 $Cp(CO)(PPh_3)FeR$ apparently add CO under considerably milder conditions. Treichel and co-workers[4] thus observed $Cp(CO)(PPh_3)FeCH_3$ (**3**) providing its acetyl $Cp(CO)(PPh_3)FeCOCH_3$ (**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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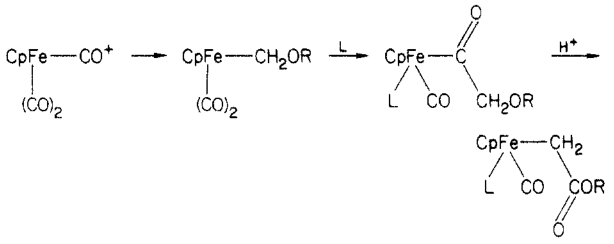
[8] Flood[6] and Brunner[7] have investigated the stereochemistry engendered in carbonylating optically active $Cp(CO)(PPh_3)Fe$ alkyl complexes. Their results substantiate the alkyl-to-ligated CO migratory insertion mechanism,[8] with incoming CO occupying the terminal CO position. It should be noted 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.

alkyl ligand on Cp(CO)(L)FeR, how does one then design the remainder of the molecule (e.g., choice of L), pick the mildest possible carbonylation conditions, and optimize the yield of the resulting acyl compound in eq 1?

In this paper we report synthetic options for carbonylating (η-C_5H_5)(CO)(L)Fe alkyl complexes under conditions of low and medium CO pressure (1–6 and 70 atm, respectively). Two problems are addressed. First, mild conditions for carbonylating methyl complexes and procuring their acetyl compounds (eq 1) are desired. Our approach is to carbonylate a series of iron methyl complexes—while systematically varying the reaction conditions (especially solvent and protic acid catalyst), the ancillary ligands [η^5-indenyl and η^5-$C_5(CH_3)_5$ instead of Cp; L = CO, $P(OCH_3)_3$, PPh_3], and the metal (Ru for Fe). Second, once optimal carbonylation reaction conditions and organoiron systems are identified, then carbonylating their substituted methyl complexes $FeCH_2Z$ (Z = CH_3, Ph, OCH_3, CO_2CH_3) may prove possible. Particular importance is placed on converting (alkoxymethyl)iron complexes to their CO-inserted alkoxyacetyl derivatives.

We are using kinetically nonlabile and thermodynamically robust (C_5H_5)Fe(CO) complexes for elucidating viable coordinated ligand pathways extant in converting two CO ligands to C_2 organic oxygenates.[9] Central to these studies is the phosphine- or phosphite-induced CO-insertion reaction[10] that converts the C_1-alkoxymethyl to C_2-alkoxyacetyl ligand (eq 2). Both the alkoxyacetyl[9b] and carboalkoxymethyl[9c] ligands function as C_2 templates, and subsequent coordinated ligand transformations afford other C_2 ligands and organic molecules. We would like (1) to use CO in place of the phosphine nucleophiles in generating alkoxyacetyl complexes (L = CO) and (2) to carbonylate the carboalkoxymethyl or other C_2 ligands as a means of procuring C_3-coordinated ligands.



(2)

In recent studies on carbonylating these CpFe alkyl complexes[10] the emphasis has shifted toward their catalysis (at 1 atm of CO) by Lewis acids[11,12] and by electron-transfer processes.[13-15] In particular, Shriver demonstrated that Al(III) halides and other Lewis acids (in 1:1 stoichiometry with 1) promote the CO-insertion process depicted in (eq 1) (L = CO),[11] and others showed that BF_3 catalyzes the same reaction in transforming 3 to 4 (L = PPh_3).[6,7] Upon oxidation, both methyl complexes 1 and 3 undergo redox-catalyzed carbonylation via radical chain processes (1 atm of CO, 0 °C) and give 2 and 4, respectively.[13b,d] In the present study, catalysis by only proton donor additives or solvent was addressed.

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.[16] Solvents for synthetic work and for recording spectral data were deoxygenated by bubbling nitrogen through for ca. 20 min. Camag alumina (neutral, activity 3) was used in column chromatography. Carbonylation studies were carried out under conditions of vigorous stirring, using either a Fischer and Porter Lab-Crest pressure bottle (80 psig), containing a magnetic stirring bar, or a Parr Instrument Co. mini-reactor (1000 psig) fitted with an overhead stirrer. A glass liner (400-mL capacity) contained the reaction mixture when using the Parr system. Heating of pressurized reactions was accomplished by using an oil bath/temperature regulator with the pressure bottle and an automatic temperature regulator with the Parr apparatus.

Infrared spectra were taken of 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 297 spectrophotometer. The ν(CO) frequencies (2200–1450 cm^{-1}) were calibrated against the polystyrene 1601 cm^{-1} absorption; they are accurate to ±2 cm^{-1} below and ±5 cm^{-1} above 2000 cm^{-1}. IR spectra of the alkyl and acyl complexes used in this study exhibited straight-line Beer's law behavior in CH_2Cl_2 solution. Thus, IR spectral monitoring of carbonylation reactions was accomplished quantitatively through analysis of absorptivity changes in the terminal and/or acyl ν(CO). By this procedure as little as 2% acetyl complex can be detected in the presence of excess methyl compound. ^1H NMR spectra were taken of concentrated $CDCl_3$ solutions after trace amounts of insoluble residues were centrifuged Varian Model T-60

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[10] Lewis bases promote CO insertion—the ubiquitous phosphine-induced alkyl–CO migratory insertion, 1 and PPh_3 → **4**,[10a–f] being an example. Other nucleophines that induce CO insertion on 1 include CN^-[10g] and even $Cp(CO)_2FeLi$.[10h] These are not true carbonylation reactions as exogeneous CO is not used; the Lewis base used instead coordinates to the acyl complex. (a) Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* **1966**, *5*, 889. Butler, I. S.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1967**, *6*, 2074. (b) Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1971**, 367. (c) Su, S.; Wojcicki, A. *J. Organomet. Chem.* **1971**, *27*, 231. (d) Nicholas, K.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *78*, 133. (e) Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171. Cotton, J. D.; Markwell, R. D. *Ibid.* **1982**, *63*, 13. (f) Brunner, H.; Vogt, H. *Chem. Ber.* **1981**, *114*, 2186. (g) Kruck, T.; Höfler, L.; Liebig, L. *Chem. Ber.* **1972**, 1174. (h) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620.

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[14] Oxidation of 1 or **2** in alcohol, the carboalkoxylation or oxidative carbonylation reaction, provides methyl ester CH_3CO_2R. The presumed mechanism entails solvolysis of the cation radical Cp(L)(ROH)FeC-$OCH_3^{+}\cdot$. 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.; Demers, J. P.; Whitesides, G. M. *Ibid.* **1974**, *96*, 2814. Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521.

[15] In certain cases discerning between Lewis acid catalyzed and redox-catalyzed CO insertion proves difficult. For example, the organometallic Lewis acid $Cp(CO)_3Mo^+$ promotes CO insertion: With 1 it gives the bimetallic μ-(η^1-*C*,*O*)-acetyl complex $Cp(CO)_2FeC(CH_3)OMo$-$(CO)_3Cp^+$,[15a,b] as well as **2** as products. A mechanistic ambiguity surfaces for this reaction since $Cp(CO)_3Mo^+$ can react with other organometallic alkyl complexes as an oxidating agent and as a Lewis acid. In future publications, however, we will document that $Cp(CO)_3Mo^+$ reacts with 1 and **3** via electron transfer and Lewis acid catalyzed pathways, respectively, in forming their bimetallic complexes.[15c] (a) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312. (b) Forschner, T. C.; Cutler, A. R., submitted for publication in *Inorg. Synth.* (c) Forschner, T. C.; Menard, K. P.; Cutler, A. R., manuscript in preparation.

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Table I. Carbonylation of Methyl Complexes (80 psig of CO)

	solv[a]						
	CH_2Cl_2	CH_3NO_2		CF_3CH_2OH			$(CF_3)_2CHOH/Cl_2$
methyl complex	(20 °C)	20 °C	45 °C	20 °C	45 °C	65 °C	(1:1)
(1) $Cp(CO)_2RuCH_3$ (**9**)	NR		NR			NR	NR (45 °C)[b]
(2) $[C_5(CH_3)_5](CO)_2FeCH_3$ (**7**)	NR		NR		57%	87%	
(3) $Cp(CO)_2FeCH_3$ (**1**)	NR	NR[c]	NR	NR[d]	38%[e]	95%	31%
(4) $Cp(CO)[P(OCH_3)_3]FeCH_3$ (**5**)		NR		95%			
(5) $In(CO)_2FeCH_3$ (**11**)	16%	31%		83%			
(6) $Cp(CO)(PPh_3)FeCH_3$ (**3**)	NR	87%		95%[f]			
(7) $In(CO)(PPh_3)FeCH_3)$ (**13**)	95%[g]			*h*			

[a] NR: 95% recovery of starting methyl complex and no detectable (by IR spectroscopy) acetyl complex. [b] 41% **10** and 36% **9** (after chromatography) for 0.43-mmol scale reaction in 30 mL: 1000 psig/24 h/60 °C. [c] Also no reaction using Me_2SO. [d] 10% **2** after 0.40-mmol scale reaction in 20 mL: 1000 psig/24 h. [e] 88% **2** at 1000 psig/24 h, as in *d*. [f] 95% **4** also for reaction using 1 atom of CO/2 h. [g] After 6 h; 32% **14** for reaction using 1 atm of CO/24 h. [h] 95% **14** for 1 atm reaction/3 h: 0.30 mol/30 mL of CF_3CH_2OH/CH_2Cl_2 (1:1).

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.

Organic reagents were procured commercially and used as received. Tetrahydrofuran (THF) was additionally distilled under nitrogen from sodium benzophenone ketyl; methylene chloride and nitromethane were likewise obtained as needed from P_2O_5. For preliminary carbonylation runs each new solvent was removed from a reagent-grade bottle, degassed, and used directly. When these runs gave positive results, they were repeated by using solvent purified of trace amounts of acid. Thus, CH_2Cl_2 was filtered through activity 1, basic alumina; trifluoroethanol was treated with sodium carbonate and distilled; nitromethane was treated with anhydrous sodium carbonate and passed through an alumina column (neutral, activity 1) prior to fractional distillation (30 mm/57–58 °C). Only with nitromethane do these purification treatments result in a diminished carbonylation rate. Unless otherwise noted, results using the purified nitromethane are cited. Both pyridinium and diphenylammonium tetrafluoroborate salts were prepared by protonating the free base in ether, reprecipitating the solid for CH_2Cl_2/ether four times, and vacuum drying.

Metal alkyl complexes $Cp(CO)_2FeCH_3$[17] (**1**), $Cp(CO)(PPh_3)FeCH_3$[4] (**3**), $Cp(CO)[P(OCH_3)_3]FeCH_3$[10b,c] (**5**), $[C_5(CH_3)_5](CO)_2FeCH_3$[18] (**7**), $Cp(CO)_2RuCH_3$[19] (**9**), $Cp(CO)(PPh_3)FeCH_2CH_3$[10c] (**19**), $Cp(CO)(PPh_3)FeCH_2OCH_3$[20] (**21**), $Cp(CO)(PPh_3)FeCH_2Ph$[21] (**23**), and $Cp(CO)(PPh_3)FeCH_2CO_2CH_3$[9] (**25**) were prepared by literature procedures and were judged pure by IR and NMR spectroscopy. A modification of Rosenblum's procedure[22] was used to convert $Cp(CO)_2Fe[CH_2{=}C(CH_3)_2]^+BF_4^-$ to $Cp(CO)_2Fe(THF)^+BF_4^-$, which then was recrystallized four times from CH_2Cl_2/ether inorder to remove traces of acid.

Organoiron alkyl and acyl complexes containing the η^5-indenyl ring (In) are new: $In(CO)_2FeCH_3$ (**11**), $In(CO)_2FeCOCH_3$ (**12**), $In(CO)(PPh_3)FeCH_3$ (**13**), $In(CO)(PPh_3)FeCOCH_3$ (**14**), and $In(CO)(PPh_3)FeCH_2OCH_3$ (**31**). These were prepared by modifying procedures used for their Cp analogues;[23] an exemplary procedure for **31** is included. Authentic samples of $Cp(CO)_2FeCOCH_3$[24] (**2**), $Cp(CO)(PPh_3)FeCOCH_3$[4,10a-d,25] (**4**), $Cp(CO)[P(OCH_3)_3]FeCOCH_3$[9c] (**6**), $Cp(CO)_2RuCOCH_3$[26] (**10**), $Cp(CO)(PPh_3)FeCOCH_2CH_3$[10b,c] (**20**), $Cp(CO)(PPh_3)FeCOCH_2OCH_3$[9] (**22**), and $Cp(CO)(PPh_3)FeCOCH_2Ph$ (**24**)[27] were available from previous studies for direct spectroscopic comparison.

Exploratory Scale Carbonylating of Methyl Complexes. A Fischer and Porter Lab-Crest 3-oz. glass pressure bottle (aerosol reaction vessel) was used at 80 psig of CO; it was kept in a wire-mesh bag and operated behind a $^3/_4$ in. Plexiglass safety shield in the hood. A bottle first was loaded under nitrogen with 0.10–0.20 mmol of methyl complex, 10 mL of solvent (nitrogen-purged), and a magnetic stirring bar. The apparatus then was pressurized to 80 psig of CO and vented—for a total of five cycles—before pressurizing again and magnetically stirring. (Presence of even trace amounts of air during carbonylation runs is deleterious, especially with **3**.) A CO pressure of 80 psig and the designated temperature were maintained by using a pressure-release valve and oil bath, respectively; the rate of stirring was sufficiently vigorous to have the vortex reach the bottom of the glass bottle. At the end of the reaction period, the vessel was vented and opened and the contents were removed under nitrogen. The resulting solution and combined CH_2Cl_2 rinses (15 mL) were evaporated on a Büchi rotovaporator, and the product was dissolved in CH_2Cl_2 (1.5 mL/0.10 mmol vessel). Conversion of methyl to acetyl complex then was ascertained by quantitative IR spectral studies on these clear CH_2Cl_2 solutions.

When positive results were obtained for a given solvent/alkyl complex combination, the reaction was repeated on a larger scale (0.2–0.5 mmol/same concentration), but with a 6-oz. pressure bottle and purified solvents. These reactions were worked up by column chromatography on alumina. Columns (4 × 2.5 cm) were made up in pentane, crude product was added in a minimum volume of CH_2Cl_2, methyl complex was eluted with pentane (**1**, **7**, **9**, **11**) or 1:2 CH_2Cl_2/pentane (**3**, **13**), and the acetyl complex was removed cleanly with CH_2Cl_2. Weights of these materials are in excellent agreement with those obtained by quantitative IR spectroscopy, both for these reactions as well as for those run on a smaller scale. Yields reported in Tables I and II —except for the 95% values—correspond to the actual weights obtained after chromatography. The 95% values represent quantitative conversion (by IR and NMR spectroscopy) of starting methyl to acetyl complex. In all reactions, mass balances (apportioned between methyl and acetyl compounds, unless otherwise noted) ranged between 88 and 95%, with neither decomposition nor other organometallic products evident.

Carbonylation of $(C_5H_5)(CO)(PPh_3)FeCh_3$ (3) in Nitromethane and in Acetonitrile. A clear, red-orange solution of $Cp(CO)(PPh_3)FeCH_3$ (**3**) (213 mg, 0.50 mmol) in 60 mL of nitromethane (purged with nitrogen, but not otherwise purified) was carbonylated (80 psig of CO/20 °C/12 h). The resulting lighter orange to yellow solution was evaporated under reduced pressure and redissolved in 7.5 mL CH_2Cl_2. IR spectral quantification of this solution indicated complete conversion of **3** [ν(CO) 1905 cm^{-1}] to $Cp(CO)(PPh_3)FeCOCH_3$ (**4**) [ν(CO) 1915, 1600 cm^{-1}], with no evidence of starting **3**, insoluble residues, or other or-

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Table II. Acid-Catalyzed Carbonylation of Methyl Complexes

methyl complex[a]	acid[b]	pressure, psig	time, h	results[c]
(1) $Cp(CO)(PPh_3)FeCH_3$ (**3**)	p-$NO_2C_6H_4OH$	80	24	95% **4**
(2) $Cp(CO)(PPh_3)FeCH_3$ (**3**)	p-$NO_2C_6H_4OH$	1 atm	12	6% **4**
(3) $Cp(CO)(PPh_3)FeCH_3$ (**3**)	$C_5H_5NH^+BF_4^-$	80	4	92% **4**
(4) $Cp(CO)(PPh_3)FeCH_3$ (**3**)	$C_5H_5NH^+BF_4^-$	1 atm	3	90% **4**
(5) $Cp(CO)(PPh_3)FeCH_3$ (**3**)	$HBF_4{\cdot}O(CH_3)_2$	80	1	83% **4**
(6) $Cp(CO)(PPh_3)FeCH_3$ (**3**)	$HBF_4{\cdot}O(CH_3)_2$	1 atm	12	95% **4**
(7) $Cp(CO)(PPh_3)FeCH_3$ (**3**)	p-ClC_6H_4OH	80	24	NR
(8) $Cp(CO)_2FeCH_3$ (**1**)	p-$NO_2C_6H_4OH$	80	24	NR
(9) $Cp(CO)_2FeCH_3$ (**1**)	2,4-$(NO_2)_2C_6H_3OH$	80	24	NR
(10) $Cp(CO)_2FeCH_3$ (**1**)	$C_5H_5NH_2^+BF_4^-$	80	36	NR
(11) $Cp(CO)_2FeCH_3$ (**1**)	$Ph_2NH_2^+BF_4^-$	80	24	91% **2**
(12) $Cp(CO)_2FeCH_3$ (**1**)	$Ph_2NH_2^+BF_4^-$	1 atm	36	85% **2**
(13) $Cp(CO)_2FeCH_3$ (**1**)	$HBF_4{\cdot}O(CH_3)_2$	80	7	91% **2**
(14) $Cp(CO)_2FeCH_3$ (**1**)	$HBF_4{\cdot}O(CH_3)_2$	1 atm	8	22% **2**
(15) $Cp(CO)_2FeCH_3$ (**1**)	$Cp(CO)_2Fe(THF)^+BF_4^-$ (**21**)	80	12	NR[d]
(16) $Cp(CO)_2FeCH_3$ (**1**)	$Cp(CO)_2FeC(CH_3)OFe(CO)_2Cp^+BF_4^-$ (**22**)	80	12	NR
(17) $Cp(CO)_2RuCH_3$ (**9**)	$Ph_2NH_2^+BF_4^-$	1000	24	NR
(18) $Cp(CO)_2RuCH_3$ (**9**)	$HBF_4{\cdot}O(CH_3)_2$	80	24	NR

[a] 0.20 mmol in 20 mL of CH_2Cl_2 or (entries 2 and 3) CH_3NO_2. All reactions at 22 °C, except for 8 (45 °C). [b] 10% (stoichiometric) added, except for entries 5, 6, 13, 14, and 18 where 1% $HBF_4{\cdot}O(CH_3)_2$ was used. [c] NR: no detectable acetyl complex by IR spectroscopy, recovery of 87–95% of starting methyl complex, and no other organometallic products or decomposition materials detected. [d] $Cp(CO)_2Fe(THF)^+BF_4^-$ recrystallized four times (CH_2Cl_2/ether) to remove trace amounts of acid. (With one recrystallization essentially quantitative carbonylation was observed.)

ganometallic materials. Removal of CH_2Cl_2 and vacuum drying (10^{-2} mm/4 h)—neither **3** nor **4** are volatile—left 215 mg of orange solid, which was spectroscopically pure (by NMR) $Cp(CO)(PPh_3)FeCOCH_3$ (**4**) (94% yield).

Similar carbonylations over shorter periods gave incomplete conversion of **3** to **4**. Both complexes were isolated after chromatography: their weights were in excellent agreement with their concentrations as determined by quantitative IR spectroscopy. After a 6-h reaction, 76% **4** and 22% **3** and, after a 3-h reaction, 44% **4** and 55% **3** were obtained.

If the nitromethane used in this procedure is carefully purified, including a final distillation, then the yield of **4** drops. Repeating the above experiment in nitromethane that had been distilled immediately before use provided 59% **4** and 39% **3** after chromatography.

An acetonitrile/methylene chloride solution (5 mL/55 mL) containing **3** (213 mg, 0.50 mmol) was carbonylated (80 psig) for 24 h. Removal of solvent and column chromatography provided 142 mg (67%) **3** and 56 mg (24%) **4**.

Carbonylation of $(C_5H_5)(CO)(PPh_3)FeCH_3$ (3) in 2,2,2-Trifluoroethanol. $Cp(CO)(PPh_3)FeCH_3$ (**3**) (213 mg, 0.50 mmol) was dissolved in trifluoroethanol (30 mL) only after adding CH_2Cl_2 (5 mL) and stirring. Under CO pressure (80 psig) this red-orange solution turned bright yellow within 20 min. Solvent was removed on a Büchi rotovaporator (30 mm, 22 °C), and the resulting orange solid (218 mg) was vacuum dried. Results of IR and NMR spectroscopic analyses indicated quantitative conversion of **3** to **4**. Identical results were obtained when this reaction was repeated by using 1 atm of CO for 2 h at 22 °C.

Carbonylation using lower concentrations of trifluoroethanol also was possible. Thus 0.5 mmol of **3** in 1:1 CH_2Cl_2/CF_3CH_2OH (20 mL) turns from dark orange to bright yellow after being stirred under 80 psig of CO for 1 h. IR and NMR spectral analysis is consistent with 96% **4** and 4% **3**. Substitution of a solvent mixture 15 mL of CH_2Cl_2/5 mL of CF_3CH_2OH in this reaction afforded 34% **4** and 65% **3**.

Carbonylation of $[\eta^5\text{-}C_5(CH_3)_5](CO)_2FeCH_3$ (7). A clear, yellow solution of $[C(CH_3)_5](CO)_2FeCH_3$ (**7**) (56 mg, 0.21 mmol) in trifluoroethanol (10 mL) was pressurized with CO (82 psig) for 24 h at 45 °C. No physical change was apparent for the reaction mixture. The solvent was then evaporated, and the yellow residue was chromatographed on alumina. Both methyl **7** and product acetyl $[C_5(CH_3)_5](CO)_2FeCOCH_3$ (**8**) compounds were eluted as separate yellow bands, **7** coming off first. Removal of solvent left yellow crystalline solids: 22 mg (38%) of **7** recovered [IR (CH_2Cl_2) 1986, 1924 cm^{-1}; NMR ($CDCl_3$) δ 1.70 (s, 15 H, CCH_3), −0.16 (s, 3 H, $FeCH_3$)] and 35 mg (57%) of **8** [mp 58–60 °C; IR (CH_2Cl_2) 1998, 1939 cm^{-1} (C≡O), 1620 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.46 (s, 3 H, $COCH_3$), 1.74 (s, 15 H, CCH_3)].

Anal. Calcd for $C_{14}H_{18}O_3Fe$: C, 57.95; H, 6.25. Found: C, 58.06; H, 6.29.

Carbonylation of $(\eta^5\text{-}C_9H_7)(CO)(PPh_3)FeCH_3$ (13) in Methylene Chloride. A reddish brown CH_2Cl_2 solution (10 mL) of $In(CO)(PPh_3)FeCH_3$ (**13**) (238 mg, 0.50 mmol) was carbonylated (80 psig) over 24 h. This orange-brown solution then was concentrated and chromatographed on 50 g of activity 3 alumina/pentane. Development of the column with 1:4 CH_2Cl_2/pentane cleanly eluted a yellow band containing $In(CO)_2FeCH_3$ (**11**) (9 mg, 7%), and CH_2Cl_2 eluted an orange band containing $In(CO)(PPh_3)FeCOCH_3$ (**14**): 231 mg of reddish orange crystalline solid (92%) after vacuum drying; IR (CH_2Cl_2) 1914 cm^{-1} (C≡O), 1608 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.6–6.2 (complex mult, 19 H, benzo + PPh_3), 5.08 (br s, 1 H, C_9H_7:$C_{1\text{or}3}$H), 4.91 (t, J = 7 Hz, 1 H, C_9H_7:C_2H), 4.56 (br s, 1 H, C_9H_7:$C_{3\text{or}1}$H), 2.26 (s, 3 H, CH_3); mp 166–169 °C.

Anal. Calcd for $C_{30}H_{25}O_2PFe$: C, 71.44; H, 4.99. Found: C, 71.12; H, 4.93.

$In(CO)(PPh_3)FeCH_3$ (**13**) was carbonylated by also using 1 atm of CO. A CH_2Cl_2 solution (40 mL) containing **13** (380 mg, 0.80 mmol) was stirred vigorously under an atmosphere of CO for 24 h. Chromatography of the orange-brown solution as before separated $In(CO)_2FeCH_3$ (**11**) with pentane (8 mg, 4%), $In(CO)(PPh_3)FeCH_3$ (**13**) with 1:2 CH_2Cl_2/pentane (253 mg, 53%), and $In(CO)(PPh_3)FeCOCH_3$ (**14**) with CH_2Cl_2 (128 mg, 32%).

Acid-Catalyzed Carbonylation of $(C_5H_5)(CO)(PPH_3)FeCH_3$ (3) in Methylene Chloride. An orange CH_2Cl_2 solution (50 mL) containing $Cp(CO)(PPh_3)FeCH_3$ (**3**) (1.00 g, 2.34 mmol) and pyridinium tetrafluoroborate (33 mg, 0.20 mmol) was stirred vigorously under 1 atm of CO for 3 h. IR spectral analysis of the resulting yellow-orange solution indicated essentially quantitative conversion of **3** to **4**. The solution was concentrated to ca. 15 mLf it was filtered through a 2.5-cm bed of alumina using a total of 90 mL of CH_2Cl_2 to remove all orange material. Removal of solvent and vacuum drying left 965 mg of $Cp(CO)(PPh_3)FeCOCH_3$ (**4**) (90%), which was pure by NMR spectroscopy.

Acid-Catalyzed Carbonylation of $(C_5H_5)(CO)_2FeCH_3$ (1) in Methylene Chloride. To $Cp(CO)_2FeCH_3$ (**1**) (150 mg, 0.78 mmol) as a yellow CH_2Cl_2 solution (20 mL) was added diphenylammonium tetrafluoroborate (20 mg, 0.08 mmol) before stirring with 80 psig of CO for 24 h. No physical change was apparent during this reaction. The reaction was worked up by column chromatography; no starting **1** was detected on the column. Development of the column with CH_2Cl_2 subsequently removed a yellow band, which afforded $Cp(CO)_2FeCOCH_3$ (**2**) as a yellow solid (158 mg, 91%) after distilling solvent and vacuum drying. It was spectroscopically pure: IR (CH_2Cl_2) 2020, 1960 cm^{-1} (C≡O), 1646 cm^{-1} (C=O); NMR ($CDCl_3$) δ 4.83 (s, 5 H, Cp), 2.56 (s, 3 H, CH_3).

A CH_2Cl_2 solution (60 mL) of $Cp(CO)_2FeCH_3$ (**1**) (95 mg, 0.50 mmol) was treated with 5 μL (0.50 mmol) of $HBF_4{\cdot}O(CH_3)_2$, and then it was vigorously stirred with 1 atm of CO for 12 h. The resulting yellow solution, unchanged in appearance, was concentrated under reduced pressure and chromatographed. The first yellow band that was eluted in pentane corresponded to recovered **1** (37 mg, 38%); the second yellow band that was removed in CH_2Cl_2 afforded 64 mg of $Cp(CO)_2FeCOCH_3$ (**2**) (58%). The same reaction but using 80 psig of CO over 7 h gave **2** exclusively, which was isolated by column chromatography in 91% yield.

Acid-Catalyzed Carbonylation of (η^5-C_9H_7)$(CO)_2FeCH_3$ (11) in Methylene Chloride. A dark yellow-brown methylene chloride solution (50 mL) containing $In(CO)_2FeCH_3$ (**11**) (1.805 g, 7.45 mmol) and $Ph_2NH_2^+BF_4^-$ (40 mg, 0.16 mmol) was treated with CO (80 psig/22 °C) for 48 h. The resulting yellow-orange solution was concentrated and filtered through a 3-cm bed of alumina; another 80 mL of CH_2Cl_2 was used to remove all color from the alumina. Evaporation of solvent from the combined filtrates and vacuum drying left yellow-orange crystals (1.902 g) that correspond to spectroscopically pure $In(CO)_2FeCOCH_3$ (**12**) (94%): IR (CH_2Cl_2) 2019, 1959 cm^{-1} ($C{\equiv}O$), 1664 cm^{-1} ($C{=}O$); NMR ($CDCl_3$ δ 7.42, 7.18 (A_2B_2 mults, 4 H, benzo), 5.58 (d, J = 2.9 Hz, 2 H, $C_9H_7{:}C_{1,3}H$), 4.99 (t, J = 2.9 Hz, 1 H, $C_9H_9{:}C_2H$), 2.49 (s, 3 H, $COCH_3$); mp 66–67 °C.

Anal. Calcd for $C_{13}H_{10}O_3Fe$: C, 57.80; H, 3.73. Found: C, 58.07; H, 3.70.

Preparation of (η^5-C_9H_7)(CO)(PPh_3)$FeCH_2OCH_3$ (27). To a nitrogen-flushed 500-mL amalgam flask, fitted with a nitrogen inlet adapter and overhead stirrer, was added 250 mL of deoxygenated THF, excess of 1% sodium amalgam (70 mL), and 7.50 g (16.5 mmol) of recrystallized $[In(CO)_2Fe]_2$.[23,28] The mixture then was stirred vigorously for 1 h; the initially red-brown THF solution formed an orange-brown suspension. Remaining sodium amalgam was drained from the bottom of the flask, and the THF suspension was transferred via 18 gauge stainless-steel double-ended needle to a second reaction flask.

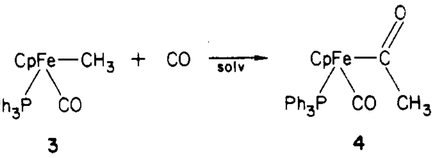
This reaction flask, a 500-mL three-necked flask fitted with a nitrogen inlet adapter, rubber septa, and a magnetic stirring bar, now containing the $In(CO)_2Fe^-Na^+$ suspension was cooled to +5 °C by immersing in a ice-water slush. Excess chloromethyl methyl ether (2.7 mL, 35 mmol) [*Caution*! Suspected human carcinogen.] then was injected into the stirred anion suspension. The resulting brownish yellow suspension was brought to room temperature (1 h) and evaporated on a rotary evaporator (25 mm, 22 °C). Pentane extracts (6 × 25 mL) of the yellow-brown residue were filtered through a 4-cm bed of activity 3 alumina/pentane, which was washed with an additional 50 mL of pentane to extract all of the yellow material. Removal of solvent from the combined pentane fractions left $In(CO)_2FeCH_2COCH_3$ as a yellow-brown oil (7.32 g, 82%): IR (CH_2Cl_2) 2000, 1940 cm^{-1}; NMR ($CDCl_3$) δ 7.53–7.06 (complex mult, 4 H, benzo), 5.32 (d, J = 2.6 Hz, 2 H, $C_9H_7{:}C_{1,3}H$), 4.86 (t, J = 2.6 Hz, 1 H, $C_9H_7{:}C_2H$), 4.30 (s, 2 H, $FeCH_2$), 3.18 (s, 3 H, OCH_3). This material was used without further purification in the next step.

A CH_2Cl_2 solution (60 mL) containing $In(CO)_2FeCH_2OCH_3$ (3.70 g, 13.6 mmol) and PPh_3 (4.27 g, 16.3 mmol) was irradiated (Hanovia medium-pressure Hg-vapor lamp) at 0 °C (4 h) during a gentle nitrogen purge. The resulting dark red solution was passed through a 3-cm bed of activity 3 alumina, which was washed with additional CH_2Cl_2 (40 mL) to remove all color from the alumina. The combined red filtrates were diluted with absolute ethanol (50 mL), and the CH_2Cl_2 was removed under reduced pressure (30 mm, 22 °C). The resulting red crystals were filtered, washed with ethanol, and vacuum dried: 4.82 g of In(CO)(PPh_3)$FeCH_2OCH_3$ (**27**) (71%); decomp pt 124 °C; IR (CH_2Cl_2) 1908 cm^{-1}; NMR ($CDCl_3$) δ 7.5–6.3 (complex mult, 19 H, benzo + PPh_3), 5.10 (t, J = 3 Hz, 1 H, $C_9H_7{:}C_2H$), 4.82 (br s, 1 H, $C_9H_7{:}C_{3or1}H$), 4.42 (br s, 1 H, $C_9H_7{:}C_{1or3}$), 3.91 (dd, J = 4, 7 Hz, 1 H, FeC*H*H), 3.88 (dd, J = 3, 4 Hz, 1 H, FeCHH*H*), 2.80 (s, 3 H, OCH_3).

Anal. Calcd for $C_{30}H_{27}O_2PFe$: C, 71.16; H, 5.37. Found: C, 71.90; H, 5.50.

Results

Carbonylation of Methyl Complexes: Results of Varying Solvent and Ancillary Ligands. The methyl complex $Cp(CO)(PPh_3)FeCH_3$ (**3**) served as our test substrate for evaluating solvent effects during carbonylation reactions (eq 3). This choice of *3* was arrived at as a result of preliminary observations in which **3** easily carbonylated (80 psig of CO/22 °C) in nitromethane, but not in THF or CH_2Cl_2. In contrast, $Cp(CO)_2FeCH_3$ (**1**) proved inert under these conditions.



3 **4** (3)

Standard conditions for carbonylating **3** in different solvents—0.10 mmol of **3**/10 mL of solvent and 80 psig of CO at 22 °C for 24 h—as vigorously stirred solutions were used. Under these conditions no carbonylation took place in $CHCl_3$, CH_2Cl_2, THF, benzene, acetone, methanol (100 mL required), $HCON(CH_3)_2$(DMF), $(CH_3)_2SO(Me_2SO)$, or $\overline{CH_2(CH_2)_2CH_2SO_2}$ (sulfolane). A special workup procedure was required for reactions using the high-boiling dipolar aprotic solvents DMF, Me_2SO, and sulfolane: they were removed by an aqueous vs. CH_2Cl_2 extraction. The combined CH_2Cl_2 extracts recovered 75–80% of **3**, with no detectable **4**. (The presence of as little as 5% **4** would have been detected during this workup procedure, as verified by results of control experiments.) With the remaining solvents, the reactions were evaporated, redissolved in a known volume of CH_2Cl_2, and assayed by IR spectroscopy. In each case no **4** was observed (vs. a 2% detection limit), and up to 5% $Cp(CO)_2FeCH_3$ (**1**) and unchanged **3** (92–97% yields) constituted the only organometallic materials.

When acetonitrile, nitromethane, or 2,2,2-trifluoroethanol were used as solvents the carbonylation of **3** proved to be quantitative under our standard conditions. The minimum time required to for converting **3** to **4** was studied by rerunning these reactions on a larger scale, breaking them down after the indicated time, and working them up by column chromatography. Convenient procedures thus are recorded in the Experimental Section for completely transforming 0.5 mmol of **3** to **4** with 80 psig of CO in nitromethane (between 6 and 12 h) and in trifluoroethanol (as short as 1 h). These results for nitromethane, however, refer to using reagent-grade solvent that was only degassed before using. When the nitromethane is distilled immediately before using as the carbonylation solvent, then the yield for **4** drops by nearly 40%. Acetonitrile proved much less efficient than nitromethane in mediating CO addition to **3** for the 0.5-mmol scale reaction.

Trifluoroethanol (picked because of its relatively high hydrogen bond donor capability, vide infra) as a solvent facilitates carbonylation reactions. Although **3** is only very slightly soluble—less than one-third of 0.50 mmol of **3** dissolved in 60 mL—the orange suspension turns to a yellow solution under 80 psig of CO pressure in less than 0.5 h. Complete transformation of **3** to **4** is also possible in mixed-solvent systems of trifluoroethanol/CH_2Cl_2 that conserve the former solvent; details are in the Experimental Section. An even more dramatic role of trifluoroethanol is evident in it promoting CO insertion on **3** with only 1 atm of CO. Thus, 0.5 mmol of **3** in CF_3CH_2OH (25 mL)/CH_2Cl_2 (5 mL) and under 1 atm of CO quantitatively converts to **4** in less than 2 h.

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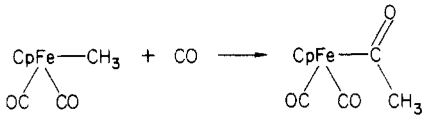
(28) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 646.

We next investigated the effects of structurally modifying the methyl complex **3** in an attempt to expedite the carbonylation chemistry. In particular, consequences of altering the ancillary ligand L (eq 1), the Cp ligand, or even the metal as a means of "fine tuning" the reactivity of the metal center toward methyl–CO insertion were probed. Results of carbonylating (80 psig of CO) one Ru and six Fe methyl complexes in the four solvents CH_2Cl_2, CH_3NO_2, CF_3CO_2OH, and $(CF_3)_2CHOH$ are presented in Table I. Each complex eventually carbonylated, albeit using widely varying conditions, to give its independently prepared acetyl compound. Three of these acetyl compounds $[C_5(CH_3)_5]CO_2FeCOCH_3$ (**8**), $In(CO)_2FeCOCH_3$ (**12**), and $In(CO)(PPh_3)FeCOCH_3$ (**14**) are new and are fully characterized.

The methyl complexes of $Cp(CO)_2FeCH_3$ (**1**) and $Cp(CO)[P(OCH_3)_3]FeCH_3$ (**5**) proved to be more resistant toward carbonylation (eq 4 and 5) than **3**. Whereas **3** adds CO in trifluoroethanol or nitromethane solution (80 psig/0.067 M/22 °C/24 h), **1** does not react under these conditions, and **5** only gives its acetyl **6** in trifluoroethanol. $Cp(CO)_2FeCH_3$ (**1**), however, does carbonylate after appropriately modifying the reaction conditions.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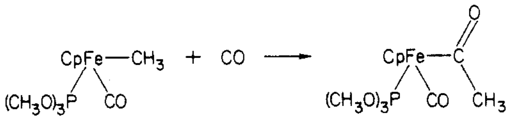
1 **2**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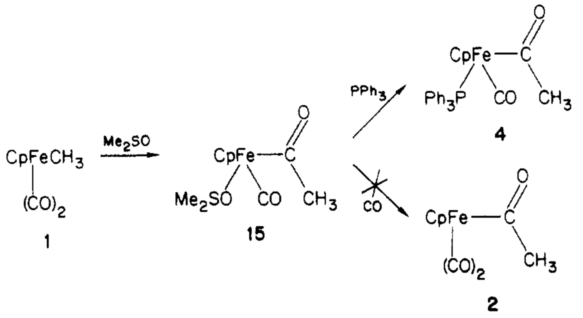
5 **6**

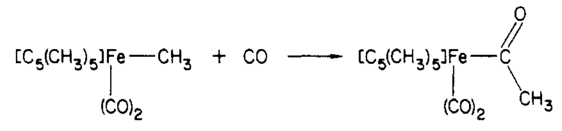
Three procedures were used to carbonylate **1**. (1) Just increasing the temperature of the reaction mixture in trifluoroethanol (but not nitromethane) completely transformed **1** to its acetyl **2** (at 65 °C). (2) Raising both CO pressure (80–1000 psig) and temperature (to 45 °C) in trifluoroethanol efficiently converted **1** to **2**, although just raising the pressure at 22 °C had minimal effect (10% conversion to **2** after 24 h). (3) Substituting hexafluoro-2-propanol as the solvent (80 psig of CO, 22 °C) also increased yields of **2**.

One surprising observation is the total inertness of $Cp(CO)_2FeCH_3$ (**1**) toward CO (80 psig/22 °C/24 h) in Me_2SO. Unchanged **1** (85%) was the only detected organometallic species after aqueous CH_2Cl_2 extraction and workup. This result contrasts the lability of the Me_2SO–acetyl complex **15**, which forms on dissolution of **1** in Me_2SO, toward PPh_3 (eq 6).[10d]


(6)

1 **15** **4** **2**

Carbonylation tendencies of methyl complexes of $[\eta^5\text{-}C_5(CH_3)_5](CO)_2Fe$ and $Cp(CO)_2Ru$ (eq 7 and 8) were then compared with that of $Cp(CO)_2FeCH_3$ (**1**). Interestingly, **7** resembles **1** rather closely in terms of the reaction conditions required for forming its acetyl compound (Table I). The ruthenium methyl **9**, in contrast, carbonylates much less readily. Only at 60 °C and at 1000 psig of CO did **9** affords its acetyl derivative **10** in moderate yield. The compound was previously prepared by acylating $Cp(CO)_2Ru^-Na^+$ with acetyl chloride.[26]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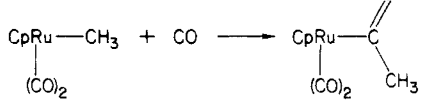
7 **8**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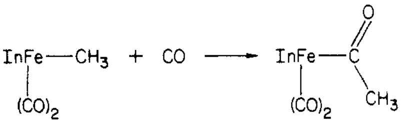
9 **10**

Replacing the Cp group by the η^5-indenyl ligand (In) markedly enhances carbonylation reactivity of the iron methyl complexes. Reaction conditions required to convert $In(CO)_2FeCH_3$ (**11**) and $In(CO)(PPh_3)FeCH_3$ (**13**) into their acetyl derivatives **12** and **14**, respectively (eq 9 and 10), are much milder than those needed for carbonylating **1** and **3** (Table I). For example, both **11** and **13** pick up CO in CH_2Cl_2, a reaction that is not observed for either **1** or **3**. The phosphine-substituted complex **13** even undergoes 32% transformation to **14** with 1 atm of CO after only 6 h—certainly under the mildest conditions that we have observed in the absence of an acid catalyst.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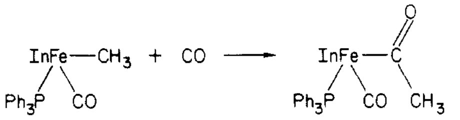
11 **12**


(10)

13 **14**

Carbonylating Methyl Complexes: Acid Catalysis. We wanted to carbonylate the methyl complexes $Cp(CO)_2FeCH_3$ (**1**) and $Cp(CO)(PPh_3)FeCH_3$ (**3**) in CH_2Cl_2 using catalytic amounts of protonic acids. The proton donor used for this purpose clearly must not preferentially cleave the $Fe–CH_3$ bond of the starting methyl complex, yet it must be acidic enough to associate with the incipient acetyl ligand[29] —either by hydrogen bonding[30] or by complete proton transfer to the acetyl O. This problem was addressed previously by Shriver on using $CHCl_2CO_2H$, although in excess, to promote CO insertion on $(CO)_5MnCH_3$.[11b] Table II summarizes our results on using a variety of acids in catalytically carbonylating **1** and **3** in CH_2Cl_2.

When tetrafluoroboric acid is used in catalytic amounts (1%), the carbonylation of **3** in CH_2Cl_2 (eq 11) proceeds smoothly at either 80 psig or 1 atm of CO. We feel that with additional study the high yields already attained

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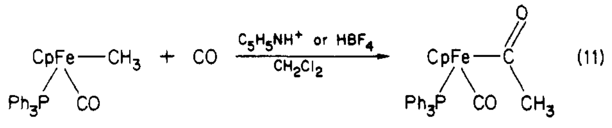
[29] For comparison, the acetyl ligand on $Cp(CO)_2FeCOCH_3$ (**2**) is "significantly more basic than acetone toward the hard acid BF_3". Stimson, R. E.; Shriver, D. F. *Inorg. Chem.* **1980**, *19*, 1141.

[30] (a) Rochester, C. H. In "The Chemistry of the Hydroxyl Group"; Patai, S., Ed.; Wiley-Interscience: New York, 1971; Part 1, Chapter 7. (b) Joesten, M. D.; Schaad, L. J. "Hydrogen Bonding"; Marcel Dekker: New York, 1974. (c) Bellamy, L. J. "The Infrared Spectra of Complex Molecules", 2nd ed.; Chapman and Hall: New York, 1980; Vol. 2, Chapter 8.

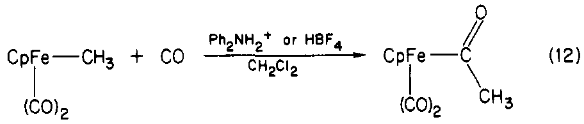


3 4

(Table II) for this convenient preparation of acetyl **4** will be optimized further. Weaker acids also were investigated as potential catalysts for this CO insertion reaction, since extension of these carbonylation studies to include complexes bearing more acid-sensitive alkyl ligands (e.g., η^1-alkoxymethyl) was anticipated.

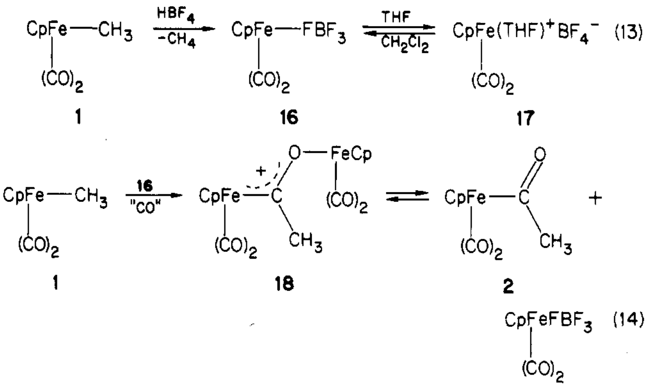
The relatively weak acids[31] *p*-nitrophenol (pK_a = 7.2) and pyridinium tetrafluoroborate (pK_a = 5.3), present in catalytic amounts (10%), thus promote CO uptake (at 80 psig) by **3** in CH_2Cl_2. Quantitative yields of **4** result from these reactions, as well as from those using pyridinium as a catalyst with 1 atm of CO over 3 h. (The $C_5H_5NH^+BF_4^-$ had been carefully purified to eliminate any traces of free acid.)

Acid-catalyzed carbonylation of $Cp(CO)_2FeCH_3$ (**1**) is, as expected, much more difficult—neither *p*-nitrophenol nor pyridinium promote this reaction (Table II). The more acidic diphenylammonium salt $Ph_2NH_2^+BF_4$ (pK_a = +0.8), however, functions as an excellent catalyst (eq 12) in CH_2Cl_2 at 80 psig of CO and even at 1 atm of CO. Tetrafluoroboric acid also catalyzes the carbonylation of **1**. Excellent yields of acetyl **2** result after using only 1% $HBF_4·O(CH_3)_2$ in CH_2Cl_2 with **1** and 80 psig of CO, although moderate yields of **2** are available even upon using only 1 atm of CO. It is of interest to ascertain whether HBF_4 or a product derived from degrading **1** with HBF_4 actually functions as the catalyst.



1 2

Protolytic cleavage of **1**[32] with HBF_4 initially generates the extremely reactive Lewis acid precursor $Cp(CO)_2FeFBF_3$[33] (**16**). We have reported procedures using excess $HBF_4·O(CH_3)_2$ to convert **1** to **16**, which subsequently functions as a convenient precursor to the labile tetrahydrofuran adduct $Cp(CO)_2Fe(THF)^+BF_4^-$ (**17**) (eq 13).[15b,34] With 1 equiv of HBF_4, however, **1** gives complex mixtures containing **16** and the bimetallic μ-(η^1-*C*,*O*)-acetyl $Cp(CO)_2FeC(CH_3)OFe(CO)_2Cp^+BF_4^-$[35] (**18**) (eq 14)—all without exogeneous CO.[36] Recently we have further demonstrated that this μ-acetyl compound **18** equilibrates with **16** and its acetyl **2**.[37] Clearly **16** and/or **18** must be considered as potential catalysts or catalyst precursors during the HBF_4-mediated carbonylation of **1**.



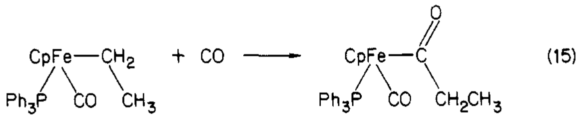
1 16 17

1 18 2

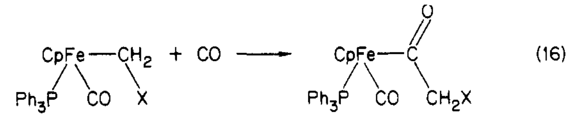
16

We attempted to use the THF adduct **17** and the μ-acetyl salt **18** as catalysts in converting **1** to **2** under 80 psig (Table II). The THF salt **17** was used in place of $Cp(CO)_2FeFBF_3$ (**16**), since we deemed it would be exceedingly difficult to procure **16** free from trace amounts of acid. Indeed, in order to get consistent results using **17**, it had to be reprecipitated four times to free it completely of acid. Nevertheless, neither **17** or **18** catalyzed carbonylation of **1** to **2**. Therefore HBF_4-stimulated CO addition to **1** apparently requires the free acid as the catalyst.

Attempted Carbonylation of Substituted Methyl Complexes. $Cp(CO)(PPh_3)Fe$ alkyl complexes are ideal systems for investigating the carbonylation of substituted methyl complexes $Cp(CO)(PPh_3)FeCH_2X$ (eq 15 and 16).



19 20



21, X=OCH_3 22
23, X=Ph 24
25, X=CO_2CH_3 26

The required alkyl complexes **19**, **21**, **23**, and **25** and three of their acyl derivatives **20**, **22**, and **24**, all well-known, were already available to us as a result of previous endeavors. Most importantly, the corresponding methyl complex **3** readily carbonylates at or below 80 psig of CO in nitromethane or trifluoroethanol and with acid catalysis in methylene chloride.

In Table III a sampling of the results from numerous attempts at carbonylating **19**, **21**, **23**, and **25** in nitromethane and/or trifluoroethanol and in methylene chloride with 10% $Ph_2NH_2^+BF_4^-$ are presented. Only the ethyl complex **19** inserted CO (at 80 psig) and gave its propionyl derivative **20** (eq 15). The other alkyl complexes remained inert toward CO insertion, even though CO pressures up to 1000 psig were used routinely. With the carbomethoxymethyl **25**, however, higher CO pressures or higher temperatures at 80 psig of CO partially replaced the PPh_3 ligand and provided $Cp(CO)_2FeCH_2CO_2CH_3$ in up to 50%

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[31] pK_a values taken from: (a) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972; p 54. (b) Reference 30a.

[32] (a) Flood, T. C.; Miles, D. L. *J. Organomet. Chem.* **1977**, *127*, 33. (b) Rogers, W. N.; Baird, M. C. *Ibid.* **1979**, *182*, C65. (c) DeLuca, N.; Wojcicki, A. *Ibid.* **1980**, *193*, 359. (d) Anderson, S. N.; Cooksey, C. J.; Holton, S. G.; Johnson, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 2312. (e) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57.

[33] $Cp(CO)_2FeFBF_3$ has been independently prepared [$Cp(CO)_2FeI/AgBF_4$] and fully characterized. Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186.

[34] $Cp(CO)_2Fe(THF)^+$ in CH_2Cl_2 solution is regarded as a labile precursor of the putative Lewis acid $Cp(CO)_2Fe^+$: Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153. See also reference 22.

[35] (a) Sünkel, K.; Schlotter, K.; Beck, W.; Ackermann, K.; Schubert, U. *J. Organomet. Chem.* **1983**, *241*, 332. Sünkel, K.; Nagel, U.; Beck, W. *Ibid.* **1983**, *251*, 227. (b) Reference 15a,b.

[36] Details for this synthesis of **18** will be reported separately. Also, relevant is the observation that when **1** reacts with **16**/**17** (in the absence of exogeneous CO), small amounts of $Cp(CO)_2FeCOCH_3$ (**2**) (up to 20%) form in addition to the Fe_2 μ-acetyl **18**. Forschner, T. C.; Cutler, A. R., work in progress.

[37] A CH_2Cl_2 solution of **18** readily incorporates (η^5-$C_5H_4CH_3$)-$(CO)_2FeCOCH_3$ and gives (η^5-$C_5H_4CH_3$)$(CO)_2FeC(CH_3)OFe(CO)_2Cp^+$-$BF_4^-$. Guiseppetti, M.; Todardo, A.; Cutler, A., manuscript in preparation.

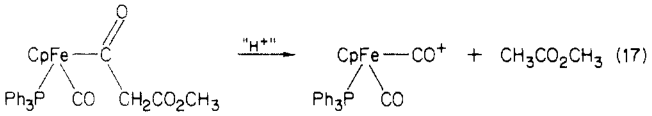
Table III. Carbonylation of Substituted Methyl Complexes

alkyl	solv/acid cat.[a]	pressure, psig	time, h	results[b]
(1) $Cp(CO)(PPh_3)FeCH_2CH_3$ (**19**)	1:1 CH_2Cl_2/CF_3CH_2OH	80	1	95% **20**
(2) $Cp(CO)(PPh_3)FeCH_2OCH_3$ (**21**)	$CH_2Cl_2/Ph_2NH_2^+BF_4^-$	80	24	NR
(3) $Cp(CO)(PPh_3)FeCH_2OCH_3$ (**21**)	$CH_2Cl_2/Ph_2NH_2^+BF_4^-$	1000	12	NR
(4) $Cp(CO)(PPh_3)FeCH_2Ph$ (**23**)	1:1 CH_2Cl_2/CF_3CH_2OH	80	24	NR
(5) $Cp(CO)(PPh_3)FeCH_2Ph$ (**23**)	CH_3NO_2	80	24	NR
(6) $Cp(CO)(PPh_3)FeCH_2Ph$ (**23**)	$CH_2Cl_2/Ph_2NH_2^+BF_4^-$	1000	24	NR
(7) $Cp(CO)(PPh_3)FeCH_2CO_2CH_3$ (**25**)	1:1 CH_2Cl_2/CF_3CH_2OH	80	24	NR[c]
(8) $Cp(CO)(PPh_3)FeCH_2CO_2CH_3$ (**25**)	1:1 CH_2Cl_2/CF_3CH_2OH	800	12	NR
(9) $Cp(CO)(PPh_3)FeCH_2CO_2CH_3$ (**25**)	CH_3NO_2	1000	12	50% **25**[d]
(10) $In(CO)(PPh_3)FeCH_2OCH_3$ (**27**)	CH_2Cl_2	1000	14	NR
(11) $In(CO)(PPh_3)FeCH_2OCH_3$ (**27**)	CH_3NO_2	80	24	NR[e]

[a] 0.2–0.4 mmol of alkyl complex in 20–50 mL of solvent and 10% acid catalyst (where noted). [b] NR: no detectable acyl complex by IR spectroscopy, recovery ca. 90% starting alkyl, and no other organometallic products or decomposition products detected. [c] At 60 °C, recovery 59% **25** and 18% $Cp(CO)_2FeCH_2CO_2CH_3$ after chromatography. [d] By IR spectroscopy: 1:1 mixture **25** and $Cp(CO)_2FeCH_2CO_2CH_3$ as only products. [e] At 70 °C, obtain ca. 1:1 mixture **27** and $In(CO)_2FeCH_2OCH_3$ as only IR detectable materials.

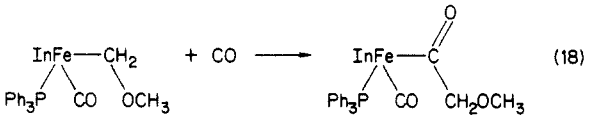
yield. Otherwise, at least 87% of all starting alkyl complexes **21**, **23**, and **25** were recovered.

This recovery of unreacted alkyl after attempted carbonylation is particularly significant in the case of the carbomethoxymethyl complex **25**. Its acyl derivative **26** recently has been reported by Davies[50] as being unstable with respect to the fragmentation process outlined in eq 17. (In the Davies' study **26** was generated in situ by acylating $Cp(CO)(PPH_3)FeCOCH_2^-$.) During attempted carbonylation of **25** no trace of the well-known[4] $Cp(CO)_2PPh_3^+BF_4^-$ [IR ν(CO) 2061, 2016 cm^{-1}] appeared, however.


$$Cp(Ph_3P)(CO)Fe{-}C(=O)CH_2CO_2CH_3 \xrightarrow{\text{"}H^+\text{"}} Cp(Ph_3P)(CO)Fe{-}CO^+ + CH_3CO_2CH_3 \quad (17)$$

26

The methoxymethyl complex $In(CO)(PPh_3)FeCH_2OCH_3$ (**27**) (bearing an η^5-indenyl ligand) presents an optimal ligand array, on the basis of experience with the parent methyl complexes in Table I, for carbonylating its methoxymethyl ligand. This complex was synthesized via standard procedures given in the Experimental Section and was subjected to the carbonylation conditions listed in Table III. Surprisingly, no methoxyacetyl ligand formed (eq 18), even up to 1000 psig of CO in CH_2Cl_2; more forcing reaction conditions instead replaced PPh_3 by CO, giving $In(CO)_2FeCH_2OCH_3$. It is worth recalling that the corresponding methyl complex **13** readily converts to its acetyl **14** with only 80 psig of CO in methylene chloride.


$$In(Ph_3P)(CO)Fe{-}CH_2OCH_3 + CO \longrightarrow In(Ph_3P)(CO)Fe{-}C(=O)CH_2OCH_3 \quad (18)$$

27

Discussion

Solvent Effects and Acid Catalysis. Choice of solvent often proves to be critical in effecting alkyl–CO migratory insertion reactions,[1,2] yet these "solvent effects" are poorly understood. Figure 1 represents such a CO insertion process on $Cp(CO)_2FeCH_3$ (**1**) using either PPh_3[10a,f] or CO[6] as the incoming ligand (L). Polar solvents (S) accordingly enhance CO insertion rates through operation of at least two pathways. (1) Solvent, S, behaving as a nucleophile/donor ligand, intercepts the acetyl intermediate **29a** or **29b** and forms the solvated acetyl compound **30**,[38] which subsequently dissociates solvent and coordinates CO or PPh_3 as the product acetyl complex **2** or **4**, respectively. Efficiency of this pathway of course suffers as the lability of ligated S on **30** decreases. (2) Solvent stabilizes the transition state involved either in forming the coordinatively unsaturated acetyl intermediate **29a** (which perhaps equilibrates with its saturated η^2-acetyl derivative **29b**) or in promoting bimolecular PPh_3- or CO-induced alkyl migration.

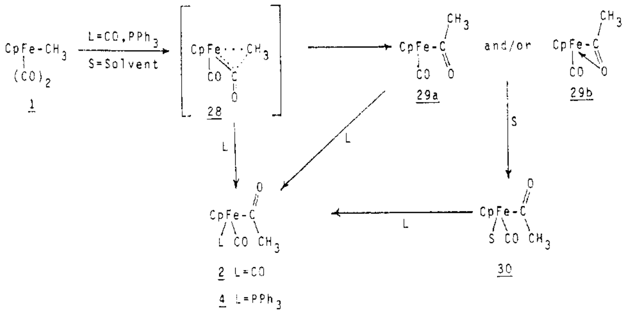


Figure 1.

The former pathway may prove kinetically nonproductive—no rate enhancement for product acyl formation that is due to the polar solvent—when the solvated intermediate **30** is sufficiently long-lived. For example, **1** dissolves in Me_2SO to give an observable Me_2SO–acetyl adduct **15** (eq 6) that upon treating with PPh_3 affords $Cp(CO)(PPh_3)FeCOCH_3$ (**4**).[10d,e] No rate acceleration for this phosphine-induced CO insertion, however, was attributed to the polar solvent Me_2SO vs. CH_2Cl_2.[10d] Calderazzo and Cotton[39] arrived at a similar conclusion for carbonylation of $(CO)_5MnCH_3$ in THF: the THF–acetyl intermediate $(CO)_4(THF)MnCOCH_3$ detected evidently is not kinetically significant. It therefore comes as no surprise that our attempted carbonylation (80 psig) of **1** in Me_2SO/**15** (eq 6) provided only starting material.

$Cp(CO)(PPh_3)FeCH_3$ (**3**), a more convenient substrate for assessing the significance of solvent effects during its carbonylation, does not pick up CO (80 psig) in methylene chloride or in most routine organic solvents (eq 3). Likewise **3** does not pick up CO in the dipolar aprotic

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(38) By studying the $P(CH_3)_2Ph$-promoted CO insertion on $Cp(CO)_3MoCH_3$ in THF, Wax and Bergman were able to demonstrate a second process involving THF as a nucleophile in a bimolecular rate-determining step. In this step methyl migration takes place concomitant with S_N2 attack of THF at the Mo center and directly produces the labile $Cp(CO)_2(THF)MoCOCH_3$. Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

(39) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 30.

Table IV. IR Spectral Data: Acetyl Complexes 1 and 3 with Proton Donors

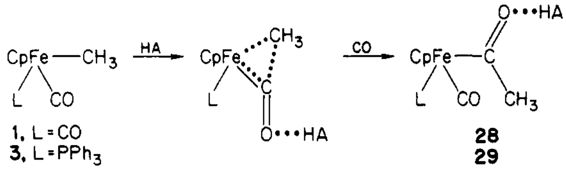
compound	solv[a]	ν(C≡O)	ν(C=O)	ν(COH)
(1) $Cp(CO)(PPh_3)FeCOCH_3$ (**3**)	CH_2Cl_2	1917	1601	
(2) $Cp(CO)(PPh_3)FeCOCH_3$ (**3**)	CH_3NO_2	1915		*b*
(3) $Cp(CO)(PPh_3)FeCOCH_3$ (**3**)	CF_3CH_2OH	1937		1575 (br)[c]
(4) 3/1 equiv of $HOC_6H_4NO_2$	CH_2Cl_2	1925		1498[d]
(5) $Cp(CO)(PPh_3)FeC(CH_3)OH^+BF_4^-$ (**31**)	CH_2Cl_2	1975		
(6) $Cp(CO)_2FeCOCH_3$ (**2**)	CH_2Cl_2	2022, 1963	1649	
(7) $Cp(CO)_2FeCOCH_3$ (**2**)	CF_3CH_2OH	2037, 1980		1609[f]
(8) 2/1 equiv of $Ph_2NH_2^+BF_4^-$	CH_2Cl_2	2022, 1963 (br)	1649	*e*
(9) $Cp(CO)_2FeC(CH_3)OH^+BF_4^-$ (**30**)	CH_2Cl_2	2068, 2023		*f*

[a] 0.10 mmol of **2** or **4**/1.5 mL of solvent; IR spectral data in cm^{-1}. [b] Acyl ν(C=O) not detected due to solvent interference; a CH_2Cl_2 solution of **3** with 0.35 mmol of CH_3NO_2 has ν(C=O) at 1601 cm^{-1} with undiminished intensity. [c] In CH_2Cl_2 solution, **4** and 2 equiv of CF_3CH_2OH yields a 40:60 mixture of **4** and its H-bonded adduct [ν(C=O) 1575 cm^{-1} (br)]. The terminal ν(CO) remains at 1918 cm^{-1}, and the CF_3CH_2OH ν(OH) decreases from 3590 to 3240 cm^{-1} (br). [d] Extent of H bonding uncertain as phenolic absorptions interfere with ν(C=O) and with assigning Δν(OH) for **29**. [e] With 1.0 equiv of $Ph_2NH_2^+$ a 45% intensity decrease ν(C=O), but ν(COH) assignment at ca. 1590 cm^{-1} is tentative due to the presence of interfering Ph_2NH absorptions. 2 or 3 equiv of $Ph_2NH_2^+$ give up to 30% hydroxycarbene salt **30**. [f] 1.0 equiv of $HBF_4 \cdot O(CH_3)_2$ and **1** effects 80% conversion to **30**.

solvents Me_2SO, DMF, and sulfolane, in agreement with Flood's results on carbonylating the analogous ethyl complex **19**.[6] Although he reported very low yields of the propionyl product **20** (eq 15) in Me_2SO or HMPA, these can be accounted for by the higher proclivity of an ethyl vs. methyl complex toward CO insertion.[1,10e] Fortunately we found three solvents—acetonitrile, nitromethane, and trifluoroethanol—that supported extraordinarily facile carbonylation of **3** at or below 80 psig of CO.

We offer no convincing rationale as to why these three solvents support CO atom of **3**; further mechanistic studies are required. Two observations pertaining to the probable role of these solvents, however, have emerged during these synthetic studies. First, presence of even trace amounts of presumably acidic impurities have a profound effect on the carbonylation rate. With nitromethane, for example, solvent taken directly from a reagent-grade bottle, purged with nitrogen, and then used in carbonylating **3** works far more efficiently than nitromethane that has been percolated through alumina (neutral or basic, activity 1) and/or distilled under vacuum.[40] The second and possibly related observation is that catalytic amounts of strong protonic acids and/or hydrogen bond donors when added promote these carbonylation reactions (with both **1** and **3**) to the extent that they are possible even in CH_2Cl_2 at 1 atm of CO.

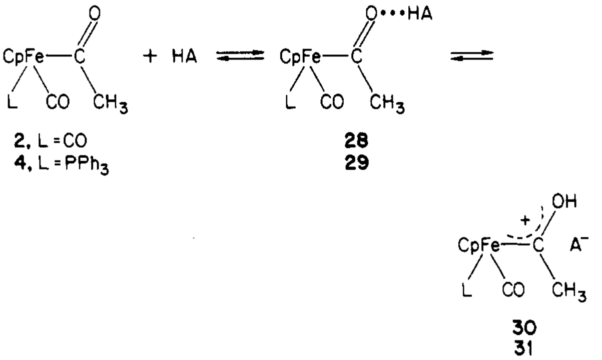
Acid-promoted CO insertion has precedent in the work of Shriver and others.[11,12] A variety of Lewis acids, for example, greatly facilitate CO insertion on metal carbonyl methyl complexes in general and on $Cp(CO)(L)FeCH_3$ (**1**, **3**) in particular. The mechanism advanced by Shriver for acid-promoted carbonylation of $(CO)_5MnCH_3$[11b] is depicted in eq 19 as it applies to CO insertion on the iron methyl complexes **1** and **3**.



(19)

An acid, in order to promote carbonylation of **1** or **3**, must effect a hydrogen bond with or otherwise protonate the incipient acetyl ligand[29] developing during methyl–CO migratory insertion (eq 19). Just how HBF_4, other successful acid catalysts, or even the more acidic solvents might interact with such an acetyl ligand (and thus promote the CO insertion process) is unknown. Since the simplest model for this interaction corresponds to the product acetyl/acid adduct (**28** or **29**), reactions between the acetyl complexes **2** and **4** and the above acids were investigated.

Equivalent amounts of $HBF_4 \cdot O(CH_3)_2$, p-$NO_2C_6H_4OH$, $C_5H_4NH^+BF_4^-$, or $Ph_2NH_2^+BF_4^-$, were added to CH_2Cl_2 solutions of acetyl complexes **2** and **4**, and the nature of the acid–acetyl ligand interaction (eq 20) was probed by



(20)

IR spectroscopy. Table IV summarizes the results of these experiments. HBF_4 transfers its proton to **2** and **4** and gives the hydroxycarbene compounds **30** and **31**, respectively. Hydroxycarbene salt **31** is a known compound,[41] and structural assignment for **30** follows from the close match of its IR spectral data with that of the analogous alkoxycarbene complexes.[42] Both **30** and **31** deprotonate upon adding triethylamine and regenerate their acetyl compounds **2** and **4**. The remaining three acids provide hydrogen bond interactions[30] with the acetyl ligands,[11b] as manifested by both diminution in intensity of the acetyl IR spectral ν(C=O) and formation of a new ν(COH) below 1600 cm^{-1}. Weak hydrogen bond associations on **28** and **29**, rather than hydrogen-bonding ion pairing $Cp(CO)(L)FeC(CH_3)OH^+\cdots A^-$, are in accord with the relatively small shift (<20 cm^{-1}) in the IR stretching frequencies for the terminal carbonyls. These ion pairs (analogous to their hydroxycarbene salts **30** and **31**), in contrast, should exhibit terminal ν(C≡O) shifted to higher energy (>40 cm^{-1}).

Solvents functioning as proton or hydrogen bond donors also should promote carbonylation of methyl complexes

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[40] The possibility of an oxidatively catalyzed radical chain process cannot be completely discounted. Flood[6] has presented cogent arguments that preclude such a mechanism for enhancing the carbonylation of **19** in nitroethane, however.

[41] Green, M. L. H.; Hurley, C. R. *J. Organomet. Chem.* **1967**, *10*, 188.

[42] (a) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (b) Bodnar, T. W.; Cutler, A. R. *Synth. React. Inorg. Met.-Org. Chem.*, in press. (c) Casey, C. P.; Miles, W. H.; Tukoda, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

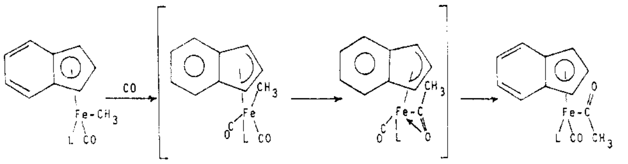
1 and 3 by a mechanism analogous to that in eq 19. Indeed, we found that trifluoroethanol, even though it is less acidic than nitromethane (pK_a = 12.4 vs. 10.2), effectively converts 1 and 3 to their respective acetyl complexes. A possible clue to this efficiency may be derived by examining its interaction with the product acetyls (Table IV). Trifluoroethanol, an excellent hydrogen bond donor,[30] clearly converts both 2 and 4 to their hydrogen bond adducts 28 and 29, whereas nitromethane elicits no such interaction.[43]

To summarize, with proper choice of solvent and/or protonic acid catalyst either methyl complex 1 or 3 carbonylates between 1 and 6.3 atm of CO. Methylene chloride, significantly, can be used as the solvent with acid catalysis. The possibility that the more acidic solvents or acid catalysts used may drive these reactions by protonating or by forming a hydrogen bond to the incipient acetyl ligand (as depicted in eq 19) is of course appealing, especially since the acetyl ligand on the final products 2 and 4 binds the same acids (eq 20). Extrapolating these results to provide a mechanism by which these same proton donors stabilize the transition state, the intermediates, and/or the products during the actual carbonylation reaction, however, would be highly speculative at this time.

Fine Tuning the Metal Center by Varying the Ancillary Ligands. The relative carbonylation tendencies of the methyl complexes noted in Table I, without benefit of added acid catalysts, can be qualitatively ranked: In(CO)(PPh$_3$)Fe > In(CO)$_2$Fe ≥ Cp(CO)(PPh$_3$)Fe > Cp(CO)[P(OCH$_3$)$_3$]Fe > Cp(CO)$_2$Fe ≈ [C$_5$(CH$_3$)$_5$](CO)$_2$Fe ≫ Cp(CO)$_2$Ru. One striking conclusion from the data supporting this overall ranking is the enormous range in reaction conditions required to carbonylate their methyl complexes. Whereas In(CO)(PPh$_3$)FeCH$_3$ (13) readily reacts with 1 atm of CO in CH$_2$Cl$_2$, Cp(CO)$_2$RuCH$_3$ (9) only carbonylates in the acidic hexafluoro-2-propanol (pK_a = 9.3) at 1000 psig of CO and 60 °C. Even the parent methyl complex Cp(CO)$_2$FeCH$_3$ (1) only adds CO in CF$_3$CH$_2$OH using 80 psig of CO above 40 °C.

Comparing the carbonylation reactivity of Cp(CO)$_2$FeCH$_3$ (1) with [C$_5$(CH$_3$)$_5$](CO)$_2$FeCH$_3$ (7) and Cp(CO)$_2$RuCH$_3$ (9) is especially opportune, since for these latter systems a variety of C$_1$ ligands derived from ligated CO have been reported recently.[44] These C$_1$-formyl, hydroxymethyl, and μ-methylene ligands evidently form more thermodynamically robust complexes than do their counterparts coordinated to Cp(CO)$_2$Fe. As we are ultimately interested in chain-extension ligand reactions that transform C$_1$ to C$_2$ and C$_3$ ligands using CO, it is informative to gauge how readily 7 and 9 insert CO. The results in Tables I and II indicate, however, that Cp(CO)$_2$RuCH$_3$ (7) only inserts CO under the most severe reaction conditions, whereas [C$_5$(CH$_3$)$_5$](CO)$_2$FeCH$_3$ (7) resembles 1 in its carbonylation tendency.[45] Even acid catalysis fails to facilitate carbonylation of 9 (up to 1000 psig of CO in CH$_2$Cl$_2$ with 10% Ph$_2$NH$_2$$^+BF_4$$^-$ present).

We do not know how the η^5-indenyl (in place of Cp ligand) facilitates carbonylation of its methyl complexes. One plausible explanation may be related to the "indenyl effect": η^5-indenyl complexes exhibit substantially increased rates over their analogous η^5-Cp complexes for CO ligand replacement by phosphines or phosphites.[46] Kinetic studies for these replacement reactions are generally in accord with an associative mode of reactivity (S$_N$2) at the metal center at least partially accounting for these increased rates. (A similar S$_N$2 mechanism is evident in the triphenylphosphine-induced CO-insertion reaction observed by Hart-Davis and Mawby[47] for η^5-In(CO)$_3$MoCH$_3$). The driving force for these associative reactions is attributed to the facile η^5-to-η^3 shift of the indenyl ligand incumbent upon S$_N$2 attack at the metal center. The resulting ene–η^3-allylindenyl intermediate is presumably stabilized through benzenoid resonance involving the ene fragment. We postulate a similar role for the indenyl ligand in facilitating the carbonylation of 11 and 13 (eq 21).[48]



11 L=CO
13 L=PPh$_3$

12
14

Even incorporating an indenyl ligand onto a substituted methyl complex, however, did not afford productive carbonylation chemistry. Thus, In(CO)(PPh$_3$)FeCH$_2$OCH$_3$ (27) does not give a methoxyacetyl complex (eq 18). Also, the substituted methyl complexes Cp(CO)(PPh$_3$)CH$_2$X (21, 23, and 25)—bearing relatively electronegative methoxymethyl, benzyl, or carbomethoxymethyl ligands—either do not react with or at most exchange their PPh$_3$ ligand with CO. Attempted acid catalysis of these reactions (eq 16) likewise failed, although it must be noted that reaction

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[43] Any hydrogen bond interaction between nitromethane and 2 or 4 could prove difficult to observe for at least two reasons. (1) Solvent absorption during IR spectral studies obscures the acetyl ν(C=O) region below 1650 cm^{-1}. (2) Any hydrogen bond interaction involving nitromethane derives from its more acidic *aci*-tautomer CH$_2$=N(O)OH, which only exists in very low concentrations: Turnbull, D.; Maron, S. H. *J. Am. Chem. Soc.* **1943**, *65*, 212. Since the hydrogen bond interaction between 2 or 4 and *aci*-nitromethane is not likely to be very strong, then rather low concentrations of the adducts 28 or 29 will exist in solution.

[44] (a) [C$_5$(CH$_3$)$_5$](CO)$_2$Fe-C$_1$ complexes: Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 430. Reference 18 also. (b) Cp(CO)$_2$Ru-C$_1$ complexes: Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43. Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679. Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461. (c) [C$_5$(CH$_3$)$_5$](CO)$_2$Ru-C$_1$ complexes: Nelson, G. O. *Organometallics* **1983**, *2*, 1474. Sumner, C. E.; Nelson, G. O. *J. Am. Chem. Soc.* **1984**, *106*, 432.

[45] It is worth noting that a number of Fe and Ru(II) alkyl complexes not containing a Cp ligand carbonylate under extremely mild conditions and give their acyl derivatives. For example, complexes (CO)$_2$(L)$_2$M(R)X [where X = halide and L = P(CH$_3$)$_3$ (for Fe, Ru),[45a] P(CH$_3$)$_2$Ph (for Ru),[45b] P(OCH$_3$)$_3$ (for Fe),[45c] and *o*-(Ph$_2$As)$_2$C$_6$H$_4$ (for Fe)[45d]] add CO under mild conditions to produce their acyl derivatives (CO)$_2$(L)$_2$M(X)(COR). The corresponding Os(II) complexes are expected to be much less reactive, although Roper recently has reported the facile carbonylation of (PPh$_3$)$_2$(CO)$_3$OsCH$_2$CH$_3$$^+$.[45e] (a) Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30*, 227; **1983**, *251*, 333. Reichenbach, G.; Cardaci, G.; Bellachioma, G. *J. Chem. Soc., Dalton Trans.* **1982**, 847; **1983**, 2593. (b) Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1331. (c) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353. (d) Jablonski, C. R. *Inorg. Chem.* **1981**, *20*, 3940. Jablonski, C. R.; Wang, Y. P. *Ibid.* **1982**, *21*, 4037. (e) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1. Grundy, K. R.; Roper, W. R. *Ibid.* **1981**, *216*, 255.

[46] Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740; *J. Chem. Soc., Chem. Commun.* **1983**, 1208. White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261. White, C.; Mawby, R. J.; Hart-Davis, A. J. *Ibid.* **1970**, *4*, 441. Jones, D. J.; Mawby, R. J. *Ibid.* **1972**, *6*, 157.

[47] Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. A* **1969**, 2403.

[48] We have no evidence for direct involvement of η^3-indenyl intermediates depicted in eq 21 during the actual carbonylation reactions. An alternative suggestion by one reviewer is that the indenyl ligand could promote CO insertion through steric acceleration. This mechanism derives from that proposed by Barnett and Pollman to account for enhanced decarbonylation of CpMo acetyl complexes with increased steric bulk of an ancillary phosphine ligand. Briefly, the bulk of the indenyl ligand could favor the methyl—CO migratory insertion—through reducing steric congestion at the Fe center (e.g., 28 in Figure 1)—during carbonylation of 11 or 13. Why steric acceleration should apply with the η^5-indenyl but not with the η^5-C$_5$(CH$_3$)$_5$ ligands is not clear. Studies in progress are attempting to probe the precise role of the indenyl ligand in this chemistry. Barnett, K. W.; Pollman, T. G. *J. Organomet. Chem.* **1974**, *69*, 413.

conditions reported in Table III are those without acid-induced decomposition of starting alkyls.

Our inability to carbonylate these methoxymethyl, benzyl, and carbomethoxymethyl complexes under rather severe reaction conditions is rather surprising. Certainly these results are of kinetic origin: the anticipated methoxyacetyl (**22**) and phenylacetyl (**24**) complexes are stable under the reported reaction conditions, and, as already noted, transcience of of carbomethoxyacetyl (**26**) would have generated $Cp(CO)_2(PPh_3)Fe^+$. In contrast, precedent exists for other organometallic benzyl and alkoxymethyl complexes exhibiting a rate-retarding effect (with respect to corresponding methyl or ethyl complexes),[1] but their substituted acetyl derivatives do form with the $(CO)_5Mn$ system, for example.[49] In marked contrast to the above results, the ethyl complex **19** carbonylates under the same (and possibly even milder) reaction conditions (eq 15) as its corresponding methyl complex **3**. Such behavior is well documented for both carbonylation[1] as well as phosphine-induced CO insertion[10b,e] of higher alkyl complexes vs. their methyl analogues. The enhanced electron-releasing ability of the higher alkyl ligand is at least partly responsible for this rate enhancement.

Conclusions

Three procedures are now available for promoting CO insertion on the $Cp(CO)_2FeCH_3$ system using 1–6.3 atm of CO.

1. Incorporating an η^5-indenyl and/or a 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 $In(CO)(PPh_3)FeCH_3$ in CH_2Cl_2 thus adds CO at 1 atm and gives its acetyl derivative. In contrast, switching from $Cp(CO)_2FeCH_3$ to $(\eta^5\text{-}C_5(CH_3)_5)(CO)_2FeCH_3$ has no effect on the facility in the carbonylation chemistry, whereas $Cp(CO)_2RuCH_3$ is much less reactive.

2. Choosing the appropriate solvent often is critical. Most organic solvents (including Me_2SO and DMF) do not support CO insertion (80 psig) on $Cp(CO)(PPh_3)FeCH_3$, although acetonitrile, nitromethane, and trifluoroethanol work. Trifluoroethanol in particular appears promising, probably because it can function as a hydrogen bond donor (i.e., acid catalyst) to an incipient acetyl ligand. IR spectral evidence is available for hydrogen bond complexation to the acetyl ligand on $Cp(CO)_2Fe$ and $Cp(CO)(PPh_3)Fe$ complexes.

3. Adding an acid catalyst (protonic) permits carbonylation of either $Cp(CO)_2FeCH_3$ or $Cp(CO)(PPh_3)FeCH_3$ under exceedingly mild conditions. With HBF_4 (1% stoichiometrically), both methyl complexes in CH_2Cl_2 add CO at 1 atm. Other useful catalysts include $Ph_2NH_2^+$ for the former and *p*-nitrophenol or pyridinium $C_5H_5NH^+BF_4^-$ for the latter.

None of the above procedures, however, are successful for carbonylating the substituted methyl complexes $Cp(CO)(PPh_3)FeCH_2X$ ($X = OCH_3$, Ph, CO_2CH_3) or $In(CO)(PPh_3)FeCH_2OCH_3$.

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Registry No. **1**, 12080-06-7; **2**, 12108-22-4; **3**, 12100-51-5; **4**, 12101-02-9; **5**, 32680-12-9; **6**, 77307-42-7; **7**, 52409-66-2; **8**, 34808-35-0; **9**, 53449-90-4; **10**, 32610-56-3; **11**, 71498-19-6; **12**, 96412-64-5; **13**, 96412-65-6; **14**, 96412-66-7; **19**, 32824-72-9; **20**, 32611-01-1; **21**, 53521-55-4; **22**, 77805-32-4; **23**, 33135-99-8; **24**, 31871-83-7; **25**, 77805-35-7; **26**, 96412-67-8; **27**, 96412-68-9; **30**, 96412-71-4; **31**, 96412-73-6; $In(CO)(PPh_3)FeCOCH_2OCH_3$, 96412-69-0; $HBF_4{\cdot}O(CH_3)_2$, 67969-83-9; $[In(CO)_2Fe]_2$, 36632-68-5; $In(CO)_2Fe^-Na^+$, 52326-30-4; $In(CO)_2FeCH_2COCH_3$, 96427-32-6; $Cp(CO)_2FeCH_2CO_2CH_3$, 12214-69-6; $In(CO)_2FeCH_2OCH_3$, 96412-74-7; CH_2Cl_2, 75-09-2; CO, 630-08-0; $Ph_2NH_2^+BF_4^-$, 40888-73-1; CH_3NO_2, 75-52-5; CH_3CN, 75-05-8; CF_3CH_2OH, 75-89-8; $C_5H_5NH_2^+BF_4^-$, 505-07-7; PPh_3, 603-35-0; *p*-$NO_2C_6H_4OH$, 100-02-7; *p*-ClC_6H_4OH, 106-48-9; 2,4-$(NO_2)_2C_6H_3OH$, 51-28-5; chloromethyl methyl ether, 107-30-2.

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