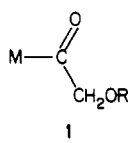
The Carbalkoxymethyl Ligand on $(\eta\text{-}C_5H_5)(CO)[P(OCH_3)_3]FeCH_2CO_2CH_3$ as a CO-Derived C_2 Template for Generating C_2 Organic Ligands and Molecules

Edward J. Crawford,[‡] Carol Lambert,[†] Kevin P. Menard,[†] and Alan R. Cutler*[‡]

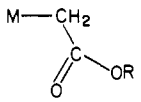
Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457, and Rensselaer Polytechnic Institute, Troy, New York 12181. *Received August 2, 1984*

Abstract: The carbalkoxymethyl ligand on $Cp(CO)[P(OCH_3)_3]FeCH_2CO_2R$ (**7**) (R = CH_3, CH_2CH_3) serves as a C_2 template for generating other C_2-coordinated ligands and organic molecules. In this study **7** is procured by acid isomerization of the alkoxyacetyl complexes $Cp(CO)[P(OCH_3)_3]FeCOCH_2OR$ (**5**), which are obtained by $P(OCH_3)_3$-induced CO-insertion on $Cp(CO)_2FeCH_2OR$. (Overall, the carbalkoxymethyl ligand on **7** derives from two CO groups on $Cp(CO)_3Fe^+$.) A mechanism for this alkoxyacetyl–carbalkoxymethyl ligand isomerization is advanced whereby protonation of **5** generates a ligated ketene intermediate that regioselectively adds alcohol and gives **7**. In excess acid either **5** or **7** quantitatively releases acetic acid ester, a selective generation of this C_2 organic from CO. The carbalkoxymethyl ligand on **7** is activated as a hydride acceptor by converting it to the (dialkoxycarbenio)methyl salt $Cp(CO)[P(OCH_3)_3]FeCH_2C(OR)_2^+$ (**8**). (Interestingly, **8** cannot be generated from the alkoxycarbene system $Cp(CO)[P(OCH_3)_3]FeC(OR)CH_2OR^+$ (**6**).) BH_4^- converts **8** into a mixture of η^2-ethylene and η^1-ethyl complexes of $Cp(CO)[P(OCH_3)_3]Fe$, whereas $(sec\text{-}Bu)_3BH^-Li^+$ generates the corresponding η^2-ethyl vinyl ether and η^1-formylmethyl compounds. The conversion of these latter two into acetaldehyde is discussed.

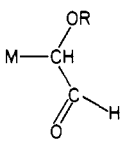
Synthesis of C_2-oxygenated organic molecules from synthesis gas, CO plus H_2, represents an important objective of studies on homogeneous reduction of ligated CO.[1] Results of studies using mononuclear organometallic systems, either in homogeneous catalysis or in stoichiometric experiments, have implicated the hydroxy- or alkoxyacetyl ligand **1** as the progenitor of ethylene glycol and some other C_2 oxygenates.[2] Mechanistic discussions that account for generating **1** and then converting it to glycol-



1



2



3

aldehyde/ethylene glycol generally follow from the collective experience gained in hydroformylation chemistry,[3] Relatively little is known, however, concerning the coordinated ligand reaction chemistry once the alkoxyacetyl complexes have been generated.

In recent years much effort involving synthetic transition organometallic chemistry instead has been directed toward understanding the ligand reactions involved in procuring **1** using CO and H_2. For example, the special problems associated in generating and in working with formyl[4] and hydroxymethyl[5] ligands (as opposed to their homologous acyl and alkoxymethyl ligands) have been extensively commented on.[1b,e] Subsequent carbonylation[2b,6] or phosphine-induced alkyl migration[7,8] of alkoxymethyl and in one case[9] hydroxymethyl ligands, to give the C_2 alkoxyacetyl complexes **1**, also has precedent. With one compound, $(CO)_5MnCOCH_2OR$, Dombek[2b] further demonstrated that its hydrogenation gives initially glycolaldehyde then glycol ethers.[10]

Two isomers of **1**, the carbalkoxymethyl **2** and alkoxyformylmethyl **3** systems, also could serve as precursors to C_2 organics. Their hydrogenation,[11] for example, could give acetic acid (ester) from **2**[12] and glycolaldehyde (ether) from **3**. Three questions now must be posed concerning the relevance of **2** and **3** in converting ligated CO into organic molecules: (1) Can **1–2–3** interconvert, and under what conditions will each predominate? Although **1** may be a kinetic product in reductive oligomerization of CO on a metal center, conditions conceivably could exist where **2** and/or **3** would be thermodynamically favored. (2) Can **2** and/or **3** derive selectively from combination of appropriate

[†] Wesleyan University.
[‡] Rensselaer Polytechnic Institute.

(1) Reviews of homogeneous analogues of or on model-systems approaches to understanding Fischer–Tropsch Chemistry: (a) Dombeck, B. D. *Adv. Catal.* **1983**, *32*, 325. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (c) Sneedon, R. P. A. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Chapter 50.2. (d) Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17. (e) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (f) Frohning, C. D. In "New Syntheses with Carbon Monoxide"; Falbe, J., Ed.; Springer-Verlag: Berlin and New York, 1980; Chapter 4. (g) Eisenberg, R.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79. (h) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (i) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

(2) (a) Pruett, R. L. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 239; *Science (Washington, D.C.)* **1981**, *211*, 11. (b) Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466. (c) Dombeck, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855; *J. Organomet. Chem.* **1983**, *250*, 467; *Ann. N. Y. Acad. Sci.* **1983**, *451*, 176. (d) Feder, H. M.; Rathke, J. W. *Ann. N. Y. Acad. Sci.* **1980**, *333*, 45. (e) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136. (f) Keim, W.; Berger, M.; Schlupp, J. *J. Catal.* **1980**, *61*, 359. Keim, W.; Berger, M.; Eisenbeis, A.; Kadelka, J.; Schlupp, J. *J. Mol. Catal.* **1981**, *13*, 95. (g) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959.

(3) Pino, P.; Piacenti, F.; Bianchi, M. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, Chapter 2. Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; p 421. Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. Cornils, B. In "New Syntheses with Carbon Monoxide"; Falbe, J., Ed.; Springer-Verlag: Berlin and New York, 1980; Chapter 1. Orghin, M. *Acc. Chem. Res.* **1981**, *14*, 259.

(4) Formyl complexes evidently decompose (react) also by radical-initiated routes: (a) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351. (b) Sumner, C. E.; Nelson, G. O. *J. Am. Chem. Soc.* **1984**, *106*, 432.

(5) Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461. Nelson, G. O. *Organometallics* **1983**, *2*, 1474 and references cited. Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 430.

(6) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405. Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056. Forschner, T. C.; Cutler, A. R. *Organometallics*, in press.

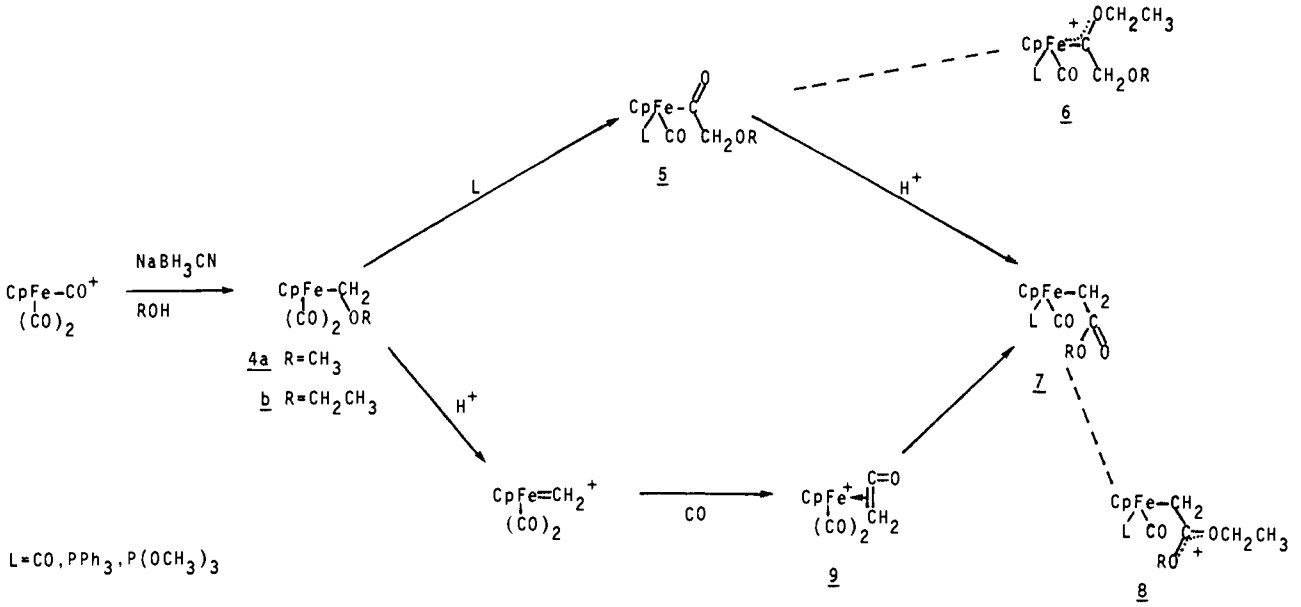
(7) Heck, R. F.; Breslow, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 2499.

(8) (a) Bodnar, T.; Coman, G.; LaCroce, S. J.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* **1981**, *103*, 2571. (b) Cutler, A.; Bodnar, T.; Coman, G.; LaCroce, S.; Lambert, C.; Menard, K. *ACS Symp. Ser.* **1981**, *No. 152*, p 279.

(9) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353.

0002-7863/85/1507-3130$01.50/0

Scheme I



C_1-coordinated ligands?[13] Alternative reaction pathways can be envisioned whereby C_1 ligands derived from CO combine on a metal center and form precursors to kinetic products **2** and **3**. (3) Can **2** or **3** afford either C_2 organic products or, after using the appropriate chain-extension reactions, larger organic molecules? We are interested in establishing the viable coordinated ligand reactions available to systems **1–3**, through stoichiometric experiments using well-defined organometallic complexes. Answers to some of the above questions are now available for the carbalkoxymethyl system **2**.

In preliminary papers we reported two routes for transforming two carbon monoxide molecules into the carbalkoxymethyl ligand on **7** (Scheme I). As the first route, C_1 alkoxymethyl complexes **4a,b**, arrived at by reducing ligated CO,[14] undergo a phosphine- or phosphite-promoted CO insertion to give alkoxyacetyl compounds **5**.[8,15] Isomerization of **5** in the presence of acid then gives the carbalkoxymethyl complexes **7** [L = CO,[18] PPh_3, $P(OCH_3)_3$[8]] in good yields. In the second route, solvolysis of a stable η^2-ketene-*C,C* compound **9**, which results from carbonylating the unstable methylidene complex derived from **4**,[19] affords **7** (L = CO). The ease with which the C_2 carbalkoxymethyl system (**2** ≡ **7**)[20] is generated enhanced our interest in using this ligand as a C_2 template. Full details are now reported for procuring trimethyl phosphite substituted carbalkoxymethyl complexes **7a,b** [L = $P(OCH_3)_3$] from the requisite alkoxyacetyl compounds **5**, for eliminating methyl acetate from **7a** with excess acid, and for carrying out subsequent ligand reduction transformations by activating (as **8**) then reducing at the β-position of the carbalkoxymethyl ligand.

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere using standard syringe/septum and Schlenk-type bench-top techniques for handling moderately air-sensitive organometallics.[21] Solvents for synthetic work and recording of spectral data therefore were deoxygenated by bubbling nitrogen through for ~20 min. Camag alumina (neutral, activity 3) was used in column chromatography. Cationic organometallic products generated in this study are not oxygen sensitive, but being moisture sensitive their precipitates must be filtered under nitrogen in Schlenk filters in order to avoid condensing moisture as the residual solvent is evaporated. The precipitation of these products,

(10) As a complementary strategy early transition and actinide organometallic complexes convert CO/H_2 into η^2-enediolate-*O,O'* OCH=CHO ligands. Formally, at least, such ligands correspond to glycolaldehyde. Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959. Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723. Moore, E. J.; Strauss, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. Gambarota, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

(11) By "hydrogenation" we mean that either H_2 or a metal hydride complex MH will formally cleave the metal–carbon (alkyl) bond. Synthetic precedent abounds, although mechanisms for these hydrogenation reactions have not been fully delineated. Plausible mechanisms,[11a] however, include oxidative addition of H_2 or MH to the alkyl complex (with reductive elimination of RH) and free radical or binuclear reductive elimination reactions between MH/MR. In addition, heterolytic cleavage of H_2 (MH?) by the alkyl metal center operates in some cases.[11b] (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415. Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360. Pino, P. *Ann. N. Y. Acad. Sci.* **1983**, 415, 111. Collman, J. P.; Belmont, J. A.; Brauman, J. I. *Ann. N. Y. Acad. Sci.* **1983**, *105*, 7288. Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147. Azram, J.; Orchin, M. *Organometallics* **1984**, *3*, 197. (b) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

(12) The stoichiometric reaction between $(CO)_4CoCH_2CO_2CH_2CH_3$ and $(CO)_4CoH$ cleanly produces ethyl acetate: Tasi, M.; Galamb, V.; Pályi, G. *J. Organomet. Chem.* **1982**, *238*, C31. Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *209*, 183.

(13) Deeming, A. J. *J. Mol. Catal.* **1983**, *21*, 25.

(14) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.

(15) (a) Alkylation of **5** affords α,β-dialkoxyethylidene salts **6**; in these the α-carbon is now a hydride acceptor. In this α-activation route,[8] nucleophilic hydride donors convert **6** first to α,β-dialkoxyethyl complexes, which are isolable with L = CO, $P(OCH_3)_3$, and then to formylmethyl and η^2-vinyl ether complexes. Bodnar, T. W.; Crawford, E. J.; Cutler, A. R., manuscript in preparation. (b) Metal hydride complexes MH also function as the hydride donor,[16] and the corresponding organometallic Lewis acid M^+ replace the carbocation electrophile as the acyl ligand-activating functionality.[17] This bimetallic activation of the alkoxyacetyl ligand amounts to forming the μ-(η^1:C,O) acyl complex. LaCroce, S. J.; Todaro, A.; Tso, C.; Cutler, A. R., manuscript in preparation.

(16) Bodnar, T.; LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 3292.

(17) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312.

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

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

(20) We have found conditions to convert an example of **1** to its isomer **3**. Thus, **6** (L = CO) isomerizes to $Cp(CO)_2Fe[(E)$-η^2-$(RO)CH{=}CH(OR)]^+$, which in turn affords $Cp(CO)_2FeCH(OR)CHO$.[15a]

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

however, can be carried out in open Erlenmeyer flasks, provided that *anhydrous* ether is used.

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 (2200–1500 cm^{-1}) were calibrated against the polystyrene 1601-cm^{-1} absorption. ^1H NMR spectra were taken of concentrated $CDCl_3$ or CD_3NO_2 solutions, after centrifugation of insoluble residues. Varian Models EM-360 and XL-200 NMR spectrometers supplied the NMR spectra, which were reported as δ values in parts per million downfield from internal Me_4Si. GLC analyses were performed by using a Gow-Mac Model 505 instrument equipped with 4 ft by $^1/_4$ in. Cu columns packed with Carbowax-20M (20%) or DC-200 (20%) on Chromosorb P (80/100 mesh) (He carrier, column temperature 127 °C). 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 was distilled under nitrogen from P_2O_5, and CH_3NO_2 was dried by storing (under nitrogen) over freshly activated molecular sieves, 4 Å. The *anhydrous* ether used either was taken from a freshly opened can or was distilled under nitrogen from sodium benzophenone ketyl. A modification of Dauben's procedure was used to prepare $Ph_3C^+PF_6^-$.[22] Although stored under nitrogen at +5 °C, trityl carbocationic salts slowly decompose (as evidenced by appearance of acid fumes), which necessitates periodic reprecipitation from CH_2Cl_2–ethyl acetate and vacuum drying. Metal carbonyl complexes $[Cp(CO)_2Fe]_2$ and $Cp(CO)_2FeCH_3$[21d] were prepared by literature procedures and judged pure by IR and NMR spectroscopy.

The efficient alkylation of organoiron acyl complexes with triethyoxonium hexafluorophosphate proved to be a critical step. All other carbocationic alkylating agents at our disposal inevitably produced significant amounts of $Cp(CO)[P(OCH_3)_3]FeCO^+$ (**13**) upon attempted alkylation of **5**. Even with $(CH_3CH_2)_3O^+PF_6^-$, commercial samples always contained acid (sometimes fuming as a white smoke) that had to be removed in order to successfully ethylate **5**. Reprecipitating the triethyloxonium salt from $PhNO_2$–ether (using an all-glass Schlenk line), washing with ether, and briefly vacuum drying (10^{-2} mm, 20 °C, 0.5 h) left this salt free of acid. (Reprecipitation from CH_3NO_2– or CH_2Cl_2–ether does not remove the acid.) This oxonium salt is best stored under nitrogen at −5 °C; it is periodically assayed for its acid content through the reaction with $[Cp(CO)Fe]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)$. IR monitoring of this reaction (in CH_2Cl_2) easily discerns between the μ-hydride salt [ν(CO) 1953 cm^{-1}] due to protonation and the μ-ethoxycarbyne salt [ν(CO) 1759 cm^{-1}] due to alkylation of a bridging carbonyl.[23]

Preparation of $(C_5H_5)(CO)_2FeCH_2OR$ (R = CH_3, CH_2CH_3) (4a,b). To a nitrogen-flushed three-necked 500-mL amalgam flask, fitted with a nitrogen inlet adapter and overhead stirrer, was added 350 mL of deoxygenated THF and 20.00 g (56.0 mmol) of recrystallized $[Cp(CO)_2Fe]_2$. The mixture then was stirred vigorously in the presence of a slightly positive nitrogen atmosphere for 1 h; over this time the solution turned from deep purple to dark yellow-orange. Sodium amalgam was then drained from the bottom of the flask, after allowing the mixture to settle (~0.5 h). [The presence of mercury "dust" and other insoluble residues is minimized if both recrystallized iron dimer (from CH_2Cl_2–heptane) and decanted sodium amalgam are used.] The remaining dark yellow-orange solution of $Cp(CO)_2Fe^-Na^+$ was transferred via 50-mL syringe or stainless-steel double-ended needle to the reaction flask. (**Caution**: This sodium ferrate solution is extremely air sensitive; exposure to air results in its immediate decomposition to a brown pyrophoric material.)

The reaction flask, a 500-mL three-necked flask fitted with a nitrogen inlet adapter, rubber septa, and a magnetic stirring bar, containing the $Cp(CO)_2Fe^-Na^+$ solution was cooled in a dry ice–acetone slush bath. Excess chloromethyl methyl ether (9.0 mL, 118 mmol) then was injected into the cold anion solution. (**Caution**: Chloromethyl ethers are suspected human carcinogens.) Within a few minutes a dark solid settled out from the olive-brown mixture. The reaction mixture was warmed to room temperature and was concentrated on a rotary evaporator (25 mm, 20 °C) to a greenish-brown gum. Methylene chloride extracts (5 × 25 mL) of this residue were filtered through a Celite pad, evaporated, and transferred to a short-path distillation apparatus. Distillation in vacuo (0.025 mm min) to a dry ice–acetone cooled receiver by using a heat gun produced $Cp(CO)_2FeCH_2OCH_3$[14,24] as an amber fluid that possesses a camphoraceous odor. Yield 22.01 g, 88%; IR (CH_2Cl_2) ν(CO) 2004, 1943 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.83 (s, 2, CH_2), 4.78 (s, 5, Cp), 3.22 (s, 3, OCH_3). This material may be stored indefinitely in the freezer in rubber-septum-sealed vials.

The ethoxymethyl complex $Cp(CO)_2FeCH_2OCH_2CH_3$[24] was prepared by using the identical procedure but with $ClCH_2OCH_2CH_3$ (11.5 mL, 117 mmol). Yield of distilled brown oil 19.62 g, 74%; IR (CH_2Cl_2) 2005, 1943 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.84 (s, 2, CH_2Fe), 4.73 (s, 5, Cp), 3.34 (quartet, J = 7.0 Hz, 2, OCH_2), 1.14 (t, J = 7.0 Hz, 3, CH_2CH_3).

Preparation of $(C_5H_5)(CO)[P(OCH_3)_3]FeCOCH_3$ (10). A mixture of $Cp(CO)_2FeCH_3$ (5.00 g, 26.0 mmol) and $P(OCH_3)_3$ (6.45 g, 52.0 mmol) in 300 mL of deoxygenated acetonitrile was refluxed for 20 h, at which time an IR spectrum was consistent with quantitative conversion to the desired acetyl complex. The reaction solution, which had turned from yellow to light orange, was then cooled to room temperature and evaporated. Methylene chloride extracts (4 × 20 mL) of the orange oily residue were filtered and evaporated. The residue was evacuated (10^{-2} mm) for 24 h (20 °C) to remove excess $P(OCH_3)_3$ and traces of unreacted iron methyl complex. Spectroscopically pure $Cp(CO)[P(OCH_3)_3]FeCOCH_3$ (**10**) remained as a yellow-orange, semicrystalline gum, 7.68 g (93%): IR (CH_2Cl_2) 1936 (C≡O), 1599 cm^{-1} (C═O); ^1H NMR ($CDCl_3$) δ 4.67 (s, 5, Cp), 3.63 (d, J = 11.5 Hz, 9, $POCH_3$), 2.52 (s, 3, $COCH_3$).

Anal. Calcd for $C_{11}H_{17}O_5PFe$: C, 41.81; H, 5.42. Found: C, 42.03; H, 5.88.

Preparation of Alkoxyacetyl Complexes $(C_5H_5)(CO)[P(OCH_3)_3]FeCOCH_2OR$ (5a, R = CH_3; 5b, R = CH_2CH_3). In a 250-mL three-necked flask fitted with a Friedrich's condenser, nitrogen inlet adapter connected to an oil bubbler, and a magnetic stirring bar an acetonitrile solution (100 mL) containing $Cp(CO)_2FeCH_2OCH_3$ (10.45 g, 47.0 mmol) and trimethyl phosphite (11.66 g, 94 mmol) was refluxed for 10 days. No further physical changes of this brown solution were apparent during this reflux period, although IR spectral monitoring indicated ~60% conversion to **5a**. The reaction mixture was then cooled to room temperature and the solvent was removed on a rotary evaporator. A resulting brown fluid was vacuum dried (10^{-2} mm) 16 h to remove excess trimethyl phosphite.

This crude material was dissolved in a minimum volume (100 mL) of anhydrous ether (containing 5% CH_2Cl_2 to enhance solubility of **5a**), and the orange-gold solution was cooled to −80 °C while scraping. Small increments (5 mL) of pentane were added slowly to induce crystallization. The mixture remained in the cold bath for an additional 5 min, before removing and warming until about half of the yellowish-orange crystals redissolved. The flask was recooled, additional pentane was added, and the solution was left at −80 °C for 20 min to ensure complete crystallization of **5a**. (The final solvent mixture was ~2:1 ether/pentane.) This flask was kept cold while the pale yellowish-orange supernatant was removed using a double-ended needle; then the remaining crystals were washed several times with pentane, the cold washes were removed, and the cold flask containing the wet crystals was immediately placed on the vacuum line. By warming this flask to room temperature under vacuum (10^{-2} mm) and drying the resulting yellow-orange crystals for an additional 2 h, 8.01 g (49%) of **5a** were obtained. IR (CH_2Cl_2) 1934 (C≡O), 1619 cm^{-1} (C═O); ^1H NMR ($CDCl_3$) δ 4.61 (s, 5, Cp), 4.07 (s, 2, CH_2), 3.67 (d, J = 11 Hz, 9, $POCH_3$), 3.29 (s, 3, OCH_3).

Anal. Calcd for $C_{12}H_{19}O_6PFe$: C, 41.60; H, 5.50. Found: C, 41.66; H, 5.59.

For the preparation of **5b**, $Cp(CO)_2FeCH_2OCH_2CH_3$ (11.25 g, 48.0 mmol) and trimethyl phosphite (11.82 g, 95.0 mmol) were dissolved in 100 mL of acetonitrile in a 250-mL three-necked flask. The reaction was run and the product was isolated as described for **5a**. Ethoxyacetyl complex **5b** was isolated as yellow crystals (5.78 g, 33%) and was characterized spectroscopically: IR (CH_2Cl_2) 1935 (C≡O), 1620 cm^{-1} (C═O); ^1H NMR ($CDCl_3$) δ 4.62 (s, 5, Cp), 4.13 (s, 2, CH_2COFe), 3.64 (d, J = 11 Hz, 9, $POCH_3$), 3.50 (m, 2, OCH_2CH_3), 1.14 (t, J = 7 Hz, 3, OCH_2CH_3).

Preparation of $(C_5H_5)(CO)[P(OCH_3)_3]FeC(OCH_2CH_3)CH_2OCH_3^+PF_6^-$ (6). To a CH_2Cl_2 solution (40 mL) containing $Cp(CO)[P(OCH_3)_3]FeCOCH_2OCH_3$ (**5a**) (1.73 g, 5.0 mmol) was added triethyloxonium hexafluorophosphate (1.24 g, 5.0 mmol). No color change of the amber solution was apparent after 0.5 h, although its IR spectrum was consistent with complete alkylation of **5a**. The reaction mixture was concentrated to a brown gum under reduced pressure, and this crude material was added dropwise with scraping into excess ether (300 mL). A reddish-brown gum formed, and after removing the supernatant via syringe, the gum redissolved in a minimum volume of CH_2Cl_2 (20 mL). Addition of this solution to ether again produced a gum, even with

(22) (a) Forschner, T. C.; Cutler, A. R. *Inorg. Synth.*, submitted for publication. (b) Dauben, H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

(23) LaCroce, S. J.; Menard, K. P.; Cutler, A. R. *J. Organomet. Chem.* **1980**, *190*, C79.

(24) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. Green, M. L. H.; Ishag, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508.

scraping, cooling, and/or prolonged storage. This gum was collected, washed with ether, and vacuum dried (2 h) to give spectroscopically pure **6**, 2.25 g (86%): IR (CH_2Cl_2) 1998 cm^{-1} (CO); ^1H NMR (acetone-d_6) δ 5.29 (s, 5, Cp), 4.92 (quart, J = 7 Hz, 2, OCH_2), 4.44 (s, 2, CH_2OCH_3), 3.82 (d, J = 12 Hz, 9, $POCH_3$), 3.45 (s, 3, OCH_3), 1.61 (t, J = 7 Hz, 3, OCH_2CH_3).

Isomerization of $(C_5H_5)(CO)[P(OCH_3)_3]FeCOCH_2OR$ (5a,b) to $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2CO_2R$ (7a,b) (R = CH_3, CH_2CH_3). An amber CH_2Cl_2 solution (200 mL) of $Cp(CO)[P(OCH_3)_3]FeCOCH_2OCH_3$ (**5a**) (6.23 g, 18.0 mmol) and trifluoromethanesulfonic acid (0.61 g, 4.0 mmol) darkened slightly over 3.5 h. This reaction was then concentrated under reduced pressure and chromatographed on 40 g of alumina using CH_2Cl_2. A wide, gold band quickly and cleanly eluted, leaving behind a second yellow band. This latter band was not removed with ethyl acetate. Solvent was stripped from the eluate and the resulting brown oil was vacuum dried 3 h. Yield of **7a** as a brown oil 4.56 g (73%); IR (CH_2Cl_2) 1947 (C≡O), 1669 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.54 (s, 5, Cp), 3.58 (d, J = 11 Hz, 9, $POCH_3$), 3.53 (s, 3, OCH_3), 1.45 (dd, J = 6.0, 2.0 Hz, 1, FeC*H*H), 0.89 (dd, J = 9.5, 6.0 Hz, 1, FeC*H*H).

A similar procedure was used to isomerize $Cp(CO)[P(OCH_3)_3]FeCOCH_2OCH_2CH_3$ (**5b**) (2.16 g, 6.0 mmol) to $Cp(CO)[P(OCH_3)_3]FeCH_2CO_2CH_2CH_3$ (**7b**) (1.50 g, 69%). This product also was isolated as a brown oil: IR (CH_2Cl_2) 1945 (C≡O), 1668 cm^{-1} (C═O); ^1H NMR ($CDCl_3$) δ 4.58 (s, 5, Cp), 4.04 (quart, J = 7 Hz, 2, OCH_2CH_3), 3.61 (d, J = 12 Hz, 9, $POCH_3$), 1.45 (m, 1, FeC*H*H), 1.23 (t, J = 7 Hz, 3, OCH_2CH_3), 0.87 (dd, J = 10.0, 6.0 Hz, 1, FeC*H*H).

Anal. Calcd for $C_{13}H_{21}O_6PFe$: C, 43.36; H, 5.88. Found: C, 43.16; H, 6.01.

Protonolysis of $(C_5H_5)(CO)[P(OCH_3)_3]FeCOCH_2OCH_3$ (5a). A solution of $Cp(CO)[P(OCH_3)_3]FeCOCH_2OCH_3$ (**5a**) (35 mg, 0.10 mmol) in CH_2Cl_2 (1.5 mL) was treated with trifluoromethanesulfonic acid (20 μL, 0.23 mmol). After sitting 26 h the orange solution had turned brown with black sediment evident. Quantitative IR spectral analysis of the methyl acetate ν(C═O) at 1738 cm^{-1}, using a Beer's law plot of methyl acetate, indicated a 100% yield.

GC analysis of the methyl acetate produced during protonation of **5a** (0.181 g, 0.523 mmol) in 3.0 mL of CH_2Cl_2 with CF_3SO_3H (0.20 mL, 2.26 mmol) was also performed. The black reaction mixture after sitting 24 h under nitrogen was trap-to-trap distilled at 10^{-2} mm to a −80 °C trap. The resulting clear CH_2Cl_2 solution of methyl acetate was identified by comparing its retention time with an authentic sample on two GLC columns of different polarity (Carbowax 20 M and DC-200, both on Chromosorb P). Quantitative analysis with the aid of an absolute calibration curve for methyl acetate gave 98% yield.

Preparation of $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (8). An amber CH_2Cl_2 solution (120 mL) containing $Cp(CO)[P(OCH_3)_3]FeCH_2CO_2CH_3$ (**7a**) (2.68 g, 7.74 mmol) and $(CH_3CH_2)_3O^+PF_6^-$ (1.92 g, 7.74 mmol) turned dark red after sitting 24 h. It was concentrated under reduced pressure and added dropwise to a 3:1 mixture of ether/benzene (80 mL); vigorous and continuous scraping was necessary to crystallize the product. Additional ether (100 mL) was added to ensure complete precipitation of $Cp(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (**8**). The resulting orange crystals were collected, washed with several small portions of ether, dried in a stream of nitrogen, and finally vacuum dried (10^{-2} mm, 2 h) to give 3.50 g (87%) of **8**: IR (CH_2Cl_2) 1961 cm^{-1} (CO); ^1H NMR (acetone-d_6) δ 4.94 (s, 5, Cp), 4.36 (quart, J = 7 Hz, 2, OCH_2CH_3), 4.03 (s, 3, OCH_3), 3.77 (d, J = 11 Hz, 9, $POCH_3$), 2.23 (dd, J = 6.0, 2.0 Hz, 1, FeC*H*H), 1.43 (t, J = 7 Hz, 3, OCH_2CH_3), 1.09 (dd, J = 9.0, 6.0 Hz, 1, FeC*H*H). Only one diastereomer of **8** was detected.

Anal. Calcd for $C_{14}H_{24}O_6P_2FeF_6$: C, 32.33; H, 4.65. Found: C, 32.51; H, 4.79.

A solution of $Cp(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (**8**) (260 mg, 0.50 mmol) in CH_2Cl_2 (12 mL) was treated with $(n\text{-}Bu)_4N^+I^-$ (0.37 g, 1.0 mmol). After 10 min of stirring the red-orange solution had turned yellow-brown. Chromatography of this reaction product on 4.0 g of alumina with CH_2Cl_2 eluted a wide, gold band, which was collected, stripped of solvent under reduced pressure, and extracted with 1:1 pentane–ether (100 mL) until all color was removed from the very pale yellow solid. These extracts were combined, filtered, and evaporated to leave a yellow-brown oil (160 mg), which was identified by its ^1H NMR spectrum as $Cp(CO)[P(OCH_3)_3]FeCH_2CO_2CH_2CH_3$ (**7b**) (89% yield).

Borohydride Reduction of $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (8). Sodium borohydride (19 mg, 0.50 mmol) was added to a suspension of $Cp(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (**8**) (260 mg, 0.50 mmol) in 8 mL of absolute ethanol. Within a few minutes the orange starting material dissolved and in its place a golden-yellow solid appeared. The reaction was stirred magnetically for a total of 2 h as the supernatant gradually darkened to a deep gold with a small amount of gold precipitate remaining. Solvent was then removed under reduced pressure and the resulting dark gold solid was extracted with pentane (90 mL) until no further color was removed. The combined extracts were filtered, stripped of solvent, and vacuum dried (10^{-2} mm, 1 h) as a dark gold oil (43 mg), which was spectroscopically pure $Cp(CO)[P(OCH_3)_3]FeCH_2CH_3$ (**16**) (28% yield): IR (CH_2Cl_2) 1920 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 4.46 (s, 5, Cp), 3.50 (d, J = 11 Hz, 9, $POCH_3$), 1.67–0.55 (br m, 5, CH_2CH_3).

The pentane-insoluble residue was extracted with CH_2Cl_2 (25 mL); these extracts were filtered and evaporated to a yellow-gold crystalline solid (82 mg). This was identified as spectroscopically pure $Cp(CO)[P(OCH_3)_3]Fe(CH_2{=}CH_2)^+PF_6^-$ (**15**) (36% yield): IR (CH_2Cl_2) 2018 cm^{-1} (CO); ^1H NMR (acetone-d_6) δ 5.42 (d, J = 1.5 Hz, 5, Cp), 3.90 (d, J = 11.5 Hz, 9, $POCH_3$), 3.25 (br s, 4, CH_2).

Treatment of **8** (52 mg, 0.10 mmol) in CH_2Cl_2 solution (1.5 mL) with $Ph_3PCH_3^+BH_4^-$[25] (29 mg, 0.10 mmol) immediately produced a deep yellow solution. Its NMR spectrum was consistent with quantitative reduction of **8** to the ethyl complex **16**.

Preparation of $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2CH_3$ (16) and $(C_5H_5)(CO)[P(OCH_3)_3]Fe(CH_2{=}CH_2)^+PF_6^-$ (15). A colorless suspension containing $CH_3C(OCH_3)_2^+PF_6^-$ was generated by adding trimethyl orthoacetate (2.04 mL, 16.0 mmol) to a CH_2Cl_2 solution (100 mL) of purified $Ph_3C^+PF_6^-$ (5.05 g, 13.0 mmol) at room temperature. This mixture after magnetically stirring 10 min was treated with $Cp(CO)[P(OCH_3)_3]FeCOCH_3$ (**10**) (4.11 g, 13.0 mmol). An orange solution was obtained after 30 min. IR spectral examination of an aliquot established quantitative conversion to $Cp(CO)[P(OCH_3)_3]FeC(CH_3)OCH_3^+PF_6^-$ (**17**) [ν(CO) 1997 cm^{-1}], as judged by absence of carbonyl stretching frequencies of starting **10** [ν(C≡O) 1936, ν(C═O) 1599 cm^{-1}].

Dropwise addition of this reaction solution into excess ether (500 mL) with swirling and scraping produced yellow crystals in a few minutes. These were filtered, washed with ether (3 × 20 mL), and dried with a nitrogen flow. A total of 25 mL of CH_2Cl_2 extracted the product, which was slowly filtered into 400 mL of ether. The resulting yellow crystals after filtering, washing with ether, and vacuum drying correspond to $Cp(CO)[P(OCH_3)_3]FeC(CH_3)OCH_3^+PF_6^-$ (**17**) (5.45 g, 88%): ^1H NMR (CF_3CO_2H) δ 5.07 (s, 5, Cp), 4.39 (s, 3, OCH_3), 3.82 (d, J = 12 Hz, 9, $POCH_3$), 2.94 (s, 3, CCH_3).

Anal. Calcd for $C_{11}H_{20}O_5P_2FeF_6$: C, 30.28; H, 4.23. Found: C, 30.33; H, 3.73.

A CH_2Cl_2 solution (50 mL) containing $Cp(CO)[P(OCH_3)_3]FeC(CH_3)OCH_3^+PF_6^-$ (**17**) (3.00 g, 6.30 mmol) was treated with $Ph_3PCH_3^+BH_4^-$ (2.20 g, 7.53 mmol). Vigorous gas evolution ensued, with darkening of the initial orange solution to orange-yellow. The solution was stirred for 20 min, after which an IR spectrum indicated quantitative conversion to $Cp(CO)[P(OCH_3)_3]FeCH_2CH_3$ (**16**), ν(CO) 1921 cm^{-1}. The reaction was evaporated and the combined benzene extracts (10 × 5 mL) of all yellow material were filtered through Celite. Concentration to 5 mL and chromatography of this extract on alumina (50 g, benzene) cleanly eluted a bright yellow band, which afforded **16** as an analytically pure yellow-brown oil (1.77 g, 93%).

Anal. Calcd for $C_{11}H_{19}O_4PFe$: C, 43.74; H, 6.34. Found: C, 43.89; H, 6.67.

To a CH_2Cl_2 solution (25 mL) containing $Cp(CO)[P(OCH_3)_3]FeCH_2CH_3$ (**16**) (459 mg, 1.50 mmol) was added $Ph_3C^+PF_6^-$ (582 mg, 1.50 mmol) with stirring. The solution turned from yellow to dark greenish-yellow, and its IR spectrum corresponded to complete consumption of **16**, with a new ν(CO) (br) evident at 2019 cm^{-1}. This mixture was added slowly with constant scraping to 75 mL of ether in order to produce yellow crystals. These were filtered, washed with ether, and vacuum dried as yellow crystals of $Cp(CO)[P(OCH_3)_3]Fe(CH_2{=}CH_2)^+PF_6^-$ (**15**) (361 mg, 54%).

Anal. Calcd for $C_{11}H_{18}O_4P_2FeF_6$: C, 29.62; H, 4.07. Found: C, 30.02; H, 4.21.

Reduction of $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (8) with $LiHB(sec\text{-}Bu)_3$. A THF solution of L-Selectride (Aldrich), $LiHB(sec\text{-}Bu)_3$ (1.0 mL, 1.0 mmol), was added via syringe to a reddish-orange THF solution (15 mL) of $Cp(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (**8**) (520 mg, 1.0 mmol) cooled to −80 °C. The reaction solution, which had instantly turned golden brown, was magnetically stirred for 45 min before warming to room temperature. IR spectral examination of the reaction indicated a 1:1.2 mixture of $Cp(CO)[P(OCH_3)_3]Fe(CH_2{=}CHOCH_2CH_3)^+PF_6^-$ (**18**) [ν(CO) 1997 cm^{-1}] and $Cp(CO)[P(OCH_3)_3]FeCH_2CHO$ (**19**) [ν(C≡O) 1942, ν(C═O) 1618 cm^{-1}]. Attempts to extract **19** with ether and leave **18** were only partially successful, since the gummy **18** so obtained could not be crys-

(25) Hertz, R. K.; Johnson, H. D.; Shore, S. G. *Inorg. Synth.* **1977**, *17*, 21.

tallized. Also, its IR spectrum indicated the presence of impurities.

The crude reaction product was converted to the formylmethyl complex **19** by stirring its CH_2Cl_2 solution (25 mL) with 10 g of activity 3 alumina for 2 h. The alumina then was filtered from the reddish-orange solution and the residual orange was removed from the alumina with 10% (v/v) ethyl acetate/CH_2Cl_2. These washes were combined with the initial filtrate, and the solvent was removed (rotovaporator) to leave an orange-brown oil. This crude product was dissolved in a minimum volume of CH_2Cl_2 and chromatographed on 50 g of alumina. Development of the column with CH_2Cl_2 separated a diffuse brown band containing borane residues from a broad gold band following it. This latter band was cleanly eluted with 5% (v/v) ethyl acetate/CH_2Cl_2. Solvent was evaporated from this golden eluate and the resulting golden-brown gum was vacuum dried 1 h. **19**: 136 mg (43%); ^{1}H NMR ($CDCl_3$) 9.29 (dd, J = 7.0, 4.0 Hz, 1, COH), 4.54 (s, 5, Cp), 3.63 (d, J = 11 Hz, 9, $POCH_3$), 1.67 (m, 1, FeC*H*H), 1.20 (m, 1, FeCH*H*).

Anal. Calcd for $C_{11}H_{17}O_5PFe$: C, 41.80; H, 5.42. Found: C, 41.57; H, 5.17.

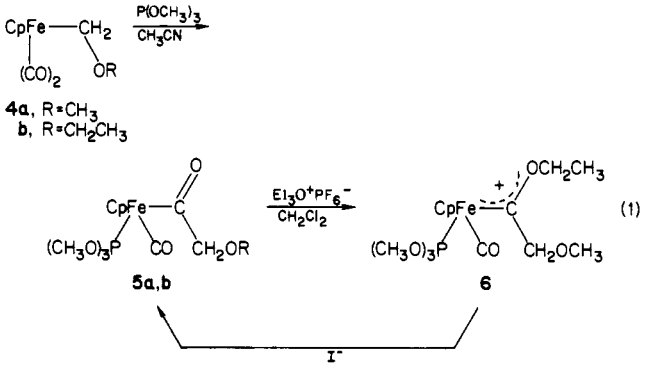
Ethylation of $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2CHO$ (19) with $(CH_3CH_2)_3O^+PF_6^-$. $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2CHO$ (**19**) (772 mg, 2.44 mmol) as a reddish-brown CH_2Cl_2 solution (35 mL) was treated with $(CH_3CH_2)_3O^+PF_6^-$ (606 mg, 2.44 mmol). IR spectral monitoring of the unchanged solution after 10 min indicated quantitative conversion of **19** to $Cp(CO)[P(OCH_3)_3]Fe(CH_2{=}CHOCH_2CH_3)^+PF_6^-$ (**18**), ν(CO) 1997 cm^{-1}. Solvent was evaporated under reduced pressure, and the resulting brown oil was redissolved in 10 mL of 1:10 (v/v) absolute ethanol/acetone (which destroys any lingering triethyloxonium). This ethanol solution then was added dropwise into ether (75 mL) while scraping; the resulting yellow-orange crystals were filtered, washed with ether, and dried first in a stream of nitrogen and then under vacuum. The vinyl ether salt **18** (692 mg, 58%) was obtained as a 2:1 mixture of diastereomers A and B: ^{1}H NMR (acetone-d_6) δ 7.89 (dd, J = 5.0, 11.5 Hz, 1, =C*H*OEt (A)), 6.77 (dd, J = 5, 11 Hz, 1, =C*H*OEt (B)), 5.30 (s, 5, Cp), 4.25 (quart, J = 7 Hz, 2, OCH_2CH_3), 3.93 (d, J = 11 Hz, 9, $POCH_3$ (A)), 3.81 (d, J = 11 Hz, 9, $POCH_3$ (**B**)), three multiplets centered at 2.64, 2.37, and 2.09 for the remaining two vinyl H's on both diastereomers, 1.31 (t, J = 7 Hz, 3, OCH_2CH_3 (B)), 1.28 (t, J = 7 Hz, 3, OCH_2CH_3 (A)).

Anal. Calcd for $C_{13}H_{22}O_5P_2FeF_6$: C, 31.86; H, 4.52. Found: C, 31.60; H, 4.31.

A yellow CH_2Cl_2 solution (10 mL) containing $Cp(CO)[P(OCH_3)_3]Fe(CH_2{=}CHOCH_2CH_3)^+PF_6^-$ (**18**) (250 mg, 0.51 mmol) was chromatographed on alumina as described. The yellow eluate was evaporated to a yellow gum (140 mg) that was spectrally identified as $Cp(CO)[P(OCH_3)_3]FeCH_2CHO$ (**19**) (83% conversion).

Results

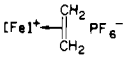
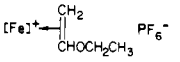
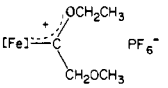
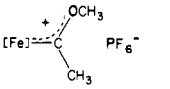
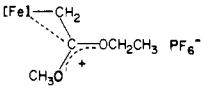
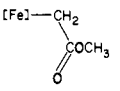
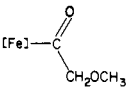
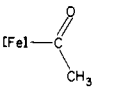
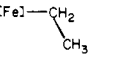
Isomerization of Alkoxyacetyl $(C_5H_5)(CO)[P(OCH_3)_3]FeCOCH_2OR$ to Carbalkoxymethyl $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2CO_2R$. Preparation of β-alkoxyacetyl **5a,b** and α,β-dialkoxyethylidene **6a** compounds follows straightforward synthetic routes (eq 1). Thus, conversion of the requisite alkoxymethyl



complex **4a,b** to the β-alkoxyacetyl compounds **5a,b** proceeds by phosphite-induced alkyl migration (i.e., CO insertion)[26] in refluxing acetonitrile over 10 days. After crystallization from CH_2Cl_2–ether–pentane both **5a** and **5b** were retrieved in ~40% yields as yellow to yellow-orange crystals. This rather lengthy reaction time for CO insertion is actually optimal, as ascertained by IR spectral monitoring, for **4** converting to **5** vs. decomposing. These vigorous reaction conditions, analogous to those observed during carbonylation of other alkoxymethyl complexes,[6] undoubtedly derive from a rate-retarding effect of the α-alkoxy group on **4a,b**. For comparison, the unsubstituted methyl complex $Cp(CO)_2FeCH_3$ and trimethyl phosphite, under comparable reaction conditions, afforded $Cp(CO)[P(OCH_3)_3]FeCOCH_3$ (**10**) (93% yield) after only 20 h of refluxing,[27]

Alkylation of the methoxyacetyl complex **5a** with triethyloxonium hexafluorophosphate yields α-ethoxy-β-methoxyethylidene **6**, an alkoxycarbene compound analogous to those derived from other CpFe acyl complexes.[8,28] Precipitation with ether and subsequent workup afforded **6** (86% yield) as a reddish-brown gum that was pure by IR and NMR spectral analysis. Its IR spectral data in CH_2Cl_2 (Table I) signal the alkoxycarbene structure. Furthermore, treatment of these solutions with 1 equiv of $(Bu)_4N^+I^-$ quantitatively regenerates the starting acyl complex **5**, as evidenced by the diagnostic acyl stretching frequency ν(C=O), 1619 cm^{-1}. NMR results, as expected, are in accord with **6** converting with iodide exclusively to **5a** and not **5b**. Proton

Table I. Spectral Data of $(C_5H_5)(CO)[P(OCH_3)_3]Fe$ Complexes

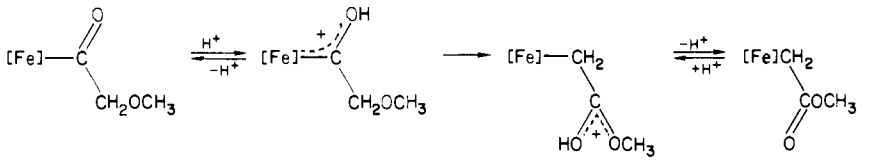
		IR (CH_2Cl_2) ν(CO), cm^{-1}	^{1}H NMR δ (Cp)
	**15**	2018	5.42[a]
	**18**	1997	5.30[a]
	**6**	1998	5.29[a]
	**17**	1997	5.29[a]
	**8**	1961	4.94[a]
	7a	1947, 1669[b]	4.54[c]
	**19**	1942, 1618[b]	4.54[a]
	5a	1934, 1619[b]	4.61[c]
	10	1936, 1599[b]	4.67[c]
	**16**	1921	4.46[c]

[a] In acetone-d_6. [b] ν(C=O). [c] In $CDCl_3$.

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

(27) Tributyl and triphenyl phosphine substituted acetyl complexes $Cp(CO)[P(OR)_3]FeCOCH_3$ have been prepared by analogous procedures: Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* **1966**, *5*, 889.

(28) (a) Green, M. L. H.; Michard, L.; Swanwick, M. *J. Chem. Soc. A* **1971**, 794. (b) Davison, A.; Reger, D. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (c) Casey, C. P.; Cyre, C. R.; Boggs, R. A. *Synth. React. Inorg. Met.-Org. Chem.* **1973**, *3*, 249. (d) Treichel, P. M.; Wagner, K. P. *J. Organomet. Chem.* **1975**, *88*, 199. (e) Brookhart, M.; Tucker, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (f) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (g) Casey, C. P.; Miles, W. H.; Tukoda, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (h) Kremer, K. A. M.; Duo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (i) Grotsch, G.; Malisch, W. *J. Organomet. Chem.* **1982**, *246*, C42, C49. (j) Bodnar, T. W.; Cutler, A. R. *Synth. React. Inorg. Met-Org. Chem.*, in press.

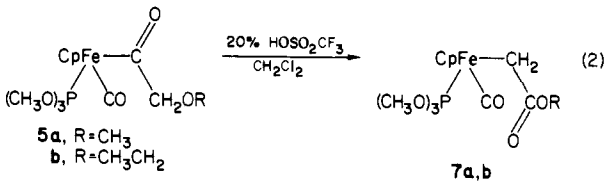


(3)

	5a	11	12	7a
IR ν(CO)	1934	1998	1969	1944
(CH_2Cl_2)	1619			1668

NMR spectral assignments for **6** also parallel those for four other α,β-dialkoxyethylidene salts[8] $Cp(CO)(PPh_3)FeC(OR')CH_2OR^+$ (R, R' = CH_3, CH_2CH_3).

Both alkoxyacetyl complexes **5a,b** isomerize smoothly to their carbalkoxymethyl compounds **7a,b** (eq 2) in the presence of 20%



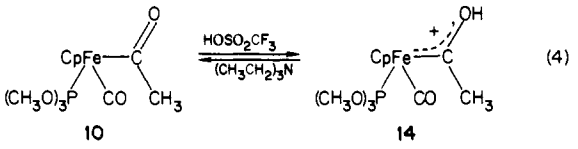
(2)

(stoichiometric) triflic acid. Chromatography of the crude reaction mixtures provided **7a,b** as spectroscopically and analytically (**7b**) pure brown gums in ~70% yields. Spectral data for **7a,b** are distinctive: magnetically nonequivalent $FeCH_2$ hydrogens absorb in the ^1H NMR spectrum, and low-energy IR ν(CO) frequencies appear for the carbalkoxy ligand at 1670 cm^{-1}. These diastereotopic and magnetically nonequivalent methylene hydrogens absorb as separate ABX multiplets (with ^{31}P coupling), because of their proximity to a chiral (iron) center.[29]

Results of IR spectral monitoring during protic isomerization of **5a,b** to **7a,b** are consistent with the reaction sequence depicted in eq 3. Several stages of this reaction, in terms of the progression of species illustrated, in fact, are qualitatively modeled by examining independently the protonation/deprotonation sequences of the individual components. Thus, treating a lemon-yellow CH_2Cl_2 solution of **5a** (0.10 mmol/1.5 mL) with 0.5 mmol of $HBF_4{\cdot}OEt_2$ immediately provided an orange solution that by IR spectroscopy contained the hydroxycarbene complex **11**. Quenching this reaction within 1 min with triethylamine regenerated >90% of **5a**. Without the amine quench, the reaction solution turned orange-brown and the IR spectral absorption for **12** replaced that of **11** within 2 h. Small amounts of $Cp(CO)[P(OCH_3)_3]FeCO^+$ (**13**)[30] also appeared [ν(CO) 2069, 2028 cm^{-1}]; its exact concentration depended on the initial concentration of **5a**. [With less than stoichiometric amounts of acid (as in the preparative-scale experimental), the buildup of this carbonyl salt **13** can be minimized.] A triethylamine quench of the reaction after 2 h transformed **12** into its carbalkoxymethyl complex **7a**. If the reaction instead was permitted to sit for longer times (~12 h), then **13** gradually built up as the only organometallic product and the IR absorption for methyl acetate [ν(CO) 1738 cm^{-1}] likewise grew in.[31]

Treatment of an orange solution containing the carbalkoxymethyl complex **7a** with excess acid gave a darker orange solution of **12**; a triethylamine quench within 2 min recovered **7a** (>90%). With continued sitting, the solution of **12** degraded as already noted and released methyl acetate.

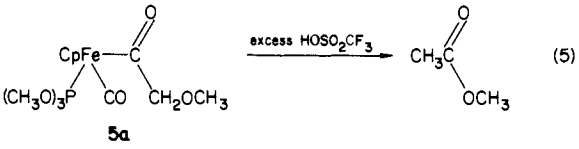
Results of protonating the alkoxyacetyl complex **7a** can be compared with those for the parent acetyl complex $Cp(CO)[P(OCH_3)_3]FeCOCH_3$ (**10**). A yellow CH_2Cl_2 solution of **10** (ν(CO) 1937, 1598 cm^{-1}], upon treatment with excess triflic acid, immediately turned orange due to the presence of its hydroxycarbene salt **14** (eq 4). Triethylamine (excess added) quantitatively



(4)

reversed this reaction. This protonation–deprotonation sequence for **10** closely parallels (by IR spectroscopy) that rigorously established with the triphenylphosphine-substituted acetyl complex $Cp(CO)(PPh_3)FeCOCH_3$.[32] Significantly, solutions of **14** remain stable for at least 24 h; deprotonation at this time regenerates at least 85% of starting **10** plus a small amount (<10%) of the carbonyl salt **13**. Clearly, the aforementioned acid degradation of the alkoxyacetyl system **5** derives from the presence of the β-alkoxy substituent and not as an inherent reaction of the acyl ligand.

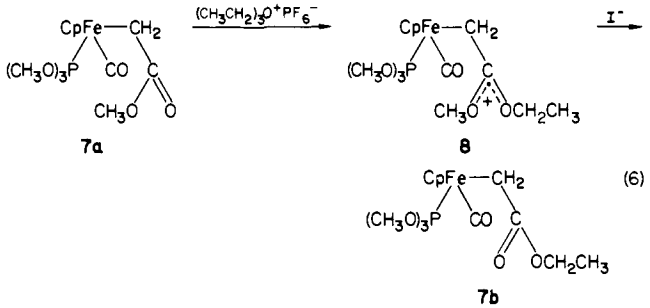
Cleavage of methyl acetate from either of **5a** or **7a** in the presence of excess acid (eq 5) is of interest. Using **5a** and excess



(5)

triflic acid in CH_2Cl_2, we quantified the methyl acetate formed after 24 h, by both IR spectral and GLC techniques. Results of both techniques are in excellent agreement—100% yield by quantitative IR spectroscopy and 98% by GLC.

Characterization of the (Dialkoxycarbenio)methyl Compound $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (8). Treatment of the carbomethoxymethyl complex **7a** with triethyloxonium hexafluorophosphate gives $Cp(CO)[P(OCH_3)_3]$-$FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (**8**) as a stable, crystalline salt in high yield. Iodide readily reverses this reaction, an interesting application being the selective transformation of **7a** to **7b** by iodide dealkylation of **8** (eq 6). A similar selectivity in S_N2 displacement



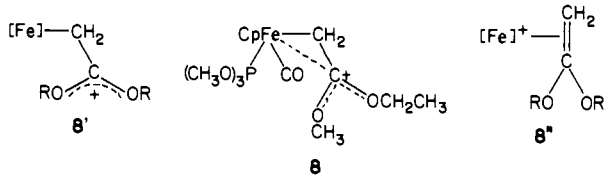
(6)

(using iodide) of methyl vs. ethyl groups from alkoxycarbene complexes has been documented.[33]

As for the structure of **8**, its spectral data are consonant with the Fe-stabilized β-dialkoxycarbenium ion depicted. Alternatively, the structure of **8** contains features of the two tautomers: η^1-

(29) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1969**, *91*, 1550. Brunner, H.; Schmidt, E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 616.
(30) Davies, S. G. *J. Organomet. Chem.* **1979**, *179*, C5.
(31) Identity of methyl acetate was confirmed through NMR spectral monitoring of similar protonation reactions in $CDCl_3$. The δ 2.10 CH_3C absorption for $CH_3CO_2CH_3$ was used for this purpose, as the OCH_3 δ 3.72 resonance was obscured by the trimethyl phosphite absorption. Nevertheless, the δ 2.10 peak growing in during the course of this reaction further increased in intensity when authentic methyl acetate was added.
(32) Green, M. L. H.; Hurley, C. R. *J. Organomet. Chem.* **1967**, *10*, 188.
(33) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604.

(dialkoxycarbenio)methyl complex **8′** (with sp^3-hydridized CH_2)

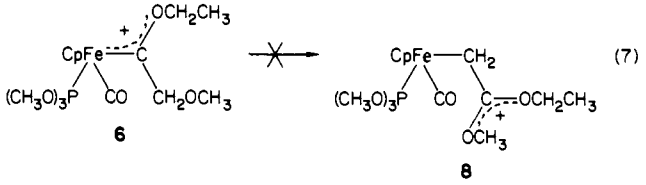


and ketene acetal **8″** (sp^2-hybridized CH_2 and charge delocalization to Fe). The structural assignment for **8** parallels that for its $Cp(CO)_2Fe$ or Fp analog.[18]

The δ Cp and terminal carbonyl ν(CO) data in the ^1H NMR and IR spectra of **8** (as for the Fp analogue)[18] thus are intermediate between analogous data (Table I) for η^1-alkyl structures **7** and **1b** and for η^2-alkenes **20** and **15**, Such data along with $^1J_{CH}(CH_2)$ information from ^{13}C NMR spectra for the Fp analogues have been further refined in favor of the Fp-stabilized β-dialkoxycarbenium ion structure analogous to **8**.[19] (Results of single-crystal X-ray structural determinations of several metal Fp-stabilized β-carbenium ions are now on record.)[34]

Supporting evidence for structural assignment of **8** derives from further examination of its ^1H NMR spectrum. The two multiplets for the diastereotopic methylene hydrogens appear very similar (although shifted slightly downfield) to those of its neutral carbalkoxymethyl precursor **7a**. Moreover, the coupling constants of the corresponding ABX multiplets on **8** and **7a** are rather similar. An alternative structure **8″** possessing an η^2-ketene acetal structure would, in contrast, have a much simpler methylene resonance, due to the lack of geminal coupling[35] and the smaller vicinal $J(H-^{31}P)$ coupling expected for a π-complex. (The methylene hydrogens on $Cp(CO)[P(OCH_3)_3]Fe(\eta^2\text{-}CH_2{=}CH_2)^+PF_6^-$, for example, absorb in its NMR spectrum as a broad singlet.) Thus, overall resemblance of the NMR spectra for **8** and **7a** and the presence of an obvious metal interaction with the β-carbon (e.g., IR spectral ν(CO) results) are most consistent with the β-dialkoxycarbenium ion structure depicted.

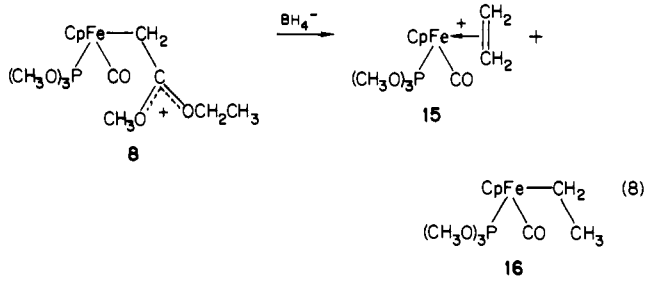
Given that an alkoxyacetyl complex **5** in acid isomerizes to its carbalkoxymethyl compound **7**, and that their alkylated alkoxycarbene **6** and dialkoxycarbenium ion **8** derivatives are available, it is of interest to note if **6** isomerizes to **8** (eq 7). We found no



(7)

evidence for this isomerization. IR spectral monitoring (before and after adding excess iodide to each aliquot) of solutions of **6a** in CH_2Cl_2 (room temperature, 24 h; reflux, 12 h) and in $CHCl_2CH_3$ (reflux, 57 °C, 5 h) indicated no alteration of the starting **6a**. Refluxing 1,2-dichloroethane (83 °C) decomposed **7a** within an hour to nonsoluble residues that contained no CO ligands (by IR spectroscopy).

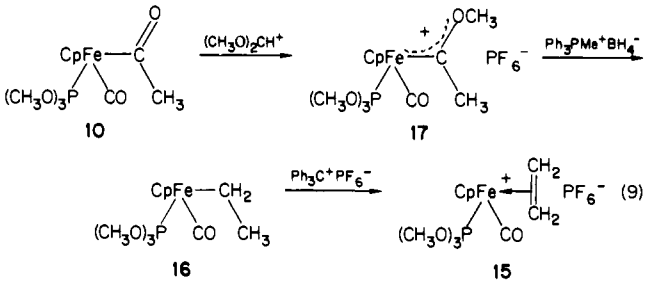
Reductive Chemistry of $(C_5H_5)(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$ (8). The real advantage of alkylating the carbalkoxymethyl **7a** is that the resulting dialkoxycarbenium ion derivative **8** is activated as a hydride acceptor. Certainly this activation is required, as **7a** is inert toward $Ph_3PCH_3^+BH_4^-$ in CH_2Cl_2 solution (20 °C). With **8**, however, sodium borohydride (1 equiv) in ethanol gives a 1:1 mixture (total, 65% yield) of the iron ethylene and ethyl complexes **15** and **16** (eq 8). A similar



(8)

reduction using $Ph_3PCH_3^+BH_4^-$ in CH_2Cl_2 affords only **16**. Compounds **15** and **16** were readily separated by pentane extraction: pentane-soluble **16** resulted as a yellow-brown oil after column chromatography, and the pentane-insoluble residue afforded yellow, crystalline **15** after recrystallization from CH_2Cl_2–ether. Although **15** and **16** are new compounds, they resemble their triphenyl phosphite analogues[35b] in solubility and spectral properties.

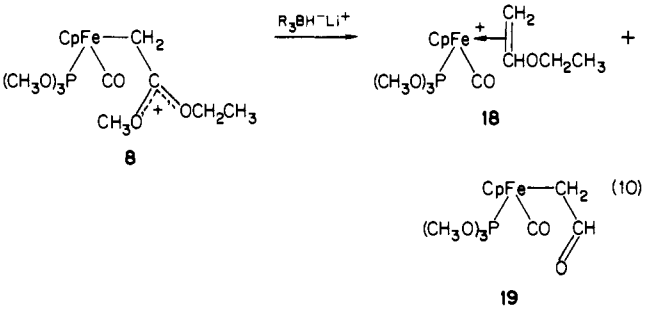
Since **15** and **16** are new compounds, they were prepared also by a more traditional route summarized in eq 9. Synthetic



(9)

procedures that we had developed[8] were used to first convert the acetyl complex $Cp(CO)[P(OCH_3)_3]FeCOCH_3$ (**10**) to the requisite α-methoxyethylidene complex **17**, and then to reduce it selectively to **16** using borohydride. The use of triphenylcarbenium ion in converting **16** to **15** is a standard procedure for converting η^1-alkyl complexes to their η^2-alkene salts.[36] For example, both iron ethyl complexes $Cp(CO)(L)FeCH_2CH_3$ (L = CO,[37] PPh_3[38]) also give their η^2-ethylene salts upon reaction with the triphenylcarbenium salts. As detailed in the Experimental Section, the aforementioned ligand transformations were uncomplicated both in their execution and in their isolation procedures.

L-Selectride, $LiHB(sec\text{-}Bu)_3$, cleanly reduces **8** in THF (−80 °C) to a 1:1,2 mixture of the ethyl vinyl ether **18** and formylmethyl **19** complexes (eq 10). Attempts to fractionate this mixture into



(10)

ether-soluble **19** and -insoluble **18** were only partly successful. Each fraction instead remained contaminated by the other component and trace amounts of other identified materials—as in-

(34) Kerber, R. C.; Ehntholt, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 2927. Laing, M.; Moss, J. R.; Johnson, J. *J. Chem. Soc., Chem. Commun.* **1977**, 656. Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C, *J. Am. Chem. Soc.* **1981**, *103*, 7361.

(35) A rather large number of monosubstituted alkene complexes $Cp(CO)(L)Fe(\eta^2\text{-}CH_2{=}CHR)^+$ [L = CO,[35a] $P(OPh)_3$[35b]] have been reported with the alkene $^2J_{HH} \sim 0$. (a) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149. Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. (b) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155.

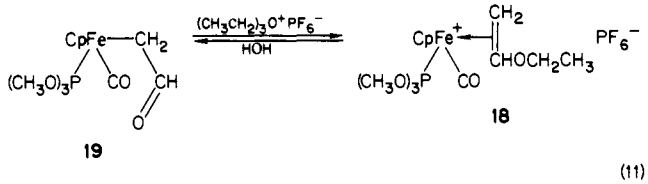
(36) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291.

(37) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58.

(38) Jensen, J. E.; Campbell, L. L.; Nakanishi, S.; Flood, T. C. *J. Organomet. Chem.* **1983**, *244*, 61.

dicated by peak broadening of the IR spectral ν(CO) absorptions and by our inability to crystallize **18**. The entire reaction mixture, therefore, was converted to the formylmethyl complex **19** by hydrolyzing it over alumina, which left **19** as an analytically pure yellow-brown gum. That the ethyl and not methyl vinyl ether compound was initially formed during the L-Selectride reduction of **8** was demonstrated by comparing NMR data of the ether-insoluble fraction with that for an authentic sample of **18**.

The vinyl ether compound **18** was independently prepared by alkylating **19** with triethyloxonium hexafluorophosphate (eq 11).



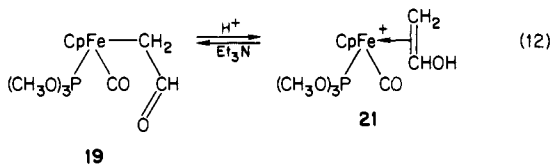
(11)

After reprecipitating from CH_2Cl_2–ether, **18** resulted as an air-stable, yellow solid that from its NMR spectrum consisted of a 2:1 mixture of diastereomers. Formation of this diastereomeric mixture—due to the chiral iron center—was anticipated, since a number of other monosubstituted (and hence prochiral) alkenes likewise produce diastereomeric mixtures as $Cp(CO)[P(OPh)_3]Fe(CH_2{=}CHR)^+$ compounds.[35b] The overall appearance of the NMR spectrum of **18** (each diastereomer), however, closely resembles that of analogous $Cp(CO)_2Fe$ complexes $Fp(CH_2{=}CHOCH_2CH_3)^+$ (**20**).[18] In particular, a diagnostic doublet of doublets absorbing downfield (δ >6) for the vinyl hydrogen geminal to the alkoxy substituent is common to the NMR data of **18** and **20**.

The chemical reactivity of **18** differs from that of its $Cp(CO)_2Fe$ counterpart $Fp(CH_2{=}CHOEt)^+$ (**20**) in two ways. First, the vinyl ether ligand on **18** is much less labile than on **20**. Excess $(n\text{-}Bu)_4N^+I^-$ in CH_2Cl_2 accordingly does not react with **18** over 2 h, whereas with **20** the iodide quantitatively releases the vinyl ether and leaves FpI within $^1/_2$ h. After 10 h at room temperature, the solution of **18** and excess iodide affords a 1:1 mixture of starting **18** and formylmethyl **19**. Second, **18** is less susceptible to hydrolysis than is **20**. A few drops of water in a vigorously stirred CH_2Cl_2 solution of **18** thus does not produce any **19** over 2 h, whereas the Fp vinyl ether compound **20** under comparable conditions hydrolyzes in a few minutes and quantitatively (as ascertained by IR spectral monitoring) gives its formylmethyl complex $FpCH_2CHO$. The phosphite–vinyl ether compound **18** will hydrolyze, however, upon column chromatography with activity III neutral alumina: CH_2Cl_2–ethyl acetate elutes **19**, which is collected in 83% yield. Therefore, replacement of a CO ligand by trimethyl phosphite on these organoiron η^2-vinyl ether salts evidently diminishes the reactivity of **18**, as expected,[39] toward nucleophilic displacement of the vinyl ether and toward nucleophilic addition to the coordinated ligand.

We also qualitatively evaluated the formylmethyl complex **19** as a precursor to free acetaldehyde. Certainly strong acids slowly transform **19** to $Cp(CO)[P(OCH_3)_3]FeCO^+$ (**13**) (in less than 50% yield) and evolve acetaldehyde. Unfortunately acetaldehyde, which is barely observable by IR spectroscopy [ν(C=O) 1728 cm^{-1}], does not accumulate in large concentrations. Attempts to trap the released acetaldehyde as its (2,4-dinitrophenyl)-hydrazone—although successful during protonation studies on $Cp(CO)(PPh_3)FeCH_2CHO$[8,15]—only partially worked with **19**. In this case the acetaldehyde (2,4-dinitrophenyl)hydrazone continuously presented itself as a gum even after column chromatography. (A yellow crystalline solid was expected.) Attempts to assay this yellow gum for the desired 2,4-DNP derivative by NMR and by IR (using Beer's law plots of authentic material) spectral studies support an acetaldehyde yield greater than 50%.

In another approach to cleaving acetaldehyde from **19** the η^2-vinyl alcohol salt, obtained by protonating **19**, was treated with iodide. With the analogous $Cp(CO)_2Fe$ system $FpCH_2CHO$, this approach works extremely well; the vinyl alcohol (acetaldehyde) displaced was distilled trap to trap and assayed by GLC.[15a] Treatment of **19** with tetrafluoroboric acid etherate or triflic acid in CH_2Cl_2 also produces the η^2-vinyl alcohol salt **21** (eq 12), as



(12)

evidenced by its IR ν(CO) shift to 1999 cm^{-1} and by its reversion to **19** with triethylamine. Vinyl alcohol complex **21** was not further characterized; its IR stretching frequency corresponds to the analogous value (1998 cm^{-1}) observed for the vinyl ether compound **18**. Unfortunately, excess iodide does not react with solutions containing **21**, a result not surprising in view of the lack of reactivity of the vinyl ether salt **18** with iodide. In conclusion, strong acids react with **19** initially to give the vinyl alcohol salt **21** and after sitting to slowly evolve acetaldehyde. Analytical procedures for acetaldehyde that worked well with analogous formylmethyl complexes $Cp(CO)LFeCH_2CHO$ (L = PPh_3, CO), however, proved unacceptable when applied to **19**.

Discussion

Many examples of transition organometallic carbalkoxymethyl complexes **2** have been reported, nearly all of which were prepared by reacting an organometallic nucleophile with chloro- or bromomethyl acetate.[12,18,40] Thus $Cp(CO)_2FeCH_2CO_2CH_3$ was synthesized initially by this route[40b] (in less than 10% yield), although more convenient procedures of isomerizing the methoxyacetyl $Cp(CO)_2FeCOCH_2OCH_3$[18] (i.e., **1** → **2**) or of adding CO then methanol to $Cp(CO)_2Fe{=}CH_2{}^+$[19] are now available. In effect, this carbomethoxymethyl ligand can be built up from CO (Scheme I), but once formed it maintains its implicit C_2 selectivity, even in the presence of higher carbon monoxide pressures. Carbalkoxymethyl systems **2** accordingly resist inserting CO and generating the C_3 carbalkoxyacetyl ligand $MCOCH_2CO_2R$.[41]

Acid-induced isomerization of the alkoxyacetyl complexes **5** serves as a convenient synthesis of carbalkoxymethyl compounds. Although the mechanism of this rearrangement has not been investigated in detail, that advanced in Scheme II is consistent

(39) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148.

(40) (a) Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* **1969**, 1309. Engelbrecht, J.; Greiser, T.; Weiss, E. *J. Organomet. Chem.* **1981**, *204*, 79. (b) King, R. B.; Bisnette, M. B.; Franzaglia, A. *J. Organomet. Chem.* **1966**, *5*, 341.

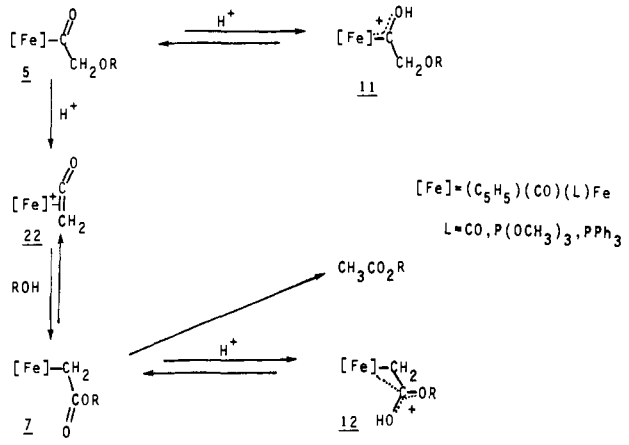
(41) We have been unable to carbonylate (η^5-Cp)- or (η^5-indenyl)(CO)(L)$FeCH_2CO_2CH_3$ (L = CO, PPh_3) with procedures employing up to 80 atm of CO, whereas the corresponding Fe methyl complexes carbonylate under conditions as mild as 1 atm CO/20 °C/1 h. Starting carbomethoxymethyl complexes, instead, were quantitatively recovered. Forschner, T. C.; Cutler, A. R. *Organometallics*, in press. There is further evidence that if the desired C_3 system $[Fe]COCH_2CO_2CH_3$ did form then it would fragment by ejecting acetic acid ester. Davies, S. G.; Watts, O.; Aktogu, N.; Felkin, H. *J. Organomet. Chem.* **1983**, *243*, C51.

(42) Flood also has noted this proclivity toward electrophilic cleavage of the iron–carbon bond of analogous PPh_3-substituted carbalkoxymethyl complexes. Flood, T. C.; Miles, D. L. *J. Organomet. Chem.* **1977**, *127*, 33.

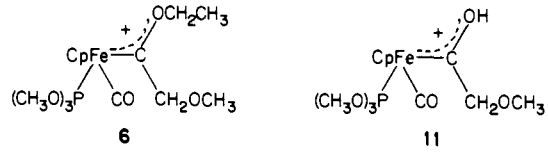
(43) The main shortcoming in using the $P(OCH_3)_3$-substituted system is that the corresponding alkyl and even cationic alkene and alkoxycarbene complexes crystallize with great difficulty (compared with the Fp and its PPh_3- or $P(OPh)_3$-[44]substituted systems), if at all. In contrast, we previously reported syntheses of the Cp(CO)(L)Fe complexes [L = PPh_3, $P(OPh)_3$]: acetyl, α-alkoxyethylidene, α-alkoxyethyl, η^1-ethylidene, and η^2-ethylene. All were characterized as yellow, crystalline solids possessing high solubilities and easily interpreted NMR spectra.[28f]

(44) Triphenyl phosphite and the caged phosphite $P(OCH_2)_3CCH_3$ have enjoyed rather more use than $P(OCH_3)_3$ in synthetic chemistry with the Cp(CO)(L)Fe system, Reger, in particular, has noted useful stability and preparative attributes of the $Cp(CO)[P(OPh)_3]Fe$ moiety in its η^1-alkyl and η^2-alkene, alkyne complexes:[35b] Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101. Rosenblum also has employed several phosphites in studies with analogous η^1-alkyl, allyl and their η^2-alkene compounds. Rosenblum, M.; Waterman, P. S. *J. Organomet. Chem.* **1980**, *187*, 267; **1981**, *206*, 197.

Scheme II



with our observations on protonating both the iron phosphite complexes **5**/**7** and the analogous Fp alkoxyacetyl/carbalkoxymethyl compounds. Accordingly, the η^2-ketene-*C*,*C* salt **22** is postulated as the primary intermediate during this isomerization, with alcohol then adding to give the carbalkoxymethyl system,[19] Our inability to isomerize dialkoxyethylidene **6** to the stable



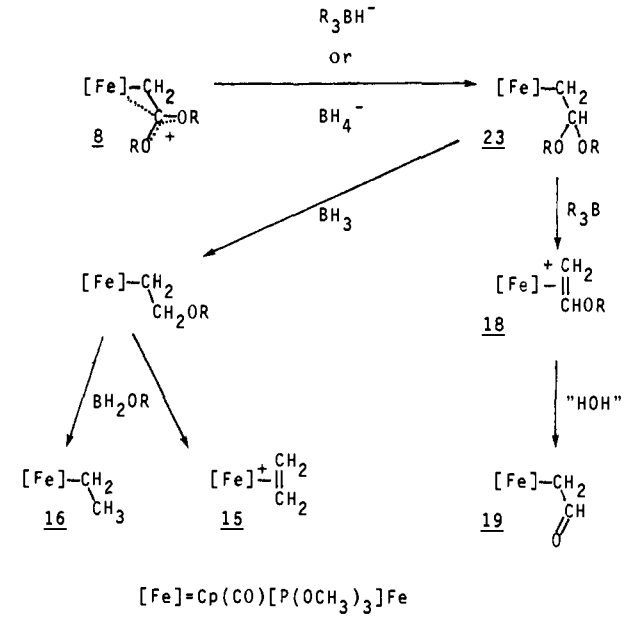
6 **11**

(dialkoxycarbenio)methyl **8** (eq 7), in contrast to the facile conversion of the analogous hydroxycarbene **11** to **7a** in acid (eq 3), is consistent with this postulated mechanism. With **11** it is quite possible that a ketene intermediate **22** irreversibly forms as the **5**/**11** equilibrium shifts back to **5** (Scheme II). The alkoxycarbene **6**, however, by not equilibrating with its neutral alkoxyacetyl **5**,[28] cannot isomerize via **22** to the (dialkoxycarbenio)methyl compound **8**.

Prolonged sitting of either **5a** or **7a** in the presence of excess acid quantitatively eliminates methyl acetate, which is another example of protonolysis of Cp organoiron alkyl compounds to eliminate alkanes,[45] In our system we favor ultimate protonolysis taking place on **7a**, since it is unlikely that **12** would simply dissociate $CH_2C(OR)OH$ (the tautomer of CH_3CO_2R) under conditions where the (dialkoxycarbenio)methyl complex **8** is so robust.

Carbalkoxymethyl ligands function as C_2 templates through their high reactivity toward electrophiles, This reactivity illustrates operation of the "β effect",[40a] which is also manifested spectroscopically, on these organometallic alkyl ligands, Carbalkoxymethyl complexes accordingly exhibit unusually low IR spectral ν(C=O) for the organic ligand; moreover, their free carboxylic acids are very weak acids. Both phenomena have been interpreted as the metal center transferring electron density, apparently via both through-space and through-bond mechanisms, to the β-position on the alkyl ligand. As a result the iron center on **7a** stabilizes a positive charge on the β-carbon in forming the Fe-stabilized β-dialkoxycarbenium compound **8** (eq 6), which serves as the key intermediate in refunctionalizing the carbalkoxymethyl ligand.

Scheme III



Choice of ancillary ligand L on the carbalkoxymethyl complexes $Cp(CO)(L)FeCH_2CO_2R$ (**7**) was critical. With L = PPh_3, we were unable to cleanly alkylate the known[8] **7**. Its attempted alkylation always gave mixtures containing the desired (dialkoxycarbenio)methyl compound contaminated by at least 50% of $Cp(CO)(PPh_3)FeCO^+$.[42] With L = $P(OPh)_3$, we were unable to prepare the appropriate starting **5** and **7**. With L = CO, we were unable to reproducibly reduce the previously reported[18] (dialkoxycarbenio)methyl salt **8** to discrete alkyl complexes. Choice of L = $P(OCH_3)_3$, however, proved propitious. The requisite examples of **5**, **7**, and **8** were readily prepared, and the reduction products of the (dialkoxycarbenio)methyl salt **8** were readily characterized.[43,44]

The reductive chemistry of the carbalkoxymethyl ligand on **7**, suitably activated as its (dialkoxycarbenio)methyl derivative **8**, engenders other C_2 ligands and their organic products. Interestingly, BH_4^- and the monohydride donor L-Selectride [(*sec*-Bu)$_3$BHLi] selectively reduce **8** to different products **15**/**16** and **18**/**19**, respectively. A mechanism accounting for these transformations appears in Scheme III. The formylmethyl acetal complex **23** that would result from the initial hydride transfer (by either borohydride reagent) to **8** was not detected; analogous formylmethyl acetal complexes $Cp(CO)(L)FeCH_2CH(OR)_2$ [L = CO,[18] PPh_3[8]], however, have been prepared by other routes. These acetals generally ionize a β-alkoxide and "hydrolyze" to their formylmethyl complexes in the presence of even trace amounts of Lewis acids. For example, L-Selectride reduces **8** to an ~1:1 mixture of **18** plus **19**; the driving force (if not the precise mechanistic details) for converting **23** and/or **18** to formylmethyl **19** thus follow.

Borohydride (BH_4^-) reduces **8** to the η^2-ethylene salt **15** and/or the fully reduced ethyl complex **16**. The latter derives from BH_3 effectively abstracting β-alkoxide functionalities on **23** and transferring back hydride. Precedent exists for electrophilic BH_3-reducing alkoxide from coordinated alkyl ligands as it converts α-alkoxyethyl,[8,28b] alkoxymethyl,[33] and even acetyl[47] complexes to their parent hydrocarbon ligands. Indeed, BH_4^- reduction of $Cp(CO)[P(OCH_3)_3]FeC(CH_3)OCH_3^+$ (**17**) (eq 9) likewise entails a similar conversion of $Cp(CO)[P(OCH_3)_3]FeCH(OCH_3)CH_3$ to the final ethyl complex **16** by BH_3. Given the analogous lability of β-alkoxide substituents toward Lewis acids,[48]

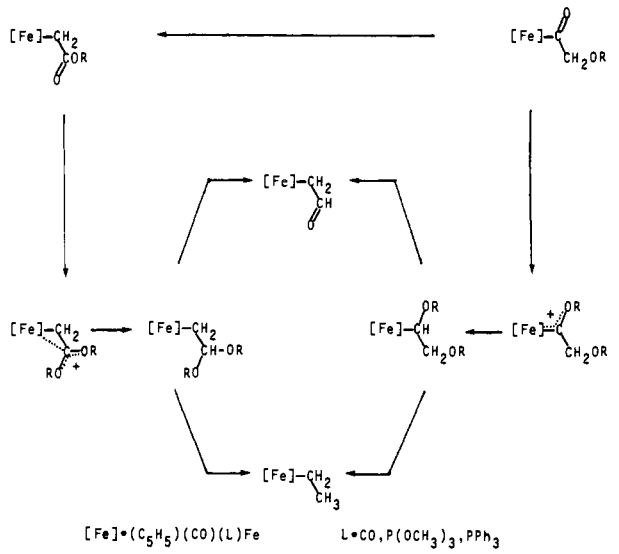
(45) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57. Rogers, W. N.; Baird, M. C. *J. Organomet. Chem.* **1979**, *182*, C65. Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619. Anderson, S. N.; Cooksey, C. J.; Holton, S. G.; Johnson, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 2312. DeLuca, N.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *193*, 359. Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

(46) Other organometallic carbalkoxymethyl compounds bearing more sterically hindered metal centers might preferentially dissociate ketene hemiacetal upon acid treatment, as previously proposed for the $Cp(CO)(PPh_3)Fe$[42] and cob(III)alamin systems. Reenstra, W. M.; Abeles, R. H.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1016.

(47) van Doorn, J. A.; Masters, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245. Stimson, R. E.; Shriver, D. F. *Organometallics* **1982**, *1*, 787.

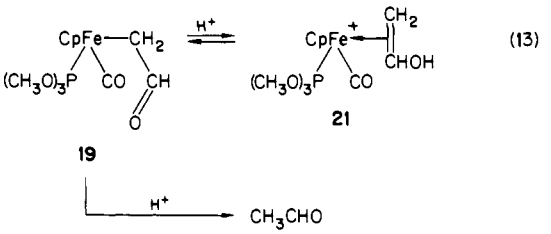
(48) Busetto, L.; Palazzi, A.; Ros, R.; Belluco, U. *J. Organomet. Chem.* **1970**, *25*, 207. Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93.

Scheme IV



it is quite reasonable that an alkoxyborane could abstract β-alkoxide with or without hydride transfer and give (perhaps competitively) the mixture of **15** and **16**, respectively.

Release of acetaldehyde with acid from the formylmethyl complex **19** was demonstrated although as already noted the analytical chemistry was both tedious and of limited accuracy. Nevertheless, significant amounts of acetaldehyde did form. A plausible mechanism for this release of acetaldehyde, which will be documented for our results with the analogous Fp system,[15] entails protonolysis of **19** by electrophilic attack on iron rather than by dissociation of vinyl alcohol from **21** (eq 13). (The



(13)

corresponding η^2-vinyl ether complex **18** does not dissociate vinyl ether under comparable—or more extreme—reaction conditions.]

In summary, the carbalkoxymethyl ligand serves as a viable C_2 template in selectively generating other C_2 ligands and organic molecules. Certainly with the aforementioned availability and reactivity of the carbalkoxymethyl ligand, it would prove interesting to generate these systems using more labile organometallic complexes—particularly those that might add H_2 and reductively eliminate acetic acid esters. In terms of procuring acetaldehyde, Scheme IV outlines our "β-activation" route in generating a formylmethyl complex from the carbalkoxymethyl system. It is also worth noting that these results complement those that define the α-activation coordinated ligand route for transforming a C_2 alkoxyacetyl ligand into the same formylmethyl and ethyl groups. Progress of studies using either (1) more labile metal complexes and H_2 or (2) organometallic Lewis acids and hydrido complexes in place of the carbocationic activating groups and borohydride reagents to selectively (but stoichiometrically) generate C_2 and C_3 ligands and organic products will be reported in due course.

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

(49) Vinyl alcohol or vinyl ether complexes with a more sterically hindered metal center, such as Co(III) in cobaloxime η^2-vinyl ether compounds can directly dissociate the vinyl ether and possibly vinyl alcohol (acetaldehyde) in analogous reactions. Silverman, R. B.; Dolphin, D. *J. Am. Chem. Soc.* **1976**, *98*, 4633.

Structure of Rhodium in an Ultradispersed Rh/Al_2O_3 Catalyst as Studied by EXAFS and Other Techniques

H. F. J. van 't Blik,[†] J. B. A. D. van Zon, T. Huizinga,[‡] J. C. Vis, D. C. Koningsberger, and R. Prins*

Contribution from the Laboratory for Inorganic Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands. *Received June 25, 1984*

Abstract: The structure of rhodium in an ultradispersed 0.57 wt % Rh/γ-Al_2O_3 catalyst before and after CO adsorption was studied with extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), temperature programmed reduction (TPR), CO infrared spectroscopy, and H_2 and CO chemisorption. With the aid of these complementary techniques, it could be established that the structure of the rhodium catalyst was completely different before and after CO adsorption. Before CO adsorption and after reduction of the catalyst at 593 K, all the rhodium was reduced and in the form of three-dimensional metallic crystallites. CO adsorption disrupted the metal–metal bonds in the crystallites, leading to isolated rhodium geminal dicarbonyl species in which the rhodium was present as Rh^+. Each rhodium ion was surrounded by two carbon monoxide molecules and three oxygen anions of the support.

As a result of many industrial applications, such as the hydrogenation of carbon monoxide, the reduction of nitrogen monoxide in automobile exhaust gas, and the hydroformylation of olefins, catalysts consisting of finely dispersed rhodium supported on alumina are studied extensively. The use of very well dispersed rhodium on a support is not only of obvious importance from an economical point of view but also from the point of view of activity and selectivity of the catalysts. Thus Yao et al.[1] reported that in going from a well dispersed rhodium phase to a particulate phase the specific activity for *n*-pentane hydrogenolysis decreased and the activity for reduction of NO by hydrogen increased. Alterations in the reaction parameters and in the product dis-

[†] Present address: Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands.

[‡] Present address: Koninklijke/Shell-Laboratorium, Badhuisweg 3, 1031 CM Amsterdam, The Netherlands.

(1) Yao, H. C.; Yu Yao, Y. F.; Otto, K. *J. Catal.* **1979**, *56*, 21.

0002-7863/85/1507-3139$01.50/0