spin decoupled from the d^4 core electrons to make the $ClCr^+$ bond. This allows the CrR^+ bond to form without further loss of intraatomic exchange energy. This is in contrast to the mechanism in Scheme I which requires the high-spin d^4 electrons on Cr^+ to decouple in order to form two additional bonds (at the cost of exchange energy) and then recouple following the loss of H_2.

Conclusions

1. The exothermic reactions of $ClCr^+$, $ClMn^+$, and $ClFe^+$ with small alkanes in the gas phase have been measured. $ClFe^+$ is unreactive. The Cl in $ClMn^+$ is displaced by alkanes larger than ethane. $ClCr^+$ activates C-C and C-H bonds of the alkanes leading to $ClCr^+$-alkene products resulting from loss of H_2 or CH_4.

2. The reactivity of $ClCr^+$ is remarkable because Cr^+ is unreactive. This is the first example of chemical activation of an unreactive transition-metal ion in the gas phase.

3. Electronic structure calculations were performed to obtain a description of the bonding in $ClCr^+$, $ClMn^+$, and $ClFe^+$. (a) These calculations indicate that the singly occupied Cl p orbital overlaps the singly occupied metal s orbital to form a covalent σ bond in $ClMn^+$ and $ClFe^+$. (b) The calculations also indicate that there are two states which are low in energy in $ClCr^+$. One contains a covalent σ bond similar to those in $ClMn^+$ and $ClFe^+$. The other contains not a covalent σ bond but rather a covalent π bond. This finding underscores the complexities of the bonding which is possible for these highly acidic, coordinatively unsaturated transition metal ions.

4. Chemical activation of Cr^+ by the chlorine ligand can be explained by the unusual Cl-Cr^+ bond. Addition of a C-H bond *directly* across the covalent bond is proposed as a low-energy reaction pathway for the reaction with alkanes. Addition of the same C-H bond to the chromium atomic ion is known to be so high in energy that it is not observed exothermically.

Acknowledgment. We gratefully acknowledge Professor W. A. Goddard III, California Institute of Technology, for the use of computational facilities.

Registry No. $ClCr^+$, 103533-62-6; $ClMn^+$, 24436-23-5; $ClFe^+$, 23172-36-3; C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; i-C_4H_{10}, 75-28-5; *neo*-C_5H_{12}, 463-82-1.

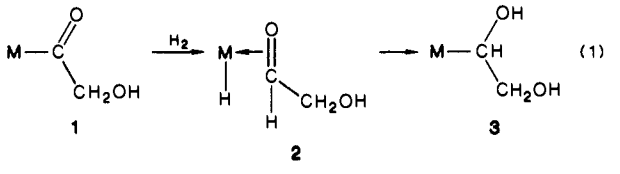
Dialkoxyethylidene and η^2-1,2-Dialkoxyethylene Iron Compounds as C_2 Templates for Generating Acetaldehyde and a Glycolaldehyde Ether

Edward J. Crawford, Thomas W. Bodnar, and Alan R. Cutler*

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received November 14, 1985. Revised Manuscript Received July 5, 1986*

Abstract: Full details on the preparation and characterization of the α-ethoxy-β-methoxyethylidene Fp **5**, on its irreversible isomerization to the η^2-1,2-methoxyethoxyethylene Fp salt **6**, and on its reduction to the α-ethoxy-β-methoxyethyl Fp **17** are presented. Other examples of *cis*-1,2-dialkoxyethylene Fp salts also are synthesized. The dimethoxy example **11** upon hydrolysis gives the α-methoxyformylmethyl Fp complex **14**, whereas reducing it gives the α,β-dimethoxyethyl complex **18**. Both spectroscopically characterized α,β-dialkoxyethyl complexes afford η^2-vinyl ether Fp compounds **19** (R = CH_3) and **20** (R = CH_2CH_3) upon treating with $Ph_3C^+PF_6^-$. β-Methoxide abstraction from **18** predominates. Hydrolysis of **19** then gives $FpCH_2CHO$ **15**, which after treating with acid and iodide yields acetaldehyde. The α-methoxyformylmethyl **14**, in turn, gives methoxyacetaldehyde. Thus, coordinated ligand reactions are presented that use the methoxyacetyl ligand on $FpCOCH_2OCH_3$ (**4**) as a C_2 template in selectively incorporating both of these skeletal carbon centers into either acetaldehyde or methoxyacetaldehyde.

Hydroxyacetyl organometallic complexes $MCOCH_2OH$ (**1**) have been suggested as intermediates in the synthesis of C_2 (and possibly larger) oxygenated organic molecules from synthesis gas ($CO-H_2$ mixtures) and homogeneous transition-metal catalysts.[1] These complexes are believed to hydrogenate their acyl ligands (eq 1) and to generate α,β-dihydroxyethyl complexes **3**. The alkyl **3**, in principle, produces ethylene glycol, or it repeats the sequence (eq 1) and extends the chain.[2] The glycolaldehyde intermediate



1 2 3 (1)

2 envisaged[3] also could serve as a branching point in the overall mechanism (and hence product distribution), since reducing **2**

(1) Hydroxyacetyl intermediates **1** could arise through carbonylating hydroxymethyl complexes MCH_2OH, which are assumed to be present in steady-state amounts as the reduction product of ligated CO. Reviews on homogeneous analogues of Fischer-Tropsch Chemistry: Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. Sneedon, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Chapter 50.2. Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17. Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. Frohning, C. D. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin and New York, 1980, Chapter 4. Eisenberg, R.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79. Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

(2) This mechanism is often discussed in the context of procuring ethylene glycol from synthesis gas by using homogeneous catalysts: (a) Pruett, R. L. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 239. Pruett, R. L. *Science (Washington, DC)* **1981**, *211*, 11. (b) Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466. (c) Dombek, B. D. *Ibid.* **1980**, *102*, 6855. Dombek, B. D. *J. Organomet. Chem.* **1983**, *250*, 467. Dombek, B. D. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 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.; Schulpp, J. *J. Mol. Catal.* **1981**, *13*, 95. (g) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959. Knifton, J. F. *J. Mol. Catal.* **1985**, *30*, 281. (h) Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1596.

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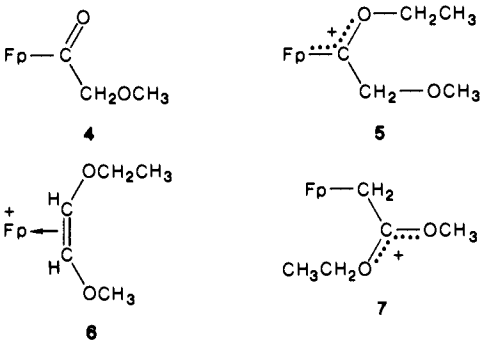
could afford either the C-bound **3** or its isomeric O-bound alkoxide $MOCH_2CH_2OH$.[4,5] This latter alkoxide, while certainly a potential ethylene glycol precursor, cannot extend the carbon–carbon chain.

The fundamental coordinated ligand reactions that operate during or even supplant the chemistry described in eq 1 are of obvious interest. Because of inherant limitations involved in procuring such mechanistic information from catalytic systems,[6] a model-systems approach has proved useful, whereby more accessible alkoxyacetyl complexes are studied under analogous but stoichiometric reaction conditions.[2b,c,7] Alternatively, alkoxyacetyl complexes, after activating with the appropriate Lewis acid,[8] are reduced by using borohydride or even transition organometallic hydride complexes[9] (instead of H_2). We have adopted this latter approach in establishing viable ligand transformations for selectively converting the methoxyacetyl ligand to oxygenated C_2 organics.[10]

In the present studies, the methoxyacetyl ligand on $Cp(CO)_2Fe$ (hereafter denoted as Fp) complex **4** serves as a template for generating other C_2 ligands and their free organic derivatives. This acyl ligand, after activating as an α,β-dialkoxyethylidene derivative **5**, reduces at the α-carbon with exogenous hydride donors. Two



isomers of **5**, an $(\eta^2$-1,2-dialkoxyethylene)Fp^+ (**6**) and a [(dialkoxycarbenio)methyl]Fp (**7**), also enter into the network of coordinated ligand reactions originating with **4**, however. A recent publication documents our studies in converting the methoxyacetyl ligand on $Cp(CO)[P(OMe)_3]FeCOCH_2OMe$ into a (dialkoxycarbenio)methyl derivative (analogous to **7**) and then into acetaldehyde.[10b] Full details are now reported on preparing and characterizing (α-ethoxy-β-methoxyethylidene)Fp^+ (**5**), on irreversibly isomerizing it to (η^2-1-methoxy-2-ethoxyethylene)Fp^+ (**6**), and on reducing it to (α-ethoxy-β-methoxyethyl)Fp. These and other examples of (α,β-dialkoxyethyl)Fp, (formylmethyl)Fp, and (mono- and dialkoxyethylene)Fp^+ complexes are involved in selectively transforming both skeletal carbon centers of (methoxyacetyl)Fp^+ (**4**) into either acetaldehyde or methoxyacetaldehyde.

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.[11]

(3) This aldehyde intermediate could arise by using H_2 or a second metal hydride complex as the reductant. Oxidative addition of H_2 or of M–H to the acyl complex thus is a prerequisite to reductive elimination (on one metal center) of aldehyde.[3a] "Binuclear reductive elimination" of aldehyde from the acyl complex with a metal hydride[3b,c] and free radical reactions[3d] are other possibilities. (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 421. Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, Chapter 2. Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. Pino, P. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 111. Mirbach, M. F. *J. Organomet. Chem.* **1984**, *265*, 205. (b) 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. Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376. Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150. Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33. (c) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. Collman, J. P.; Belmont, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 7288. Nappa, M. J.; Santi, R.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *4*, 34 and references cited. (d) Azram, J.; Orchin, M. *Organometallics* **1984**, *3*, 197.

(4) This mechanistic dichotomy has been advanced previously to rationalize product distributions during hydroformylation of alkenes[4a] and during alcohol homologation,[4b] again by homogeneous catalysis. That metal–carbon bonds form under these conditions has been independently verified during hydroformylation studies on formaldehyde, which gives glycolaldehyde.[4c] (a) Reference 3a. Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259. Wood, C. D.; Garrow, P. E. *Organometallics* **1984**, *3*, 170. (b) Slocum, D. W. In *Catalysis in Organic Synthesis*; Jones, W. H., Ed.; Academic Press: New York, 1980; p 245. Bahrmann, H.; Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin and New York, 1980; Chapter 2. Piacenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls*; Wender, I.; Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, Chapter 1. Chen, M. J.; Feder, H. M.; Rathke, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 7346. (c) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *172*, C27. Spencer, A. *J. Organomet. Chem.* **1980**, *194*, 113. Chan, A. S. C.; Carroll, W. E.; Willis, D. E. *J. Mol. Catal.* **1983**, *19*, 377.

(5) Other strategies have been employed to convert metal–acyl and η^2-aldehyde complexes to C-bound α-oxyalkyl derivatives. Oxophilicity of zirconium (or other "early" transition-metal),[5a,b,c] trialkylsilyl–metal,[5d] actinide,[5e] and lanthanide[5f] organometallic complexes, respectively, that are used accounts for the regioselectivity. Moreover, many of these systems convert CO/H_2 into η^2-O,O′-enediolate-OCH=CHO- ligands; formally, at least, such ligands correspond to glycolaldehyde.[5c,e,f] (a) Marsella, J. A.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chim. Acta* **1985**, *96*, 161, and references therein. (b) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178. Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. Planalp, R. P.; Anderson, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 7774. Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596. Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *102*, C11. (c) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103 and references therein. 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. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (d) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393. Murai, S.; Soda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837. Kaplan, L. *Organometallics* **1982**, *1*, 1102. Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147. Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326. (e) 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. Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56. (f) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671.

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(8) Nucleophilic hydride donors generally transfer hydride to ancillary terminal carbonyls rather than to an acyl ligand.[8a] Furthermore, a general trend has emerged: many nucleophiles preferentially attack at a terminal carbonyl vs. an acyl ligand[8b] but chemoselectively add to the carbenoid carbon of a metal–carbene complex.[8c,8d] Converting an acyl complex into an electrophilic alkoxycarbene derivative, therefore, activates the acyl ligand to nucleophilic attack. (a) Van Doorn, J. A.; Masters, C.; Vogler, H. C. *J. Organomet. Chem.* **1976**, *105*, 245. Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1979**, *171*, 65. Selover, J. C.; Marsi, M.; Parker, D. W.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *206*, 317. (b) Lukehart, C. M. *Acc. Chem. Res.* **1981**, *14*, 109. Casey, C. P.; Baltusis, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6347. (c) Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441. (d) For reviews on metal carbene complexes: Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. Coddard, R. J.; Hoffman, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667. Casey, C. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, Chapter 3. Fischer, H. *The Synthesis of Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

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Cationic organometallics used in this study, although not oxygen-sensitive, readily hydrolyze. Their precipitates accordingly must be filtered under nitrogen in Schlenk filters, in order to avoid condensing moisture as the residual solvent is evaporated. The precipitation of these salts (typically by using CH_2Cl_2–ether), however, can be carried out in open Erlenmeyer flasks if *anhydrous* ether is used. Solvents for synthetic work and recording of spectral data were deoxygenated by purging with nitrogen for 20 min. Camag alumina (neutral, activity 3) was used in column chromatography.

Infrared spectra were taken of CH_2Cl_2 solutions (0.10 mmol/1.5 mL) in NaCl amalgam-spaced (0.10 mm) solution cells 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; they are accurate to ±2 cm^{-1} below and ±5 cm^{-1} above 2000 cm^{-1}. IR spectra of the neutral and cationic organoiron complexes used in this study exhibit straightline Beer's law behavior (0–0.10 mmol/1.5 mL) in CH_2Cl_2 solution. Thus, IR spectral monitoring of reactions was accomplished quantitatively through analysis of absorptivity changes in the terminal and/or acyl ν(CO). By this procedure, as little as 4% FpI (0.006 mmol) can be measured in the presence of excess $FpCOCH_2OCH_3$ (**4**) (0.10 mmol).

^1H and ^{13}C NMR spectra were taken of concentrated $CDCl_3$ and CD_3NO_2 solutions, after insoluble residues were centrifuged off. Varian Model T-60 and XL-200 NMR spectrometers supplied the NMR spectra, which are reported as δ values downfield after internal Me_4Si. GLC analyses were performed by using a Gow-Mac Model 505 instrument equipped with a 4 ft by $^1/_4$ in. Cu column packed with Carbowax-20 M (20%) on Chromosorb P (80/100 mesh) (155 °C) or with a 6 ft by $^1/_8$ in. stainless-steel column packed with Poropak T (80/100 mesh) (160 °C). Combustion microanalyses were performed by Baron Consulting Company, 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 likewise obtained as needed from P_2O_5. The anhydrous ether used either was taken from a freshly opened can, or it was distilled from sodium benzophenone ketyl. A modification of Dauben's procedure was used to prepare $Ph_3C^+PF_6^-$. Although stored under nitrogen at +5 °C, trityl carbocationic salts slowly decompose (as evidenced by appearance of white acid fumes),[12] which necessitates periodic reprecipitation from CH_2Cl_2–ethyl acetate and vacuum drying. Commercial samples of $(CH_3CH_2)_3O^+PF_6^-$ inevitably contained acid (sometimes fuming as a white smoke); this oxonium salt was reprecipitated from $PhNO_2$–ether (by using an all-glass Schlenk line), washed with ether, and briefly vacuum dried (10^{-2} mm, 20 °C, 0.5 h). (Reprecipitation from CH_3NO_2– or CH_2Cl_2–ether does not eliminate the acid.) The white, crystalline $(CH_3CH_2)_3O^+PF_6^-$, which is best stored under nitrogen at −5 °C, is assayed periodically for acid through its reaction (1:1) with $[Cp(CO)Fe]_2$-μ-$(Ph_2PCH_2CH_2PPh_2)$.[13] IR spectral monitoring of this reaction (in CH_2Cl_2) easily discerns between the μ-hydride salt [ν(CO) 1954 cm^{-1}], resulting from immediate protonation, and the μ-ethoxycarbyne salt [ν(CO) 1760 cm^{-1}], resulting from slower alkylation of a bridging carbonyl [ν(CO) 1677 cm^{-1}]. The titer of the borohydride reagent $LiHB(CH_2CH_3)_3$ (as its commercially available solution in THF) was periodically assayed by spectral monitoring (IR and NMR) of its reaction with $Cp(CO)(PPh_3)FeC(OCH_3)CH_3^+PF_6^-$ in CH_2Cl_2.[14]

Metal carbonyl complexes $[Cp(CO)_2Fe]_2$,[11d] $Fp[CH_2{=}C(CH_3)_2]^+BF_4^-$,[15] $FpC(OCH_3)CH_3^+PF_6^-$,[16] $Fp(CH_2{=}CHOCH_3)^+BF_4^-$, and $Fp(CH_2{=}CHOCH_2CH_3)^+BF_4^-$,[17] were prepared by literature procedures and judged pure by IR and NMR spectroscopy. Authentic samples of FpI,[11d] $FpCOCH_3$,[18] and $FpCO^+BF_4^-$[19] were available from previous studies for direct spectroscopic comparison.

The *cis*-$(CH_3O)CH{=}CH(OCH_3)$ was prepared, by using a minor modification of an established procedure,[20] by passing $CH_3OCH_2CH(OCH_3)_2$ through activated, 3.2 mm alumina pellets (300 °C, 10^{-2} mm). The fraction subsequently distilling 85–95 °C corresponded to the desired product, 46% yield and greater than 95% spectroscopically pure [^1H NMR (acetone-d_6) δ 5.20 (s, 2 H, CH=), 3.48 (s, 6 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 129.8 (CH=), 59.9 (OCH_3)]. Methoxyacetaldehyde was prepared by acid hydrolysis of its commercially available dimethyl acetal:[21] IR (CH_2Cl_2) 1738 cm^{-1}; NMR ($CDCl_3$) δ 9.77 (br s, 1 H, CHO), 4.02 (br s, 2 H, OCH_2), 3.44 (s, 3 H, OCH_3).

Preparation of $FpCOCH_2OCH_3$ (4). The following procedure is a modification of that reported by Rosenblum.[17] A THF solution (300 mL) of Fp^-Na^+ (0.112 mol) was generated by Na(Hg) reduction of Fp_2 (10.0 g, 56 mmol) in a 500-mL, three-necked amalgam flask. After the Hg dust had settled, the dark yellow-orange solution was transferred via a double-ended stainless steel needle into a 500-mL, three-necked reaction flask. To the cold (−78 °C) anion solution was then injected methoxyacetyl chloride (5.5 mL, 60 mmol), and the resulting dark yellow-green suspension was stirred 20 min before warming to room temperature. Removal of solvent on a rotovaporator (25 mm, 22 °C) left a dark red-orange oil. This was extracted with CH_2Cl_2 and passed through a 3.5 × 8 cm pad of alumina with CH_2Cl_2 (total volume 150 mL). The red-orange filtrate was reduced to 75 mL, heptane (40 mL) was added, and the solution was further reduced to 70 mL before it was cooled (−78 °C). Scraping then produced an orange-red crystalline mass. The remaining light orange solution was removed (by using a double-ended needle fitted with a sintered-glass frit), and the crystals were washed successively with 3 × 15-mL portions of heptane (at −78 °C). Traces of residual solvent finally were removed under vacuum from the *cold* crystals, which melted at −10°C to yield spectroscopically pure[17] $FpCOCH_2OCH_3$ (**4**) as an amber fluid (10.78 g, 77%): IR (CH_2Cl_2) 2024, 1963 (C≡O), 1657 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.83 (s, 5 H, Cp), 3.93 (s, 2 H, $FeCH_2$), 3.33 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 254.8 (C=O), 213.9 (C≡O), 90.6 (CH_2), 86.4 (Cp), 59.0 (OCH_3).

Preparation of $Fp[cis\text{-}(CH_3O)CH{=}CH(OCH_3)]^+BF_4^-$ (11). The following represents a modification of the procedure reported by Baird, Heberhold, et al.[22] When an orange 1,2-dichloroethane suspension (45 mL) containing $Fp[CH_2{=}C(CH_3)_2]^+BF_4^-$ (498 mg, 1.56 mmol) and *cis*-$(CH_3O)CH{=}CH(OCH_3)$ (2 mL, 18 7 mmol) was warmed to 65 °C for 15 min, it gave a red-orange solution (with gas evolution). The mixture was cooled to room temperature, diluted with ether (35 mL) to give yellow-orange crystals, and then filtered. The crystals were extracted with CH_2Cl_2 (30 mL), filtered, and reprecipitated with ether (40 mL). Bright yellow crystals of **11** remained after vacuum drying (425 mg, 77% yield):[22] IR (CH_2Cl_2) 2063, 2023 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.42 (s, 5 H, Cp), 6.35 (s, 2 H, =CH), 3.96 (s, 6 H, OCH_3); (CD_3COCD_3) δ 5.68 (s, 5 H, Cp), 6.79 (s, 2 H, =CH), 4.01 (s, 6 H, OCH_3); ^{13}C NMR (CD_3NO_2) 210.6 (C≡O), 104.7 (=CH), 89.1 (Cp), 62.5 (OCH_3).

A CH_2Cl_2 solution of $Fp[(CH_3O)CH{=}CH(OCH_3)]^+BF_4^-$ (**11**) upon treating with 4 equiv of n-$Bu_4N^+I^-$ quantitatively released FpI (within ca. 10 min).

Reaction of $Fp[(CH_3O)CH{=}CH(OCH_3)]^+BF_4^-$ (11) and Ethanol. An orange slurry of $Fp[(CH_3O)CH{=}CH(OCH_3)]^+BF_4^-$ (**11**) (140 mg, 0.40 mmol) in 5 mL of anhydrous ethanol was stirred for 10 min, before it was treated with ether (30 mL). The resulting bright yellow crystals were filtered, washed with ether (20 mL), and dried in vacuo for 1 h. Yield was 126 mg of analytically pure $Fp[cis\text{-}(CH_3CH_2O)CH{=}CH(OCH_2CH_3)]^+BF_4^-$ (**12**) (83%): IR (CH_2Cl_2) 2062, 2022 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.49 (s, 5 H, Cp), 6.48 (s, 2 H, =CH), 4.56–4.20 (br m, 4 H, OCH_2CH_3; solvent), 1.38 (t, J = 7 Hz, 6 H, OCH_2CH_3); ^1H NMR (CD_3COCD_3) δ 5.68 (s, 5 H, Cp), 6.85 (s, 2 H, =CH), 4.42 (d quart, J = 10 Hz, 7 Hz, 2 H, $OCH_AH_BCH_3$), 4.27 (d quart, J = 10, 7 Hz, 2 H, $OCH_AH_BCH_3$), 1.32 (t, J = 7 Hz, 6 H, OCH_2CH_3); ^{13}C NMR (CD_3NO_2) δ 211.2 (C≡O), 103.5 (=CH), 89.2 (Cp), 72.4 (OCH_2), 15.1 (CH_3). Anal. Calcd for $C_{13}H_{17}BF_4FeO_4$: C, 41.09; H, 4.52. Found: C, 40.96; H, 4.48.

Preparation of $Fp[cis\text{-}[(CH_3)_2CHCH_2CH_2O]CH{=}CH[OCH_2CH_2CH(CH_3)_2]]^+BF_4^-$ (13). A yellow-orange slurry of $Fp[(CH_3O)CH{=}CH(OCH_3)]^+BF_4^-$ (**11**) (64 mg, 0.18 mmol) in 5 mL of i-amyl alcohol was stirred for 20 min, which left a more finely divided crystalline deposit and a darker supernatant. Pentane (35 mL) was added, and the reaction was cooled (−20 °C) for 12 h. Filtering the pale yellow suspension left

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yellow-orange crystals, which were recrystallized from CH_2Cl_2–ether, washed with ether, and vacuum dried. Bright yellow-orange crystals of $Fp\{[(CH_3)_2CHCH_2CH_2O]CH{=}CH[OCH_2CH_2CH(CH_3)_2]\}^+BF_4^-$ (**13**) (71 mg, 84% yield) were recovered: IR (CH_2Cl_2) 2061, 2022 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.40 (s, 5 H, Cp), 6.74 (s, 2 H, =CH), 3.80–4.36 (m, 4 H, OCH_2), 1.01–1.81 (m, 6 H, CH_2CH), 0.89 (d, J = 6 Hz, 12 H, CH_3). Anal. Calcd for $C_{19}H_{29}BF_4FeO_4$: C, 49.14; H, 6.31. Found: C, 49.28; H, 6.28.

Hydrolysis of $Fe[(CH_3O)CH{=}CH(OCH_3)]^+BF_4^-$ (11): Synthesis of $FpCH(OCH_3)CHO$ (14). To a yellow-orange solution of $Fp[(CH_3O)CH{=}CH(OCH_3)]^+BF_4^-$ (**11**) (60 mg, 0.17 mmol) in CH_2Cl_2 (5 mL) was added 0.12 mL of water, and the reaction was stirred for 20 min. IR spectral monitoring of the clear orange solution (interspersed with red water droplets) then indicated quantitative conversion of **11** to $FpCH(OCH_3)CHO$ (**14**): IR (CH_2Cl_2) 2020, 1966 (C≡O), 1664 (C=O) cm^{-1}. Granular sodium sulfate (1 g) was added to absorb the water (10 min); the reaction was evaporated on a rotovaporator and extracted with ether (4 × 10 mL). These extracts were combined and filtered, before the clear yellow solution was stripped to an orange-yellow oil and chromatographed with ether-alumina (20 g, activity 3). Pentane eluted trace amounts of Fp_2 (red-brown band), and 1:1 CH_2Cl_2–ethyl acetate cleanly removed a bright yellow band from the brown residue remaining on the column. The yellow band afforded $FpCH(OCH_3)CHO$ (**14**) (21 mg, 49% yield) as a yellow solid after evaporating the solvent: ^1H NMR (CS_2) δ 4.72 (s, 5 H, Cp), 8.90 (s, 1 H, CHO), 4.55 (s, 1 H, FeCH), 3.23 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 215.8 (s, C≡O), 214.0 (s, C≡O), 191.2 (d, J = 168 Hz, CHO), 86.9 (Cp), 82.8 (d, J = 122 Hz, FeCH), 59.9 (quart, J = 138 Hz, OCH_3). Anal. Calcd for $C_{10}H_{10}FeO_4$: C, 48.03; H, 4.00. Found: C, 47.57; H, 4.30.

Reaction of $(CH_3CH_2)_3O^+PF_6^-$ and $FpCH(OCH_3)CHO$ (14). $FpCH(OCH_3)CHO$ (**14**) was generated by hydrolysis (5 drops of water) of $Fp[(CH_3O)CH{=}CH(OCH_3)]^+BF_4^-$ (**11**) (151 mg, 0.43 mmol) in 6.5 mL of CH_2Cl_2 over 20 min. The resulting yellow-orange solution, after stirring with anhydrous Na_2SO_4 and filtering, was treated with triethyloxonium hexafluorophosphate (750 mg, 0.30 mmol). Quantitative conversion of **14** to $Fp[cis\text{-}(CH_3O)CH{=}CH(OCH_2CH_3)]^+PF_6^-$ (**6**) was evident by IR spectral monitoring (30 min) of the reddish-orange solution [IR (CH_2Cl_2) 2068, 2028 cm^{-1}]. Concentration of this solution and attempted precipitation using CH_2Cl_2–ether (excess) (with/without cooling, sitting, scraping, etc.) inevitably gave an orange-red gum, 109 mg (69%) after vacuum drying. Its NMR spectrum is in accord with 6 [^1H NMR (CD_3NO_2) δ 5.46 (s, 5 H, Cp), 6.53 (d, J = 2 Hz, 1 H, =$CHOC_2H_5$), 6.36 (d, J = 2 Hz, 1 H, =$CHOCH_3$), 4.3 (m, 2 H, OCH_2), 4.02 (s, 3 H, OCH_3), 1.38 (t, J = 7 Hz, 3 H, OCH_2CH_3), contaminated with 10% $FpCO^+PF_6^-$ (δ 5.93, Cp) and small amounts of ether. ^1H NMR (CD_3COCD_3) δ 5.70 (s, 5 H, Cp), 6.89 (d, J = 2.2 Hz, 1 H, =$CHOC_2H_5$), 6.74 (d, J = 2.2 Hz, 1 H, =$CHOCH_3$), 4.38 (d quart, J = 7.0, 10.2 Hz, 2 H, OCH_2), 4.04 (s, 3 H, OCH_3), 1.35 (t, J = 7.0 Hz, OCH_2CH_3)]. Coupling constants for the d quartet of δ 4.38 were assigned from the results of a homonuclear spin decoupling experiment. Irradiation at δ 1.35 reduced this multiplet to two doublets centered at δ 4.45, 4.28. ^{13}C NMR (CD_3NO_2) δ 211.0 (C≡O), 104.6 (=CHOMe), 103.8 (=CHOEt), 89.3 (Cp), 72.6 (OCH_2), 62.8 (OCH_3), 15.2 (CH_3).

Small samples of spectrally and analytically pure 6 were obtained by carefully recrystallizing the crude material from CH_2Cl_2–ether (with scraping). Anal. Calcd for $C_{14}H_{19}FeF_6O_4P$: C, 34.00; H, 3.54. Found: C, 33.53; H, 3.40.

Protonation of $FpCH(OCH_3)CHO$ (14). To a cold (0 °C) CH_2Cl_2 solution (10 mL) of $FpCH(OCH_3)CHO$ (**14**) (129 mg, 0.52 mmol) was added excess $HBF_4{\cdot}OEt_2$ (0.1 mL) with stirring. A yellow-brown precipitate immediately settled as the solution turned dark brown; addition of ether (35 mL) precipitated additional solid. The supernatant was decanted, the solid was washed with ether (2 × 10 mL), and the resulting $Fp[(CH_3O)CH{=}CH(OH)]^+BF_4^-$ (**22**) was vacuum dried (10^{-2} mm, 1 h) as an amorphous yellow solid, 146 mg (84% yield): IR (CH_3NO_2) 2062, 2023 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.49 (s, 5 H, Cp), 6.97 (br s, 1 H, =CHOH), 6.58 (br s, 1 H, =CH(OMe)), 6.8–7.2 (br s, OH), 4.02 (s, 3 H, OCH_3); ^{13}C NMR (CH_3NO_2) δ 209.1 (C≡O), 103.6 (=CHOMe), 100.1 (=CHOH), 88.7 (Cp), 61.4 (OCH_3).

Attempts to further purity this yellow salt were unsuccessful. The extremely hygroscopic solid neither is soluble in CH_2Cl_2 nor is stable at room temperature (over several hours). Treatment of a CH_3NO_2 solution of **22** with ether afforded only dark brown gums. The salt, however, was derivatized by three procedures. (1) Treating its CH_2Cl_2 suspension with triethylamine (50% excess) immediately and quantitatively regenerated $FpCH(OCH_3)CHO$ (**14**), as ascertained by IR spectral monitoring. (2) Dissolving the yellow solid (**22**) in absolute ethanol (as an orange-brown solution) and adding ether (after 5 min) precipitated $Fp[(CH_3CH_2O)CH{=}CH(OCH_2CH_3)]^+BF_4^-$ (**12**) (88% yield, based on **14**), as identified by IR and NMR spectral data. (3) Reacting its CH_2Cl_2 suspension with $(n\text{-}Bu)_4N^+I^-$ (4 equiv) generated FpI (80–90%) and CH_3OCH_2CHO, as identified by its IR spectral ν(C=O) 1738 cm^{-1}. Methoxyacetaldehyde was quantified by GLC.

Methoxyacetaldehyde from $Fp[(CH_3O)CH{=}CH(OH)]^+PF_6^-$ (22). A light brown slurry of $Fp[(CH_3O)CH{=}CH(OH)]^+PF_6^-$ (**22**) (135 mg, 0.40 mmol) in 4 mL of $ClCH_2CH_2Cl$, maintained at 50 °C, was treated with excess $(n\text{-}Bu)_4N^+I^-$ (2.0 g). The resulting black solution (15 m) was distilled trap-to-trap (−30 °C), and the clear distillate (5.0 mL after rinsing the receiving trap with $ClCH_2CH_2Cl$) was examined by IR spectroscopy, ν(CO) 1738 cm^{-1}, and by GLC. Retention times of aliquots from this solution on both GLC columns matched those of an authentic sample of CH_3OCH_2CHO. Quantitative analysis using an absolute calibration graph further established a 38% yield of methoxyacetaldehyde.

Preparation of $FpC(OCH_2CH_3)CH_2OCH_3^+PF_6^-$ (5). To a yellow-orange methylene chloride solution (26.2 mL) containing $Cp(CO)_2FeCOCH_2OCH_3$ (**4**) (463 mg, 1.74 mmol) was added $(CH_3CH_2)_3O^+PF_6^-$ (347 mg, 1.40 mmol, 0.80 equiv). After sitting for 5 h, the resulting dark red-orange solution was concentrated (5 mL) and added dropwise into ether (30 mL). This precipitated a red-orange gum, which was collected, washed with ether, and vacuum dried (383 mg). [Numerous attempts at crystallizing the product by using ethyl acetate–CH_2Cl_2–benzene or ether di- and trisolvent mixtures, with or without cooling, inevitably afforded gums. Adding the CH_2Cl_2 solution to cold ether (−78 °C), for example, deposited yellow solid, but this formed a gum upon warming to room temperature.] This gum by NMR spectral analysis consisted of a 5.8:1 mixture of $FpC(OCH_2CH_3)CH_2OCH_3^+PF_6^-$ (**5**) and $Fp[CH_3OCH{=}CHOCH_2CH_3]^+PF_6^-$ (**6**), as deduced from the relative intensities of the methoxy singlets, plus trace amounts of ether and $(CH_3CH_2)_3O^+PF_6^-$. Yield **5**: 259 mg, 0.61 mmol (44%); IR (CH_2Cl_2) 2073, 2027 (CO) cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.45 (s, 5 H, Cp), 4.87 (quart, J = 7.0 Hz, 2 H, OCH_2CH_3), 4.30 (s, 2 H, CH_2), 3.59 (s, 3 H, OCH_3), 1.76 (t, J = 7.0 Hz, 3 H, OCH_2CH_3); ^{13}C NMR (CH_3NO_2) δ 332.8 (Fe=C), 209.1 (C≡O), 89.9 (Cp), 87.2 (CH_2OMe), 79.7 (OCH_2), 61.2 (OCH_3), 14.1 (OCH_2CH_3).

Treatment of this 5.8:1 mixture of **5** (222 mg, 0.52 mmol) and **6** (37 mg, 0.09 mmol) with tetra-*n*-butylammonium iodide (148 mg, 0.40 mmol) in 9 mL of CH_2Cl_2 afforded immediately a black solution. Within 1 h, only $FpCOCH_2OCH_3$ (**4**) and FpI, in 5.5:1 ratio, were evident by IR spectroscopy. Solvent was evaporated, and the greenish brown residue was chromatographed on a 45 g alumina–CH_2Cl_2 column. Development of this column with pentane cleanly eluted a black band, which contained spectroscopically pure FpI (25 mg, 96% yield from 6). A second yellow band then was eluted with 1:1 CH_2Cl_2–pentane, which contained spectroscopically pure $FpCOCH_2OCH_3$ (**4**) (85 mg, 65% yield from **5**). A small amount of brown residue remained at the top of the column.

Reaction of $(CH_3CH_2)_3O^+PF_6^-$ and $FpCOCH_2OCH_3$ (4). $Cp(CO)_2FeCOCH_2OCH_3$ (**4**) (1.156 g, 4.62 mmol) in CH_2Cl_2 solution (70 mL) was treated with $(CH_3CH_2)_3O^+PF_6^-$ (1.147 g, 4.62 mmol). and the reaction progress was monitored by IR spectroscopy. Starting **4** was consumed within 8 h, as evidenced by disappearance of the acyl ν(CO) at 1656 cm^{-1}. After 12 h, the red-orange solution was concentrated to 5 mL and added dropwise to ether (60 mL). The mixture was decanted, and the remaining gum was washed with ether and reprecipitated from CH_2Cl_2–ether as a red-orange gum (1.407 g, after vacuum drying). This material exhibited two sharp IR stretching [ν(CO) 2073, 2027 cm^{-1}], although its NMR spectrum (CD_3NO_2) indicated a 2.6:1.0 mixture of $FpC(OCH_2CH_3)CH_2OCH_3^+$ (**5**) (52% yield), $Fp[CH(OCH_2CH_3){=}CH(OCH_3)]^+PF_6^-$ (**6**) (20%), and small amounts (<8%) of $FpCO^+PF_6^-$, ether, and $(CH_3CH_2)_3O^+PF_6^-$.

The above product in CH_2Cl_2 solution (50 mL) was treated with $n\text{-}(Bu)_4N^+I^-$. After 10 min, the resulting black solution corresponded to a 2.5:1.0 mixture of $FpCOCH_2OCH_3$ (**4**) [ν(CO) 2018, 1961, 1656 cm^{-1}] and FpI [ν(CO) 2042, 1997 cm^{-1}].

The CH_2Cl_2 solution of the isolated reaction products (**5** and **6**) was refluxed for 2 h; essentially no change was evident by IR spectroscopy, although the solution darkened. NMR spectral analysis of the ether-precipitated gum, however, indicated a 1:1 mixture of **5** and **6**. Continued refluxing of the CH_2Cl_2 solutions gradually produced insoluble black residues as **5** isomerized into **6**. After 8 h refluxing, **5** no longer was detected, and **6** was isolated (in variable 25–35% yields) as a red-orange gum.

Preparation of $FpCH(OCH_3)CH_2(OCH_3)$ (18). To a cold (−78 °C) yellow-orange CH_2Cl_2 solution (6.6 mL) containing $Fp\{(CH_3O)CH{=}CH(OCH_3)\}^+BF_4^-$ (**11**) (155 mg, 0.44 mmol) was added 0.50 mL (0.45 mmol) of a $LiHB(CH_2CH_3)_3$ solution in THF, which immediately turned the reaction solution darker red-orange. After 20 min, the reaction was warmed to room temperature, and the solvent was evaporated to leave a dark red-orange gum. This was extracted with a 2:1 ether–pentane

mixture (35 mL) until the extracts were colorless; the combined orange extracts then were concentrated to an orange gum. An ether solution (30 mL) of this gum was diluted with pentane (20 mL), before cooling to −78 °C with scrapping.

The resulting light brown precipitate, containing only unidentified organic residues, was filtered and washed with ether (2 × 5 mL) at −78 °C. The red-orange filtrate and ether washings were combined, evaporated, and vacuum dried to leave a dark orange oil (89 mg). IR and NMR spectral data for this oil were consistent with the presence of $FpCH(OCH_3)CH_2(OCH_3)$ (**18**) (73 mg, 63%), Fp_2 (11%), and trace amounts of organic residues and ether [for **18**, IR (CH_2Cl_2) 2016, 1954 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.85 (s, 5 H, Cp), 4.87 (br triplet, J = 8 Hz, 1 H, Fe−CH), 3.89 (m, 1 H, $FeCHCH_AH_B$), 3.58 (d, J = 11.2 Hz, $FeCHCH_AH_B$), 3.40 (s, 3 H, $FeCCOCH_3$), 3.34 (s, 3 H, $FeCOCH_3$)]. NMR spectral methine and methylene assignments were confirmed from the results of homonuclear decoupling experiments. Irradiation at δ 4.87 gave two doublets (J = 11.2 Hz) at δ 3.89, 3.58, and irradiation at δ 3.89 collapsed the FeCH methine multiplet to a broad singlet (δ 4.87): ^{13}C NMR (C_6D_6) δ 218.1, 216.7 (C≡O), 85.6 (Cp), 83.8 (Fe−CH), 71.3 (CH_2OMe), 59.0, 58.2 (OCH_3).

Reduction of $FpC(OCH_2CH_3)CH_2OCH_3^+PF_6^-$ (5). A 5.8:1 mixture (585 mg, 1.13 mmol) of **5** and **6**, as a cold (−78 °C) and vigorously stirred CH_2Cl_2 solution (21 mL), was treated dropwise with $LiHB(CH_2CH_3)_3$ in THF (1.28 mL, 1.15 mmol). The orange solution turned dark yellow-black within 15 min; an IR spectrum of this reaction solution at room temperature indicated quantitative conversion of **5** and **6** to a Fp alkyl complex [ν(CO) 2014, 1957 cm^{-1}]. Solvent was evaporated, and the resulting yellow-black gummy residue was extracted with ether (3 × 5 mL). The red-yellow ether extracts, after filtering through Celite, were concentrated to 15 mL, diluted with 15 mL of pentane, and cooled to −78 °C. A yellow-green film was deposited. The remaining red supernatant was removed; the insoluble residue was washed with 20 mL of ether (which was previously cooled to −78 °C), and the combined supernatant and ether washings were evaporated to an orange gum (135 mg). This gum assayed by IR and NMR spectroscopy as $FpCH(OCH_2CH_3)CH_2OCH_3$ (**17**) (117 mg, 37% yield) that was contaminated by Fp_2 (3–7%) [NMR ($CDCl_3$) δ 4.77 (Cp)] plus traces of organic residues and ether [for **17** IR (CH_2Cl_2) 2014, 1957 cm^{-1}; NMR ($CDCl_3$) δ 4.87 (s, 5 H, Cp), 4.90 (m, 1 H, FeCH), 4.02 (t, J = 10.8 Hz, $FeCCH_AH_B$), 3.82–3.62 (m, 3 H, OCH_2 + $FeCCH_AH_B$), 3.42 (s, 3 H, OCH_3), 1.24 (t, J = 7.0 Hz, 3 H, OCH_2CH_3)]. Results of NMR spectral double-irradiation experiments were used to confirm these assignments. Irradiation at δ 1.2 (OCH_2CH_3) pulled out a triplet (δ 3.73, J = 10.8 Hz) for $FeCCH_AH_B$ and left a singlet (δ 3.76) for OCH_2CH_3; irradiation at δ 4.90 (FeCH) collapsed the δ 4.02 triplet to a doublet (J = 10.8 Hz).

The pentane insoluble residues contained unidentified organic residues along with some Fp_2 and **17**, as ascertained by IR and NMR spectral analyses Alternative workup procedures (e.g., using larger volumes of 2:1 ether–pentane for the product extraction) often recovered more **17**, but it inevitably contained more organic contaminants. Attempted chromatography of crude **17** on activity 3 alumina both decomposed it and transformed it to $FpCH_2CHO$ (**15**). $FpCH(OCH_2CH_3)CH_2OCH_3$ (**17**) obtained from the ether–pentane supernatant has been stored for 6 days at −10 °C, with less than 20% loss as CH_2Cl_2 insoluble brown residues. When left in methylene chloride solution at room temperature, however, crude **17** degraded (@50%) to one or more cationic Fp complexes [ν(CO) 2072, 2023 cm^{-1}] after only 3 h. This decomposition proved quantitative after 10 h, and a 1:1 mixture of the above unidentified cationic species and $FpCH_2CHO$ remained.

Reaction of $FpCH(OCH_2CH_3)CH_2(OCH_3)$ (17) and $Ph_3C^+PF_6^-$. A CH_2Cl_2 solution (8 mL) containing a 5.8:1 mixture of $FpC(OCH_2CH_3)CH_2OCH_3^+PF_6^-$ (**5**) and $Fp[(CH_3CH_2O)CH{=}CH(OCH_3)]^+PF_6^-$ (**6**) (200 mg, 0.37 mmol) was reduced with $LiHB(CH_2CH_3)_3$, as detailed above. To the resulting orange-brown solution at 0 °C was added $Ph_3C^+PF_6^-$ (138 mg, 0.36 mmol), and the solution was warmed to room temperature (1 h). Adding this solution to excess ether (35 mL) precipitated a yellow-brown solid, which was recrystallized from acetone–ether (10–40 mL) as pale yellow crystals. These were collected, washed with ether, and vacuum dried (63 mg) [IR (CH_2Cl_2) 2067, 2028 cm^{-1}]. NMR spectral analysis indicated a 7.5:1 mixture of the vinyl ether salts $Fp[CH_2{=}CH(OR)]^+PF_6^-$ (**20**, R = CH_2CH_3; **19**, R = CH_3),[17] by using the δ 4.04 singlet (OCH_3) of the latter salt and the δ 1.39 triplet (OCH_2CH_3) of the former: for $Fp[CH_2{=}CH(OCH_2CH_3)]^+PF_6^-$ (**20**) NMR (CD_3NO_2) δ 7.89 (dd, J = 4.5, 12 Hz, 1 H, =CH(OEt)), 5.49 (s, 5 H, Cp), 4.36 (quart, J = 7 Hz, 2 H, OCH_2CH_3), 3.05 (dd, J = 3.0, 12 Hz, 1 H, (*Z*)-H−CH=), 2.69 (dd, J = 3.0, 4.5 Hz, 1 H, (*E*)-H−CH=), 1.39 (t, J = 7 Hz, 3 H, OCH_2CH_3). An overall 33% yield of **20** thus was realized.

Hydrolysis of $Fp[CH_2{=}CH(OCH_3)]^+PF_6^-$ (19). An orange methylene chloride–nitromethane solution (8.0–2.5 mL) of $Fp[CH_2{=}CHOCH_3]^+PF_6^-$ (**19**) (200 mg, 0.53 mmol) was treated with 0.2 mL of water and was stirred for 20 min. Anhydrous K_2CO_3 (0.5 g) was added, while the mixture was stirred for another 10 min. An IR spectrum of the supernatant then indicated quantitative conversion of **19** to $FpCH_2CHO$ (**15**) [IR (CH_2Cl_2) 2022, 1968 cm^{-1} (C≡O), 1649 cm^{-1} (C=O)]. Removal of solvent under reduced pressure left an orange gum; it was redissolved in 1:1 ether–pentane (30 mL), concentrated to 10 mL, and cooled (−78 °C). The resulting yellow-orange precipitate was filtered, washed with 10 mL of pentane, and vacuum dried. This yielded 79 mg (68%) of **15**[17] as an amorphous yellow solid: ^1H NMR ($CDCl_3$) δ 9.42 (t, J = 5.2 Hz, 1 H, CHO), 4.80 (s, 5 H, Cp), 1.70 (d, J = 5.2 Hz, 2 H, $Fe\text{-}CH_2$); ^{13}C NMR ($CDCl_3$) δ 214.9 (CO), 201.3 (CHO), 85.8 (Cp), 10.9 ($FeCH_2$).

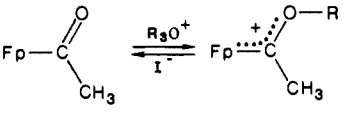
A CH_2Cl_2 solution (15 mL) containing $FpCH_2CHO$ (**15**) (220 mg, 1.00 mmol) was cooled to 0 °C and treated dropwise with excess $HBF_4{\cdot}O(CH_3)_2$ (0.2 mL). The dark orange solution immediately turned yellow-brown and deposited a yellow solid; addition of ether (25 mL) after 5 min precipitated the remaining product. The yellow crystalline solid (280 mg) that remained after filtering, washing with ether, and recrystallizing from acetone–ether was identified as spectroscopically pure $Fp[CH_2{=}CHOH]^+BF_4^-$ (**21**)[17] (91%): IR (CH_3NO_2) 2065, 2021 cm^{-1}; NMR (acetone-d_6) δ 8.37 (t, J = 8.0 Hz, 1 H, =CHOH), 5.63 (s, 5 H, Cp), 2.96 (d, J = 8.0 Hz, 2 H, $=CH_2$).

Acetaldehyde from $Fp[CH_2{=}CHOH]^+BF_4^-$ (21). Into a nitrogen-flushed, 25-mL, three-necked, flask was added $Fp[CH_2{=}CHOH]^+BF_4^-$ (**21**) (196 mg, 0.64 mmol) and $(n\text{-}Bu)_4N^+I^-$ (2.1 g, 5.8 mmol). This solid mixture was warmed to 55 °C, before $ClCH_2CH_2Cl$ (4 mL) was injected. The resulting dark yellow-brown suspension was stirred vigorously, and after 10 min, all volatiles were distilled (10^{-2} mm) into a trap that was maintained at −30 °C. The brown pot residue remaining consisted of a 3:1 mixture of FpI and $FpCH_2CHO$, as ascertained by IR spectroscopy. This mixture then was treated with $HBF_4{\cdot}O(CH_2CH_3)_2$ (60 mg, 0.37 mmol) and 1.5 mL of $ClCH_2CH_2Cl$ (55 °C), and again the volatiles were distilled (after 5 min) into the same cold trap. The remaining brown pot residue now consisted entirely of FpI. The combined volatile fraction—a pale yellow solution—contained CH_3CHO [IR ($ClCH_2CH_2Cl$) 1726 cm^{-1}]. Quantitative GLC analysis of this solution on the Carbowax 20 M column (150 °C), using $CH_3CH_2CO_2CH_2CH_3$ as the internal standard, indicated a 96% yield of acetaldehyde.

Attempted Isomerization of $FpC(OCH_3)CH_3^+PF_6^-$ (9). A CH_2Cl_2 solution (12 mL) containing $FpC(OCH_3)CH_3^+PF_6^-$ (**9**)[16] (266 mg, 0.67 mmol) was refluxed for 18 h. Treatment of aliquots of the unchanged yellow solution with excess $(n\text{-}Bu)_4N^+I^-$ quantitatively regenerated (10 min) $FpCOCH_3$ (**8**), as ascertained by IR spectroscopy. Less than 5% FpI, the product derived from independently treating $Fp[CH_2{=}CHOCH_3]^+PF_6^-$ (**19**) with excess $(n\text{-}Bu)_4N^+I^-$, would have been detected under these conditions.

Results

Alkylation of $FpCOCH_2OCH_3$ (4). The progress of the reaction between $(CH_3CH_2)_3O^+PF_6^-$ and **4** resembles, at first glance, analogous reactions between $FpCOCH_3$ (**8**) and oxonium salts or other carbocationic alkylating reagents that afford alkoxycarbene compounds **9** (eq 2).[14,16,23] Over 5–8 h, IR spectral ν(CO)



(2)

8 **9**

R = CH_3, CH_2CH_3

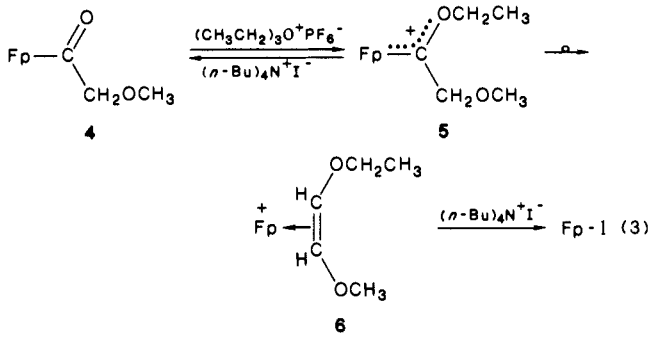
absorptions of **4** [2024, 1963 (C≡O); 1657 cm^{-1} (C=O)] were replaced by two terminal carbonyl absorptions at 2073 and 2027 cm^{-1}, which are consistent with $FpC(OCH_2CH_3)CH_2OCH_3^+PF_6^-$ (**5**). Moreover, adding iodide or acetone to the reddish-yellow CH_2Cl_2 solutions of **5** regenerated **4**; this result also is consistent with the presence of a Fp(alkoxycarbene) compound (eq 2).

Significant differences exist between triethyloxonium PF_6^- alkylating **4** vs. **8**, however.[24] Treating reaction mixtures containing **5** with iodide did not quantitatively regenerate **4**, as significant amounts of FpI also formed. These iodide reversion reactions were conducted by treating aliquots of the **4**/$(CH_3CH_2)_3O^+$ mixture (1:1 stoichiometry) with $(n\text{-}Bu)_4N^+I^-$. Within minutes, the mixture darkened, and the relative amounts of **4** and FpI were quantified by IR spectroscopy in situ and by isolation (via chromatography). Interestingly, the proportion of FpI increased with the reaction time, progressing from 15% (8

h) to 29% (12 h) to 50% (2 h refluxing), even though IR spectra of the original **4**/$(CH_3CH_2)_3O^+$ solution remained essentially unchanged. Another discrepancy observed in alkylating **4** is that the product inevitably precipitated with ether as a red-orange gum. Similar preparations of other Fp(alkoxycarbene)$^+PF_6^-$ salts, in contrast, generally afford yellow—frequently crystalline—solids. Continued handling of this gum decomposed it to insoluble residues.

The NMR spectrum of this gum clearly exhibited two independent sets of absorptions that are linked to a single broadened Cp resonance (δ 5.45, CD_3NO_2), in addition to small but variable amounts of $FpCO^+$, $(CH_3CH_2)_3O^+$, and ether. One set for the component in higher concentration corresponds to **5** (e.g., OCH_3 singlet at δ 3.59). The other set contains two vinyl C–H doublets (δ 6.53, 6.36 with J = 2.2 Hz) and a OCH_3 singlet at δ 4.02. For comparison, the OCH_3 singlet of **9** (R = CH_3) resonates under similar conditions even further downfield at δ 4.67.

These observations are consistent with $(CH_3CH_2)_3O^+PF_6^-$ alkylating **4** to give the α-ethoxy-β-methoxyethylidene compound **5**, which subsequently isomerizes (half-life @24 h) to the *cis*-1,2-methoxyethoxyethylene complex **6** (eq 3). Both **5** and **6** have



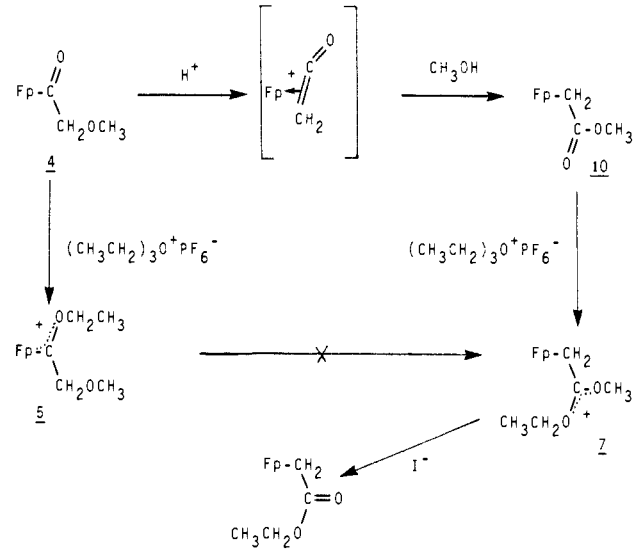
essentially overlapping IR spectral ν(CO) and NMR spectral Cp resonances. The reaction of η^2-dialkoxyethylene salt **6**, which was independently synthesized (vide infra), with iodide can explain the formation of FpI.

By appropriate choice of the reaction conditions between **4** and $(CH_3CH_2)_3O^+PF_6^-$, it is possible to greatly enrich the product in either **5** or **6**. A procedure employing 0.8 equiv of $(CH_3CH_2)_3O^+$ and a reaction time of 5 h thus optimizes the proportion of **5** (5.8:1.0 isomeric mixture) with an overall 44% yield. This product supplied our purest samples of **5**, which were reacted with borohydride reagents and were used in collecting NMR spectral data. Complete ^1H and ^{13}C NMR spectral assignments for **5** (Experimental Section) follow from those of analogous ethoxycarbene compounds **9**.[16]

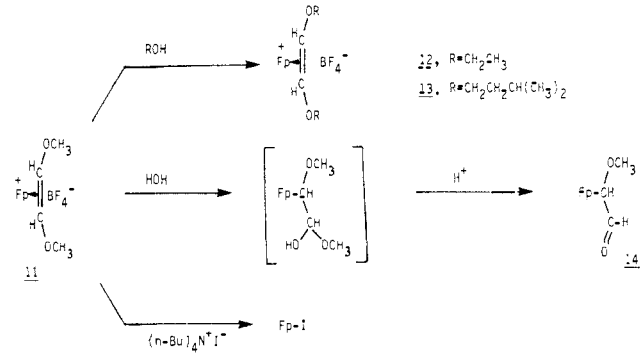
Longer reaction times increased the concentration of **6**. A 1:1 stoichiometry and a 12-h reaction time thus reduced the proportion of **5**:**6** to 2.6:1.0 (52% overall yield), as ascertained both by direct NMR spectral observation and by results of iodide degradation. Further increases in **6** resulted from either refluxing the reaction (2–8 h) or conducting it at room temperature for prolonged periods of time—up to 5 days. If the reaction refluxed for more than 2 h or sat at room temperature for more than 2.5 days, however, it decomposed; black insoluble residues formed, and unidentified organic residues collected. Nevertheless, this reaction after sitting 3 days afforded a 1:2.7 mixture of **5** and **6** (total yield 55–63%). Prolonged sitting for 5 days at room temperature or refluxing 8 h afforded only **6** in at least 40% and 25–35% yields, respectively.

One requirement for alkylating **4** is that the $(CH_3CH_2)_3O^+PF_6^-$ must be scrupulously free of acid. Otherwise, traces of free acid isomerize **4** to the carbomethoxymethyl complex **10**[17,25,26] (Scheme I), and over 8–12 h **10** then alkylates and gives the known (methoxyethoxycarbenio)methyl compound **7**[17] as an impurity (up to 18% of product). Treatment of **7** with iodide quantitatively and immediately generates $FpCH_2CO_2Et$.[27] After recrystallizing the commercially available oxonium salt from $PhNO_2$–ether, however, neither **7** nor $FpCH_2CO_2Et$ (after reacting with iodide) were detected during the alkylation of **4**.

Scheme I



Scheme II



η^2-[*cis*-1,2-Dialkoxyethylene]Fp$^+$ and η^1-(Methoxyformylmethyl)Fp Complexes. (*cis*-1,2-Dimethoxyethylene)Fp^+ (**11**) was prepared via the standard isobutylene exchange reaction[15] (eq 4), as initially reported by Baird and Heberhold.[22,28] Recrystallizing

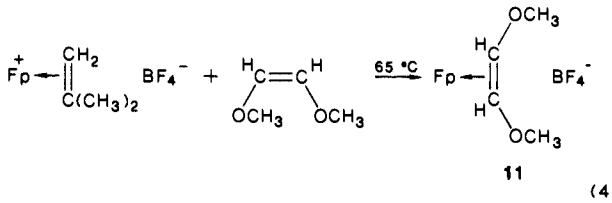
(23) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258; **1981**, *103*, 979. (b) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924. Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *Ibid.* **1982**, *104*, 3761.

(24) Attempts at using other alkylating agents, including $(CH_3)_3O^+BF_4^-$; $RC(OCH_3)_2^+PF_6^-$ (R = H, CH_3), and CH_3OSO_2F, that convert **8** to **9**[14,16,23] were unsuccessful. Only very small amounts of the desired $FpC(OCH_3)CH_2OCH_3^+$ formed, as $FpCO^+$ was the major organometallic product. Although we don't know why these reactions failed, it is unlikely that these electrophilic methylating agents abstract methoxide from **4** and give the ketene compound $Fp(CH_2{=}C{=}O)^+$. This intermediate, unstable under the workup conditions, would have been detected either by its facile hydrolysis to give $FpCH_2CO_2H$ [IR ν(CO) 2024, 1972, 1651 cm^{-1}] or by its reaction with iodide to give $FpCH_2COI$ [IR ν(CO) 2022, 1977, 1754 cm^{-1}].[25] Neither byproduct was observed under the appropriate reaction conditions. A future publication will elaborate on generating $Fp(CH_2{=}C{=}O)^+$ from **4** by using strong acids.

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

(26) (a) King, R. B.; Bisnette, M.; Fronzaglia, A. *J. Organomet. Chem.* **1966**, *5*, 341. (b) Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A.* **1969**, 1309.

(27) We independently prepared **7** from the reaction between **10** and $(CH_3CH_2)_3O^+PF_6^-$. (n-Bu)$_4N^+I^-$ (1 equiv) in CH_2Cl_2 quantitatively converts **7** to $FpCH_2CO_2Et$. Certainly the carbalkoxy IR ν(C=O) at 1676 cm^{-1} is extremely diagnostic for the carbethoxymethyl ligand, and the NMR spectrum of **7** moreover exhibits a particularly definitive $FeCH_2$ singlet at δ 2.01 (CD_3NO_2). The regioselectivity of this iodide dealkylation reaction has been established by using $Cp(CO)[P(OCH_3)_3]FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$; also, intermediacy of the ketene compound $Fp(CH_2{=}C{=}O)^+$ during isomerization of **4** to **10** has been discussed.[10b]



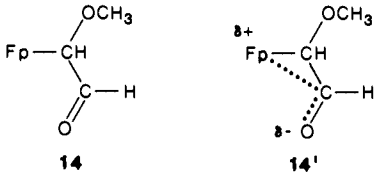
11 (4)

the initial product from CH_2Cl_2–ether afforded analytically pure **11** as an air-stable, yellow salt in 77% yield. It proved to be a convenient starting material for investigating the reactions of (1,2-dialkoxyethylene)Fp^+ complexes with alcohols, water, iodide, and borohydride reagents (Scheme II).

Methoxy groups on **11** easily exchange in ethyl or isoamyl alcohols to give the corresponding dialkoxyethylene salts **12** and **13** in over 80% yield.[29] Both products physically resemble **11**, although the bisamyloxy **13** is much more soluble in $CHCl_3$, for example. The NMR spectrum of the bisethoxy **12** has a vinyl singlet (δ 6.48 in CD_3NO_2) that is downfield from the corresponding resonance of **11** by 0.13 ppm (in CD_3NO_2). Also, the magnetically nonequivalent[30] methylene hydrogens give two distinct quartets. Only a single isomer was detected by NMR spectroscopy for **12** and **13**, to which we assign thermodynamically favored cis configurations[35] in analogy with **11**.[22,28]

Dimethoxy **11**, upon adding a few drops of water to its vigorously stirred CH_2Cl_2 solution, hydrolyzes to (methoxyformylmethyl)Fp **14**. Although this hydrolysis proceeds to completion (within 20 min by IR spectral monitoring), the product **14**, a yellow solid, resulted in only 49% yield after chromatography. Product loss in part arises from its solution instability. Crude **14** degrades in CH_2Cl_2 solution (@20% in 1 h) to variable mixtures of Fp_2, $FpCO^+$, and insoluble residues. Nevertheless, analytically pure **14** was further characterized spectroscopically.

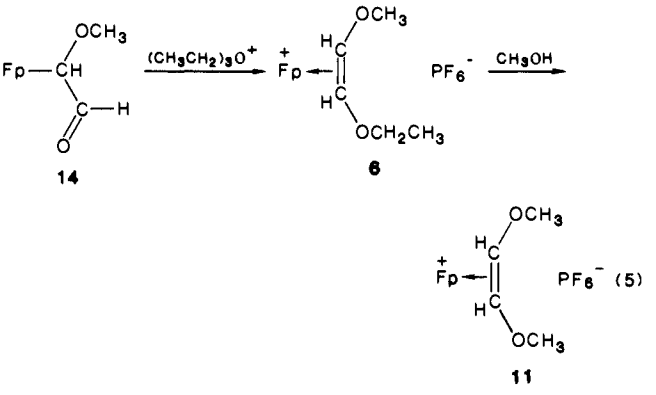
Spectral data for **14** is similar to that of the known formylmethyl complexes $FpCH_2CHO$ (**15**)[17,31] and $FpCH(CH_3)CHO$ (**16**).[32] The ^1H NMR spectrum of **14** thus exhibits a downfield singlet (δ 8.90) for the formyl hydrogen, vs. δ 9.10 for **15** and 9.2 for **16** (all data in CS_2). Absence of vicinal coupling for this hydrogen in **14** (both formyl and methine singlets broadened, but $J < 1$ Hz)



14 **14'**

agrees with the small vicinal couplings observed for the aldehyde hydrogen on aliphatic aldehydes.[33] (The corresponding hydrogens on **16** do, however, exhibit a small coupling of 3 Hz.[32]) The ^{13}C NMR spectrum of **14** has two resonances for the diastereotopic terminal carbonyls[34] (δ 216 and 214), vs. the single resonance detected for **15**. Finally, the IR spectrum of **14** exhibits a moderately intense acyl absorption ν(CO) at 1664 cm^{-1}, vs. 1650 cm^{-1} for **15** and 1640 cm^{-1} for **16** (all data in CH_2Cl_2). These low-energy acyl stretching frequencies [with respect to ν(CO) 1715 cm^{-1} for CH_3CHO] could indicate a through-space interaction that involves the Fe (e.g., **14'**, depicted as vertical stabilization) lowering the formyl CO bond order and transferring electron density to the oxygen terminus. This polarization, often referred to as the "β-effect",[26b] would account for the facile reactivity of **16** and **15** with electrophiles.

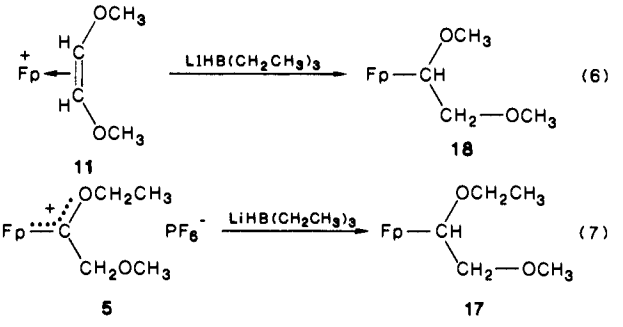
$FpCH(OCH_3)CHO$ (**14**) reacts with $(CH_3CH_2)_3O^+PF_6^-$ in CH_2Cl_2 solution and gives **6** (eq 5), which is isolated analytically pure as a yellow solid (69% yield). The **14** used in this reaction must be carefully dried, or substantial amounts of the 1,2-diethoxyethylene complex **12** also form. Nevertheless, this reaction does constitute a convenient and independent synthesis of **6**.



14 **6** **11** (5)

The spectral data and chemical reactivity of **6** matches those of the symmetrically substituted **11** and **12**. Structural assignment of **6** accordingly follows from analysis of its ^1H NMR spectrum. The small coupling (J = 2.0 Hz) of the two doublets (δ 6.53 and 6.36, CD_3NO_2), ascribed to the two magnetically nonequivalent vinyl hydrogens,[30] supports the cis disubstituted ethylene ligand configuration. For comparison, vinyl CH absorptions on Fp-$(CH_2{=}CHOR)^+$ have coupling interactions of J(cis) = 4.5 Hz and J(trans) = 12 Hz.[17] Chemical shifts of the vinyl absorptions and of the methoxy and ethoxy absorptions on **6**, recorded in both CD_3NO_2 and CD_3COCD_3, closely match the corresponding values for **11** and **12**.[35] In addition, the ethoxymethylene hydrogens on **6**, as with **12**, are magnetically nonequivalent and resonate as a doublet of quartets. All dialkoxyethylene complexes **6**, **11**, and **12** react with iodide within a few minutes to quantitatively eliminate FpI.

η^1-α,β-Dialkoxyethyl Fp Complexes. Both (dimethoxyethylene)Fp^+ **11** and (α-ethoxy-β-methoxyethylidene)Fp^+ **5** salts reduce with 1 equiv of $LiHB(CH_2CH_3)_3$ at −80 °C to give the α,β-dialkoxyethyl complexes **18** and **17** (eq 6 and 7), respectively.



11 **18** (6)

5 **17** (7)

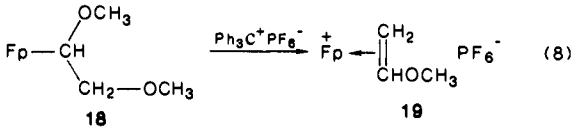
IR spectral monitoring of these reactions in CH_2Cl_2 indicated that the cationic starting materials rapidly converted to neutral Fp alkyl complexes [ν(CO) 2015, 1954 cm^{-1}] with <10% Fp_2 evident as the only other IR-detectable organometallic. These reactions, however, had to be worked up immediately. Upon sitting at room temperature (>2 h), both crude products decomposed to largely Fp(vinyl ether) salts **19** and **20**,[17] Fp_2, $FpCO^+$, and unidentified organics.

Workup procedures for these reactions proved to be critical. The mixtures were evaporated, and pentane–ether extracts containing crude **17** and **18** were cooled (−80 °C)—this precipitated unwanted borane and other unidentified organic residues. Evaporating the remaining solution left orange gums that contained 80–90% **17** and **18** (by NMR spectral analysis). Also present were Fp_2, ether, and trace amounts of organic residues.

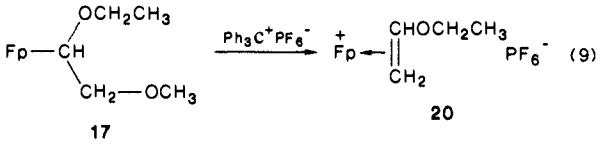
(28) Marsi, M.; Rosenblum, M. *J. Am. Chem. Soc.* **1984**, *106*, 7264.
(29) Subsequent to our completing this work, Marsi and Rosenblum reported the preparation of **12**.[28] Crawford, E. J.; Cutler, A. R. 188th National Meeting of the American Chemical Society, Philadelphia, PA, Aug 1984; INOR 266.
(30) Van Gorkum, M.; Hall, G. E. *Q. Rev. Chem. Soc.* **1968**, *22*, 14.
(31) Ariyaratne, J. K. P.; Green, M. L. H. *J. Chem. Soc.* **1964**, 1.
(32) Klemarczyk, P.; Rosenblum, M. *J. Org. Chem.* **1978**, *43*, 3488.
(33) Karabatsos, G. J.; Hsi, H. *J. Am. Chem. Soc.* **1965**, *87*, 2864. The vicinal coupling constant for CH_3OCH_2CHO is 0.77 Hz. Karabatsos, G. J.; Fenoglio, D. J. **1969**, *91*, 3577.
(34) Orlova, T. Y.; Petrovskii, P. V.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1974**, *67*, C23.

With this procedure, 37% (**18**) to 63% (**17**) yields of relatively clean pentane-insoluble products were obtained. Some loss (particularly **18**) can be attributed to the initial precipitate. Further attempts at purifying **17** and **18** by low-temperature crystallization, sublimation, or chromatography failed. The latter two procedures inevitably caused product decomposition. Longevity of **17** and **18** purified as described varied from batch to batch, although these gums were stable for at least 8 h at −5 °C.

Unambiguous structural assignments for both **17** and **18** follow from analysis of their ^{1}H NMR spectral data. Isolated ABX spin systems for $FpCH_x(OR)CH_AH_B(OR)$, having diastereotopic methylene hydrogens H_AH_B, were assigned by using decoupling experiments. The methine $FeCH_x$ absorbs near the Cp resonance (δ 4.9), and the distinct methylene H_AH_B multiplets appear between δ 3.6–4.0. The spectrum of **18** also exhibits separate



18 **19**

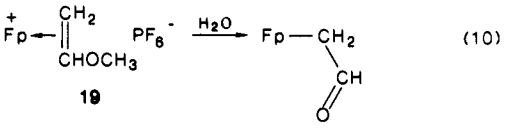


17 **20**

methoxy singlets (δ 3.34, 3.40), assigned to the α- and β-positions, respectively, whereas **17** has one methoxy singlet (δ 3.42). Accordingly, the regioisomer of **17**, $FpCH(OCH_3)CH_2(OCH_2CH_3)$, if formed at all, must account for less than 10% of the product. The ^{13}C NMR spectrum of **18** also supports the structure assigned; its diastereotopic terminal carbonyls (δ 216.7, 218.1) further indicate the presence of the chiral center.

A useful reaction of **17** and **18** is that either HBF_4 or $Ph_3C^+PF_6^-$ convert them into (η^2-vinyl ether)Fp^+ (**19** and **20**). Thus, interacting **18** and $Ph_3C^+PF_6^-$ affords the known methylvinyl ether salt **19**,[17] which is obtained in 48% yield after reprecipitating from acetone–ether. Under similar reaction conditions **17** gives a 7.5:1.0 mixture of ethyl-to-methylvinyl ether salts **20**/**19**.

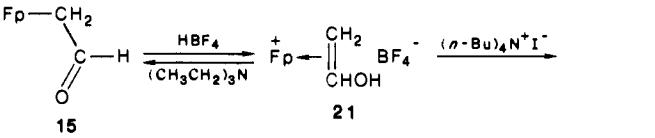
Formylmethyl Complexes FpCH(R)CHO (15, R = H; 14, R = OCH_3) as Aldehyde Precursors. (Methyl vinyl ether)Fp^+ (**19**) hydrolyzes to $FpCH_2CHO$ (**15**) (eq 10) under precisely the same reaction conditions used for the hydrolysis of **11**. After precipitating from ether–pentane (−78 °C), **15** resulted in 68% yield. Both formylmethyl complexes **14** and **15** now are available from $FpCOCH_2OCH_3$ (**4**).



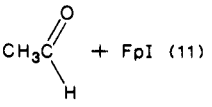
19 **15**

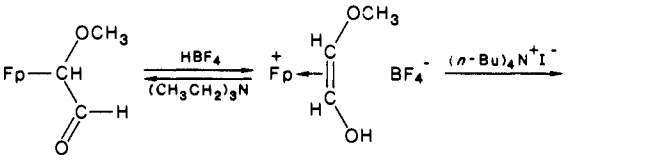
Formylmethyl **14** and **15** upon protonating afford their respective η^2-vinyl alcohol complexes **22** and **21** (eq 11 and 12). These reactions are reversed quantitatively upon adding 1 equiv of triethylamine. (This behavior has been documented previously for **15**/**21**.[17]) The (η^2-1,2-hydroxymethoxyethylene)Fp^+ complex **22** forms in 84% yield as a sparingly soluble, gummy precipitate that was not obtained analytically pure. Nevertheless, results of derivatizing **22** (deprotonation, conversion to **12** with ethanol, and reaction with iodide) and analyzing its spectral data firmly establish its structure. The NMR spectrum of **22**, in particular, exhibits two broadened singlets for the vinyl hydrogens plus methoxy and Cp singlets (δ 4.02, 5.49 in CD_3NO_2) that agree with those values for **11** (δ 3.96, 5.42) or for **6** (δ 4.02, 5.46).

The η^2-vinyl alcohol salts **21** and **22**, in turn, serve as precursors to acetaldehyde and methoxyacetaldehyde (eq 11 and 12), respectively. In both reactions, excess iodide cleaved the aldehyde from **21** or **22** in 1,2-dichloroethane solutions (50–55 °C), and then the aldehyde plus solvent was distilled trap-to-trap (−30 °C).

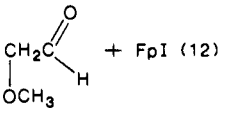


15 **21**





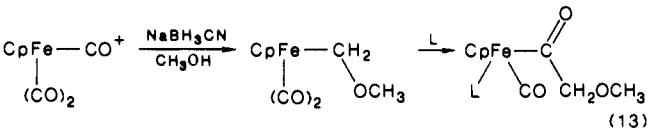
14 **22**



Both IR spectroscopy and GLC analysis confirmed the identity of the aldehydes (the only organic products) and established yields of 96% for acetaldehyde and 38% for methoxyacetaldehyde.

Discussion

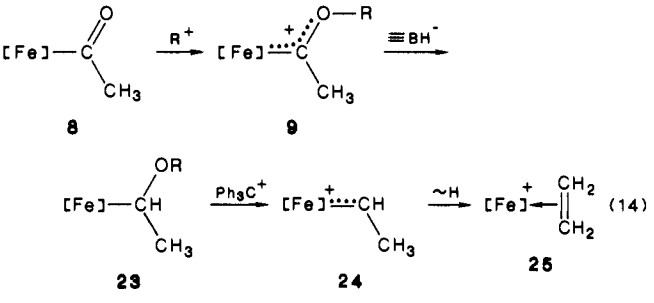
In previous studies, phosphine- and phosphite-substituted methoxyacetyl complexes[10] were prepared by incorporating two terminal carbonyls of $Cp(CO)_3Fe^+$ into the two acyl skeletal carbons (eq 13).[19] This synthetic route, however, does not apply



L = PPh_3, $P(OCH_3)_3$

to $FpCOCH_2OCH_3$ (**4**), in that we have been unsuccessful in carbonylating $FpCH_2OCH_3$ (even with Lewis acid catalysts).[37,38] Rather, **4** was procured by acylating Fp^-Na^+, which afforded large quantities of this starting C_2 template as a stable, amber oil.[17]

Activating then reducing the acyl ligand on **4** is well precedented. A variety of electrophilic alkylating agents transform iron acetyl complexes **8** to their α-methoxy- or ethoxyethylidene (i.e., alkoxycarbene) derivatives **9**,[14,16,23,39] which then reduce (by using



8 **9** **23** **24** **25**

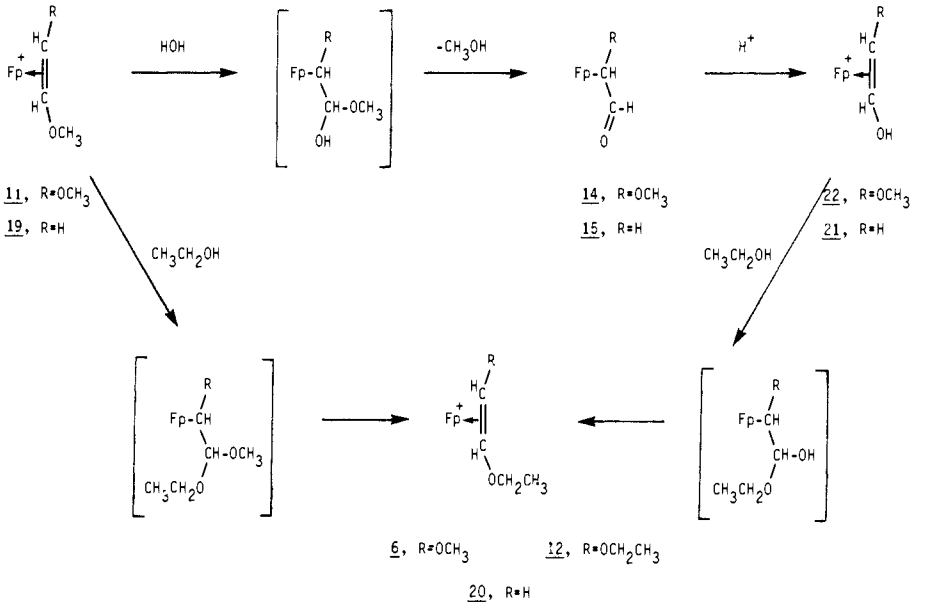
[Fe] = Cp(CO)(L)Fe; L = CO, PPh_3, $P(OPh)_3$; R = CH_3, CH_2CH_3

(35) Matching of NMR vinyl CH chemical shifts of **6** with those of the symmetrical dimethoxy **11** and diethoxy **12** analogues, plus the established cis dialkoxy configurations of **6**[22,28] and **11**, also establishes the cis stereochemistry of **12**. The NMR singlet for the vinyl hydrogens of **12**, along with the analogous singlet for **11**, are within 0.05 ppm of the two vinyl doublets of the η^2-methoxyethoxyethylene complex **6**. Furthermore, vinyl C–H singlets for cis and trans stereoisomers of uncoordinated 1,2-dimethoxyethylene, in contrast, differ by 1.0 ppm (data also in acetone-d_6).[36] Assuming that this chemical shift difference extrapolates the ligated η^2-dialkoxyethylene complexes **11** and **12**, then **12** must also have a cis alkene configuration.

(36) Heberhold, M.; Wiedersatz, G. O.; Kreiter, C. G. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1976**, *31*, 35.

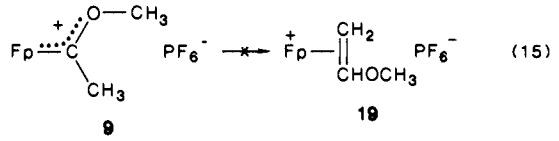
(37) Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247.

Scheme III



borohydride[14,23a,39a,c,d] or transition-metal hydride[9] reagents) to stable α-alkoxyethyl compounds **23** (eq 14). These examples of **23** were then used to generate ethylidene compounds **24** (after abstracting alkoxide) that then isomerize to their η^2-ethylene complexes **25** (eq 14).[14,23a]

Initial attempts at alkylating $FpCOCH_2OCH_3$ (**4**) were complicated by the initially formed $FpC(OCH_2CH_3)CH_2OCH_3^+PF_6^-$ (**5**) readily isomerizing[40] to its η^2-α,β-dialkoxyethylene compound **6** (eq 3). Inseparable mixtures of **4** and **5** thus resulted. With proper control of the reaction conditions, however, **5** is isolated containing less than 15% of **6**. In contrast to this irreversible **5**-to-**6** isomerization, the (α-methoxyethylidene)Fp^+ salt **9** does not rearrange to the known η^2-vinyl ether compound **19** (eq 15) in refluxing CH_2Cl_2.



9 **19** (15)

The **5** → **6** isomerization resembles the well-known rearrangement of η^1-alkylidene ligands bearing a β-hydrogen but not an alkoxy substituent to η^2-alkene ligands.[8d,41] Several examples of this transformation with cationic CpFe compounds, e.g., **24** → **25** (eq 14), have been documented.[14,23,39c,42] Brookhart has characterized this reaction as a hydride migration.[23a] The Fp-stabilized α-carbenium ion **5** likewise undergoes a hydride migration, and the resulting Fp-stabilized β-carbenium ion then gives the η^2-dialkoxyethylene salt **6**.[43,44] Presence of the second alkoxy substituent at the β-position of the starting alkylidene complex **5** apparently is critical[45]—its absence (i.e., **9**)) precludes this isomerization.

Although only recently prepared, (η^2-1,2-dialkoxyethylene)Fp^+ complexes already have found applications. Rosenblum and coworkers used **11** as a vinylene dication equivalent: sequential reaction of carbon nucleophiles, e.g., R_1Li and R_2Li, then protonation stereoselectively affords alkene complexes $Fp(R_1CH{=}CHR_2)$[4].[28] Equation 16 depicts the first half of this sequence. In the second half, R_2Li regioselectively adds to the alkoxy vinyl carbon of **26** (now a vinyl cation equivalent)[46] and after proton-

(38) A rather limited number of alkoxyacetyl and other β-oxoacyl complexes, most as derivatives of the $Mn(CO)_5$ moiety,[2b,38a] have been characterized. All were prepared by either carbonylation or phosphine-induced CO insertion on the requisite α-hydroxy-, alkoxy-, or siloxyalkyl compound. (a) 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. Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1596. Gladysz, J. A.; Selover, J. C.; Strause, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766. Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147. (b) Heck, R. F.; Breslow, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 2499. Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353. Pelling, S.; Botha, C.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* **1983**, 1495. Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887. Milstein, D.; Fultz, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1336. Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1473.

(39) (a) Green, M. L. H.; Michard, L.; Swanwick, M. *J. Chem. Soc. A* **1971**, 794. Davison, A.; Reger, D. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Casey, C. P.; Cyre, C. R.; Boggs, R. A. *Synth. React. Inorg. Met.-Org. Chem.* **1973**, *3*, 249. Treichel, P. M.; Wagner, K. P. *J. Organomet. Chem.* **1975**, *88*, 199. Grotsch, G.; Malisch, W. *J. Organomet. Chem.* **1982**, *246*, C42. (c) Bly, R. S.; Silverman, G. S. *Organometallics* **1984**, *3*, 1765. (d) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* **1984**, *3*, 1764. Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. *J. Chem. Soc., Chem. Commun.* **1984**, 745.

(40) The only other α,β-dialkoxyalkylidene complexes known, $(CO)_5WC(OCH_2CH_3)CH(OCH_3)Ph$ and Cr analogues, evidently are stable. Schubert, U.; Fischer, E. O. *Justus Liebigs Ann. Chem.* **1975**, *393*. Fischer, E. O.; Schubert, U.; Kalbfus, W.; Kreiter, C. G. *Z. Anorg. Allg. Chem.* **1975**, *416*, 135.

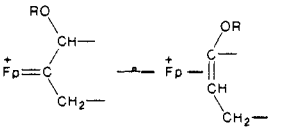
(41) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354.

(42) (a) Kremer, K. A. M.; Duo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. Kremer, K. A. M.; Helquist, P.; Kerber, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1862. (b) Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069.

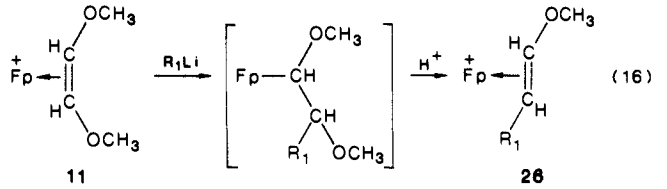
(43) (a) Other examples (not containing CpFe or Ru) of alkylidene complexes isomerizing, presumably via a 1,2-hydrogen shift, to their η^2-alkene complexes have been documented[8d] by Hatton and Gladysz (Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157). (b) In work germane to this study, Gladysz and co-workers established that the (siloxy)carbene complex $(CO)_4Fe{=}C(CH_3)OSi(CH_3)_3$ readily isomerizes to the η^2-(siloxy)-vinyl ether compound $(CO)_4Fe[CH_2{=}CHOSi(CH_3)]$. In contrast, the analogous (α-alkoxy)carbene complexes $(CO)_4Fe{=}C(CH_2R)OCH_3$ characterized by Semmelhack and Tamura apparently are stable. Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325. Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099, 6750.

(44) Analogous hydride migration reactions on other examples of **5**, $Cp(CO)(L)FeC(OCH_2CH_3)CH_2OCH_3^+$, L = PPh_3, $P(OCH_3)_3$, have not been detected. We also note that analogous substituted ethylidene salts **24** only isomerize very slowly to their requisite η^2-ethylene compounds **25** (eq 14).

(45) Indeed, Fp(alkylidene) salts bearing β-hydroxy or -alkoxy substituents on the structural unit



regioselectively isomerize to their η^2-vinyl alcohol or ether complexes.[32] Marten, D. C. *J. Chem. Soc., Chem. Commun.* **1980**, 341. Marten, D. C. *J. Org. Chem.* **1981**, *46*, 5422. Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069.



ating eliminates $Fp(R_1CH{=}CHR_2)^+$. It is worth noting that *trans*-**26**, the kinetic product (eq 16), rapidly isomerizes to *cis*-**26** and that the stereochemistry of the final product $Fp(R_1CH{=}CHR_2)^+$ depends on whether *cis*- or *trans*-**26** is used in the final reaction sequence.

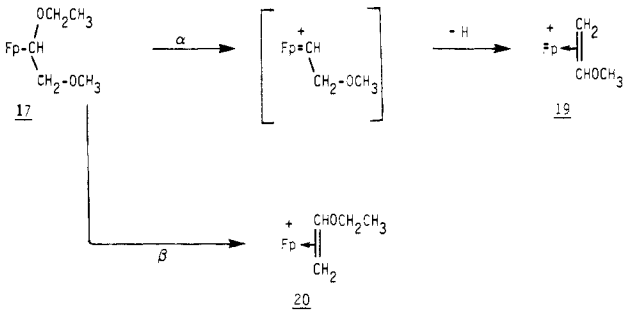
We found that alcohols and water also add to **11**, giving the *cis*-1,2-dialkoxyethylene compounds **12** and **13** and (η^1-methoxyformylmethyl)Fp (**14**), respectively. These solvolytic reactions, as those of the (η^2-vinyl ether)Fp^+ salts **19** and **20**, entail the intermediacy of undetected η^1-formylmethyl hemiacetals (using water) and acetals (using alcohols) (Scheme III). $FpCH_2CH(OCH_3)_2$ (**27**), which has been independently prepared, gives $Fp(CH_2{=}CHOCH_3)^+$ (**19**) upon reacting with acid or Ph_3C^+, produces $FpCH_2CHO$ (**15**) upon chromatographing, and generates $Fp(CH_2{=}CHOH)^+$ (**21**) upon chromatographing and adding acid.[17] We also report that water hydrolyzes **19** (eq 10) to $FpCH_2CHO$ (**15**). Solvolytic reactions of **11** now reported that give **14**, **22**, and **12** (Scheme III) accordingly parallel analogous reactions of **19**.

Although transition-metal alkyl complexes bearing an alkoxy group either α or β to the metal center are common, those containing both structural features on one ethyl ligand have not been characterized previously. Related examples, as carbonate derivatives $CoCHO(C{=}O)OCH_2$ of Co(III) complexes having a synthetic macrocyclic system, have been reported by Finke et al.[47] The reactivity of the dihydroxyethyl complex, resulting from removal of the carbonate protecting group, however, is dominated by facile homolytic cleavage of the Co–C bond. Subsequent free radical reactions with and without Co(II) involvement afford acetaldehyde and glycolaldehyde, respectively. Also related to the dialkoxyethyl Fp compounds **17** and **18** are several examples of carbohydrate complexes. $(PPh_3)(CO)_3Co$-, $Mn(CO)_5$-,[48] and Fp-[49] substituted C-glycoside polyethers were prepared by metallating the glycosyl halide with a metallate nucleophile.

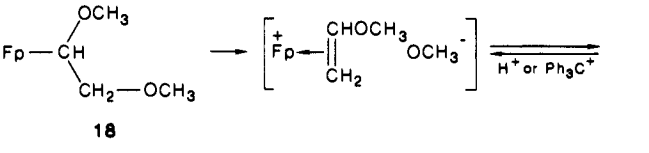
The two α,β-dialkoxyethyl complexes **17** and **18** that resulted from reducing **5** and **11** (eq 6 and 7) were not obtained analytically pure due to limitations imposed by the workup procedure and by their limited stability. Since these products are insoluble in pentane, they had to be extracted from the crude reaction (before it degraded) with ether. Unfortunately, this also removed organic contaminants that were never completely eliminated. In contrast, the α-alkoxyethyl complexes **16** (eq 14) extract with pentane as analytically pure products from their crude reaction mixtures.[14] NMR spectra of **17** and **18**, nevertheless, support the assigned structures and establish at most 10–15% of Fp_2 plus trace amounts of organic contaminants, appearing upfield (<3 δ) from most absorptions for **8a,b**.

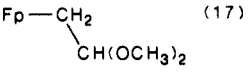
We were especially concerned that formylmethyl acetal complexes, e.g., $FpCH_2CH(OCH_3)_2$ (**27**), might be present with **17** and **18**. These acetal complexes, which would undergo the same reactions with electrophiles, could derive from two sources. (1) $FpCH_2CH(OCH_3)(OCH_2CH_3)$ could arise from reducing the (dialkoxycarbenio)methyl complex **7**[50] (Scheme I), but the latter

Scheme IV



does not form when **4** alkylates. That **5** does not isomerize to **7**, however, agrees with results of a previous study using Cp(CO)[$P(OCH_3)_3$]$FeC(OCH_2CH_3)CH_2OCH_3^+$.[10b] (2) Alternatively, **17** and **18** once formed by reducing **5** and **11** could isomerize to their requisite formylmethyl acetal compounds (eq 17). Loss

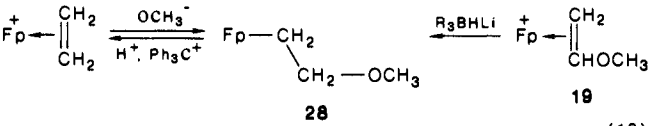




(17)

of β-methoxide from **18**, then regioselective readdition,[46] for example, would account for this isomerization product. The first step evidently occurs as a decomposition pathway for crude **17** and **18**. No trace (<5%) of **27** in purified **18**, however, is detected by NMR spectroscopy, even though all three ligand absorptions (**27**)[17] would have occurred in otherwise blank regions of the spectrum.

We expected **17** and **18** to be extremely sensitive toward electrophiles, given the high reactivity of α- and β-alkoxyethyl complexes. Acid or $Ph_3C^+PF_6^-$, for example, abstracts the α-alkoxide from **23** (eq 14) and generates ethylidene compounds **24**.[14,23a] Analogous β-methoxy complexes **28**, obtained by adding methoxide to $Fp(CH_2{=}CH_2)^+$[51] or by adding hydride to **19**[9] (eq 18), likewise transfer the β-methoxide to electrophiles. Both **17** and **18** accordingly afford vinyl ether complexes upon treating with $Ph_3C^+PF_6^-$ or with acid (eq 8 and 9).



(18)

The question of whether α- or β-alkoxide abstraction from **17** and **18** ensues was settled by studying **17**. Removal of α-ethoxide would generate **19** (Scheme IV), via an alkylidene–alkene isomerization of the β-methoxyethylidene intermediate, whereas loss of the β-methoxide would afford **20**. Treatment of **17** [containing less than 10% of its regioisomer $FpCH(OMe)CH_2(OEt)$] with $Ph_3C^+PF_6^-$ affords both vinyl ether salts **19** and **20**, although less than 12% of the product is **19**. Clearly β-alkoxide abstraction predominates, if not occurs exclusively, which agrees with Rosenblum's results, eq 16.

Conclusions

With conclusion of this work, we now delineate a network of coordinated ligand reactions (Scheme V) for selectively converting the methoxyacetyl ligand on Cp(L)(CO)Fe complexes [L = CO, PPh_3, $P(OMe)_3$] into the C_2 organics acetaldehyde, methoxyacetaldehyde, or methyl acetate.[10] (Compounds depicted in

(46) Rosenblum, M.; Bucheister, A.; Chang, T. C. T.; Cohen, M.; Marsi, M.; Samuels, S. B.; Scheck, D.; Sofen, N.; Watkins, J. C. *Pure Appl. Chem.* **1984**, *56*, 129.

(47) Finke, R. G.; McKenna, W. P.; Schiraldi, D. A.; Smith, B. L.; Pierpont, C. *J. Am. Chem. Soc.* **1983**, *105*, 7592. Finke, R. G.; Schiraldi, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 7605.

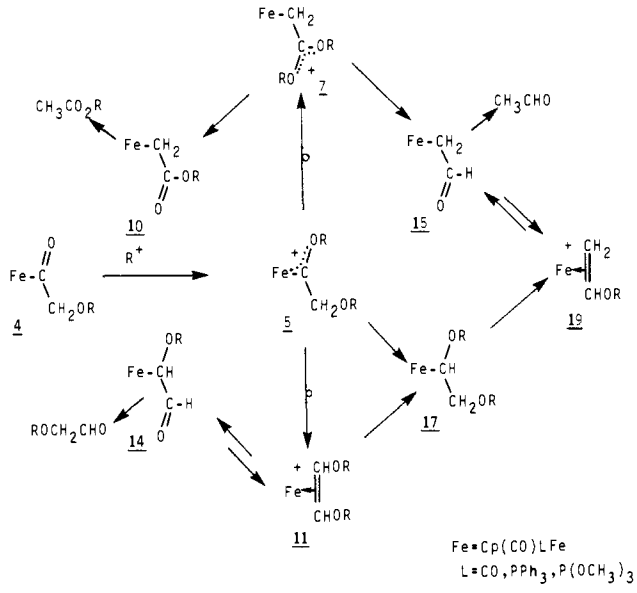
(48) (a) Rosenthal, A.; Koch, H. J. *Tetrahedron Lett.* **1967**, 871. (b) DeShong, P.; Slough, G. A.; Elango, V.; Trainor, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7788.

(49) Trainor, G. L.; Swart, B. E. *J. Org. Chem.* **1983**, *48*, 2447. Trainor, G. L. *J. Organomet. Chem.* **1985**, *282*, C43.

(50) An example of this reduction has been reported[10b] by using Cp(CO)[$P(OCH_3)_3$]$FeCH_2C(OCH_3)(OCH_2CH_3)^+PF_6^-$.

(51) 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 V



Scheme V are numbered as their Fp derivatives.) Carbocationic alkylating agents convert **4** into its α,β-dialkoxyethylidene complexes **5**, which can be reduced to the α,β-dialkoxyethyl compounds **17** (isolated for L = CO). These then convert either directly (L = PPh_3, $P(OCH_3)_3$) or indirectly via isolable **19** (L = CO) into their respective formylmethyl derivatives **15** and then (after protonating) acetaldehyde. Alternatively, **5** may rearrange to the (η^2-1,2-dialkoxyethylene) complex **11** (L = CO); this in turn provides its η^1-methoxyformylmethyl compound **14**, then methoxyacetaldehyde (after hydrolysis, protonation) or **17** (after reduction). Protonating **4** on the other hand delivers a α-hydroxy-β-methoxyethylidene salt that subsequently isomerizes to its ketene hemiacetal complex **7** [L = CO, PPh_3, $P(OMe)_3$]. These afford the carbalkoxymethyl ligand on **10**, which is a precursor to **15** or to methylacetate.

Complexes $FpCH(OR)CH_2OCH_3$ **17** and **18**, obtained by reducing either **5** or **11**, are stable once purified. Certainly, they are no less stable than other Fp-η^1-alkyl complexes bearing β-alkoxy substituents (e.g., **27** and **28**); all degrade or react with electrophiles via β-alkoxide cleavage. This β-alkoxide lability for **17** and **18** does not presage their isomerizing to formylmethyl acetal complexes **27** (eq 17), however. We must emphasize that analogous α,β-dihydroxyethyl complexes **3**, as with other α-hydroxyalkyl compounds,[52] should prove to be much less stable by virtue of having alternative degradation pathways available. They could, for example, homolytically cleave the metal–carbon σ-bond and generate a hydroxyalkyl radical $RCH(OH)^{\bullet}$,[47] or they could deinsert metal–hydride[2]—both reactions ultimately give free aldehyde. Nevertheless, it is conceivable that α,β-dialkoxyethyl complexes **17** and **18**, or other protected forms of α,β-dihydroxyethyl complexes **3**, could chain extend by successively incorporating CO, activating (with organic or other electrophiles), and then reducing the new acyl to homologous α, β, γ,··· alkoxyalkyl derivatives.[53] Work is in progress toward this goal using labile cobalt–carbonyl systems.

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Biphasic Kinetics and Temperature Dependence of Iron Removal from Transferrin by 3,4-LICAMS

Suzanne A. Kretchmar and Kenneth N. Raymond*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received March 3, 1986*

Abstract: The kinetics of iron removal from transferrin by the synthetic catechol sequestering agent *N,N',N''*-tris(5-sulfo-2,3-dihydroxybenzoyl)-1,5,10-triazadecane (3,4-LICAMS) have been investigated at pH 7.4 and a range of temperatures. In contrast to an earlier report, biphasic kinetics are observed for iron removal from diferric transferrin. This is attributed to kinetic inequivalence between the two sites, and the absorbance–time curves are fit to a model incorporating this assumption. Elucidation of the two observed macroscopic rate constants is achieved by exclusively labeling the individual sites of the protein with ^{55}Fe or ^{59}Fe. At 25 °C iron is removed from the N-terminal site at approximately twice the rate as from the C-terminal site. The two microscopic rate constants agree within experimental error with those obtained from the first-order processes of iron removal from N-terminal and C-terminal monoferric transferrins. The activation enthalpy for iron release from C-terminal monoferric transferrin by 3,4-LICAMS is 20 (1) kcal/mol over the entire range 4–20 °C. The corresponding values for N-terminal monoferric transferrin are 21 (2) kcal/mol below 20 °C and 15 (1) kcal/mol above 20 °C. These activation enthalpies agree with the observation that the rates of iron removal from the two monoferric transferrins are similar in the low-temperature regime but differ by a factor of about 2 in the high-temperature regime. It is proposed that the N-terminal site undergoes a conformational change at 20 °C which results in more facile iron release at physiological temperature.

Serotransferrin, the iron transport protein found in blood serum, has been well characterized.[1-4] The protein is bilobal, and each lobe contains an iron-binding site. Estimates of the metal–metal distance indicate that the sites are too distant (35 nm) for direct interaction.[1,5] Although similar, the two sites are not chemically identical.[6,7] For example, the C-terminal site has three more

* Author to whom correspondence should be addressed.

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