J. Am. Chem. Soc. **1986**, *108*, 1940-1949

Oxidatively Induced Insertion and Cleavage Reactions of Alkenyliron Complexes. New Routes to Highly Functionalized Alkenes

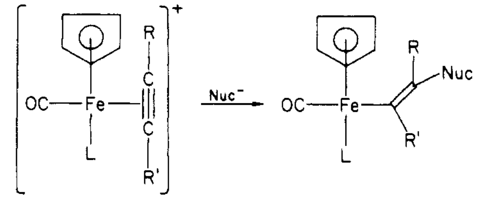
Daniel L. Reger,* Edward Mintz, and Lukasz Lebioda

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received July 12, 1985*

Abstract: Catalytic amounts of $[Cp_2Fe]BF_4$ or Ce(IV) in solution at −78 °C under CO at 1 atm converts $CpFeCO[P(OPh)_3](\eta^1\text{-}C(R_3){=}C(R_1)R_2)$ (R_1 cis to Fe) to $CpFeCO[P(OPh)_3](\eta^1\text{-}C(O)C(R_3){=}CR_1R_2)$ complexes in high yield. The stereochemistry of the products is dependent on the R groups. For most cases ($R_1 = R_3 = Me$, $R_2 = Me$, SPh, $CH(CO_2Et)_2$; $R_1 = H$, $R_2 = Me$, $R_3 = CO_2Me$; $R_1 = H_1$, $R_2 = Ph$, $R_3 = Me$; $R_1 = Ph$, $R_2 = Me$, $R_3 = Me$, Ph), the reaction proceeds with complete retention of the carbon–carbon double-bond stereochemistry. For $R_1 = Me$, $R_2 = Ph$, $R_3 = Me$, Ph and $R_1 = R_3 = Et$, $R_2 = Ph$ complexes, the stereochemistry of the double bond is reversed in the acyl products. These stereochemical assignments were made by carrying out the solid-state structures of $CpFeCO[P(OPh)_3](\eta^1\text{-}(Z)\text{-}C(O)C(Me){=}C(Ph)Me)$ and $CpFeCO[P(OPh)_3](\eta^1\text{-}(E)\text{-}C(O)C(Me){=}C(Me)SPh)$. The Lewis acid $AlCl_3$ also promotes this migratory insertion reaction, but a mixture of isomers of the acyl products are obtained in low yield. The conditions of 3–5 equiv of Ce(IV) in a mixed CH_2Cl_2/ROH solvent system at −78 °C under 1 atm of CO cleave the alkenyl ligand from iron to produce alkenyl esters in good yield. The stereochemistry of the esters parallels that outlined above for the alkenylacyl syntheses. These reaction conditions also convert the alkenylacyl complexes to alkenyl esters with complete retention of double-bond stereochemistry. Thus, highly functionalized alkenes can be selectively prepared by these methods.

The use of transition-metal organometallic complexes in both catalytic and stoichiometric syntheses of organic complexes is a growing and diverse field.[1] One area with considerable promise is the use of metal complexes to activated π-bonds toward nucleophilic addition reactions. Many different types of π-systems have been studied,[2] and a series of rules[3] have been developed for 18-electron cationic π-complexes that order the reactivity of unsaturated hydrocarbons. There have also been theoretical calculations on the origin of the activation by a metal, particularly in regard to addition reactions to η^2-alkene complexes.[4] Despite the great amount of activity in this area, prior to our studies, addition reactions with η^2-alkyne complexes leading to η^1-alkenylmetal complexes had only been briefly studied for two 16-electron systems. Chisholm and Clark[5] had reported the addition of alkoxides to Pt–alkyne complexes, and M. Green[6] had reported on the addition of hydride to Mo–alkyne complexes. These latter studies have been extended, but generally η^2-alkenyl complexes are isolated.[7]

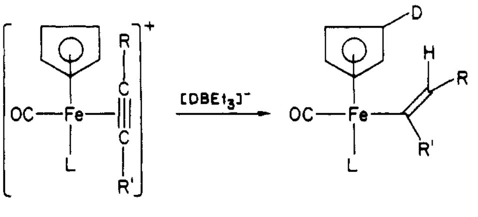
We have reported that a wide variety of nucleophiles will add to internal alkynes coordinated to cationic iron complexes, eq 1.[8,9] The reaction is stereoselective, as shown, with trans addition of the nucleophiles listed.[8c,9] It is also regioselective with the nucleophile adding away from an electron withdrawing ester group on the alkyne[8b] and at the alkyne carbon atom bearing a phenyl group.[8c]



(1)

L = PPh_3, $P(OPh)_3$
Nuc = Me, Ph, $CH(CO_2Et)_2$, $CH{=}CH_2$, $C{\equiv}CMe$, CN, SPh
R = R' = Me; R = Me, R' = CO_2Me; R = Ph, R' = Me

Surprisingly, hydride generally adds overall cis, eq 2, via a mechanism in which the hydride (or deuteride as shown in eq 2) reacts exo at the Cp ring followed by transfer of the endo hydrogen atom (from the C_5H_6 group formed in the addition step) to the alkyne ligand.[10]



(2)

L = PPh_3, $P(OPh)_3$
R = R' = Me; R = Me, R' = CO_2Me; R = Ph, R' = Me

Complexes containing a terminal alkenyl ligand can be prepared by addition to the η^2-allene complex, but as shown in eq 3, they rearrange[11] to *E*-internal alkenyl complexes.

Finally, alkenyl complexes can be prepared by the addition of anionic nucleophiles (or amines followed by base[12]) to vinylidene cations,[13] eq 4. This reaction places the nucleophile at the α-

---

(1) (a) Alper, H. "Transition Metal Organometallics In Organic Synthesis"; Academic Press: New York, 1976; Vol. 1. (b) Davies, S. G. "Organotransition Metal Chemistry: Applications to Organic Synthesis"; Pergamon Press: New York, 1982.

(2) Reference 1b, Chapter 4.

(3) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

(4) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

(5) (a) Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 2557. (b) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532. (c) Chisholm, M. H.; Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 1269.

(6) (a) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795. (b) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Bottrill, M.; Green, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 927.

(7) (a) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1267. (b) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V.; Manojlovic-Muir, L.; Muri, K. W. *J. Chem. Soc., Chem. Commun.* **1981**, 1059. (c) Davidson, J. L.; Vasapool, G.; Manojlovic-Muir, L.; Muri, K. W. *Ibid.* **1982**, 1025. (d) Allen, S. R.; Green, M.; Orpen, A. G.; Williams, I. D. *Ibid.* **1982**, 826. (e) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *Ibid.* **1985**, 435.

(8) (a) Reger, D. L.; McElligott, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5923. (b) Reger, D. L.; McElligott, P. J.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1982**, *1*, 443. (c) Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. A. *Ibid.* **1983**, *2*, 101.

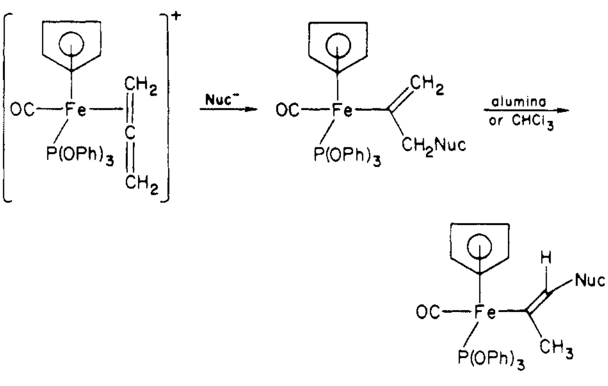
(9) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* **1984**, *3*, 134.

(10) Reger, D. L.; Belmore, K. A.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 5710.

(11) Reger, D. L.; Belmore, K. A. *Organometallics* **1985**, *4*, 305.

(12) Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics*, in press.

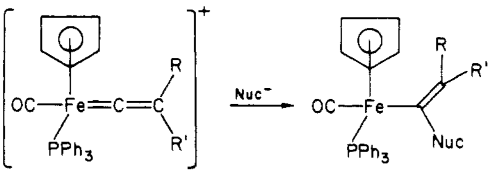
0002-7863/86/1508-1940$01.50/0



(3)

Nuc = Me, Ph, CH=CH$_2$, C≡CMe, SPh, H

alkenyl carbon atom whereas the chemistry shown in eq 1–3 place it at the β-alkenyl position.



(4)

R = R' = Me; Nuc = Ph, CH=CH$_2$, SPh
R = Ph, R' = Me; Nuc = Me

Thus, a variety of reactions are now well-developed for the preparation of tri- and tetrasubstituted alkenyliron complexes in which the type and location of the alkenyl substituents can be readily controlled. To be of use in organic syntheses, reactions that cleave the iron in a selective manner are needed. We have briefly reported on halide cleavage reactions,[8a] but generally these are not very successful. A better reaction would be cleavage of the iron group with concomitant formation of a new carbon–carbon bond on the alkene at the cleavage site. To this end, we report here that CO can be induced to undergo insertion into the iron–alkenyl bond using catalytic amounts of oxidant[14] or an equivalent of $AlCl_3$[15] to prepare alkenylacyliron complexes. In the presence of excess oxidant and an alcohol solvent,[16] alkenyl esters are prepared in good yield. Although the reactions are highly stereoselective, in certain cases the stereochemistry of the insertion process is surprising. In order to definitively assign the stereochemistry of the alkenylacyliron complexes, we report details on the crystal and molecular structure of CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(O)C(Me)=C(Ph)Me) and CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)SPh) as determined by X-ray crystallography. A communication on some of these findings has been published.[17]

Experimental Section

General Procedure. The iron–alkenyl complexes in eq 1[9] and eq 2[10,11] and cuprate reagents[9] were prepared via published procedures. Insertion and cleavage reactions were carried out under 1 atm of carbon monoxide. All other operations on organometallic compounds were conducted under a nitrogen atmosphere. All solvents were purified and degassed prior to use. In the alumina plug filtrations, elution with CH_2Cl_2 was continued until the washings were colorless. Column chromatography of organometallic complexes was carried out by using Alcoa F-20 alumina. Proton NMR spectra were recorded at 60 or 90 MHz, and chemical shifts are reported as δ vs. Me_4Si. Carbon-13 spectra were recorded at ca. −12 °C with proton decoupling at 20 MHz using $CDCl_3$ (δ 76.9) or CD_2Cl_2 (δ 53.8) as the solvent and internal standard and are also reported as δ vs. Me_4Si. The $AgBF_4$ was purchased from Ozark-Mahoning and was stored and weighed out in a drybox. Alkyllithium reagents and ceric-ammonium nitrate were purchased from Aldrich and CuCN from Fisher. Carbon monoxide was purchased from Matheson. Ferrocenium tetrafluoroborate[18] was prepared via literature procedures. Elemental analyses were performed by Robertson Laboratory. In the acyl preparations listed below, $[Cp_2Fe]^+$ is the preferred oxidant, if successful,[17] because Ce(IV) necessitates the use of an alcoholic cosolvent that can lead to some cleavage, yielding the alkenyl ester.

CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Ph)=C(Ph)Me). Cold (−78 °C) THF (50 mL) was added to a flask charged with [CpFeCO[P(OPh)$_3$](η^2-PhC≡CPh)]BF$_4$ (2.00 g, 2.76 mmol). To this mixture, a cold (−50 °C) THF solution of $Me_2Cu(CN)Li_2$ (2.76 mmol, 25 mL) was added. The resulting mixture was stirred cold (−78 °C) for 10 min and then removed from the bath and stirred an additional 50 min. The solvent was evaporated, affording a green oil. This oil was redissolved in CH_2Cl_2 (20 mL) and filtered through an alumina plug. The orange filtrate was collected and the solvent evaporated, affording an orange oil. This oil was dissolved in benzene (5 mL) and chromatographed on an alumina column (15 × 3 cm). Elution with 50% benzene/hexane developed a single yellow/orange band that was collected, and the solvent was evaporated, yielding an orange oil (1.62 g, 90%): ^{1}H NMR ($CDCl_3$) δ 7.2 (25, m, P(OPh)$_3$, Ph's), 4.12 (5, s, Cp), 1.78 (3, s, Me); IR (CH_2Cl_2) ν(CO) 1939 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 217.9 (d, J = 52 Hz, Fe—C≡O), 158.8 (d, J = 4.8 Hz, =*C*MePh), 151.6, 129.7, 122.0, 124.9 (d, s, s, d; J = 9.9, 3.9 Hz; P(OPh)$_3$), 151.6 (d, J = 1.2 Hz, C1 on α-Ph ring), 144.0 (s, C1 on β-Ph ring), 141.2 (d, J = 33 Hz, Fe—C=), 84.8 (s, Cp), 27.6 (d, J = 2.6 Hz, Me). There were an appropriate number of peaks corresponding to the remaining phenyl carbon atoms that were not definitively assigned. Anal. Calcd for $C_{39}H_{33}FeO_4P$: C, 71.79; H, 5.10. Found: C, 71.45; H, 5.35.

CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Ph)=C(H)Ph). Cold (−78 °C) THF (50 mL) was added to a flask charged with [CpFeCO[P(OPh)$_3$](η^2-PhC≡CPh)]BF$_4$ (1.50 g, 2.07 mmol). L-Selectride (2.4 mL of 1.0 M solution) was added to the cold (−78 °C) mixture with stirring. The resulting mixture was stirred at −78 °C for 10 min and then removed from the bath and stirred an additional 50 min. The solvent was evaporated, affording a green oil. This oil was redissolved in CH_2Cl_2 (20 mL) and filtered through an alumina plug. The orange filtrate was collected and the solvent evaporated, affording an orange oil. This oil was dissolved in benzene (5 mL) and chromatographed on an alumina column (17 × 3 cm). Elution with hexane (80 mL) and then 50% benzene/hexane developed one yellow band that was collected and the solvent evaporated, affording an orange oil (1.22 g, 92%): ^{1}H NMR ($CDCl_3$) δ 7.1 (26, m, P(OPh)$_3$, Ph's, =CH), 4.42 (5, s, Cp); IR (CH_2Cl_2) ν(CO) 1952 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 217.9 (d, J = 48 Hz, Fe—C≡O), 157.2 (d, J = 2.3 Hz, =*C*HPh), 157.0 (d, J = 41.6 Hz, Fe—C=), 151.4, 129.5, 124.6, 121.5 (d, s, s, d; J = 10.1, 3.9 Hz, P(OPh)$_3$), 139.2, 138.7, 128.0, 127.6, 127.4, 125.0, 123.7, 123.3 (d, d, s, s, s, s, s, s; J = 1.4, 7.9 Hz; Ph's), 83.6 (d, J = 1.4 Hz, Cp). Anal. Calcd for $C_{38}H_{31}FeO_4P$: C, 71.48; H, 4.89. Found: C, 71.37; H, 4.97.

The stereochemistry of this compound was confirmed by conducting an analogous reaction by using Superdeuteride in place of L-Selectride. Analysis of the product by ^{13}C NMR indicates that each Cp ring contains one deuterium atom with none located on the alkenyl ligand. Thus, the hydrogen atom on the alkenyl ligand was delivered in an intramolecular fashion as shown in eq 2, yielding the *E* isomer.[10]

CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Et)=C(Et)Ph). Cold (−78 °C) THF (40 mL) was added to a flask charged with [CpFeCO[P(OPh)$_3$](η^2-EtC≡CEt)]BF$_4$ (2.26 g, 3.6 mmol). A cold (−50 °C) THF solution (25 mL) of $Ph_2Cu(CN)Li_2$ (3.6 mmol) was added and the resulting solution stirred at −78 °C for 10 min and then removed from the cold bath and stirred an additional 50 min. Solvent evaporation afforded a green oil. This oil was dissolved in CH_2Cl_2 (25 mL) and filtered through an alumina plug. Elution with CH_2Cl_2 (ca. 60 mL) afforded an orange filtrate that, upon solvent evaporation, yielded an orange oil. This oil was dissolved in benzene (4 mL) and chromatographed on an alumina column (22 × 3 cm). Elution with 50% benzene/hexane developed a single orange band. This band was collected and the solvent evaporated, affording an orange oil (1.62 g, 73%): ^{1}H NMR (benzene-d_6) δ 7.2 (20, m, Ph), 4.43 (5, s, Cp), 2.82 (4, br m, CH$_2$'s), 1.03 (6, t, J = 9 Hz, Me's); IR (CH_2Cl_2) ν(CO) 1949 cm^{-1}; ^{13}C NMR (CD_2Cl_2) δ 220.1 (d, J = 51 Hz, Fe—C≡O), 151.7, 129.6, 124.6, 121.5 (d, s, s, d; J = 9.9, 4.3 Hz; P(OPh)$_3$), 147.7, 128.9, 127.6, 127.2 (all s, Ph), 147.5 (d, J = 2.5 Hz, =*C*EtPh), 143.5 (d, J = 39.6 Hz, Fe—C=), 84.4 (d, J = 1.7 Hz, Cp), 41.3, 35.5 (d, s; J = 4.3 Hz; CH$_2$'s), 15.6, 13.5 (s, s; Me's). Anal. Calcd

---

(13) Reger, D. L.; Swift, C. A. *Organometallics* **1984**, *3*, 876.

(14) (a) Magnuson, R. H.; Zulu, S.; Tsai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *Ibid.* **1982**, *104*, 5790. (c) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* **1983**, *2*, 460.

(15) (a) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766. (b) Butts, S. B.; Richmond, T. G.; Shriver, D. F. *Inorg. Chem.* **1981**, *20*, 278. (c) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093. (d) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272. (e) Lacroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312.

(16) Anderson, S. N.; Fong, C. W.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1973**, 163.

(17) Reger, D. L.; Mintz, E. *Organometallics* **1984**, *3*, 1759.

(18) Nesmeyanov, A. N.; Perevalova, E. G.; Yuryeva, L. P.; Grandberg, K. I. *Izv. Akad Nauk SSSR, Ser. Khim.* **1962**, 1772.

for $C_{36}H_{35}FeO_4P$: C, 69.91; H, 5.70. Found: C, 70.03; H, 5.80.

CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)SPh) (1). A CH_2Cl_2 solution of CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)SPh) (0.25 g, 0.40 mmol, 30 mL) and an EtOH solution of $(NH_4)_2Ce(NO_3)_6$ (0.03 g, 0.06 mmol, 10 mL) were prepared and placed under a CO atmosphere. Both flasks were cooled to -78 °C and the contents stirred vigorously for 30 min. While the CO atmosphere was maintained, the Ce(IV) solution was added, via cannula, to the iron–alkenyl solution. Upon addition of the oxidant, the solution became green/brown in color. The resulting solution was stirred at -78 °C under CO for 30 min and then removed from the cold bath and stirred an additional 40 min. The green/brown color quickly dissipated, and the solution became orange. The solvent was evaporated, affording an orange oil. This oil was dissolved in CH_2Cl_2 (15 mL) and filtered through an alumina plug. The orange filtrate was collected and the solvent evaporated, affording an orange oil. This oil was dissolved in benzene (4 mL) and chromatographed on an alumina column (23 × 2 cm). Elution with 50% benzene/hexane, 100% benzene, and finally CH_2Cl_2 developed two yellow bands. The first band was CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)SPh) and a small amount of the alkenyl ester cleavage product (vide infra). The second band was CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)SPh) (0.11 g, 42%): ^{1}H NMR ($CDCl_3$) δ 7.4 (20, m, P(OPh)$_3$, SPh), 4.23 (5, s, Cp), 2.2, 1.95 (3, 3; q, q; *J* = 1.5 Hz; Me's); IR (CH_2Cl_2) ν(CO) 1951 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 269.4 (d, *J* = 32.7 Hz, Fe*C*(O)C), 217.7 (d, *J* = 44.7 Hz, Fe—C≡O), 155.6 (d, *J* = 6 Hz, C(O)*C*=), 151.0, 129.5, 124.9, 121.6 (d, s, s, d; *J* = 8.3, 4.5 Hz; P(OPh)$_3$), 135.3, 128.7, 125.6, (all s; SPh), 117.5 (s, =*C*(Me)SPh), 84.1 (d, *J* = 1 Hz, Cp), 20.7, 18.5 (s, s; Me's). Anal. Calcd for $C_{35}H_{31}FeO_5PS$: C, 64.62; H, 4.80. Found: C, 64.46; H, 4.73.

CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)CH(CO$_2$Et)$_2$) (2). Separate CH_2Cl_2 solutions of CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)CH(CO$_2$Et)$_2$) (0.30 g, 0.45 mmol, 25 mL) and [Cp$_2$Fe]BF$_4$ (0.03 g, 0.09 mmol, 10 mL) were placed under a CO atmosphere (1 atm). Both solutions were cooled to -78 °C and stirred vigorously for 20 min. While the CO atmosphere was maintained, the [Cp$_2$Fe]BF$_4$ solution was added, via cannula, to the iron–alkenyl solution. Upon addition of the oxidant, the solution turned from orange to green. This solution was stirred at -78 °C under CO for 45 min and then removed from the cold bath and stirred an additional 40 min. During the course of the reaction, the green dissipated and the solution became light brown. The solution was filtered through an alumina plug (6 × 3 cm). An orange filtrate was collected and evaporation of the solvent afforded an orange oil. This oil was dissolved in benzene (4 mL) and chromatographed on an alumina column (22 × 2 cm). Elution with 100% benzene, CH_2Cl_2, and finally THF developed three yellow bands. The first band was Cp$_2$Fe. The second band was CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)CH(CO$_2$Et)$_2$) (0.02 g, 5%). The third band was CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)CH(CO$_2$Et)$_2$) (0.26 g, 82%): ^{1}H NMR ($CDCl_3$) δ 7.3 (15, m, P(OPh)$_3$), 4.27 (5, s, Cp), 4.23 (4, q, *J* = 9 Hz, OCH$_2$), 1.87, 1.82 (3, 3; s, s; vinyl-Me's), 1.30 (6, t, *J* = 9 Hz, CH$_2$*Me*); IR (CH_2Cl_2) ν(CO) 1952 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 269.8 (d, *J* = 32 Hz, Fe—*C*(O)C), 217.0 (d, *J* = 43.7 Hz, Fe—C≡O), 168.2 (s, CO$_2$), 151.5 (d, *J* = 5.7 Hz, FeC(O)*C*), 150.9, 129.2, 124.6, 121.3 (d, s, s, d; *J* = 8.7, 4.2 Hz; P(OPh)$_3$), 113.9 (s, =*C*(Me)CH(CO$_2$Et)$_2$), 84.0 (s, Cp), 61.1 (s, CH$_2$), 54.0 (s, CH), 15.9, 15.3 (s, s; vinyl-Me's), 13.8 (s, OCH$_2$*C*H$_3$). Anal. Calcd for $C_{36}H_{37}FeO_9P$: C, 61.72; H, 5.32. Found: C, 61.35; H, 5.49.

CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(H)Ph) (3). This compound was prepared in a manner similar to that for **1** using CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(H)Ph) (0.42 g, 0.73 mmol, 30 mL) and $(NH_4)_2Ce(NO_3)_6$ (0.06 g, 0.1 mmol, 10 mL). The oil obtained after the alumina plug filtration was dissolved in benzene (4 mL) and chromatographed on an alumina column (14 × 2 cm). Elution with benzene, 50% benzene/CH_2Cl_2, and finally 100% CH_2Cl_2 developed a single yellow band. This band was collected and the solvent evaporated, affording an orange oil (0.32 g, 73%): ^{1}H NMR (benzene-*d*$_6$) δ 7.4, 7.0 (21, m, P(OPh)$_3$, Ph, =CH), 4.17 (5, s, Cp), 2.13 (3, d, *J* = 1.5 Hz, Me); IR (CH_2Cl_2) ν(CO) 1951 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 269.5 (d, *J* = 33.6 Hz, Fe*C*(O)C), 218.2 (d, *J* = 46 Hz, Fe—C≡O), 153.3 (d, *J* = 6.4 Hz, C(O)*C*=), 151.4, 129.4, 128.0, 121.8 (d, s, s, d; *J* = 8.1, 4.1 Hz; P(OPh)$_3$), 137.3, 129.0, 126.7, 124.8 (all s; Ph), 130.0 (s, =*C*(H)Ph), 83.6 (d, *J* = 1.2 Hz, Cp), 15.1 (s, Me). Anal. Calcd for $C_{34}H_{29}FeO_5P$: C, 67.56; H 4.84. Found: C, 66.94; H, 5.27.

CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(CO$_2$Me)=C(H)Me) (4). This compound was prepared in a manner similar to that outlined for **2** using CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(CO$_2$Me)=C(H)Me) (0.43 g, 0.77 mmol, 25 mL) and [Cp$_2$Fe]BF$_4$ (0.04 g, 0.15 mmol, 10 mL). The oil obtained after alumina plug filtration was dissolved in 5 mL benzene and chromatographed on an alumina column (23 × 2 cm). Elution with 100% benzene, 50% benzene/CH_2Cl_2, 100% CH_2Cl_2 and 100% THF developed three yellow bands. The first yellow band was Cp$_2$Fe. The second was CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(CO$_2$Me)=C(H)Me) (0.12 g, 27%). The third band was CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(CO$_2$Me)=C(H)Me) (0.20 g, 44%): ^{1}H NMR ($CDCl_3$) δ 7.4 (15, m, P(OPh)$_3$), 6.1 (1, q, *J* = 6 Hz, =CH), 4.25 (5, s, Cp), 3.75 (3, 5, OMe), 1.9 (3, d, *J* = 6 Hz, =CMe); IR (CH_2Cl_2) ν(CO) 1949 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 261.6 (d, *J* = 35.5 Hz, Fe*C*(O)C), 217.6 (d, *J* = 44.6 Hz, Fe—C≡O), 167.2 (s, CO$_2$Me), 151.1, 129.4, 124.8, 121.7 (d, s, s, d; *J* = 8.3, 4.3 Hz; P(OPh)$_3$), 150.5 (s, *C*(CO$_2$Me)=), 134.9 (s, =*C*(H)Me), 83.9 (d, *J* = 1.2 Hz, Cp), 51.5 (s, OMe), 14.9 (s, =C(H)*C*H$_3$).

CpFeCO[P(OPh)$_3$](η^1-C(O)C(Me)=CMe$_2$) (5). This compound was prepared in a manner similar to that outlined for **2** using CpFeCO[P(OPh)$_3$](η^1-C(Me)=CMe$_2$) (0.60 g, 1.14 mmol, 25 mL) and [Cp$_2$Fe]BF$_4$ (0.06 g, 0.23 mmol, 10 mL). The oil obtained from alumina plug filtration was dissolved in 4 mL of benzene and chromatographed on an alumina column (22 × 2 cm). Elution with 50% benzene/hexane, 100% benzene, and finally 100% CH_2Cl_2 developed three yellow bands. The first band was Cp$_2$Fe. The second was starting material CpFeCO[P(OPh)$_3$](η^1-C(Me)=CMe$_2$) (0.03 g, 5%). The third band was CpFeCO[P(OPh)$_3$](η^1-C(O)C(Me)=CMe$_2$) (0.34 g, 53%): ^{1}H NMR (benzene-*d*$_6$) δ 7.5, 7.1 (15, m, P(OPh)$_3$), 4.13 (5, s, Cp), 2.03, 1.97, 1.63 (3, 3, 3; s, s, s; Me's); IR (CH_2Cl_2) ν(CO) 1952 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 270.5 (d, *J* = 31.8 Hz, Fe*C*(O)C), 218 (d, *J* = 45.1 Hz, Fe—C≡O), 151.1, 129.3, 124.6, 121.6 (d, s, s, d; *J* = 8.3, 4.0 Hz; P(OPh)$_3$), 146.4 (d, *J* = 5.9 Hz, FeC(O)*C*), 118.9 (s, =*C*Me$_2$), 83.9 (s, Cp), 21.3, 19.6, 15.7 (s, s, s; Me's). Anal. Calcd for $C_{30}H_{29}FeO_5P$: C, 64.76; H, 5.25. Found: C, 63.89; H, 5.25.

CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(O)C(Me)=C(Ph)Me) (6). This compound was prepared in a manner similar to that outlined for **2** using CpFeCO[P(OPh)$_3$](η^1-(*E* or *Z*)-C(Me)=C(Me)Ph) (1.26 g, 2.14 mmol, 25 mL) and [Cp$_2$Fe]BF$_4$ (0.06 g, 0.2 mmol, 15 mL). The oil obtained after alumina plug filtration and solvent evaporation was dissolved in benzene (4 mL) and chromatographed on an alumina column (23 × 3 cm). Elution with 50% benzene/hexane followed by 100% benzene and finally 100% CH_2Cl_2 developed two yellow bands. The first yellow band was Cp$_2$Fe. The second was the acyl product (1.19 g, 90%): ^{1}H NMR ($CDCl_3$) δ 7.4 (20, m, P(OPh)$_3$, Ph), 3.60 (5, s, Cp), 2.03, 1.95 (3, 3; s, s; Me's); IR (CH_2Cl_2) ν(CO) 1955 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 274.4 (d, *J* = 32.5 Hz, Fe—*C*(O)C), 218.3 (d, *J* = 43.9 Hz, Fe—C≡O), 151.1, 129.4, 124.7, 121.5 (d, s, s, d; *J* = 8.4, 4.4 Hz; P(OPh)$_3$), 151.1 (s, Fe—C(O)*C*), 144.1, 129.9, 127.6, 126.5 (all s, Ph), 123.9 (s, =*C*(Ph)Me), 84.5 (s, Cp), 20.1, 17.2 (s, s; Me's). Anal. Calcd for $C_{35}H_{31}FeO_5P$: C, 67.97; H, 5.05. Found: C, 68.05, H, 5.12.

CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(O)C(Ph)=C(Ph)Me) (7). This compound was prepared in a manner similar to that outlined for **1** using CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Ph)=C(Ph)Me) (0.18 g, 0.28 mmol, 25 mL) and $(NH_4)_2Ce(NO_3)_6$ (0.02 g, 0.04 mmol, 5 mL). The orange oil obtained after the alumina plug filtration was dissolved in benzene (4 mL) and chromatographed on an alumina column (23 × 2 cm). Elution with 50% benzene/hexane, 100% benzene, and finally 100% CH_2Cl_2 developed two yellow bands. The first yellow (faint) band was starting material. The second yellow band was CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(O)C(Ph)=C(Ph)Me) (0.16 g, 0.24 mmol, 84%): ^{1}H NMR ($CDCl_3$) δ 7.2 (25, m, P(OPh)$_3$, Ph's), 3.58 (5, s, Cp), 1.9 (3, s, Me); IR (CH_2Cl_2) ν(CO) 1949 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 269.9 (d, *J* = 34 Hz, Fe—*C*(O)C), 218.9 (d, *J* = 43 Hz, Fe—C≡O), 155.6 (d, *J* = 5.6 Hz, FeC(O)*C*). 150.8, 129.0, 124.4, 121.6 (d, s, s, d; *J* = 8.2, 4.5 Hz; P(OPh)$_3$), 143.7, 136.4 (s, s; Ph's), 84.7 (s, Cp), 21.5 (s, Me). There were an appropriate number of peaks for the remaining phenyl carbons that were not definitively assigned. Anal. Calcd for $C_{40}H_{33}FeO_5P$: C, 70.60; H, 4.89. Found: C, 69.94; H, 5.11. Similar results were obtained starting with a *E*:*Z* (5:1) mixture of the iron–alkenyl complex.

CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(O)C(Et)=C(Ph)Et) (8). This compound was prepared in a manner similar to that outlined for **2** using CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Et) =C(Et)Ph) (0.50 g, 0.81 mmol, 20 mL) and [Cp$_2$Fe]BF$_4$ (0.040 g, 0.16 mmol, 15 mL). The oil obtained from the alumina plug filtration was chromatographed on an alumina column (22 × 2 cm). Elution with 50% benzene/hexane, 100% benzene, and finally CH_2Cl_2 developed two yellow bands. The first band was Cp$_2$Fe. The second yellow band was CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(O)C(Et)=C(Ph)Et) (0.43 g, 82%): ^{1}H NMR ($CDCl_3$) δ 7.3 (20, m, P(OPh)$_3$, Ph), 3.57 (5, s, Cp), 2.45 (4, m, CH$_2$'s), 1.13, 0.96 (3, 3; t, t; *J* = 9 Hz; Me's). IR (CH_2Cl_2) ν(CO) 1957 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 271.2 (d, *J* = 32 Hz, Fe—*C*(O)C), 218.5 (d, *J* = 44 Hz, Fe—C≡O), 156.0 (d, *J* = 5.2 Hz, C(O)*C*=), 151.1, 129.4, 124.6, 121.4 (d, s, s, d; *J* = 8.0, 4.6 Hz; P(OPh)$_3$), 142.6, 130.5, 128.9, 127.5 (all s, Ph), 126.3 (s, *C*(Ph)Et), 84.4 (s, Cp), 26.3, 21.3 (s, s; CH$_2$'s), 14.2, 13.8 (s, s; Me's).

CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)Ph) (9). A CH_2Cl_2 (15 mL) solution of CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)Ph) (0.90 g, 1.5 mmol) and a CH_2Cl_2 (15 mL) mixture of $AlCl_3$ (0.20 g, 1.5

mmol) were prepared separately and placed under a CO atmosphere. Both flasks were cooled to −78 °C and the contents stirred for 30 min. The iron–alkenyl solution was transferred, via cannula, to the AlCl$_3$ mixture. This was stirred at −78 °C for 20 min and then the flask was removed from the cold bath and stirred an additional 40 min. During the course of the reaction, the solution became red/brown. The solution was filtered through an alumina plug (6 × 3 cm). Elution with CH$_2$Cl$_2$ afforded an orange filtrate that, upon solvent evaporation, yielded an orange oil. This oil was dissolved in benzene (4 mL) and chromatographed on an alumina column (20 × 2 cm). Elution with 50% benzene/hexane, 100% benzene, and finally CH$_2$Cl$_2$ developed a single yellow band. This band was collected in two fractions and the solvent evaporated, affording orange oils. The first fraction was a mixture of (*E*)- and (*Z*)-CpFeCO[P(OPh)$_3$](η^1-C(O)C(Me)=C(Me)Ph) in a 9:1 ratio (0.32 g, 0.52 mmol). The second fraction was pure CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)Ph) (0.12 g, 0.20 mmol). Repeated chromatography of the first fraction allowed isolation of pure E isomer in a combined 43% yield (0.41 g): ^{1}H NMR (CDCl$_3$) δ 7.4 (20, m, P(OPh)$_3$, Ph), 4.27 (5, s, Cp), 2.03, 1.80 (3, 3: br s, br s; Me's); IR (CH$_2$Cl$_2$) ν(CO) 1954 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 271.7 (d, *J* = 31.9 Hz, Fe*C*(O)C), 218.0 (d, *J* = 44.6 Hz, Fe—C$\equiv$O), 151.0, 128.2, 124.7, 121.6 (d, s, s, d; *J* = 8.1, 4.1 Hz; P(OPh)$_3$), 143.5 (s, C(O)*C*=), 129.8, 127.9, 126.4, 126.0 (all s, Ph), 122.8 (s, =*C*(Me)Ph), 84.0 (s, Cp), 21.2, 17.5 (s, s; Me's).

CpFe(CO)$_2$(η^1-C(O)C(CO$_2$Me)=CMe$_2$). This complex was prepared in a manner similar to that outlined for **2** using CpFeCO[P(OPh)$_3$](η^1-C(CO$_2$Me)=CMe$_2$) (0.51 g, 0.9 mmol, 15 mL) and [Cp$_2$Fe]BF$_4$ (0.05 g, 0.18 mmol, 15 mL). The oil obtained from the alumina plug filtration was dissolved in benzene (4 mL) and chromatographed on an alumina column (22 × 2 cm). Elution with 30% CH$_2$Cl$_2$/benzene, 100% CH$_2$Cl$_2$, and 100% THF developed three yellow bands. The first was Cp$_2$Fe. The second was CpFeCO[P(OPh)$_3$](η^1-C(CO$_2$Me)=CMe$_2$) (0.02 g, 4%). The third was CpFe(CO)$_2$(η^1-C(O)C(CO$_2$Me)=CMe$_2$) (0.27 g, 94%): ^{1}H NMR (CDCl$_3$) δ 4.87 (5, s, Cp), 3.75 (3, s, OMe), 2.05, 1.78 (3, 3; s, s; Me's); IR (CH$_2$Cl$_2$) ν(CO) 2012, 1967 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 256.8 (s, Fe—*C*(O)C), 213.6 (s, Fe(CO)$_2$), 164.3 (s, *C*O$_2$Me), 139.4 (s, C(O)*C*=), 129.4 (s, =*C*Me$_2$), 86.7 (s, Cp), 51.3 (s, OMe), 22.2, 21.0 (s, s; Me's); mass spectrum (CI, CH$_4$), *m*/*e* 319 (M$^+$ + 1), 290 (M$^+$ − CO), 263 (M$^+$ + 1 − (CO)$_2$), 205 (M$^+$ − C$_6$H$_9$O$_2$), 177 (M$^+$ − C$_7$H$_9$O$_3$).

Isomerization of CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Me)=C(Ph)Me). Separate CH$_2$Cl$_2$ solutions of CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Me)=C(Ph)Me) (0.20 g, 0.34 mmol, 20 mL) and [Cp$_2$Fe]BF$_4$ (0.02 g, 0.07 mmol, 20 mL) were prepared under a N$_2$ atmosphere. After both solutions were cooled to −78 °C, the [Cp$_2$Fe]BF$_4$ solution was added via cannula to the alkenyl complex with stirring. Upon addition of the oxidant, the solution turned from orange to green, which dissipated quickly. The solution was stirred for 10 min at −78 °C and then warmed to ambient temperature. The solution was then filtered through an alumina plug followed by elution with CH$_2$Cl$_2$. The orange filtrate was collected, and the solvent was evaporated, affording an orange oil. This oil was chromatographed on a short alumina column. Elution with 50% benzene/hexane developed a single yellow band that was collected, and the solvent was evaporated, affording an orange oil of CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)Ph) (0.18 g, 90%): ^{1}H NMR (CDCl$_3$) δ 7.1 (20, m, P(OPh)$_3$, Ph), 4.33 (5, s, Cp), 2.20, 2.00 (3, 3; br s; Me's); IR (hexane) ν(CO) 1946 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 219.6 (d, *J* = 50.7 Hz, CO), 151.8, 129.5, 124.7, 121.8 (d, s, d, d; *J* = 10.4, 0.8, 3.7 Hz; P(OPh)$_3$), 149.1 (d, *J* = 3.1 Hz, =*C*(Me)Ph), 141.4, 128.6, 127.8, 121.5 (all s, =C*Ph*), 137.7 (d, *J* = 34.2 Hz, FeC=), 84.4 (d, *J* = 1.8 Hz, Cp), 36.1, 29.7 (d, s; *J* = 4.9 Hz, Me's).

Isomerization of CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Ph)=C(Ph)Me). Separate CH$_2$Cl$_2$ solutions of CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Ph)=C(Ph)Me) (0.35 g, 0.54 mmol, 25 mL) and [Cp$_2$Fe]BF$_4$ (0.03 g, 0.11 mmol, 20 mL) were prepared under a N$_2$ atmosphere. Both solutions were cooled to −78 °C, and the oxidant was added to the alkenyl solution via cannula. This solution was stirred at −78 °C for 10 min and then warmed to ambient temperature and filtered through an alumina plug, washing with CH$_2$Cl$_2$. Evaporation of the solvent afforded an orange oil. This oil was chromatographed on an alumina column (20 × 1.9 cm). Elution with 50% benzene/hexane developed a single yellow band that, upon solvent evaporation, afforded an orange oil that was a 5:1 mixture of CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Ph)=C(Me)Ph) and CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Ph)=C(Ph)Me) (combined 0.31 g, 89%). CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Ph)=C(Ph)Me): ^{1}H NMR (CDCl$_3$) δ 7.2 (25, m, P(OPh)$_3$, Ph's), 4.12 (5, s, Cp), 1.78 (3, s, Me). CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Ph)=C(Me)Ph): ^{1}H NMR (CDCl$_3$) δ 7.23, 6.9 (25, m, P(OPh)$_3$, Ph's), 4.52 (5, s, Cp), 2.53 (3, s, Me).

Cleavage Reactions. A detailed procedure for the cleavage reactions is outlined for (*Z*)-EtO$_2$C(Me)C=C(Ph)Me. Subsequent cleavage reactions follow the same general procedure with the necessary changes indicated.

(*Z*)-EtO$_2$C(Me)C=C(Ph)Me. CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)Ph) (0.48 g, 0.81 mmol) was dissolved in a CH$_2$Cl$_2$/EtOH solution (12 mL, 1:1) and placed under a CO atmosphere. (NH$_4$)$_2$Ce(NO$_3$)$_6$ (1.11 g, 2.02 mmol) was dissolved in EtOH (30 mL) under a CO atmosphere. Both flasks were cooled to −78 °C and the solutions stirred vigorously for 30 min. While the CO atmosphere was maintained, the Ce(IV) solution was added, via cannula, to the iron–alkenyl solution. This solution was stirred at −78 °C for 40 min and then removed from the cold bath and stirred an additional 45 min. The solvent was evaporated, affording a brown oil. This oil was dissolved in CH$_2$Cl$_2$ (15 mL) and filtered through an alumina plug (7 × 3 cm). Elution with CH$_2$Cl$_2$ (60 mL) afforded a clear, faint-yellow filtrate. Solvent evaporation yielded an oil that was a mixture of (*Z*)- and (*E*)-EtO$_2$C(Me)C=C(Me)Ph in a 9:1 ratio. The oil was chromatographed on a silica gel column. Elution with 5% Et$_2$O/hexane afforded, after solvent evaporation, (*Z*)-EtO$_2$C(Me)C=C(Ph)Me (0.10 g, 61%): ^{1}H NMR (CDCl$_3$) δ 7.3 (5, m, Ph), 3.83 (2, q, *J* = 7 Hz, OCH$_2$), 2.12, 2.03 (3, 3; s, s; Me's), 0.83 (3, t, *J* = 7 Hz, OCH$_2$*Me*). These values correspond well to literature values.[19] Mass spectrum, *m*/*e* 204 (molecular ion). The pure *Z* isomer is also obtained by an analogous oxidative cleavage of CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(O)C(Me)=C(Ph)Me).

(*E*)-MeO$_2$C(Me)C=C(Me)Ph. This compound was prepared as above using CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)Ph) (0.10 g, 0.16 mmol, 8 mL) and (NH$_4$)$_2$Ce(NO$_3$)$_6$, (0.23 g, 0.42 mmol) in MeOH. The oil obtained from the alumina plug filtration was dissolved in Et$_2$O (2 mL) and chromatographed on a silica gel column. Elution with 5% Et$_2$O/hexane afforded, after solvent evaporation, (*E*)-MeO$_2$C(Me)C=C(Me)Ph as an oil (0.02 g, 66%): ^{1}H NMR (CDCl$_3$) δ 7.4 (5 m, Ph), 3.8 (3, s, OMe), 2.30, 1.77 (3, 3; q, q; *J* = 1.5 Hz; Me's); mass spectrum, *m*/*e* 190 (molecular ion). The ^{1}H NMR spectrum corresponds well with literature values.[19]

(*Z*)-MeO$_2$C(Me)C=C(Ph)Me. This compound was prepared as above using CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)Ph) (1.18 g, 2.0 mmol) in CH$_2$Cl$_2$/MeOH (15 mL, 1:1) and (NH$_4$)$_2$Ce(NO$_3$)$_6$ (2.74 g, 5.0 mmol) in MeOH (35 mL). The oil obtained from the alumina plug filtration was a mixture of (*Z*)- and (*E*)-MeO$_2$C(Me)C=C(Me)Ph in a 9:1 ratio. This oil was chromatographed on silica gel. Elution with 5% Et$_2$O/hexane afforded, after solvent evaporation, a mixture of *Z* and *E* isomers in a 9:1 ratio (0.31 g, 81% overall): *Z* isomer ^{1}H NMR (CDCl$_3$) δ 7.4 (5, m, Ph), 3.4 (3, s, OMe), 2.07, 2.0 (3, 3; s, s; Me's). *E* isomer ^{1}H NMR (CDCl$_3$) δ 7.4 (5, m, Ph), 3.8 (3, s, OMe), 2.3, 1.77 (3, 3; q, q; *J* = 1.5 Hz, Me's). These values correspond well to literature values.[20] Mass spectrum, *m*/*e* 190 (molecular ion).

(*E*)-EtO$_2$C(Me)C=C(H)Ph. This compound was prepared as above using CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(H)Ph) (0.40 g, 0.69 mmol) in CH$_2$Cl$_2$/EtOH (10 mL, 1:1) and (NH$_4$)$_2$Ce(NO$_3$)$_6$ (1.14 g, 2.08 mmol) in EtOH (30 mL). The oil obtained from the alumina plug filtration was chromatographed on a silica gel column. Elution with 10% Et$_2$O/hexane afforded, after solvent evaporation, the desired compound as an oil (0.10 g, 77%): ^{1}H NMR (CDCl$_3$) δ 7.67 (1, q, *J* = 2 Hz, HC=), 7.3 (5, m, Ph), 4.23 (2, q, *J* = 7 Hz, OCH$_2$), 2.1 (3, d, *J* = 2 Hz, C*Me*=), 1.3 (3, t, *J* = 7 Hz, OCH$_2$*Me*). These values correspond well to literature values.[21] Mass spectrum, *m*/*e* 190 (molecular ion).

(*E*)-EtO$_2$C(Me)C=C(Me)SPh. This compound was prepared as above using CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(Me)SPh) (0.31 g, 0.50 mmol) in CH$_2$Cl$_2$/EtOH (15 mL, 1:1) and (NH$_4$)$_2$Ce(NO$_3$)$_6$ (0.82 g, 1.50 mmol) in EtOH (30 mL). The oil obtained from the alumina plug filtration was chromatographed on silica gel. Elution with 10% Et$_2$O/hexane afforded, after solvent evaporation, a clear, light-yellow oil that was a mixture of (*E*)- and (*Z*)-EtO$_2$C(Me)C=C(Me)SPh in a 10:1 ratio (0.11 g, 93%): *E* isomer ^{1}H NMR (CDCl$_3$) δ 7.35 (5, m, SPh), 4.2 (2, q, *J* = 7 Hz, OCH$_2$), 2.13, 2.08 (3, 3; q, q; *J* = 1.5 Hz; vinyl-Me's), 1.30 (3, t, *J* = 7 Hz, OCH$_2$*Me*). Z isomer ^{1}H NMR (CDCl$_3$) δ 1.97, 1.83 (3, 3; s, s; vinyl-Me's). These values correspond well to literature values.[22] Mass spectrum, *m*/*e* 236 (molecular ion). The pure *E* isomer is formed from an analogous oxidative cleavage with CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)SPh).

(*E*)-MeO$_2$C(Ph)C=C(H)Ph. This compound was prepared as above using CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Ph)=C(H)Ph) (0.69 g, 1.08 mmol) in MeOH/CH$_2$Cl$_2$ (20 mL, 1:1) and (NH$_4$)$_2$Ce(NO$_3$)$_6$ (2.96 g, 5.4 mmol) in MeOH (30 mL). The oil obtained from the alumina plug filtration was dissolved in Et$_2$O (3 mL) and chromatographed on a silica

---

(19) Baboulene, M.; Sturtz, G. *J. Organomet. Chem.* **1979**, *177*, 27.

(20) Jackman, L. M.; Lown, J. W. *J. Chem. Soc.* **1962**, 1776.

(21) Tanaka, K.; Yamagishi, N.; Tanikaga, R.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1979**, *52* (12), 3619.

(22) Chalchat, J. C.; Theron, F. *Bull. Soc. Chim. Fr.* **1974**, *5–6*, 953.

gel column (20 × 2 cm). Elution with 5% Et_2O/hexane afforded a clear oil (0.19 g, 74%): ^1H NMR ($CDCl_3$) δ 7.9 (1, s, =CH), 7.3 (10, m, Ph's), 3.8 (3, s, OMe). These values correspond well to literature values.[23] Mass spectrum, m/e 238 (molecular ion).

(*Z*)-$EtO_2C(Ph)C{=}C(Ph)Me$. This compound was prepared as above using $CpFeCO[P(OPh)_3](\eta^1$-(*Z*)-C(Ph)=C(Ph)Me) (0.90 g, 1.4 mmol) in $EtOH/CH_2Cl_2$ (15 mL, 1:1) and $(NH_4)_2Ce(NO_3)_6$ (4.19 g, 7.64 mmol) in EtOH (35 mL). The oil obtained from the alumina plug filtration was dissolved in Et_2O (3 mL) and chromatographed on a silica gel column (20 × 2 cm). Elution with 10% Et_2O/hexane afforded, after solvent evaporation, a clear oil (0.16 g, 44%): ^1H NMR ($CDCl_3$) δ 7.4 (10, m, Ph's), 3.92 (2, q, J = 7 Hz, OCH_2), 2.07 (3, s, Me), 0.88 (3, t, J = 7 Hz, OCH_2Me). These values correspond well to literature values.[24] Mass spectrum, m/e 266 (molecular ion).

(*Z*)-$MeO_2C(Et)C{=}C(Ph)Et$. This compound was prepared as above using $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-C(Et)=C(Et)Ph) (0.40 g, 0.64 mmol) in $MeOH/CH_2Cl_2$ (10 mL, 1:1) and $(NH_4)_2Ce(NO_3)_6$ (1.05 g, 1.92 mmol) in MeOH (25 mL). The oil obtained from the alumina plug filtration was dissolved in Et_2O (3 mL) and chromatographed on a silica gel column (17 × 2 cm). Elution with 10% Et_2O/hexane afforded, after solvent evaporation, a clear oil (0.13 g, 92%): ^1H NMR (benzene-d_6) δ 7.2, 6.9 (5, m, m; Ph), 2.9 (3, s, OMe), 2.17, 2.0 (2, 2; q, q; J = 7 Hz, CH_2), 0.83, 0.53 (3, 3; t, t; J= 7 Hz, Me's); mass spectrum, m/e 218 (molecular ion).

(*E*)-$EtO_2C(Me)C{=}C(Me)CH(CO_2Et)_2$. This compound was prepared as above using $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-C(Me)=C(Me)CH($CO_2Et)_2$) (0.38 g, 0.57 mmol) in $EtOH/CH_2Cl_2$ (15 mL, 1:1) and $(NH_4)_2Ce(NO_3)_6$ (0.62 g, 1.14 mmol) in EtOH (25 mL). Elution of the silica gel column with 30% Et_2O/hexane afforded, after solvent evaporation, an oil (0.10 g, 61%): ^1H NMR ($CDCl_3$) δ 4.53 (1, s, CH), 4.23 (6, q, J = 9 Hz, OCH_2), 2.07, 1.95 (3, 3; q, q; J = 2 Hz; vinyl-Me's), 1.3 (9, t, J = 9 Hz, OCH_2Me); mass spectrum, m/e 286 (molecular ion).

$EtO_2C(MeO_2C)C{=}CMe_2$. This compound was prepared as above using $CpFeCO[P(OPh)_3](\eta^1$-C(CO_2Me)=CMe_2) (0.34 g, 0.59 mmol) in $EtOH/CH_2Cl_2$ (15 mL, 1:1) and $(NH_4)_2Ce(NO_3)_6$ (0.97 g, 1.77 mmol) in EtOH (25 mL). Elution of the silica gel column with 15% Et_2O/hexane afforded, after solvent evaporation, an oil (0.10 g, 98%): ^1H NMR ($CDCl_3$) δ 4.27 (2, q, J = 6 Hz, OCH_2), 3.8 (3, s, OMe), 2.1 (6, s, Me's), 1.33 (3, t, J = 6 Hz, OCH_2Me).

$EtO_2C(Ph_2NCH_2)C{=}CH_2$. This compound was prepared as above using $CpFeCO[P(OPh)_3](\eta^1$-C(CH_2NPh_2)=CH_2)[12] (0.93 g, 1.4 mmol) in $EtOH/CH_2Cl_2$ (15 mL, 1:1) and $(NH_4)_2Ce(NO_3)_6$ (1.54 g, 2.8 mmol) in EtOH (25 mL). The oil obtained from the alumina plug filtration was dissolved in Et_2O (3 mL) and chromatographed on a silica gel column. Elution with 10% Et_2O/hexane afforded, after solvent evaporation, an oil (0.25 g, 64%): ^1H NMR ($CDCl_3$) δ 7.1 (10, m, Ph's), 6.27, 5.8 (1, 1; m, m; =CH_2), 4.63 (2, dd, J = 1 Hz, CH_2N), 4.23 (2, q, J = 7 Hz, OCH_2), 1.3 (3, t, J = 7 Hz, OCH_2Me); mass spectrum, m/e 281 (molecular ion).

X-ray Structure Determinations. Crystals of $CpFeCO[P(OPh)_3](\eta^1$-(*Z*)-C(O)C(Me)=C(Ph)Me) are monoclinic, space group $P2_1/n$, with a = 18.940 (4) Å, b = 15.875 (4) Å, c = 10.286 (3) Å, V = 3070 (1) Å^3, β = 97.01 (4)°, Z = 4, D_x = 1.34 g cm^{-3}, λ = 0.71073 Å, linear absorption coefficient μ = 5.80 cm^{-1}, F_w = 618,46, and T = 291 K. The crystals were grown from hot–cold hexane. A prismatic crystal with dimensions 0.4 × 0.4 × 0.4 mm enclosed by faces {100}, {010}, and {001} was mounted in a glass capillary and used for all measurements. The data were collected with an Enraf-Nonius CAD-4 diffractometer, graphite monochromator; 25 general reflections used for orientation matrix and parameter measurements; $\omega - 2\theta$ scan mode, 0.80° + 0.35° tan θ scan range, variable scan speed; orientation checked every 100 reflections; intensity of three standard reflections were monitored every 2.5 h of exposure time. The crystals showed very little decay in the X-ray beam over 141 h of exposure. The corrections for decay were applied (max = 1.005, av = 1.003). Reflections (5562) were measured in the $3° < 2\theta < 50°$ range, with 253 symmetry equivalent. In a merge procedure, they provided 5393 unique values and R_{merge} = 1.8%. Reflections (3478) with $I > 3\sigma(I)$ were considered observed; absorption corrections were applied with minimum, maximum, and average transmission factors 0.891, 1.067, and 0.992, respectively. The iron atom position was determined from a Patterson map; the rest of the structure was found in difference Fourier maps. The structure was refined by full-matrix least-squares, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma^2(F) + 0.0004F^2)^{-1}$ with anisotropic temperature factors for all non-H atoms. In the difference Fourier maps, the methyl hydrogen atoms corresponded to the highest peaks. The hydrogen atoms bonded to the carbon atoms of the aromatic rings were used for structure factor calculations in the calculated positions. H-atom parameters were not refined. The final R = 0.034, wR = 0.036, and S = 1.77. On the final difference Fourier map, the maximum was 0.28 e Å^{-3} and was in the vicinity of iron.[25] The atomic coordinates are listed in Table I; important bond distances and angles are in Table III. An ORTEP drawing[26] of the molecule is shown in Figure 1 (33% probability).

Table I. Positional Parameters and Their Estimated Standard Deviations of $CpFeCO[P(OPh)_3](\eta^1$-(*Z*)-C(O)C(Me)=C(Ph)Me)

atom	x	y	z	B_{eqv} (Å^2)
Fe(1)	0.24282 (2)	0.02576 (3)	0.14133 (4)	3.354 (8)
P(1)	0.34588 (4)	0.07832 (5)	0.16692 (8)	3.15 (2)
O(1)	0.2747 (1)	−0.0808 (2)	0.3671 (3)	5.50 (6)
O(2)	0.1836 (2)	0.1840 (2)	0.1809 (3)	6.03 (7)
O(20)	0.4071 (1)	0.0345 (1)	0.0938 (2)	3.80 (5)
O(30)	0.3619 (1)	0.1733 (1)	0.1273 (2)	3.91 (5)
O(40)	0.3808 (1)	0.0821 (1)	0.3164 (2)	3.74 (5)
C(1)	0.2615 (2)	−0.0364 (2)	0.2807 (3)	3.95 (7)
C(2)	0.2058 (2)	0.1203 (2)	0.2364 (3)	4.03 (7)
C(3)	0.2067 (2)	0.1161 (2)	0.3839 (3)	4.44 (8)
C(4)	0.1660 (2)	0.0660 (3)	0.4471 (3)	4.74 (8)
C(5)	0.1751 (3)	0.0581 (4)	0.5934 (4)	8.3 (1)
C(6)	0.2608 (2)	0.1766 (3)	0.4537 (4)	6.8 (1)
C(11)	0.1066 (2)	0.0166 (3)	0.3790 (3)	4.38 (8)
C(12)	0.0531 (2)	0.0553 (3)	0.2974 (4)	5.35 (9)
C(13)	−0.0035 (2)	0.0092 (3)	0.2363 (4)	6.4 (1)
C(14)	−0.0075 (2)	−0.0748 (3)	0.2547 (5)	6.8 (1)
C(15)	0.0443 (2)	−0.1135 (3)	0.3362 (5)	7.3 (1)
C(16)	0.1003 (2)	−0.0687 (3)	0.3990 (4)	6.1 (1)
C(21)	0.4109 (2)	−0.0514 (2)	0.0683 (3)	3.60 (7)
C(22)	0.4199 (2)	−0.0749 (2)	−0.0572 (3)	4.42 (8)
C(23)	0.4232 (2)	−0.1598 (3)	−0.0868 (4)	5.44 (9)
C(24)	0.4169 (2)	−0.2193 (3)	0.0080 (4)	6.0 (1)
C(25)	0.4092 (2)	−0.1946 (2)	0.1333 (4)	5.45 (9)
C(26)	0.4068 (2)	−0.1103 (2)	0.1649 (3)	4.24 (8)
C(31)	0.3486 (2)	0.2045 (2)	−0.0013 (3)	3.93 (7)
C(32)	0.3968 (2)	0.1911 (3)	−0.0861 (4)	5.7 (1)
C(33)	0.3862 (3)	0.2292 (3)	−0.2079 (4)	8.0 (1)
C(34)	0.3281 (3)	0.2784 (3)	−0.2410 (4)	8.3 (1)
C(35)	0.2803 (3)	0.2899 (3)	−0.1551 (5)	7.9 (1)
C(36)	0.2892 (2)	0.2531 (3)	−0.0322 (4)	5.8 (1)
C(41)	0.4479 (2)	0.1160 (2)	0.3620 (3)	4.01 (7)
C(42)	0.4522 (2)	0.1978 (3)	0.4025 (4)	5.7 (1)
C(43)	0.5178 (2)	0.2281 (3)	0.4599 (4)	7.1 (1)
C(44)	0.5753 (2)	0.1767 (3)	0.4749 (4)	7.1 (1)
C(45)	0.5704 (2)	0.0955 (3)	0.4317 (4)	6.4 (1)
C(46)	0.5058 (2)	0.0641 (3)	0.3748 (3)	5.01 (9)
C(51)	0.1436 (2)	0.0204 (3)	0.0280 (4)	6.2 (1)
C(52)	0.1694 (2)	−0.0610(3)	0.0536 (4)	7.1 (1)
C(53)	0.2328 (2)	−0.0695 (3)	−0.0034 (4)	6.4 (1)
C(54)	0.2453 (2)	0.0051 (3)	−0.0612 (3)	5.9 (1)
C(55)	0.1912 (2)	0.0615 (3)	−0.0432 (3)	5.58 (9)

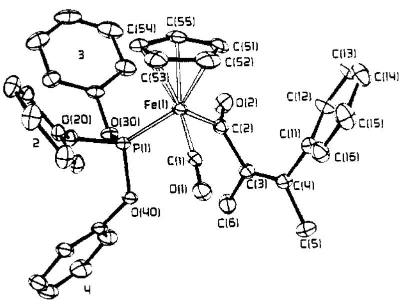


Figure 1. ORTEP diagram showing the crystal and molecular structure of $CpFeCO[P(OPh)_3](\eta^1$-(*Z*)-C(O)C(Me)=C(Ph)Me) (**6**).

Crystals of $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-C(O)C(Me)=C(Me)SPh) are triclinic, space group $P\bar{1}$, with a = 12.332 (2) Å, b = 24.801 (2) Å, c = 10.969 (3) Å, α = 101.12 (2)°, β = 93.75 (2)°, γ = 103.89 (2)°, V = 3174 (1) Å^3, Z = 4, D_x = 1.36 g cm^{-3}, λ = 0.71073 Å, linear absorption coefficient μ = 6.25 cm^{-1}; Fw = 650.52 and T = 291 K. The crystals were grown from hexane/CH_2Cl_2 (20:1). An irregular fragment of a larger crystal with dimensions 0.3 × 0.2 × 0.2 mm was mounted in a

---

(23) Slougui, N.; Rousseau, G. *Syn. Commun.* **1982**, *12*, 401.

(24) Phan, T. H.; Dahn, H. *Helv. Chim. Acta* **1976**, *59*, 335.

(25) All calculations were carried out by using Enraf-Nonius Structure Determination Package, Frenz, B. A.; 1983.

(26) Johnson, C. K. "ORTEP II" Oak Ridge National Laboratory: Oak Ridge, TN, 1970; Report ORNL-3794.

Table II. Positional Parameters and Their Estimated Standard Deviations of CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)SPh)

atom	x	y	z	B_{eqv} (Å^2)	atom	x	y	z	B_{eqv} (Å^2)
Fe(1A)	0.49487 (6)	0.39129 (3)	0.75066 (7)	3.19 (2)	Fe(1B)	0.71590 (6)	0.14839 (3)	0.91023 (7)	3.67 (2)
P(1A)	0.3337 (1)	0.33475 (6)	0.7029 (1)	3.11 (3)	P(1B)	0.6852 (1)	0.17185 (6)	0.9905 (1)	3.29 (3)
O(1A)	0.4708 (4)	0.4258 (2)	0.5152 (3)	5.9 (1)	O(1B)	0.7058 (3)	0.0307 (2)	0.9013 (4)	6.2 (1)
O(2A)	0.3856 (3)	0.4435 (1)	0.9378 (3)	4.06 (9)	O(2B)	0.6832 (3)	0.2118 (2)	1.1396 (4)	5.7 (1)
O(20A)	0.3169 (3)	0.2737 (2)	0.6108 (3)	4.4 (1)	O(20B)	0.9847 (3)	0.1766 (1)	0.9024 (3)	3.86 (9)
O(30A)	0.2560 (3)	0.3125 (2)	0.8047 (3)	3.95 (9)	O(30B)	0.9376 (3)	0.2302 (1)	1.0894 (3)	3.80 (9)
O(40A)	0.2462 (3)	0.3610 (1)	0.6359 (3)	3.87 (9)	O(40B)	0.9106 (3)	0.1289 (1)	1.0733 (3)	3.79 (9)
C(1A)	0.4798 (4)	0.4126 (2)	0.6090 (5)	4.2 (1)	C(1B)	0.7083 (4)	0.0779 (2)	0.9081 (5)	4.3 (2)
C(2A)	0.4244 (4)	0.4480 (2)	0.8408 (4)	3.2 (1)	C(2B)	0.6713 (4)	0.1637 (2)	1.0786 (5)	4.0 (1)
C(3A)	0.4240 (4)	0.5016 (2)	0.7905 (4)	3.2 (1)	C(3B)	0.6084 (4)	0.1159 (2)	1.1351 (5)	4.1 (1)
C(4A)	0.3269 (4)	0.5143 (2)	0.7689 (5)	3.6 (1)	C(4B)	0.6508 (4)	0.1042 (2)	1.2369 (5)	4.0 (1)
C(3A)	0.2143 (3)	0.4325 (2)	0.7958 (5)	4.9 (2)	C(5B)	0.7637 (5)	0.1350 (3)	1.3089 (6)	5.5 (2)
C(6A)	0.5350 (4)	0.5350 (2)	0.7668 (5)	3.9 (1)	C(6B)	0.4932 (5)	0.0850 (3)	1.0636 (6)	6.5 (2)
S(10A)	0.3254 (1)	0.57597 (6)	0.7098 (2)	5.00 (4)	S(10B)	0.5671 (1)	0.05293 (7)	1.3089 (2)	5.79 (4)
C(11A)	0.2325 (4)	0.5468 (2)	0.5693 (5)	4.1 (1)	C(11B)	0.6507 (5)	0.0067 (2)	1.3252 (5)	4.5 (2)
C(12A)	0.1578 (5)	0.5755 (2)	0.5356 (6)	5.2 (2)	C(12B)	0.7163 (5)	−0.0093 (3)	1.2346 (6)	5.9 (2)
C(13A)	0.0867 (5)	0.5542 (3)	0.4274 (6)	6.4 (2)	C(13B)	0.7772 (6)	−0.0484 (3)	1.2457 (8)	8.6 (3)
C(14A)	0.0870 (5)	0.5036 (3)	0.3522 (6)	6.3 (2)	C(14B)	0.7695 (6)	−0.0728 (3)	1.3456 (9)	9.4 (2)
C(15A)	0.1593 (5)	0.4739 (3)	0.3856 (6)	5.8 (2)	C(15B)	0.7043 (6)	−0.0591 (3)	1.4358 (7)	8.2 (2)
C(16A)	0.2339 (5)	0.4957 (3)	0.4940 (6)	5.3 (2)	C(16B)	0.6458 (5)	−0.0178 (3)	1.4280 (6)	6.1 (2)
C(21A)	0.3978 (4)	0.2375 (2)	0.5402 (5)	3.7 (1)	C(21B)	0.9751 (4)	0.1461 (2)	0.7811 (5)	3.9 (1)
C(22A)	0.4362 (5)	0.2130 (2)	0.5637 (5)	4.5 (2)	C(22B)	0.9374 (5)	0.0873 (3)	0.7495 (6)	5.0 (2)
C(23A)	0.5154 (5)	0.1956 (3)	0.4954 (6)	6.1 (2)	C(23B)	0.9302 (6)	0.0597 (3)	0.6287 (7)	7.5 (2)
C(24A)	0.5558 (5)	0.2233 (3)	0.4028 (6)	5.9 (2)	C(24B)	0.9605 (6)	0.0879 (4)	0.5374 (6)	9.6 (3)
C(25A)	0.5158 (5)	0.2668 (3)	0.3800 (5)	5.3 (2)	C(25B)	0.9999 (6)	0.1465 (3)	0.5691 (6)	7.8 (2)
C(26A)	0.4362 (5)	0.2844 (2)	0.4454 (5)	4.8 (2)	C(26B)	1.0082 (5)	0.1757 (3)	0.6902 (5)	5.0 (2)
C(31A)	0.2944 (4)	0.2853 (2)	0.8934 (5)	3.4 (1)	C(31B)	0.9539 (4)	0.2847 (2)	1.0637 (5)	3.8 (1)
C(32A)	0.2790 (4)	0.2278 (2)	0.8664 (5)	4.2 (1)	C(32B)	1.0531 (5)	0.3084 (3)	1.0251 (6)	6.2 (2)
C(33A)	0.3095 (5)	0.2016 (2)	0.9589 (6)	5.4 (2)	C(33B)	1.0739 (6)	0.3635 (3)	1.0105 (7)	8.2 (2)
C(34A)	0.3552 (6)	0.2336 (3)	1.0757 (6)	6.5 (2)	C(34B)	0.9937 (7)	0.3925 (3)	1.0278 (7)	7.9 (2)
C(35A)	0.3691 (6)	0.2911 (3)	1.0992 (6)	6.5 (2)	C(35B)	0.8953 (6)	0.3687 (3)	1.0676 (7)	7.6 (2)
C(36A)	0.3387 (5)	0.3176 (2)	1.0099 (5)	4.8 (2)	C(36B)	0.8763 (5)	0.3145 (3)	1.0871 (6)	6.0 (2)
C(41A)	0.1347 (5)	0.3337 (2)	0.5842 (5)	4.8 (2)	C(41B)	1.0152 (4)	0.1266 (2)	1.1264 (5)	3.9 (1)
C(42A)	0.0531 (5)	0.3292 (3)	0.6607 (7)	7.4 (2)	C(42B)	1.0722 (5)	0.1670 (3)	1.2281 (6)	6.2 (2)
C(43A)	−0.0606 (6)	0.3064 (3)	0.6096 (9)	11.2 (3)	C(43B)	1.1714 (6)	0.1590 (3)	1.2794 (7)	8.1 (2)
C(44A)	−0.0719 (9)	0.2912 (3)	0.483 (1)	14.5 (3)	C(44B)	1.2104 (5)	0.1154 (3)	1.2349 (6)	8.9 (2)
C(45A)	−0.0010 (8)	0.2978 (4)	0.4021 (8)	16.1 (3)	C(45B)	1.1551 (6)	0.0770 (3)	1.1350 (8)	10.3 (2)
C(46A)	0.1110 (6)	0.3188 (3)	0.4598 (6)	9.7 (2)	C(46B)	1.0568 (6)	0.0827 (3)	1.0801 (7)	7.4 (2)
C(51A)	0.6400 (5)	0.4292 (2)	0.8781 (6)	5.0 (2)	C(51B)	0.5840 (5)	0.1800 (3)	0.8514 (6)	7.9 (2)
C(52A)	0.6700 (3)	0.4095 (3)	0.7576 (6)	5.7 (2)	C(52B)	0.5873 (6)	0.1316 (3)	0.7641 (7)	9.8 (2)
C(53A)	0.6285 (5)	0.3517 (3)	0.7252 (6)	5.8 (2)	C(53B)	0.6695 (7)	0.1437 (3)	0.7184 (6)	8.7 (2)
C(54A)	0.5712 (5)	0.3346 (2)	0.8212 (6)	5.3 (2)	C(54B)	0.7424 (5)	0.1962 (3)	0.7733 (6)	8.4 (2)
C(55A)	0.5788 (5)	0.3814 (3)	0.9144 (5)	4.7 (2)	C(55B)	0.6807 (6)	0.2189 (3)	0.8521 (7)	7.3 (2)

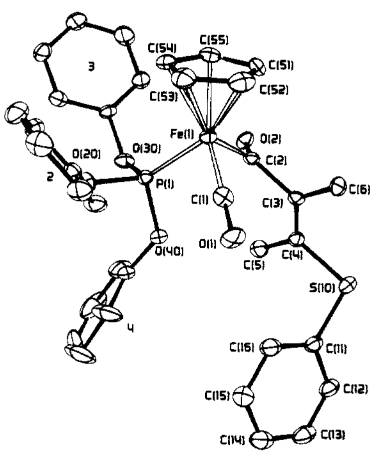


Figure 2. ORTEP diagram showing the crystal and molecular structure of CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)C(Me)=C(Me)SPh) (**1**).

glass capillary and used for all measurements. The procedures and instrument parameters were the same as described above except that data were collected only in the 3° < 2θ < 45° shell because the crystal's diffraction was weaker. The crystal showed 10% decay in the X-ray beam over 243 h of exposure. The corrections for decay were applied (max = 1.053, av = 1.025) but not for absorption. Reflections (8276) were measured, out of which 614 were Friedel pairs. In a merge procedure, they provided 7777 unique values and R_{merge} = 1.9% (on intensities). Reflections (4333) with $I > 3\ \sigma(I)$ were considered observed and used in further calculations. The intensity statistics indicated the centrosymmetric space group, and the unit cell volume suggested two molecules in the asymmetric part of the unit cell. The positions of the two symmetry independent iron atoms were determined from a Patterson map; the rest of the structure was found in a series of difference Fourier maps. The structure was refined in the same way as described above. The final R = 0.041, wR = 0.045, and S = 1.49. On the final difference Fourier map, the maximum was 0.40 e Å^{-3} and was in the vicinity of iron. The final coordinates are listed in Table II; selected bond distances and angles are in Table III. An ORTEP drawing of one of the molecules (A) is shown in Figure 2.

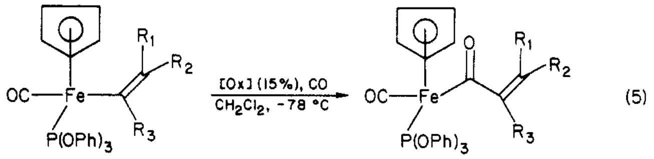
Results

Alkenylacyl Complexes. The reaction of CpFeCO[P(OPh)$_3$](η^1-alkenyl) complexes with CO gas (1 atm) at or above room temperature does not yield observable amounts of alkenylacyl derivatives. In contrast, as shown in eq 5 and 6, the conditions of a catalytic amount of oxidant ([Ox] = [Cp$_2$Fe]BF$_4$ or Ce(IV) with EtOH used as a cosolvent) under 1 atm of CO at −78 °C yields the desired alkenylacyl complexes in good to excellent yield. Note the reversal of alkene stereochemistry in eq 6. The complexes are definitively characterized by their ^{13}C NMR spectra. In addition to a set of resonances similar to those in the corresponding starting material, the acyl carbon atom resonance appears as a doublet (J_{C-P} ca. 35 Hz) in the region 255–275 ppm. This was important as we were unable to definitively locate the acyl carbonyl stretching band in the IR due to interference from a strong band at 1590 arising from the P(OPh)$_3$ ligand.

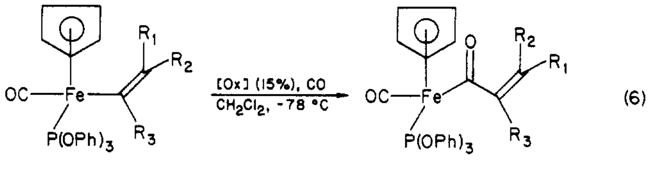
In all cases, the reaction is completely stereoselective, but the two equations seemingly present contradictory results.[27] In

---

[27] In our earlier communication, we incorrectly pictured complex **6** as the *E* isomer.



1, R_1 = Me, R_2 = SPh, R_3 = Me
2, R_1 = Me, R_2 = $CH(CO_2Et)_2$, R_3 = Me
3, R_1 = H, R_2 = Ph, R_3 = Me
4, R_1 = H, R_2 = Me, R_3 = CO_2Me
5, R_1 = R_2 = R_3 = Me
6, R_1 = Ph, R_2 = Me, R_3 = Me
7, R_1 = Ph, R_2 = Me, R_3 = Ph



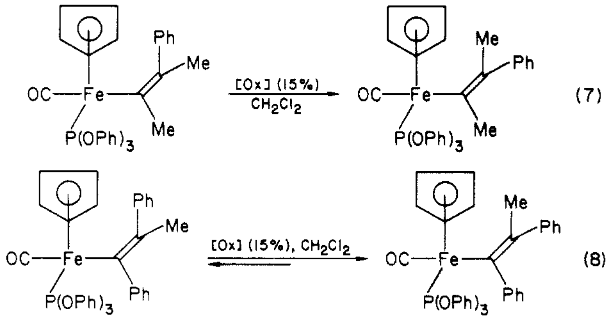
6, R_1 = Me, R_2 = Ph, R_3 = Me
7, R_1 = Me, R_2 = Ph, R_3 = Ph
8, R_1 = Et, R_2 = Ph, R_3 = Et

general, eq 5, the reactions proceed with retention of the alkenyl stereochemistry. The exceptions, eq 6 are cases where a Ph group is trans to iron with a group other than H at the cis alkenyl position.

The stereochemistry of the alkenylacyl complexes was determined by a variety of means. First, the solid state structures of **1** and **6** were determined by X-ray crystallographic means (vide infra). Second, as described below, these acyl complexes (or the starting alkenyl complexes) undergo oxidative cleavage in the presence of alcohol to yield alkenyl esters. In a number of cases, the stereochemistry of the alkenyl ester is known and we have found that a positive correlation exists between the stereochemistry of the ester and that of the alkenylacyl complex. This has been proven in two ways. First, the crystallographically determined geometries of **1** (*E*) and **6** (*Z*) (vide infra) are the same as the geometry of the esters[19,22] obtained via their oxidative cleavage. Second, using different chemistry (vide infra), we have prepared $CpFeCO[P(OPh)_3](\eta^1\text{-}(E)\text{-}C(O)C(Me){=}C(Me)Ph)$ (**9**), the opposite stereoisomer of **6**. Cleavage of **9** yields exclusively the E-alkenyl ester and, as stated above, cleavage of **6** yields the Z-alkenyl ester.

The last method to assign stereochemistry of the acyls is based on the observation that the acyl complexes **6**, **7**, and **8** that have a Ph group on the alkenylacyl ligand cis to iron show an anomolous shielding of the Cp resonance in the ^1H NMR of ca. 0.5 ppm when compared to complexes **1–5** and **9**.

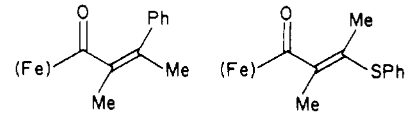
Equations 7 and 8 show that the catalytic oxidative conditions in the *absence* of CO can cause double-bond isomerization reactions and thus yield important information on how the (*E*)-alkenyl complexes shown in eq 6 yield Z-alkenylacyl complexes.



For eq 8, an equilibrium mixture of the *E*/*Z* isomers is established at a 5/1 ratio. For eq 7, none of the starting *Z* isomer is observed by NMR analysis of the reaction products.

We have observed a unique result when $CpFeCO[P(OPh)_3](\eta^1\text{-}C(CO_2Me){=}CMe_2)$ is exposed to the oxidative conditions in the presence of CO described above. Although the product of the reaction is indeed an acyl complex, it is not the expected $CpFeCO[P(OPh)_3](\eta^1\text{-}C(O)C(CO_2Me){=}CMe_2)$. Instead, displacement of $P(OPh)_3$ also occurred, affording $CpFe(CO)_2(\eta^1\text{-}C(O)C(CO_2Me){=}CMe_2)$.

Table III. Selected Bond Angles (deg) and Bond Lengths (Å) with Estimated Standard Deviations in Parentheses ([Fe] = $CpFeCO[P(OPh)_3]$)



angle/bond		A	B
P(1)–Fe–C(1)	91.69 (8)	89.1 (2)	90.6 (2)
P(1)–Fe(1)–C(2)	90.96 (8)	88.3 (1)	88.7 (1)
P(1)–Fe(1)–Cp	124.6	129.7	127.8
C(1)–Fe(1)–C(2)	91.1 (1)	93.6 (2)	94.1 (2)
C(1)–Fe(1)–Cp	124.8	125.7	125.6
C(2)–Fe(1)–Cp	121.5	119.7	119.8
O(2)–C(2)–C(3)	117.9 (3)	118.3 (4)	116.2 (5)
C(2)–C(3)–C(4)	125.3 (2)	119.0 (4)	121.8 (5)
C(2)–C(3)–C(6)	111.7 (3)	116.1 (4)	113.3 (4)
C(4)–C(3)–C(6)	123.0 (3)	124.8 (4)	124.9 (5)
C(3)–C(4)–C(5)	122.5 (3)	126.0 (4)	125.3 (5)
C(3)–C(4)–C(11)	122.7 (3)		
C(5)–C(4)–C(11)	114.8 (3)		
C(3)–C(4)–S(10)		119.4 (4)	119.9 (4)
C(5)–C(4)–S(10)		114.5 (4)	114.5 (4)
Fe(1)–P(1)	2.110 (1)	2.106 (1)	2.110 (1)
Fe(1)–C(1)	1.740 (3)	1.748 (6)	1.724 (6)
Fe(1)–C(2)	1.966 (3)	1.968 (5)	1.957 (6)
C(2)–C(3)	1.517 (4)	1.536 (6)	1.514 (6)
C(2)–O(2)	1.211 (3)	1.208 (5)	1.218 (6)
C(3)–O(4)	1.332 (4)	1.327 (6)	1.314 (6)
C(3)–C(6)	1.519 (4)	1.487 (6)	1.523 (7)
C(4)–C(5)	1.499 (4)	1.502 (7)	1.503 (7)
C(4)–C(11)	1.475 (4)		
C(4)–S(10)		1.776 (5)	1.780 (5)
Fe(1)–C(51)	2.088 (3)	2.098 (5)	2.085 (6)
C(51)–C(52)	1.394 (5)	1.423 (8)	1.395 (12)
C(1)–O(1)	1.139 (3)	1.144 (5)	1.152 (6)
P(1)–O(20)	1.615 (2)	1.608 (3)	1.607 (3)

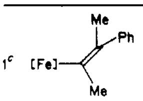
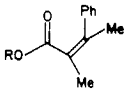
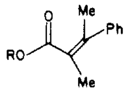
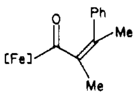
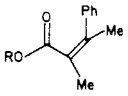
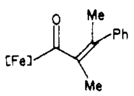
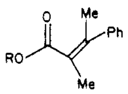
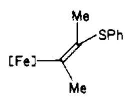
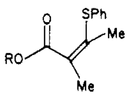
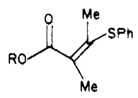
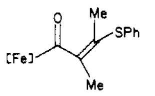
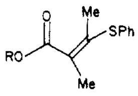
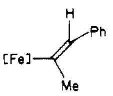
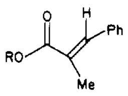
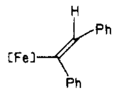
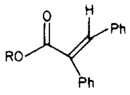
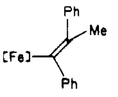
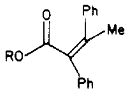
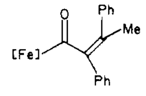
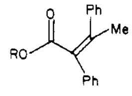
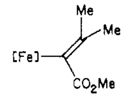
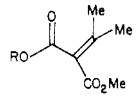
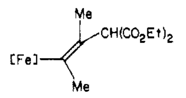
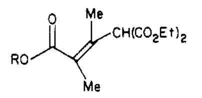
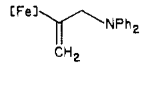
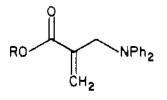
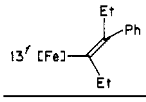
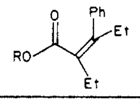
It was not possible to isomerize alkenylacyl complexes. Treating **9** with a catalytic amount of oxidant under CO led to reisolation of **9**. Also, the insertion reaction could not be oxidatively reversed. Catalytic oxidation of **6** under N_2 at −78 °C in a solution being purged with N_2 led to reisolation of **6**.

Attempts to study the electrochemical properties of these alkenyl and alkenylacyl complexes failed. Only irreversible anodic waves were observed by cyclic voltammetry (ca. 0.7 eV).

$AlCl_3$-Induced Insertion Reactions. Mixing $CpFeCO[P(OPh)_3](\eta^1\text{-}(E)\text{-}C(Me){=}C(Me)Ph)$ with 1 equiv of $AlCl_3$ in CH_2Cl_2 under 1 atm of CO at −78 °C produces mainly the *E*-acyl complex **9** contaminated with a small amount of the *Z*-acyl **6**. In a similar reaction, $CpFeCO[P(OPh)_3](\eta^1\text{-}(E)\text{-}C(Et){=}C(Et)Ph)$ produces the *E*- and *Z*-acyls in a 1/1.3 ratio. In both reactions, as in similar reactions with other alkenyl complexes that we have carried out, the yields are low. Thus, these reactions are not synthetically useful (for organic compounds) at present. However, pure **9** was isolated for the cleavage experiment shown in Table IV (vide infra). Note that if these reactions are carried out at room temperature in the absence of CO, a new ν(CO) band appears in the IR at 1990 cm^{-1}, replacing the band of the starting alkenyl complex (ca. 1950 cm^{-1}).

Cleavage Reactions. Reaction of the alkenyliron complexes with an excess of Ce(IV) in a mixed CH_2Cl_2/ROH solvent system (the CH_2Cl_2 is needed to solubilize the iron complex) under 1 atm of CO produces alkenyl esters in good to excellent isolated yield. As shown in Table IV, the stereochemistry of the products parallels the chemistry shown earlier in eq 5 and 6 for the synthesis of alkenylacyliron complexes. The alkenyl complexes in eq 5 yield esters with the retention of the double-bond stereochemistry, whereas those in eq 6 yield the opposite stereoisomer. In two cases, mixtures are observed. In the reaction shown in line 1, small

Table IV. Synthesis of Alkenyl Esters

	iron starting material[a]	product[b]
1[c]		 (9) +  (1)
2		
3		
4		 (1) +  (10)
5		
6[d]		
7		
8[d,e]		
9		
10		
11[f]		
12		
13[f]		

[a] [Fe] = CpFeCO[P(OPh)$_3$]. [b] Cleavage reactions are carried out in CH_2Cl_2/ROH (1/3) using 3 equiv of Ce(IV) as the oxidizing agent. In the two cases where mixtures form, the product ratios are given in parentheses. [c] These products can be separated by chromatography on silica. [d] Five equivalents of Ce(IV) is needed to maximize the yield. [e] The same product is formed if one starts with a 5/1 mixture of the E/Z alkenyliron isomers. [f] Stereochemistry of the product not definitively assigned by comparison to a literature value.

amounts of the *E* esters form although the main product, the *Z* isomer, can be isolated pure by chromatography. Note that this same mixture is obtained when $[Cp_2Fe]BF_4$ or $AgBF_4$ is used as the oxidant. The cleavage of the *E*-alkenyl complex shown in line 4 yields mainly the *E*-alkenyl ester, but it is contaminated with small amounts of the *Z* isomer. As shown, the *Z*- and *E*-alkenylacyl complexes for the dimethylphenyl case (line 2 and 3) each yield their corresponding alkenyl ester, the one derived from retention of the double-bond geometry. This is also true for the alkenylacyl *E* isomer in the dimethylthiophenyl case (line 5). These three cases are particularly important because the structure of the alkenylacyl complex has been assigned in each case from X-ray crystallographic results.

Description and Discussion of Structures. The molecular structure of CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(O)C(Me)=C(Ph)Me) is shown in Figure 1 and bond distances and angles are in Table III. The most important point about the structure is that the stereochemistry of the alkenyl group is *Z*, the Ph substituent is cis with respect to iron. The overall geometry around iron is best described as octahedral,[28] with the Cp group occupying three sites. The angles formed by the P(OPh)$_3$, CO and alkenylacyl ligands are all close to 90° and are very similar to those observed in our earlier structural study[8c] of CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Me)=C(Ph)Me) (**10**), a precursor of this complex. The Fe–C(2)-(acyl) bond distance is 1.966 (3) Å compared to 2.031 (8) Å for the starting alkenyl complex. We have previously argued from three structural determinations[8b,c,10] that 2.03 Å is the correct distance for an Fe–C(sp^2 hybrid) single bond in these molecules, and thus the shortening of the bond by ca. 0.06 Å indicates multiple-bond character[29] as expected for an acyl complex. The acyl group is exactly anti with respect to the carbonyl ligand[30] (C(1)Fe–C(2)O(2) torsional angle of 179.4°). This places the acyl π^* orbital in the optimum position to overlap with the π-type HOMO orbital based on iron and parallel to the P–Fe line[31] (P(1)Fe–C(2)O(2) dihedral angle of −88.8°). In the alkenyl complex **10** the alkenyl group is oriented 24.6° away from the optimum position. Calculations have indicated[32] that for alkenylmetal complexes, the repulsive interaction of a filled metal π-orbital with the π-bonding orbital of an alkenyl ligand can override any positive overlap with the π^*-orbital, and thus a normal single bond is expected. For an acyl complex, the bonding π-orbital is based mainly on oxygen and the antibonding π^*-orbital on carbon, making the interaction with the filled metal orbital much more favorable and multiple M–C bonding more likely than for alkenylmetal complexes. The C(3)–C(4) (alkene) bond distance of 1.33 Å is normal for a double bond[8b,c] and is not lengthened by any appreciable conjugation with the acyl (O(2)C(2)–C(3)C(4) torsional angle = −112°, 68° from coplanar position) or the Ph (C(3)C(4)–C(11)C(12) torsional angle = 55.1°) substituents.

Finally, the orientation of the alkenyl-phenyl group is of interest. It is oriented up toward the Cp ring much as observed by Brunner[33] in a family of CpMo(CO)$_2$–amidinato and -thioamidato complexes ("winner" molecules). As also observed in the molecules studied by Brunner, the ^{1}H NMR resonance of the Cp ligand in **6** (and **7** and **8** with a cis phenyl substituent) is shielded ca. 0.5 ppm when compared to the other alkenylacyl complexes **1**–**4** and **9**. The high-field shift was attributed[34] to the fact that the Cp hydrogen atoms lie in the region of the inner anisotropy of the phenyl ring.

The molecular structure of CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(O)-C(Me)=C(Me)SPh) has also been determined. There are two independent molecules in the unit cell. Figure 2 shows an ORTEP for one (A) of these. Comparison of bond angles and lengths in Table III shows the structures of the two independent molecules (labeled A and B) to be very similar. The overall geometry of these molecules is similar to that for **6**, but most importantly, the stereochemistry of the alkenyl group is definitely *E* in both molecules of **1**. The two carbonyl groups are still anti although the C(1)Fe–C(2)O(2) dihedral angle is lower at 160.1° for A and 165.4° for B.

The only major difference in the structures of **1** and **6** is the orientation of the alkenyl part of the molecule. For **6**, as described above, the alkenyl-phenyl group is oriented up near the Cp ring. This places C(6) down away from the Cp. In **1**, the alkene is

---

(28) Seeman, J. I.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1019.

(29) For a recent discussion of CpFe–C(sp^2) bond distances see: Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1980**, *19*, 2343.

(30) (a) Baird, J. G.; Bandy, J. A.; Davies, S. G.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1202. (b) Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. *Ibid.* **1984**, 745.

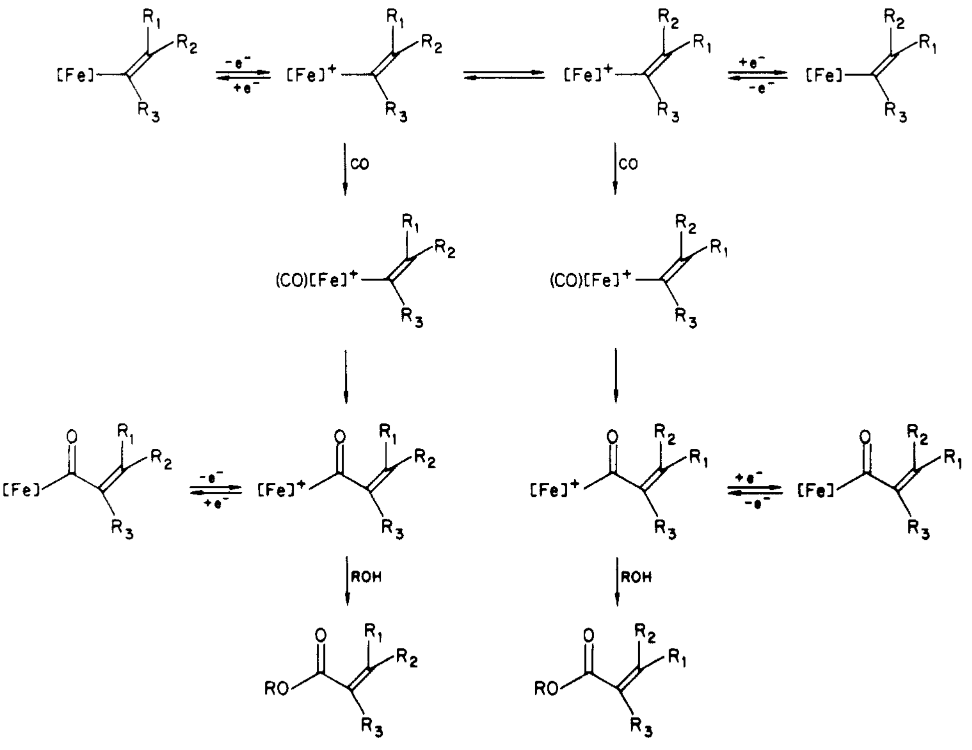
(31) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(32) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

(33) Brunner, H.; Agrifoglio, G.; Bernal, I.; Creswick, M. W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 641.

(34) Brunner, H.; Agrifoglio, G. *J. Organometal. Chem.* **1980**, *202*, C43.

Scheme I



[Fe] = CpFeCO[P(OPh)$_3$]

rotated opposite to that in **6** so that C(6) is now oriented up toward the Cp ligand. Although packing forces could be the cause of the difference, a weak interaction of the Cp group with the phenyl ring could explain the orientation of the alkenyl group in **6**. There is clearly no such interaction for **1**.

Discussion

Interpretation of the results presented here is highly dependent on assignment of alkenyl stereochemistry of the starting materials in eq 5 and 6 and Table IV. A combination of X-ray, NMR deuterium labeling, and synthetic studies have previously led to definitive assignments of the complexes prepared in eq 1 and 2. For example, the structure of CpFeCO[P(OPh)$_3$](η^1-(Z)-C(Me)=C(Ph)Me) (**10**, formed by reaction of Me$_2$Cu(CN)Li$_2$ and [CpFeCO[P(OPh)$_3$](η^2-MeC≡CPh)]BF$_4$) was determined crystallographically.[8c] This also fixed the stereochemistry of its isomer, CpFeCO[P(OPh)$_3$](η^1-(E)-C(Me)=C(Me)Ph) (**11**, formed by reaction of Ph$_2$Cu(CN)Li$_2$ and [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]BF$_4$). These isomers *do not* interconvert under the reaction or workup conditions used in their preparations. Definitive assignment of these two complexes in conjunction with NMR studies[9] clearly allows assignment of E stereochemistry to the other alkenyl derivatives (prepared as in eq 1) that form from addition of nucleophiles to the 2-butyne π-complex. The stereochemical assignment of the new complexes CpFeCO[P(OPh)$_3$](η^1-(Z)-C(Ph)=C(Ph)Me) (**12**) and CpFeCO[P(OPh)$_3$](η^1-(E)-C(Et)=C(Et)Ph) is based on the very close similarity of their preparations to that of **10** (the only difference is that the η^2-alkyne is changed from MeC≡CPh to PhC≡CPh) and **11** (alkyne changed from MeC≡CMe to EtC≡CEt), respectively. Also, complex **12** undergoes an isomerization reaction, eq 8, in the presence of an oxidant in a manner similar to that observed for **10**, eq 7. For the complexes prepared as in eq 2, the structure of CpFeCO(PPh$_3$)(η^1-(E)-C(CO$_2$Et)=C(H)Me was determined crystallographically.[10] The deuterium labeling experiment outlined in the Introduction section allows assignment of E stereochemistry to the other complexes shown in eq 2.[10] These experiments are supported by other synthetic and NMR studies.[11] E stereochemistry was assigned to the new complex CpFeCO[P(OPh)$_3$](η^1-(E)-C(Ph)=C(H)Ph) by a similar deuterium labeling experiment. The methods used to determine the alkene stereochemistry of the acyl complexes are outlined in the Results section and include two structures assigned by the X-ray crystallographic studies reported in this paper, Figures 1 and 2.

Scheme I illustrates a proposed pathway for the formation of iron–alkenylacyl complexes and alkenyl ester cleavage products. It is derived from this and our earlier work and from results cited in the literature[14,35] pertinent to oxidative migratory insertion processes. The reactions are initiated by the one-electron oxidation of 18-electron alkenyliron complexes generating the 17-electron radical cations shown. Our results clearly indicate that in the absence of CO, these intermediates can undergo a rapid $E \rightleftharpoons Z$ isomerization (eq 7 and 8). The migratory insertion step is best viewed as an associative two-step process.[35] In the reactions employing a catalytic amount of oxidant, the 17-electron acyl intermediate must undergo electron transfer with the starting alkenyliron complex, thereby generating product and more of the 17-electron alkenyliron intermediate that can continue the cycle. Under the conditions of excess oxidant and alcohol solvent, the 17-electron acyl intermediate reacts with the alcohol to afford the alkenyl ester cleavage product. These cleavage products can also be prepared by treating the 18-electron alkenylacyl complex with oxidant in a similar manner.

As it seems unlikely that isomerization of the double bond takes place after the insertion step, stereochemical selectivity must arise at an earlier stage. For the cases where an isomerization reaction has been clearly observed in the absence of the CO (eq 7 and 8), the more stable isomer places the larger (Ph vs. Me) β-substituent trans to the iron. If the 17-electron alkenyl intermediates have the same isomeric stability order, we have a very interesting situation for the three cases shown in eq 6. In these reactions, the products arise from the *less stable* isomer, the isomer with Ph cis to iron. This is analogous to the now well-known study of asymmetric catalytic hydrogenation of prochiral alkenes by Halpern[36] where the predominant hydrogenation product arises from the less stable π-alkene intermediate. In this case, the rate of addition of H$_2$ to the π-alkene complex determines the product

---

[35] Doxsee, K. M.; Grubbs, R. H.; Ansoh, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819 and references therein.

[36] Chan, A. S. C.; Pluth, J. J., Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952.

ratios. For our system, preferential CO association or, more likely, a faster rate of migratory insertion of one stereoisomer over the other determines product ratios. At present, the origin of selectivity is not at all clear. This is particularly true when one considers that starting with CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)═C(R)Ph), the *E*-isomer products are formed exclusively when R = H, but the *Z*-isomer products are predominantly (in the case of esters) or exclusively (in the case of alkenylacyl) formed when R = Me.

From a synthetic viewpoint, the completely stereoselective nature (as judged from 400-MHz NMR spectra) of alkenylacyl formation and alkenyl ester formation (in all but two cases) is of paramount importance. Even in the two instances (line 1 and 4, Table IV) where mixtures of esters are obtained, pure alkenyl ester can be prepared by effecting the oxidative cleavage on the iron-alkenylacyl complex (lines 2, 3, and 5, Table IV). An obvious complication is the inversion of alkene stereochemistry for the complexes in eq 6. However, these complexes are very similar (after finding one case of isomerization, we deliberately synthesized similar analogues) in that each possesses a phenyl group at the β-alkenyl position which is geminal to a group other than hydrogen. In general, we anticipate that the CO insertion step will proceed with retention of alkene stereochemistry.

The stereoselective synthetic route to alkenylacyliron complexes presented here allows the use of relatively mild reaction conditions, thus circumventing the potential thermal decomposition inherent in a thermally induced migration reaction. The described procedures for the preparation of tetrasubstituted alkenyl esters are quite different from the methods generally used[19–24] (mainly Horner–Emmons reactions) to prepare these compounds. Most notable is the observed high selectivity for the formation of a single stereoisomer, whereas the earlier methods generally give mixtures (ca. 2/1 of the two stereoisomers). New methodology for di- and trisubstituted alkenyl esters is also developed.[37] Overall, the ester formation is essentially a two-step sequence. The first is the η^2-alkyne complex preparation and the nucleophile addition. The second step is the oxidative cleavage. We have found the yields to be good in each step. In addition, one is afforded extensive control over the type of alkene substituents. Two of the groups are dictated by the choice of alkyne and the third by the nucleophile employed. In general, the nucleophile can be a stabilized carbanion, a carbon based nucleophile for which the lithium salt can be prepared[9] or a heteroatom nucleophile.[12] For additional flexibility, alkenyliron complexes can also be prepared via an iron–vinylidene route[13] and from η^2-allene complexes.[11] Although the reactions need to be carried out by using standard inert atmosphere techniques, they are not particularly sensitive procedures. The iron starting material, CpFeCO[P(OPh)$_3$]I, is inexpensive and can be prepared relatively easily on a large scale. The sum total is a unique and flexible route to alkenylacyliron complexes and highly functionalized alkenes.

Acknowledgment. Acknowledgment is made to the National Science Foundation (CHE 8019513 and EPSOR) and the NIH (Biomedical Research Grant S07-RR07160) for support of this research. We thank Dr. Robert Bly for helpful discussions.

Supplementary Material Available: Complete listings of bond angles, bond distances, torsional angles, positional parameters of H-atoms, general temperature factors, and structure factor amplitudes for **1** and **6** (110 pages). Ordering information is given on any current masthead page.

---

(37) (a) Marfat, A.; McGuirk, P. R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 3888. (b) Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405.

Synthesis and Characterization of a Mn^{III} Porphyrin Cation Radical and Its Conversion to Mn^{IV} by Ligand Metathesis

Larry O. Spreer,* Anthony C. Maliyackel, Stephen Holbrook, J. W. Otvos, and Melvin Calvin

Contribution from the Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720. *Received September 23, 1985*

Abstract: The complex (5,10,15,20-tetraphenylporphinato)manganese chloro hexachloroantimonate, **1**, MnTPP(Cl)(SbCl$_6$), was synthesized by the oxidation of MnTPP(Cl) with phenoxathiin hexachloroantimonte in dichloromethane. The assignment of **1** as a manganese(III) porphyrin π-cation radical species was based on its X-ray crystal structure, visible and infrared spectra, and magnetic properties. The crystal structure was determined as a tetrachloroethane solvate. The manganese in the compound is five-coordinated with the chloride anion axially bound to the Mn with 50% occupancy at sites above and below the porphyrin ring. The second anion, SbCl$_6^-$, is displaced from the Mn with a Mn–Cl–Sb angle of 132°. The porphyrin core carbon and nitrogen atoms as well as Mn are coplanar. Variable-temperature magnetic susceptibility measurements on the solid gave $\mu_{\text{eff}} = 4.9\ \mu_B$ which is close to that expected for a Mn^{III} cation (d^4) $S = 2$, π-cation radical $S = {}^1/_2$, with independent spin states. Magnetic susceptibility measurements on solutions of **1** gave a range of values for μ_{eff} between 5.7 and 6.7 μ_B. This suggests that the spin independent state of **1** in the solid changes into a ferromagnetically coupled state, resultant spin of five-halves, in the solution phase. The IR spectrum of **1**, with four solvent molecules (C$_2$H$_2$Cl$_4$) present, shows a peak at 1280 cm^{-1}. A band in this region has been suggested as diagnostic of metallotetraphenylporphyrin π-cation radical species. The 1280-cm^{-1} band observed for **1** disappeared when all the solvent molecules from **1** were removed under vacuum. The crystalline nature of the solid was lost by the removal of the solvent molecules; however, magnetic moment (4.7 μ_B) and the visible spectrum remained virtually unchanged. We believe that the 1280-cm^{-1} band in **1** is associated with the solvent molecules; neat C$_2$H$_2$Cl$_4$ also shows strong absorption in the 1280-cm^{-1} region. Treatment of **1** with basic methanol or oxidation of MnTPP(Cl) with phenoxathiin hexachloroantimonate in the presence of basic methanol gave another species whose visible and EPR spectra are identical with that reported for Mn^{IV}TPP(OCH$_3$)$_2$. These results suggest that the site of oxidation in MnTPP(Cl) is shifted from the ligand to the metal in the presence of the strong π-donating ligand, CH$_3$O$^-$.

The development of stable and efficient oxidation catalysts is difficult but essential to work aimed at producing an artificial photosynthesis assembly capable of converting solar energy to storable high energy chemical compounds. A useful oxidation catalyst in an assembly designed to split water would mediate the four-electron conversion of water to oxygen. An alternate goal would be the use of an oxidation catalyst to produce more useful

---

*To whom correspondence should be addressed. Present address: Department of Chemistry, University of the Pacific, Stockton, CA 95211.

0002-7863/86/1508-1949$01.50/0