New $CpFeCO[P(OPh)_3](\eta^1$-alkenyl) and $CpFeCO[P(OPh)_3](\eta^1$-alkenylacyl) Complexes. Crystal and Molecular Structure of $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-$COC(CH_2OMe)=C(Me)Ph)$ and an NMR Method To Assign Alkenyl Ligand Structure

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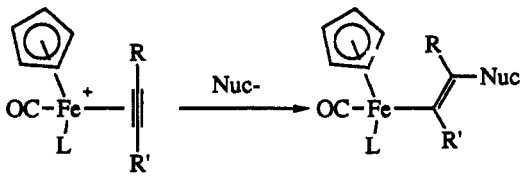
Received June 3, 1987

The reaction of $[CpFeCO[P(OPh)_3](\eta^2$-$MeC{\equiv}CCH_2OMe)]BF_4$ with three nucleophiles is stereo- and regioselective, yielding $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-$C(CH_2OMe){=}C(Me)Nuc)$ (Nuc = Me, Ph, SC_6H_4Me). These complexes react with CO using $[Cp_2Fe]BF_4$ as an oxidative catalyst to yield $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-$COC(CH_2OMe){=}C(Me)Nuc)$. The alkenylacyl ligand is cleaved with excess oxidant in the presence of alcohol to yield (*E*)-$RO_2CC(CH_2OMe){=}C(Me)Nuc$. The reaction of $[CpFeCO[P(OPh)_3](\eta^2$-$MeC{\equiv}C$-*i*-Pr)$]BF_4$ with two nucleophiles is selective, yielding $CpFeCO[P(OPh)_3](\eta^1$-(*Z*)-$C(Me){=}C(i$-Pr)Me) and $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-$C(Me){=}C(i$-Pr)SPh), but is not regioselective for Nuc = phenyl, yielding both $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-$C(Me){=}C(i$-Pr)Ph) and $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-$C(i$-Pr)$=$C(Me)Ph). For these complexes, oxidatively catalyzed CO insertion reactions go with partial or complete *Z*–*E* isomerization of the double bond to yield a mixture of products. Examination of the ^{13}C NMR spectra of previously prepared alkenyl complexes and the new complexes prepared here allow the formulation of two rules based on P–C coupling and chemical shift arguments that assign the structure of the tri- and tetrasubstituted alkenyl ligands in these types of complexes. The solid state structure of $CpFeCO[P(OPh)_3](\eta^1$-(*E*)-$COC(CH_2OMe){=}C(Me)Ph)$ was determined by X-ray crystallography and supports these new rules. The molecule crystallizes in space group $P\bar{1}$ with a = 13.318 (5) Å, b = 13.400 (3) Å, c = 10.460 (3) Å, α = 104.81 (2)°, β = 103.64 (2)°, γ = 108.10 (2)°, V = 1611 (1) Å^3, and Z = 2.

Introduction

We have shown previously that a variety of soft, anionic nucleophiles will add to cationic iron–η^2-alkyne complexes (eq 1) to yield iron–alkenyl complexes.[1,2] The reaction is regioselective for the two unsymmetrical alkynes tested, to date, and trans addition of the nucleophile is generally observed.



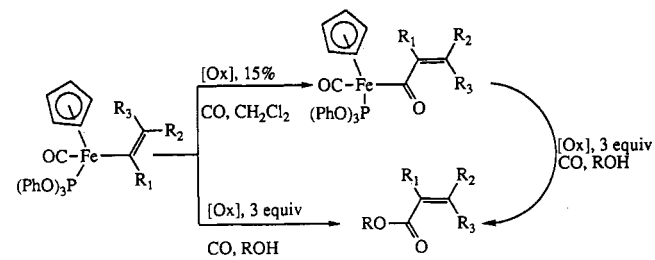
(1)

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

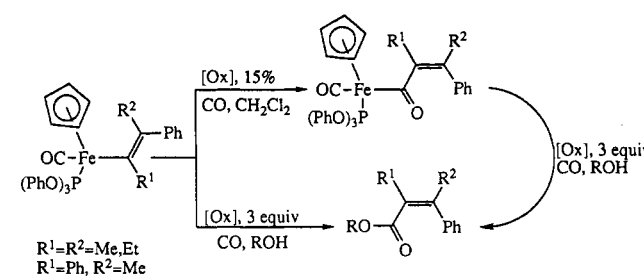
The alkenyl ligand can be further elaborated by an oxidatively ([Ox] = $[Cp_2Fe]BF_4$ or Ce(IV)) catalyzed CO insertion reaction or cleaved (starting with either an alkenyl or alkenylacyl complex) with excess oxidant in alcohol solvents to yield highly functionalized alkenes (Scheme I).

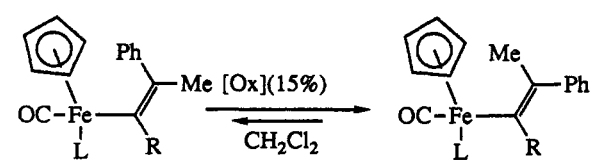
These reactions are stereoselective, generally proceeding with retention of the double-bond stereochemistry. Three exceptions to this observed in our earlier studies are alkenyl complexes that have a phenyl group trans to iron with a group other than hydrogen cis to iron. In these cases, complete inversion of stereochemistry is observed (Scheme II). Consistent with these observations, in the absence of CO these three alkenyl ligands undergo oxidatively catalyzed *E*–*Z* isomerization reactions (they do not thermally isomerize) (eq 2).[3] A surprising result is that these

Scheme I



Scheme II





(2)

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isomerization reactions highly favor the *E* isomers whereas the (alkenylacyl)iron complexes or alkenyl esters that form in the oxidatively catalyzed CO insertion or cleavage reaction are *Z* isomers.

Reported here are efforts directed at exploring the types of alkynes that can be successfully used in these reactions. We desired to determine if these reaction sequences would remain stereo- and regioselective for alkynes other than the three cases examined in the earlier work. It was important to determine what type of functional groups in addition to esters are compatible with this chemistry. We were also interested in exploring the generality of the unusual isomerization reaction shown in Scheme II. Finally, we report a method using ^{13}C NMR chemical shift and P–C coupling constant data to assign the structural arrangement of the alkenyl ligand substituents. The structure of $CpFeCO[P(OPh)_3](\eta^1\text{-}(E)\text{-}COC(CH_2OMe)=C(Me)Ph)$ has been determined crystallographically to support these methods of structural assignment.

Experimental Section

General Procedure. All operations on complexes in solution were carried out under an atmosphere of nitrogen (except CO reactions) using solvents that were dried and distilled before use. Chromatography was done with Alcoa F-20 alumina and J. T. Baker silica gel (60–200 mesh). ^1H NMR spectra were recorded at 300 MHz and ambient temperature unless otherwise specified. ^{13}C NMR spectra were recorded at either 20.1 or 75.5 MHz and also at ambient temperature, unless otherwise specified. A refocused INEPT sequence[4] was used with the alkenyliron complexes to aid in the assignment of the alkyl portions of the ^{13}C spectra. All chemical shifts are reported as δ vs Me_4Si, using the solvent as reference. Elemental analyses were performed by Robertson Laboratory. $[CpFeCO[P(OPh_3](\eta^2\text{-}MeC{\equiv}CCHMe_2)]BF_4$ and $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CCH_2OMe)]BF_4$ were prepared by using a previously reported general procedure for preparation of (η^2-alkyne)iron complexes.[3] These complexes were prepared immediately before use and were assumed to form quantitatively. $MeC{\equiv}CCH_2OMe$,[5] ferrocenium tetrafluoroborate,[6] and the cuprate reagents[3,7] were prepared via literature methods. $MeC{\equiv}CCHMe_2$ was purchased from Farchan, alkyllithium reagents were purchased from Aldrich, and $AgBF_4$ was purchased from Ozark-Mahoning.

$CpFeCO[P(OPh)_3][\eta^1\text{-}C(CH_2OMe)=CMe_2]$ (1). Cold THF (−78 °C, 25 mL) was added to a flask containing $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CCH_2OMe)]BF_4$ (1.08 g, 1.71 mmol), and this mixture was treated via cannula with a cold THF solution (−78 °C, 15 mL) of $Me_2CuCNLi_2$ (1.71 mmol). The resulting solution was stirred for 10 min, removed from the cold bath, and stirred for an additional 1–2 h. The solvent was evaporated, and the oily residue was redissolved in benzene (20 mL) and filtered through an alumina plug. The filtrate was collected, and the solvent was evaporated to yield a yellow oil (0.70 g, 73%): ^1H NMR (δ in C_6D_6 at 52 °C) 7.0 (15, m, $P(OPh)_3$), 4.43 (5, s, Cp), 4.30 (2, m, CH_2), 3.27 (3, s, OMe), 2.14, 2.01 (3, 3, s, s, vinyl Me's); IR (cm^{-1}, thin film) ν(CO) 1935; ^{13}C NMR (δ in CD_2Cl_2 at −15 °C, two rotamers in ca. 5:4 ratio are observed) 220.5, 219.7 (d, d, J = 48, 50 Hz, CO), 151.7, 151.6, 129.5, 124.9, 124.6, 121.8, 121.3 (d, d, s, s, s, d, d, J = 9, 10, 4, 4 Hz, $P(OPh)_3$), 142.1, 138.5 (s, d, J = 5 Hz, FeC=*C*), 132.0, 129.6 (d, d, J = 39, 34 Hz, FeC=), 84.5, 84.1 (s, d, J = 1 Hz, Cp), 82.9, 82.5 (d, d, J = 2, 8 Hz, OCH_2), 57.8, 56.9 (s, s, OMe), 29.8, 29.7, 22.8, 22.0 (s, s, d, d, J = 2, 3 Hz, vinyl Me's). Anal. Calcd for $C_{30}H_{31}FeO_5P$: C, 64.53; H, 5.60. Found: C, 64.50; H, 5.34.

$CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(CH_2OMe)=C(Me)Ph]$ (2). $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CCH_2OMe)]BF_4$ (1.08 g, 1.71 mmol) was treated with 1 equiv of $Ph_2CuCNLi_2$ by using a procedure analogous to that used for **1**. Chromatography of the product on alumina with hexane/CH_2Cl_2 (3:1) afforded a pure yellow oil (0.85 g, 80%): ^1H NMR (δ in C_6D_6 at 52 °C) 7.1 (20, m, Ph and $P(OPh)_3$), 4.52 (5, s, Cp), 4.12 (2, m, OCH_2), 3.12 (3, s, OMe), 2.50 (3, s, vinyl Me); IR (cm^{-1}, thin film) ν(CO) 1940; ^{13}C NMR (δ in CD_2Cl_2 at −15 °C) 220.4 (d, J = 47 Hz, CO), 151.8, 129.7, 124.7, 121.4 (d, s, s, d, J = 9, 4 Hz, $P(OPh)_3$), 148.3, 128.2, 127.8, 125.1 (d, s, s, s, J = 3 Hz, *CPh*), 145.1 (d, J = 5 Hz, =*C*Ph), 140.8 (d, J = 39 Hz, FeC=), 84.9 (d, J = 1 Hz, Cp), 83.4 (d, J = 9 Hz, OCH_2), 57.3 (s, OMe), 30.0 (s, vinyl Me). Anal. Calcd for $C_{35}H_{33}FeO_5P$: C, 67.75; H, 5.36. Found: C, 67.71; H, 4.98.

$CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(CH_2OMe)=C(Me)S\text{-}p\text{-}C_6H_4Me]$ (3). $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CCH_2OMe)]BF_4$ (1.08 g, 1.71 mmol) was dissolved in CH_2Cl_2 (25 mL), cooled to −78 °C, and added via cannula to a chilled (−78 °C) flask of *p*-$NaSC_6H_4Me$ (0.246 g, 1.71 mmol). The reaction was stirred for 8 h at −78 °C, removed from the cold bath, and stirred for an additional 2 h. The solvent was evaporated, and the residue was redissolved in benzene (20 mL) and filtered through an alumina plug. The filtrate was reduced in volume to 3 mL and chromatographed on alumina. Elution with hexane, followed by benzene, afforded a pure yellow oil (0.96 g, 84%): ^1H NMR (δ in C_6D_6 at 52 °C) 7.1 (19, m, $P(OPh)_3$ and SPh), 5.04 (2, m, OCH_2), 4.42 (5, s, Cp), 3.33 (3, s, OMe), 2.59 (3, s, vinyl Me), 2.07 (3, s, Ph*Me*); IR (*cm*$^{-1}$, *thin film*) ν(CO) 1943; ^{13}C NMR (δ *in* CD_2Cl_2 at −15 °C) (two rotamers are observed in ca. 7:4 ratio; data for the major isomer is reported here, and a partial spectrum of the minor isomer is given in Table II), 219.9 (d, J = 48 Hz, CO), 157.9 (d, J = 36 Hz, FeC=), 151.4, 129.6, 124.8, 121.3 (d, s, s, d, J = 10, 4 Hz, $P(OPh)_3$), 135.9, 134.4, 129.4, 127.8 (s, s, s, s, SPh), 135.2 (d, J = 14 Hz, =CS), 84.4 (s, Cp), 83.4 (s, OCH_2), 57.3 (s, OMe), 28.5, 20.8 (s, s, Me's). Anal. Calcd for $C_{36}H_{35}FeO_5PS$: C, 64.87; H, 5.29. Found: C, 64.55; H, 5.47.

$CpFeCO[P(OPh)_3][\eta^1\text{-}COC(CH_2OMe)=CMe_2]$ (4). Separate CH_2Cl_2 solutions of **1** (0.85 g, 1.52 mmol, 30 mL) and $[Cp_2Fe]BF_4$ (62 mg, 0.22 mmol, 15 mL) were placed under a CO atmosphere (1 atm), cooled to −78 °C, and stirred for 20 min. The $[Cp_2Fe]BF_4$ solution was added via cannula to the alkenyliron complex by using CO pressure. The resulting solution was stirred under CO at −78 °C for 45 min, removed from the cold bath, and stirred an additional 1 h. The solution was rinsed through an alumina plug, and the solvent was evaporated to yield a yellow-brown oil. Chromatography of the oil on alumina with hexane/CH_2Cl_2 (3:1) separated two yellow bands. The first band was identified as ferrocene, and the second band, obtained as a light yellow oil, was identified as **4** (0.71 g, 80%): ^1H NMR (δ in $CDCl_3$) 7.3 (15, m, $P(OPh)_3$), 4.51, 4.13 (1, 1, d, d, J = 11, 11 Hz, CH_2), 4.16 (5, s, Cp), 3.22 (3, s, OMe), 1.75, 1.71 (3, 3, s, s, vinyl Me's); IR (cm^{-1} in hexane) ν(CO) 1953; ^{13}C NMR (δ in $CDCl_3$) 267.8 (d, J = 34 Hz, C=O), 218.3 (d, J = 45 Hz, C≡O), 151.5, 129.5, 124.8, 121.9 (d, s, s, d, J = 9, 4 Hz, $P(OPh)_3$), 149.5 (s, =CMe_2), 148.2 (d, J = 4 Hz, C(O)*C*=), 84.3 (s, Cp), 68.6 (s, OCH_2), 56.9 (s, OMe), 22.0, 19.9 (s, s, vinyl Me's). Anal. Calcd for $C_{31}H_{31}FeO_6P$: C, 63.50; H, 5.33. Found: C, 64.10; H, 5.06.

$CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}COC(CH_2OMe)=C(Me)Ph]$ (5). This compound was prepared from **2** (1.89 g, 3.05 mmol) and $[Cp_2Fe]BF_4$ (125 mg, 0.46 mmol) by using a procedure analogous to that used for **4**. The crude product was purified by chromatography on alumina with hexane/CH_2Cl_2 (3:1). **5** was obtained as a yellow oil (1.80 g, 91%): ^1H NMR (δ in $CDCl_3$) 7.3 (20, m, $P(OPh)_3$ and Ph), 4.71, 3.75 (1, 1, d, d, J = 12, 12 Hz, CH_2), 4.20 (5, s, Cp), 3.07 (3, s, OMe), 2.02 (3, vinyl Me); IR (cm^{-1} in hexane) ν(CO) 1950; ^{13}C NMR (δ in $CDCl_3$ at −15 °C) 267.9 (d, J = 32 Hz, C=O), 218.4 (d, J = 46 Hz, C≡O), 150.9, 129.3, 124.6, 121.5 (d, s, s, d, J = 9, 4 Hz, $P(OPh)_3$), 148.0 (d, J = 6 Hz, C(O)*C*=), 142.4, 127.9, 127.7, 126.4 (all s, CPh), 83.8 (s, Cp), 69.8 (s, CH_2), 56.1 (s, OMe), 21.8 (s, Me). Anal. Calcd for $C_{36}H_{33}FeO_6P$: C, 66.68; H, 5.13. Found: C, 66.48; H, 5.07.

$CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}COC(CH_2OMe)=C(Me)S\text{-}p\text{-}C_6H_4Me]$ (6). This compound was prepared from **3** (0.50 g, 0.75 mmol) and $[Cp_2Fe]BF_4$ (31 mg, 0.11 mmol) by using a procedure

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analogous to that used for **4**. Chromatography of the crude product on alumina with hexane/CH_2Cl_2 (3:1) and CH_2Cl_2 separated three yellow bands. They were identified in order of elution as ferrocene, **3** (30 mg, 6%), and **6** (0.38 g, 73%). Compound **6** was obtained as a yellow oil: ^1H NMR (δ in $CDCl_3$) 7.3 (19, m, $P(OPh)_3$ and SPh), 4.70 (2, m, CH_2), 4.19 (5, s, Cp), 3.30 (3, s, OMe), 2.28, 1.89 (3, 3, s, s, Me's); IR (cm^{-1}, thin film) ν(CO) 1945; ^{13}C NMR (δ in $CDCl_3$ at −15 °C) 266.9 (d, J = 42 Hz, C=O), 217.8 (d, J = 45 Hz, C≡O), 153.6 (d, J = 6 Hz, C(O)*C*=), 150.9, 129.4, 124.8, 121.6 (d, s, s, d, J = 8, 4 Hz, $P(OPh)_3$), 136.5, 131.3, 130.3, 125.2, 125.1 (all s, =CSPh), 84.0 (s, Cp), 70.0 (s, OCH_2), 56.8 (s, OMe), 21.0, 20.6 (s, s, Me's). Anal. Calcd for $C_{37}H_{35}FeO_6PS$: C, 63.98; H, 5.08. Found: C, 64.13; H, 5.22.

(*E*)-$MeO_2CC(CH_2OMe)$=C(Me)Ph. Complex **5** (0.59 g, 0.95 mmol) was dissolved in CH_2Cl_2 (10 mL) and placed under a CO atmosphere. $[Cp_2Fe]BF_4$ (0.78 g, 2.8 mmol) was dissolved in MeOH and also placed under CO. Both solutions were cooled to −78 °C and stirred for 10 min. The CH_2Cl_2 solution was added to the MeOH solution, and the resulting solution was stirred for 2 h at −78 °C. The solution was then brought to room temperature, and the solvent was evaporated. The residue was taken up in CH_2Cl_2, rinsed through an alumina plug, reduced in volume to 2 mL, and chromatographed on silica with hexane/Et_2O (5:1). The alkenyl ester eluted shortly after the bright yellow ferrocene band and was obtained as a pale yellow oil (0.18 g, 8.2 mmol, 86%): ^1H NMR (δ in $CDCl_3$) 7.3 (5, m, Ph), 3.92 (2, s, CH_2), 3.82, 3.19 (3, 3, s, s, OMe's), 2.27 (3, s, Me); IR (cm^{-1}, thin film) ν(CO) 1721; ^{13}C NMR (δ in $CDCl_3$) 169.0 (s, C=O), 150.2, 141.4 (s, s, C=C), 128.0, 127.6, 126.9, 126.7 (all s, Ph), 70.1, 57.8, 51.7 (all s, OMe's and OCH_2), 23.2 (s, Me); MS (EI, 15 eV), m/e 220 (M^+), 205 (M^+ − Me). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.20; H, 7.54.

(*E*)-$MeO_2CC(CH_2OMe)$=C(Me)S-*p*-C_6H_4Me. This compound was prepared from **6** (0.53 g, 0.80 mmol) and MeOH in a reaction analogous to that used for the preparation of (*E*)-$MeO_2CC(CH_2OMe)$=C(Me)Ph. The crude product was purified by chromatography on silica with pentane/Et_2O (9:1) to yield a pale yellow oil (0.16 g, 0.63 mmol, 79%): ^1H NMR (δ in $CDCl_3$) 7.1 (4, m, SPh), 4.40 (2, s, CH_2), 3.65, 3.31 (3, 3, s, s, OMe's), 2.24, 2.02 (3, 3, s, s, Me's); IR (cm^{-1}, thin film) ν(CO), 1710; MS (EI, 15 eV), m/e 266 (M^+), 143 (M^+ − SPh(Me)).

$EtO_2CC(CH_2OMe)$=CMe_2 and $EtO_2CC(CMe_2OEt)$=CH_2. These compounds were prepared from **4** and EtOH in reactions analogous to that used for the preparation of (*E*)-$MeO_2CC(CH_2OMe)$=C(Me)Ph. In the completely analogous reaction, ^1H NMR analysis shows the crude product to be a 1:1 mixture of the title compounds. In a similar reaction, when the EtOH solvent was replaced with CH_2Cl_2 spiked with 3 equiv of EtOH, the product ratio of methyl to ethyl ether was 9:1. Chromatography of the 9:1 mixture on alumina with pentane/Et_2O (10:1) afforded $EtO_2CC(CH_2OMe)$=CMe_2 as a pale yellow oil (63% yield): ^1H NMR (δ in $CDCl_3$) 4.19 (2, q, J = 7 Hz, OCH_2CH_3), 4.13 (2, s, CH_2OCH_3), 3.29 (3, s, OMe), 2.02, 1.89 (3, 3, s, s, vinyl Me's), 1.27 (3, t, J = 7 Hz, OCH_2CH_3); IR (cm^{-1}, thin film) ν(CO) 1712; ^{13}C NMR (δ in $CDCl_3$ at −30 °C, all s) 168.7 (CO), 150.1, 124.6 (C=C), 68.7, 60.5 (OCH_2's), 58.2 (OMe), 23.2, 22.3, 14.1 (Me's); MS (EI, 15 eV), m/e 172 (M^+), 157 (M^+ − Me), 127 (M^+ − CH_2OMe or M^+ − OEt). Chromatography of the 1:1 mixture of products afforded $EtO_2CC(CMe_2OEt)$=CH_2 as a pale yellow oil (40% yield): ^1H NMR (δ in $CDCl_3$) 5.98, 5.67 (1, 1, d, d, J = 1, 1 Hz, CH_2), 4.18, 3.33 (2, 2, q, q, J = 7, 7 Hz, OCH_2's), 1.43 (6, s, CMe_2), 1.28, 1.13 (3, 3, t, t, J = 7, 7 Hz, OCH_2CH_3's); IR (cm^{-1}, thin film) ν(CO) 1715; ^{13}C NMR (δ in $CDCl_3$ at −30 °C, all s) 167.1 (C=O), 145.3, 123.5 (C=C), 75.9 (CMe_2), 66.0, 60.5 (OCH_2's), 26.5 (CMe_2), 15.3, 14.1 (CH_2Me's); MS (EI, 15 eV), m/e 171 (M^+ − Me). Anal. Calcd for $C_{10}H_{12}O_3$: C, 64.49; H. 9.74. Found: C, 64.71; H, 9.80.

CpFeCO[P(OPh)$_3$][η^1-(*Z*)-C(Me)=C(CHMe$_2$)Me] (7). $[CpFeCO[P(OPh)_3](\eta^2\text{-MeC}{\equiv}CCHMe_2)]BF_4$ (1.07 g, 1.70 mmol) was treated with 1 equiv of $Me_2CuCNLi_2$ by using a procedure analogous to that used for **1**. Chromatography of the crude product on alumina with hexane/CH_2Cl_2 (5:1) afforded a yellow powder (0.87 g, 91%): ^1H NMR (δ in C_6D_6) 7.0 (15, m, $P(OPh)_3$), 4.22 (5, s, Cp), 3.23 (1, m, CH), 2.55 (3, br s, vinyl Me), 1.92 (3, s, vinyl Me), 1.21, 1.09 (3, 3, d, d, J = 6, 6 Hz, $CHMe_2$); IR (cm^{-1}, in hexane) ν(CO) 1943; ^{13}C NMR (δ in CD_2Cl_2 at −13 °C) 219.4 (d, J = 52 Hz, CO), 151.7, 129.6, 124.9, 122.1 (d, s, s, d, J = 10, 4 Hz, $P(OPh)_3$), 143.2 (s, FeC=C), 84.3 (d, J = 1 Hz, Cp), 39.5 (s, CH), 33.6 (d, J = 11 Hz, vinyl Me), 21.7, 20.5 (s, s, $CHMe_2$), 14.6 (d, J = 4 Hz, vinyl Me), the Fe-bound, vinyl carbon atom resonance was not located. Anal. Calcd for $C_{31}H_{33}FeO_4P$: C, 66.92; H, 5.98. Found: C, 66.72; H, 5.90.

Mixture of CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(CHMe$_2$)=C(Me)Ph] (8) and CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(CHMe$_2$)Ph] (9). $[CpFeCO[P(OPh)_3](\eta^2\text{-MeC}{\equiv}CCHMe_2)]BF_4$ (1.07 g, 1.70 mmol) was treated with 1 equiv of $Ph_2CuCNLi_2$ by using a procedure analogous to that used for **1**. Chromatography of the crude product on alumina with hexane/CH_2Cl_2 (8:1) moved a single yellow band. The band was collected, and the solvent was evaporated to yield a yellow oil (0.87 g, 82%). ^1H NMR indicates this oil to be a ca. 5:1 mixture of regioisomers **8** and **9**. Spectral data for the mixture: ^1H NMR (δ in C_6D_6) 7.1 (**8** and **9**) (20, m, $P(OPh)_3$ and Ph), 4.43 (**8**), 4.28 (**9**) (5, s, s, Cp), 3.54 (**9**), 3.17 (**8**) (1, m, m, CH), 2.53 (**8**), 2.29 (**9**) (3, s, s, vinyl Me), 1.25 (**9**), 1.10 (**8**), 1.07 (**9**), 1.02 (**8**) (6, m, d, m, d, J = 6, 6 Hz, $CHMe_2$); IR (cm^{-1} in CH_2Cl_2) ν(CO) 1937; ^{13}C NMR (δ in CD_2Cl_2 at −15 °C) 222.0 (**8**), 220.2 (**9**) (d, d, J = 54, 51 Hz, CO), 152.2 (**8**), 151.7 (**9**) (d, d, J = 12, 10 Hz, POC), 149.3 (**8**), 136.4 (**9**) (d, d, J = 37, 31 Hz, FeC=), 145.0 (**9**), 140.3 (**8**) (d, d, J = 4, 6 Hz, =*C*Ph), 130–120 (**8** and **9**) (m, Ph and $P(OPh)_3$ except POC), 85.3 (**8**), 84.7 (**9**) (d, d, J = 2, 1 Hz, Cp), 41.4 (**8**), 38.9 (**9**) (d, s, J = 4 Hz, CH), 35.1 (**9**), 31.9 (**8**) (d, s, J = 10 Hz, vinyl Me), 25.0 (**8**), 23.4 (**8**), 22.5 (**9**), 22.2 (**9**) (all s, $CHMe_2$). Anal. Calcd for $C_{36}H_{35}FeO_4P$: C, 69.91; H, 5.70. Found: C, 69.68; H, 5.57.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(CHMe$_2$)SPh] (10). $[CpFeCO[P(OPh)_3](\eta^2\text{-MeC}{\equiv}CCHMe_2)]BF_4$ (1.07 g, 1.70 mmol) was dissolved in CH_2Cl_2 (25 mL), cooled to −78 °C, and added via cannula to a −78 °C flask of NaSPh (0.224 g, 1.70 mmol). The reaction was stirred for 8 h at −78 °C, removed from the cold bath, and stirred for an additional 2 h. The solvent was evaporated, and the residue was redissolved in benzene (20 mL) and filtered through an alumina plug. The filtrate was reduced in volume to 3 mL and chromatographed on alumina. Elution with hexane/CH_2Cl_2 (3:1) moved a single yellow band. The band was collected, and the solvent was evaporated to yield a yellow oil (0.99 g, 89%): ^1H NMR (δ in C_6H_6) 7.0 (20, m, SPh and $P(OPh)_3$), 4.15 (5, s, Cp), 3.75 (1, m, CH), 3.02 (3, s, vinyl Me), 1.49, 1.33 (3, 3, d, d, J = 6, 6 Hz, $CHMe_2$); IR (cm^{-1} in hexane) ν(CO) 1950; ^{13}C NMR (δ in $CDCl_3$ at −13 °C) 219.0 (d, J = 53 Hz, CO), 158.8 (d, J = 29 Hz, FeC=), 151.4, 129.5, 124.9, 121.6 (d, s, s, d, J = 11, 4 Hz, $P(OPh)_3$), 141.4, 128.2, 124.6, 122.8 (all s, SPh), 132.1 (d, J = 3 Hz, =CS), 83.8 (d, J = 2 Hz, Cp), 40.3 (s, CH), 36.4 (d, J = 9 Hz, vinyl Me), 22.0, 21.0 (s, s, $CHMe_2$). Anal. Calcd for $C_{36}H_{35}FeO_4PS$: C, 66.47; H, 5.42. Found: C, 66.48; H, 5.55.

CpFeCO[P(OPh)$_3$][η^1-COC(Me)=C(CHMe$_2$)Me] Mixture of Z and E Isomers. These complexes were prepared from **7** (0.59 g, 1.1 mmol, 25 mL) and $[Cp_2Fe]BF_4$ (43 mg, 0.16 mmol, 15 mL) by using a procedure analogous to that used for **4**. Chromatography of the crude product on alumina with hexane and hexane/CH_2Cl_2 (1:1) yielded a 3:2 (A:B) mixture of stereoisomers as a yellow oil (0.52 g, 84%): ^1H NMR (δ in $CDCl_3$) 7.3 (A and B) (15, m, $P(OPh)_3$), 4.19 (A), 4.15 (B) (5, s, s, Cp), 3.00 (B), 2.67 (A) (1, m, m, CH), 1.78 (B), 1.68 (A), 1.66 (A), 1.48 (B) (6, all s, vinyl Me's), 1.29 (A), 1.15 (A), 0.95 (B), 0.83 (B) (6, all d, J = 7, 7, 7, 7 Hz, $CHMe_2$); IR (cm^{-1} in CH_2Cl_2) ν(CO) 1953; ^{13}C NMR (δ in $CDCl_3$ at −15 °C) 270.5 (B), 270.4 (A) (d, d, J = 31, 30 Hz, C=O), 218.1 (A), 218.0 (B) (d, d, J = 44, 45 Hz, C≡O), 157.3 (A), 146.0 (B) (d, d, J = 5, 6 Hz, FeC(O)*C*), 151.1, 129.3, 124.5, 121.6 (A and B) (d, s, s, d, J = 9, 4 Hz, $P(OPh)_3$), 127.0 (B), 118.4 (A) (s, s, C(O)C=*C*), 84.4 (A), 84.1 (B) (d, d, J = 1, 1 Hz, Cp), 30.2 (B), 27.9 (A) (s, s, CH), 22.4, 21.6, 21.2, 20.8, 20.7, 19.8, 15.4, 10.9 (A and B) (all s, Me's).

Mixture of CpFeCO[P(OPh)$_3$][η^1-(*Z*)-COC(CHMe$_2$)=C(Ph)Me] (11) and CpFeCO[P(OPh)$_3$][η^1-(*Z*)-COC(Me)=C(Ph)CHMe$_2$] (12). This mixture was prepared from ca. 5:1 mixture of **8** and **9** (0.65 g, 1.1 mmol) and $[Cp_2Fe]BF_4$ (45 mg, 0.17 mmol) by using a procedure analogous to that used for **4**. Chromatography of the crude product on alumina with hexane and hexane/CH_2Cl_2 (3:1) separated two yellow bands. The first was identified as ferrocene and the second as ca. 4:1 mixture of **11** and **12** (0.60 g, 84%); ^1H NMR (δ in $CDCl_3$) 7.3 (**11** and **12**) (20, m, $P(OPh)_3$ and Ph), 3.49 (**11**), 3.47 (**12**) (5, d, d, J = 1, 1 Hz, Cp), 2.91 (**12**), 2.74 (**11**) (1, m, m, CH), 2.05 (**11**), 1.97 (**12**) (3, s,

s, vinyl Me), 1.33 (11), 1.28 (11), 1.18 (12), 0.72 (12) (6, all d, all J = 7 Hz, CHMe_2); IR (cm^{-1} in CH_2Cl_2) ν(CO) 1951; ^{13}C NMR (δ in $CDCl_3$ at −15 °C) 273.2 (12), 272.2 (11) (d, d, J = 32, 30 Hz, C=O), 218.9 (11), 218.5 (12) (d, d, J = 44, 44 Hz, C≡O), 159.9 (11), 149.6 (12) (d, d, J = 4, 5 Hz, C(O)C=), 150.9, 145.5, 139.6, 131.6, 129.8, 129.3, 127.6, 127.2, 126.2, 125.2, 124.5, 121.6, 121.4 (11 and 12) (d, ten s, d, d, J = 9, 4, 4 Hz, P(OPh)$_3$ and =CPh), 84.7 (11), 84.5 (12) (d, s, J = 1 Hz, Cp), 29.8 (11), 29.2 (12) (s, s, CH), 21.6 (11), 21.4 (11), 21.3 (11), 21.0 (12), 15.0 (12) (all s, Me's). Anal. Calcd for $C_{37}H_{35}FeO_5P$: C, 68.74; H, 5.46. Found: C, 68.76; H, 5.28.

CpFe[P(OPh)$_3$][η^1-(Z)-COC(Me)=C(SPh)CHMe$_2$] (13 and CpFeCO[η^1-(Z)-COC(Me)=C(SPh)CHMe$_2$] (14). Both compounds were prepared in a single reaction from **10** (0.99 g, 1.5 mmol) and $[Cp_2Fe]BF_4$ (0.21 g, 0.77 mmol) by using a procedure analogous to that used for **4**. Chromatography of the crude product on alumina with hexane/CH_2Cl_2 mixtures separated four bands that were identified, in order of elution, as ferrocene, **10** (0.30 g, 30%), **13** (0.14 g, 14%), and **14** (0.19 g, 34%). Both orange oils **13** and **14** were obtained as equilibrium mixtures of their respective two possible diastereomers. Spectral data for **13** (diastereomer ratio 4:1 (A:B)): ^1H NMR (δ in $CDCl_3$) 7.3 (A and B) (20, m, P(OPh)$_3$ and SPh), 4.26 (B), 3.42 (A) (5, s, s, Cp), 3.1 (A and B) (1, m, CH), 1.97 (A), 1.91 (B) (3, s, s, vinyl Me), 1.16 (B), 1.08 (A), 0.92 (B), 0.77 (A) (all d, all J = 7 Hz, CHMe_2); ^{13}C NMR (δ in $CDCl_3$ at −15 °C, major diastereomer only) 278.0 (d, J = 42 Hz, C=O), 155.2, 155.0, 139.8 (all d, J = 12, 16, 5 Hz, CSC=C), 152.1, 129.4, 124.3, 122.1 (d, s, s, d, J = 8, 4 Hz, P(OPh)$_3$), 131.2, 129.0, 128.5 (all s, SPh except SC), 81.8 (d, J = 2 Hz, Cp), 32.7, 29.9, 29.7, 13.6 (all s, CH and Me's). Anal. Calcd for $C_{36}H_{35}FeO_4PS$: C, 66.47; H, 5.42. Found: C, 66.48; H, 5.47. Spectral data for **14** (diastereomer ratio 3:1 (A:B)): ^1H NMR (δ in $CDCl_3$) 7.3 (A and B) (5, m, Ph), 4.55 (A), 4.22 (B) (5, s, s, Cp), 3.13 (B), 3.03 (A) (1, m, m, CH), 1.91 (A), 1.87 (B) (3, s, s, vinyl Me), 1.16 (A), 1.10 (B), 0.91 (A), 0.73 (B) (6, all d, all J = 7 Hz, CHMe_2); IR (cm^{-1} in CH_2Cl_2) ν(CO) 1935; ^{13}C NMR (δ in $CDCl_3$, major diastereomer only) 268.1 (s, C=O), 217.4 (s, C≡O), 160.0, 155.0 (s, s, C=C), 137.6, 129.5, 129.3, 129.1 (all s, SPh), 83.4 (s, Cp), 32.3, 21.5, 21.2, 12.8 (all s, CH and Me's). Anal. Calcd for $C_{19}H_{20}FeO_2S$: C, 61.97; H, 5.47. Found: C, 61.71; H, 5.49.

Crystallographic Analysis. Yellow crystals of CpFeCO[P(OPh)$_3$](η^1-(E)-COC(CH_2OMe)=C(Me)Ph) suitable for X-ray diffraction measurements were grown at 0 °C from a water–methanol mixture. The data crystal was mounted in a thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6 fully automated four-circle diffractometer by using graphite-monochromatized Mo Kα radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the diffractometer automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analysis are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library obtained from Molecular Structure Corp., College Station, TX. An empirical absorption correction was performed on the data. Neutral atom scattering factors were calculated by the standard procedures.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] Full-matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

The compound crystallizes in the triclinic crystal system. Space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of Patterson and difference Fourier techniques. All non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atom positions were determined by a difference Fourier synthesis, and their positions were refined. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement. See supplementary material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters.

(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmington, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.31, pp. 149–150.

Table I. Crystallographic Data for the Structural Analysis for Compound 5

(A) Crystal Data	
formula	$C_{36}H_{33}FePO_6$
temp, (±3 °C)	23
space group	$P\bar{1}$
a (Å)	13.318 (5)
b (Å)	13.400 (3)
c (Å)	10.460 (3)
α (deg)	104.81 (2)
β (deg)	103.64 (2)
γ (deg)	108.10 (2)
V (Å^3)	1611 (1)
M_r	648.5
Z	2
ρ_{calcd} (g/cm^3)	1.34
(B) Measurement of Intensity Data	
radiatn	Mo Kα (0.71073Å)
monochromator	graphite
detector aperture (mm)	
horizontal	2.0
vertical	2.0
cryst faces	011, 011, 100, 100, 110, 010, 110
cryst size (mm)	0.23 × 0.30 × 0.29
cryst orientatn: directn; deg from θ axis	[211]; 0.28
reflctns measd	$+h, \pm k, \pm l$
max 2 θ (deg)	48
scan type	moving crystal–stationary counter
ω-scan width (A + 0.347 tan θ) (deg)	1.2
bkgd	$^1/_4$ additional scan at end of each scan
ω-scan rate (deg/min.)	4.0[a]
no. of reflctns measd (unique)	5298
data used ($F^2 \geq 3.0\sigma(F^2)$)	3509
(C) Treatment of Data	
absorpt correctn	empirical
coeff (cm^{-1})	5.78
transmissn coeff	
max	1.00
min	0.93
P factor	0.02
final residuals	
R_F	0.038
R_{wF}	0.037
esd of unit weight observn	1.54
largest shift/error value of final cycle	0.15
largest peak in final diff fourier (e/Å^3)	0.36
no. Variables:	529

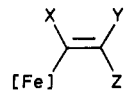
[a] Rigaku software uses a multiple scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to first scan etc. A maximum of three scans was permitted per reflection.

Results and Discussion

NMR Method To Assign Alkenyl Ligand Structure. Assignment of the structural arrangement of the tri- and tetrasubstituted alkenyl ligands in CpFeCO[P(OPh)$_3$](η^1-CR$_1$=C(R$_2$)R$_3$) complexes prepared in this and our earlier work is difficult. A combination of X-ray crystallography,[1b,c] isotope labeling,[1d,f] and variable-temperature NMR studies[2] have been used previously to make the structural assignments.

Examination of the ^{13}C NMR spectra of over 30 of these previously characterized alkenyliron complexes (Table II) shows some very consistent trends in the P–C coupling constants and chemical shifts of the alkene bound carbon atoms. These trends afford two simple rules that allow

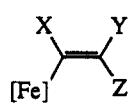
Table II. ^{13}C NMR Data[a] for Alkene-Bound Carbon Atoms in Complexes of the Type[b]



no.	complex	carbon atom position X	Y	Z
1.	[Fe](CH$_2$CH=CH$_2$)C=CH$_2$[c]	56.7 (2)		
2.	[Fe](CH$_2$SPh)C=CH$_2$[c]	53.5 (3)		
3.	(*E*)-[Fe](CO$_2$Me)C=C(H)-Me[d]	178.8	19.9 (2)	
4.	(*Z*)-[Fe](Ph)C=C(Ph)Me[e]		27.6 (3)	
5.	(*E*)-[Fe](Me)C=C(Ph)OMe[f]	28.7 (6)		
6.	(*E*)-[Fe](Me)C=C(Me)-CCMe[g]	37.9 (7)	83.2 (5)	27.3
7.	(*E*)-[Fe](Me)C=C(H)-CCMe[c]	34.5	79.7 (4)	
8.	(*E*)-[Fe](Ph)C=C(Me)Ph[h]			29.0
9.	(*E*)-[Fe](CO$_2$Me)C=C(Me)-OMe[f]	178.2		17.1
10.	(*E*)-[Fe](CO$_2$Me)C=C(Me)-Ph[h]	178.1		27.6
11.	(*E*)-[Fe](Me)C=C(Me)Ph[i]	36.1 (5)	141.4	29.7
12.	(*E*)-[Fe](Me)C=C(Me)SPh[g]	37.3 (2)		29.2
13.	(*E*)-[Fe](Et)C=C(Et)Ph[e]	41.3 (4)	147.7	35.5
14.	(*Z*)-[Fe](Me)C=C(Me)H[c]	40.9 (4)		20.7
15.	(*E*)-[Fe](Me)C=C(H)Me[c]	30.7	17.0 (2)	
16.	(*Z*)-[Fe](Me)C=C(Ph)Me[i]	34.0 (9)	23.8 (3)	142.1
17.	(*E*)-[Fe](Me)C=C(H)Ph[c]	33.6	141.1 (2)	
18.	[Fe](CO$_2$Me)C=C(Me)$_2$[g]	178.6	24.9 (2)	26.6
19.	(*E*)-[Fe](CO$_2$Me)C=C(Me)-NPh$_2$[f]	179.1 (6)		21.3 (2)
20.	[Fe](CH$_2$OMe)C=C(Me)$_2$[j]	82.5 (8) 82.9 (2)	22.8 (2) 22.0 (3)	29.8 29.7
21.	(*E*)-[Fe](CH$_2$OMe)C=C-(Me)Ph[j]	83.4 (9)	148.3 (3)	30.0
22.	(*E*)-[Fe](CH$_2$OMe)C=C-(Me)SAr[j,k]	85.3 (8) 83.4		28.3 28.5
23.	(*Z*)-[Fe](Me)C=C(*i*-Pr)Me[j]	33.6 (11)	14.6 (4)	39.5
24.	(*E*)-[Fe](Me)C=C(*i*-Pr)Ph[j]	35.1 (10)		38.9
25.	(*E*)-[Fe](*i*-Pr)C=C(Me)Ph[j]	41.4 (4)		31.9
26.	(*E*)-[Fe](Me)C=C(*i*-Pr)-SPh[j]	36.4 (9)		40.3

[a] Listed as chemical shift in ppm (P–C coupling in Hz). [b] [Fe] = CpFeCO[P(OPh)$_3$]; X, Y, and Z = alkyl, aryl, and H substituents. [c] Reference 1d. [d] Belmore, K. Ph.D. Dissertation, University of South Carolina, May, 1984. [e] Reference 3. [f] Reference 1e. [g] Reference 2. [h] Reger, D. L.; Klaeren, S. A., unpublished results. [i] Reference 1c. [j] This work. [k] Ar = *p*-C$_6$H$_4$(Me).

complete assignment of the structure of most alkenyliron complexes in this system. Rule 1: P–C coupling is observed in positions (see A below) X and Y, but *not* at Z. Rule 2: When X = Y or X = Z, the lower field resonance is assigned to X.



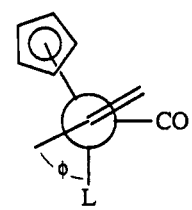
A

Evidence for the first rule is seen in cases where assignment of the resonances to either X, Y, or Z substituents is unambiguous. Entries 1–7 are examples of complexes with clearly assignable substituents (for 6 only the alkynyl carbon resonance) that show coupling at position X or Y. Cases 8, 9, and 10 are examples of a methyl group at position Z that show no coupling. Cases 6, 11, 12, 13, and 14 all have identical substituents (methyl in all cases except 13) in positions X and Z. In every case, the lower field resonance (36.1–40.9 ppm for methyl) is a doublet and the higher field resonance (20.7–29.7 ppm for methyl) is a singlet. The coupling rule allows assignment of the lower field resonance in each case to the substituent in the X position. For case 15, that has a methyl group at both positions X and Y, the coupled higher field resonance was shown to arise from the Y position methyl group from the ^{13}C NMR spectrum of the deuteriated sample CpFeCO-[P(OPh)$_3$](η^1-(*E*)-C(CD_3)=C(D)CH$_3$).[1d] In the similar entries 16 and 23 (vide infra), the higher field methyl resonance is assigned to the Y position by analogy.

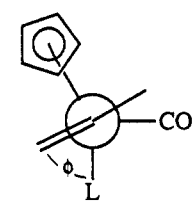
Entries 7, 15, and 17 show coupling at the Y position but not at X. These are representative of a total of nine complexes with a η^1-(*E*)-C(Me)=C(H)R ligand that all have this coupling pattern. They are the only class of alkenyl ligands that do not show P–C coupling at position X. Although no coupling is observed, chemical shift values for the X position methyl groups in these complexes (30.2–34.5 ppm) do fall in the expected range.

The coupling rule is confirmed by results on new complexes prepared in this work. The arrangement of the alkenyl substituents in cases 21, 23, and 26 has been determined by means other than the rules (vide infra). For case 21, the resonance for the methylene group at position X is clearly distinguishable from the resonance for the methyl at position Z. The methylene resonance is a doublet, the methyl resonance is a singlet. For cases 23 and 26, the Z position resonance is clearly assignable and coupling is observed at positions X and Y, but not at position Z.

Two entries are given in Table II for cases 20 and 22 because two rotamers about the Fe–C(alkenyl) bond are observed in low-temperature (ca. −15 °C) spectra. We have reported previously[2] that molecules with methyl groups at both positions X and Z (e.g., cases 6, 11, 12, and 14) exist as two rotamers in solution that interconvert with a barrier to rotation of ca. 13 kcal/mol. These two rotamers have been assigned configurations B and C based on crystallo-



B



C

graphic studies.[1b,c,f,9] The one P(OPh)$_3$-substituted complex, CpFeCO[P(OPh)$_3$](η^1-(*Z*)-C(Me)=C(Ph)Me), that has been studied crystallographically[1c] has the structure shown in B in the solid state with Φ = 55.4°. An interesting observation is that for both cases 20 and 22, one rotamer has a large coupling at position X while for the other rotamer the coupling is small or zero. These results for the low coupling rotamers are similar to those observed for the CpFeCO[P(OPh)$_3$](η^1-(*E*)-C(Me)=C(H)R) complexes noted above and both probably are the same rotamer type. While we cannot assign rotamers to the individual spectra, it is reasonable to expect that the angle Φ would be somewhat different in the two configurations, yielding different coupling constants.[10] Note that the data given in Table II for cases 6, 11, 12, and 14 are averaged data for the two rotamers.

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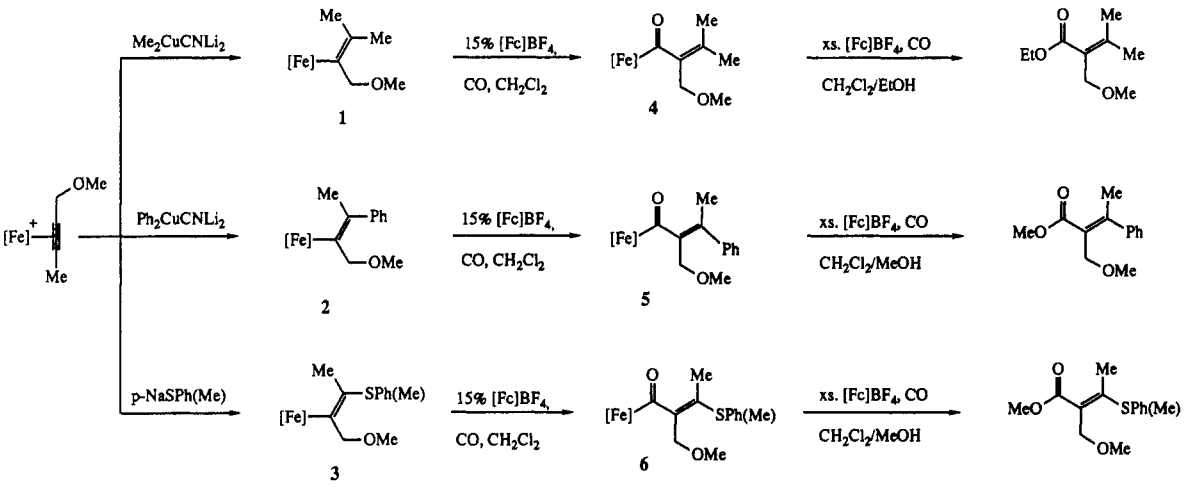
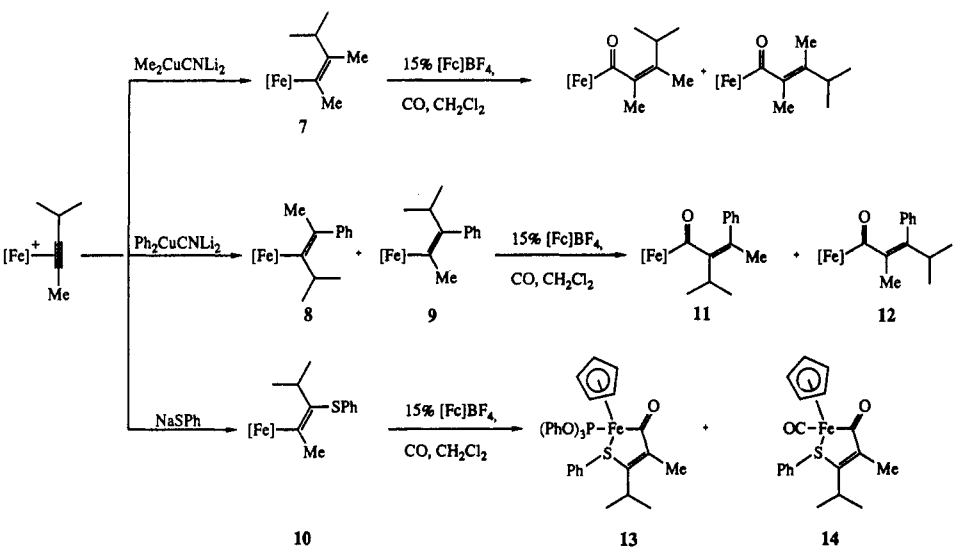
Scheme III



[Fe] = $CpFeCO[P(OPh)_3]$, [Fc] = $(Cp_2Fe)^+$

Scheme IV



[Fe] = $CpFeCO[P(OPh)_3]$, [Fc] = $(Cp_2Fe)^+$

The one exception to the coupling rule is entry 19. In this case, coupling is observed in the resonances for the ester carbon atom in position X, the ipso-phenyl carbon atom bonded through nitrogen at position Y, and the methyl group at position Z. This is the only case that coupling is observed for an ester carbon atom at position X (see cases 3, 9, 10, and 18), through a heteroatom at position Y, as well as the methyl group at Z. Possibly the bulky NPh_2 substituent causes the alkenyl ligand to adopt a configuration very different from the other molecules that results in much larger coupling constants. An alternative explanation, suggested by a reviewer, is that the coupling is due to a low barrier to rotation about the C–C double bond in this amino acylic ester.

Thus, P–C coupling and chemical shift can be used to assign the structural arrangement of the alkenyl substituents in these molecules. For the limited cases in which data are available, the rules also seem to hold for $CpFeCO(PPh_3)(\eta^1$-alkenyl) complexes.[2]

Synthesis of Alkenyl Complexes. Scheme III shows the addition reactions of $[CpFeCO[P(OPh)_3](\eta^2$-$MeC{\equiv}CCH_2OMe)]BF_4$ with three typical nucleophiles. In all cases, the reactions proceed in high yield with formation of a single alkenyl isomer. The stereochemistry of the products is known because trans addition of these nucleophiles has been demonstrated previously and isomerization of the double bond has not been observed for any of these alkenyliron complexes under the reaction conditions or isolation procedures.[1,2] The regiochemistry of the reaction to form complex **2** has been determined definitively by a solid state X-ray crystal structure analysis of the product of the reaction of **2** and CO, complex **5** (vide infra). The structure of **1** and **3** follow from the P–C coupling constant argument given in the preceding section. In all cases the methylene carbon atom of the CH_2OMe substituent shows coupling and is assigned to position X, geminal to iron. The resonance for the methyl group at position Z, cis to iron, is a singlet. The chemical shift values in each complex are very similar for the methyl and methylene carbon resonances, respectively, as expected for closely analogous alkenyl structures.

Addition reactions with the η^2-isopropylmethylacetylene complex are shown in Scheme IV. In two cases, the reactions are regioselective whereas in the phenyl addition reaction both regioisomers form. The regiochemistry of the reaction to form **7** can be assigned to that shown be-

cause in the oxidatively catalyzed CO insertion reaction of **7**, two stereoisomers form. If the regiochemistry was opposite to that assigned for **7**, a geminal dimethylalkenyl ligand would form for which only one stereoisomer would be possible. The structure of **10** is assigned from the proton-coupled ^{13}C NMR spectrum of **14**, one of the products formed in the oxidatively catalyzed reaction of **10** and CO. The acyl carbon atom resonance in **14** is a quartet with J_{C-H} = 3 Hz. This quartet arises from three-bond coupling to the geminal methyl group. The coupling constant data for **8** and **9** clearly define the alkene structure in both cases. Thus, for **8** coupling is observed in the methyne resonance but not in the methyl resonance. For **9**, the opposite pattern is observed.

These results combined with those shown in eq 1 determine the regiochemistry of the addition reaction for four unsymmetrically substituted alkynes. Nucleophilic addition reactions with similar (η^2-alkene)metal complexes have been studied theoretically.[11] The origin of the activation of the alkene to nucleophilic addition was attributed to slippage of the metal along the π-bond to an intermediate resembling η^1-coordination. It was argued that electron donor substituents on the alkene should favor slippage away from the substituent, a prediction verified experimentally.[12] For electron acceptor substituents, a prediction was not as clear because electronic effects would favor slippage toward the substituted alkene carbon atom, but steric effects would be in the opposite direction.

These ideas should apply to [CpFeCOL(η^2-alkyne)]$^+$ complexes. For the π-donating phenyl substituent in MeC≡CPh, nucleophiles add to the alkyne carbon atom bearing this donor group as predicted by theory. The strongly electron-withdrawing ester substituent in MeC≡CCO_2R does the opposite, directing the nucleophile away from the functionalized alkyne carbon atom. Similar regioselectivity to the ester-substituted case is observed with the weaker electron-withdrawing –CH_2OMe substituent for the alkyne MeC≡CCH_2OMe. Electronic effects are clearly dominant in these two cases. For MeC≡CCHMe_2, two of the reactions are regioselective and in the direction predicted by both steric and electronic arguments. The phenyl addition reaction, using $Ph_2CuCNLi_2$, is not selective, and, in fact, isomer **8** is the predominant product. This result is surprising, especially considering the complete regioselectivity observed when $Me_2CuCNLi_2$ is the reagent. Considerably more information on the mechanism of these reactions and the structure of "higher order cuprates"[7] is needed before a clear understanding of these results is possible. From a synthetic viewpoint, the reactions are nearly always regioselective.

A number of other functionalized alkynes have not proven useful in these reactions. The preparation of alkenyl complexes is a two step procedure. First, the π-complex is formed by adding the alkyne to a mixture of CpFeCO[P(OPh)$_3$]I and $AgBF_4$ in CH_2Cl_2. After filtration to remove AgI, the nucleophilic addition reaction is carried out. The η^2-alkyne complex is generally not isolated. Alkenyl products do not form in this sequence for the alkynes MeC≡C$SiMe_3$, MeC≡CCH_2OSiMe_3, MeC≡COEt, MeC≡CNEt_2, EtC≡CC(O)Me, and cyclooctyne. For the $SiMe_3$ substituted cases, the iron appears to induce cleavage of the silyl group. For cyclooctyne, the η^2-complex forms but reactions with nucleophilic reagents were not observed. With the other three alkynes, a cationic intermediate seems to form, but the nucleophilic addition reactions are not successful. It is likely that a lone pair on the heteroatom coordinates to iron rather than the triple bond. We have shown previously that nitrogen bonds to iron in preference to the double bond for ligands such as acrylonitrile.[13]

Synthesis of Alkenylacyl Complexes and Alkenyl Esters. As shown in Scheme III, compounds **1**, **2**, and **3** react with CO (1 atm) at –78 °C in the presence of a catalytic amount of [Cp_2Fe]BF_4 as an oxidant to form the alkenylacyl complexes **4**, **5**, and **6**, respectively. In our earlier work, it was shown that these oxidatively catalyzed insertion reactions proceed in most cases with retention of alkene stereochemistry. The exceptions were complexes with a phenyl group trans to iron with a substituent other than hydrogen at the cis position. As shown in Scheme II, these complexes undergo *E–Z* isomerization during the CO insertion reaction. Because of the similarity of the alkenyl substituents in **2** to these examples, it was anticipated that isomerization of the alkene would accompany CO insertion yielding a (*Z*)-alkene product. It was expected that **3** should react without isomerization to yield the *E* isomer.

We have suggested previously that the stereochemistry of acyl complexes with a cis phenyl substituent can be assigned on the basis of ^1H NMR results. Isomers of this type show a 0.5 ppm shielding of the Cp resonance when compared to other alkenylacyl complexes. This shielding is presumably caused by the proximity of the Cp hydrogen atoms to the region of inner anisotropy of the phenyl ring. This effect has been observed by others.[14] The ^1H NMR of product **5** did *not* show this anomalous shielding of the Cp resonance. In order to determine definitively the structure of the alkene, we determined the solid-state structure of **5** by X-ray crystallography (vide infra). It is the *E* isomer shown in Scheme III and predicted by NMR. The stereochemistry of **6** was assigned by analogy to **5** and the numerous examples[3] of similar complexes that undergo CO insertion with retention of alkene stereochemistry.

The alkenylacyl ligands of the **4**, **5**, and **6** can be cleaved from iron by using excess [Cp_2Fe]BF_4 in the presence of alcohol to yield alkenyl esters. Ce(IV), the oxidant used in our earlier studies, is not compatible with these cleavage reactions. In the preparation of $EtO_2CC(CH_2OMe)$=CMe_2, only a limited amount of EtOH was added to prevent formation of $EtO_2CC(CMe_2OEt)$=CH_2. This is to our knowledge the first reported preparation of the alkenyl esters shown in Scheme III. There is a brief report[15] of $EtO_2CC(CH_2OMe)$=CMe_2, but the published NMR data do not match those reported here. These syntheses represent a convenient, essentially two-step procedure for the conversion of MeC≡CCH_2OMe into tetrasubstituted alkenes. The reactions are stereo- and regioselective, with good choice of the added nucleophile. The cleavage reaction introduces an ester functional group of use for further elaboration.

Conversion of complexes **7**, **8**, **9**, and **10** to alkenylacyl complexes is not as synthetically useful because mixtures form in all cases. Complex **7**, with the bulky isopropyl group cis to iron, undergoes partial isomerization in the oxidatively catalyzed CO insertion reaction to yield a 3:2 mixture of the *E* and *Z* acyl complexes. Complexes **8** and **9** (taken into reaction as a mixture) each yield a single

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Table III. Bond Distances (Å) with Esd's in Parentheses for CpFeCO[P(OPh)$_3$](η^1-(*E*)-COC(CH$_2$OMe)=C(Me)Ph) (5)

Fe-C1	1.740 (4)	O3-C6	1.419 (4)
Fe-C2	1.967 (4)	O10-C11	1.388 (4)
Fe-C55	2.096 (4)	O20-C21	1.402 (4)
Fe-C54	2.097 (4)	O30-C31	1.407 (4)
Fe-C53	2.098 (4)	C2-C3	1.519 (5)
Fe-P	2.109 (1)	C3-C4	1.329 (4)
Fe-C51	2.111 (5)	C3-C6	1.508 (5)
Fe-C52	2.117 (4)	C4-C41	1.487 (5)
P-O30	1.598 (2)	C4-C5	1.502 (5)
P-O20	1.600 (2)	C51-C52	1.362 (6)
P-O10	1.620 (2)	C51-C55	1.384 (7)
O1-C1	1.151 (4)	C52-C53	1.396 (6)
O2-C2	1.220 (4)	C53-C54	1.400 (6)
O3-C7	1.414 (7)	C54-C55	1.405 (7)

Table IV. Bond Angles (deg) with Esd's in Parentheses for CpFeCO[P(OPh)$_3$](η^1-(*E*)-COC(CH$_2$OMe)=C(Me)Ph) (5)

C1-Fe-C2	94.6 (2)	O20-P-Fe	123.2 (1)
C1-Fe-C55	93.7 (2)	O10-P-Fe	117.7 (1)
C1-Fe-C54	122.9 (2)	C7-O3-C6	111.4 (4)
C1-Fe-C53	158.6 (2)	C11-O10-P	124.4 (2)
C1-Fe-P	91.4 (1)	C21-O20-P	123.1 (2)
C1-Fe-C51	99.2 (2)	C31-O30-P	125.5 (2)
C1-Fe-C52	133.1 (2)	O1-C1-Fe	176.8 (4)
C2-Fe-C55	115.4 (2)	O2-C2-C3	118.4 (3)
C2-Fe-C54	85.9 (2)	O2-C2-Fe	123.7 (3)
C2-Fe-C53	94.8 (2)	C3-C2-Fe	117.7 (2)
C2-Fe-P	91.7 (1)	C4-C3-C6	124.9 (3)
C2-Fe-C51	150.8 (2)	C4-C3-C2	121.4 (3)
C2-Fe-C52	131.9 (2)	C6-C3-C2	113.7 (3)
C55-Fe-C54	39.2 (2)	C3-C4-C41	122.9 (3)
C55-Fe-C53	64.9 (2)	C3-C4-C5	122.4 (3)
C55-Fe-P	151.9 (2)	C41-C4-C5	114.6 (3)
C55-Fe-C51	38.4 (2)	O3-C6-C3	111.7 (3)
C55-Fe-C52	63.8 (2)	C52-C51-C55	108.4 (5)
C54-Fe-C53	39.0 (2)	C52-C51-Fe	71.5 (3)
C54-Fe-P	145.7 (1)	C55-C51-Fe	70.2 (3)
C54-Fe-C51	65.0 (2)	C51-C52-C53	108.9 (5)
C54-Fe-C52	64.7 (2)	C51-C52-Fe	70.9 (3)
C53-Fe-P	107.5 (1)	C53-C52-Fe	69.9 (2)
C53-Fe-C51	64.5 (2)	C52-C53-C54	107.6 (5)
C53-Fe-C52	38.7 (2)	C52-C53-Fe	71.4 (2)
P-Fe-C51	113.5 (2)	C54-C53-Fe	70.5 (2)
P-Fe-C52	93.0 (1)	C53-C54-C55	106.8 (5)
C51-Fe-C52	37.6 (2)	C53-C54-Fe	70.6 (2)
O30-P-O20	98.5 (1)	C55-C54-Fe	70.4 (3)
O30-P-O10	102.6 (1)	C51-C55-C54	108.3 (5)
O30-P-Fe	114.3 (1)	C51-C55-Fe	71.4 (3)
O20-P-O10	96.8 (1)	C54-C55-Fe	70.4 (3)

stereoisomer. As described above, both of these acyl complexes are assigned *Z* stereochemistry based on the observed shielding of the Cp resonance by 0.5 ppm when compared to other complexes. Complex **10** also undergoes *E*–*Z* isomerization during the CO insertion reaction, and, in addition, the thio group, now cis to iron, displaces either a P(OPh)$_3$ or CO ligand to form a separable mixture of complexes **13** and **14**. This type of isomerization–substitution reaction was not observed in previous examples using thiophenol-substituted alkenyl complexes. Complex **10** differs from these earlier cases in that a bulky isopropyl group is cis to iron. Clearly, the isomerization reaction is much more favorable for complexes with a bulky group cis to the iron.

Description of Structure. The molecular structure of CpFeCO[P(OPh)$_3$](η^1-(*E*)-COC(CH$_2$OMe)=C(Me)Ph) is shown in Figure 1. Bond distances are listed in Table III, and bond angles are listed in Table IV. The most important feature of the structure is the arrangement of the substituents on the alkenyl ligand. The ether group is geminal to the acyl carbonyl, thus verifying the regiochemistry of the nucleophilic addition reaction to form **2** as shown in Scheme III. The phenyl group is trans to the

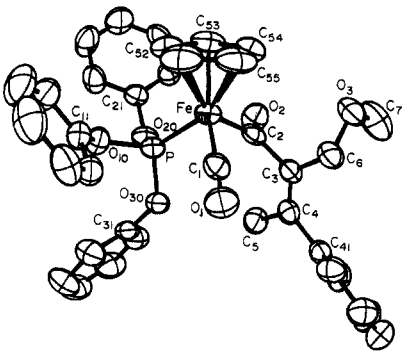

Figure 1. An ORTEP drawing of CpFeCO[P(OPh)$_3$](η^1-(*E*)-COC(CH$_2$OMe)=C(Me)Ph) (**5**) showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and *B*(eq) for CpFeCO[P(OPh$_3$)](η^1-(*E*)-COC(CH$_2$OMe)=C(Me)Ph) (5)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Fe	0.134012 (43)	0.180186 (42)	−0.158145 (52)	3.18 (2)
P	0.160462 (76)	0.351336 (75)	−0.104855 (91)	3.04 (3)
O1	0.06398 (24)	0.14448 (24)	−0.45513 (28)	5.5 (1)
O2	0.36826 (21)	0.25749 (22)	−0.01725 (27)	4.7 (1)
O3	0.31920 (28)	0.00374 (22)	−0.23482 (30)	5.4 (1)
O10	0.05515 (19)	0.38467 (19)	−0.09305 (24)	3.79 (8)
O20	0.25153 (18)	0.44677 (18)	0.03880 (22)	3.57 (8)
O30	0.19931 (19)	0.40673 (18)	−0.21260 (22)	3.39 (8)
C1	0.09494 (30)	0.15999 (29)	−0.33663 (41)	3.7 (1)
C2	0.29392 (30)	0.21520 (26)	−0.13216 (37)	3.1 (1)
C3	0.32462 (28)	0.17917 (28)	−0.26244 (35)	3.2 (1)
C4	0.38440 (28)	0.25415 (29)	−0.30638 (36)	3.3 (1)
C5	0.43623 (41)	0.37797 (34)	−0.22290 (52)	4.3 (2)
C6	0.28315 (39)	0.05354 (32)	−0.33147 (45)	4.1 (1)
C7	0.43673 (63)	0.03396 (63)	−0.19337 (91)	8.0 (3)
C11	−0.05653 (31)	0.31618 (31)	−0.17320 (40)	3.7 (1)
C12	−0.09399 (35)	0.27121 (33)	−0.31778 (42)	4.0 (1)
C13	−0.20629 (41)	0.20674 (37)	−0.39107 (56)	5.3 (2)
C14	−0.28003 (45)	0.18698 (46)	−0.32172 (74)	6.8 (2)
C15	−0.24330 (44)	0.23362 (48)	−0.17811 (72)	6.8 (2)
C16	−0.13238 (41)	0.29808 (42)	−0.10341 (56)	5.2 (2)
C21	0.25223 (29)	0.44406 (27)	0.17207 (34)	3.2 (1)
C22	0.32578 (33)	0.40886 (31)	0.24344 (38)	3.7 (1)
C23	0.33136 (39)	0.41273 (36)	0.37775 (43)	4.8 (2)
C24	0.26239 (43)	0.44995 (43)	0.43793 (48)	6.0 (2)
C25	0.19093 (44)	0.48532 (45)	0.36632 (47)	6.1 (2)
C26	0.18397 (37)	0.48262 (37)	0.23209 (43)	4.9 (2)
C31	0.21772 (31)	0.51777 (29)	−0.20433 (35)	3.3 (1)
C32	0.13079 (42)	0.53891 (40)	−0.27417 (49)	5.0 (2)
C33	0.14962 (57)	0.64529 (46)	−0.27621 (61)	6.5 (2)
C34	0.25430 (61)	0.72786 (46)	−0.21106 (62)	6.8 (2)
C35	0.34045 (53)	0.70537 (39)	−0.14202 (55)	5.9 (2)
C36	0.32259 (39)	0.60000 (34)	−0.13808 (44)	4.4 (1)
C41	0.40293 (29)	0.22290 (28)	−0.44326 (37)	3.3 (1)
C42	0.31564 (34)	0.14767 (33)	−0.56562 (41)	4.1 (1)
C43	0.33184 (41)	0.12081 (39)	−0.69309 (47)	4.7 (2)
C44	0.43519 (44)	0.17019 (40)	−0.70159 (52)	5.3 (2)
C45	0.52238 (42)	0.24570 (42)	−0.58317 (52)	5.4 (2)
C46	0.50708 (34)	0.27181 (35)	−0.45436 (45)	4.2 (1)
C51	−0.02105 (45)	0.07846 (47)	−0.15363 (59)	6.0 (2)
C52	0.04141 (44)	0.15537 (43)	−0.02180 (56)	5.3 (2)
C53	0.14148 (41)	0.14112 (36)	0.02482 (46)	4.6 (2)
C54	0.13894 (45)	0.05115 (37)	−0.08129 (52)	4.9 (2)
C55	0.03690 (51)	0.01299 (40)	−0.19215 (55)	5.9 (2)

acyl carbonyl showing that the insertion reaction proceeds with retention of alkene stereochemistry. The overall geometry around iron is best characterized as octahedral with the Cp group occupying three sites. The structure, especially the arrangement of the alkenylacyl ligand, is very similar to that observed in CpFeCO[P(OPh)$_3$](η^1-(*E*)-COC(Me)=C(Me)SPh).[3] The Fe–C(2)(acyl) bond distance is 1.967 (4) Å, 0.06 Å shorter than expected for a Fe–C(sp^2) single bond. The acyl group is anti to the carbonyl ligand (O(2)C(2)–FeC(1) torsion angle = 165.9 (3)°) as is observed

in other similar structures.[3,9a,16] The C(3)–C(4)(alkenyl) bond length is normal at 1.329 (4) Å and is not conjugated to either the acyl (O(2)C(2)–C(3)C(4) torsion angle = –70.9 (5)°) or the phenyl (C(3)C(4)–C(41)C(42) torsion angle = 45.0 (5)°) group.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this project and the NSF (CHE 84-11172) and NIH (RR-02435) for funds supporting NMR instrumentation.

Registry No. 1, 111237-17-3; 2, 111237-18-4; 3, 111237-19-5; 4, 111237-20-8; 5, 111237-21-9; 6, 111237-22-0; 7, 111237-23-1; 8, 111237-24-2; 9, 111237-25-3; 10, 111266-86-5; 11, 111237-26-4; 12, 111237-27-5; 13, 111290-83-6; 14, 111266-87-6; [CpFeCO[P(OPh)$_3$](η^2-MeC≡CCH$_i$OMe)]BF$_4$, 111237-29-7; Me$_i$CuCNLi$_2$, 80473-70-7; Ph$_2$CuCNLi$_2$, 80473-66-1; *p*-NaSC$_6$H$_4$Me, 10486-08-5; [Cp$_2$Fe]BF$_4$, 1282-37-7; (*E*)-MeO$_2$CC(CH$_2$OMe)=C(Me)Ph, 111209-36-0; (*E*)-MeO$_2$CC(CH$_2$OMe)=C(Me)S-*p*-C$_6$H$_4$Me, 111209-37-1; EtO$_2$CC(CH$_2$OMe)=CMe$_2$, 102674-24-8; EtO$_2$CCnCMe$_i$OEt)=CH$_2$, 111209-38-2; [CpFeCO[P(OPh)$_3$](η^2-MeC≡CCHMe$_2$)]BF$_4$, 111237-31-1; NaSPh, 930-69-8; (*Z*)-CpFeCO[P(OPh)$_3$][η′-COC(Me)=CCHMe$_2$)Me], 111237-32-2; (*E*)-CPFeCO[P(OPh)$_3$][η′-COC(Me)=C(CHMe$_2$)Me], 111320-43-5.

Supplementary Material Available: Tables of bond distances and angles for the phenyl rings, positional parameters of H atoms, and anisotropic thermal parameters (8 pages); a listing of structure factor amplitudes (24 pages). Ordering information is given on current masthead page.

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Iron η^2-Alkyne Complexes. Crystal and Molecular Structures of [CpFeCO[P(OPh)$_3$](η^2-MeC≡CPh)]SbF$_6$ and [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]SbF$_6$

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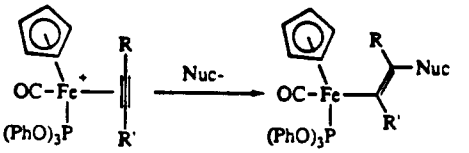
Received June 22, 1987

The complexes [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]SbF$_6$ (1) and [CpFeCO[P(OPh)$_3$](η^2-MeC≡CPh)]SbF$_6$ have been crystallized and their solid-state structures determined by X-ray crystallography. Crystals of 1 are monoclinic of space group $P2_1/n$ with $Z = 4$, $a = 18.995$ (3) Å, $b = 16.711$ (3) Å, $c = 9.434$ (1) Å, and $\beta = 101.17$ (1)°. Crystals of 2 are monoclinic of space group $P2_1/c$ with $Z = 4$, $a = 9.108$ (2) Å, $b = 20.658$ (3) Å, $c = 17.510$ Å, and $\beta = 94.57$ (1)°. The unsymmetrical alkyne in 2 is symmetrically bonded to iron with carbon–iron bond distances of 2.14 (1) and 2.146 (9) Å. For 1, a slight distortion in these bond distances is observed (2.165 (7) and 2.114 (6) Å). The alkyne is oriented orthogonal to the Fe–center Cp vector. For 1, the center Cp–Fe–center alkyne–alkyne carbon torsion angles are both 90° whereas in 2 they are –85.3 and 94.6°. Bonding to the iron does not greatly purturb the alkyne. The C≡C bond lengths are the same (1.19 (1) Å for 1, 1.21 (1) Å for 2) as in the free alkynes and C≡C—R bend back angles range from 155 (2) to 159 (1)°. Complex 1 is fluxional in solution. The alkyne rotates about the Fe–alkyne bond with a barrier to rotation of 12.5 kcal/mol at 241 K. The NMR spectra of 2 are invariant from 210 to 330 K, but the cation [CpFeCO[P(OPh)$_3$](η^2-MeC≡CCO$_2$Me)]$^+$ shows two rotamers in a 1/1.7 ratio at low temperature that interconvert with a barrier of 11.3 kcal/mol at 204 K.

Introduction

Over the past several years, a series of papers has been published[1] describing the preparation and reactivity of [CpFeCO(L)(η^2-alkyne)]$^+$ (L = CO, PPh$_3$, P(OPh)$_3$) complexes. Coordination to iron activates the alkyne toward nucleophilic addition reactions yielding an extensive series (studied most completely for L = P(OPh)$_3$) of alkenyliron complexes (eq 1).



(1)

Nuc = Me, Ph, CH(CO$_2$Et)$_2$, CH=CH$_2$, C≡CMe, CN, SPh
R = R' = Me; R = Me, R' = CO$_2$Me or CH$_2$OMe; R = Ph or i-Pr, R' = Me

To support these synthetic studies, it was desired to determine crystallographically the solid-state structures of representative examples of the η^2-alkyne starting materials. Two main features are important. Studying analogous η^2-alkene complexes, Hoffmann and co-workers[2]

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