

Reactions of Alkylolithium Reagents and Nitrogen- and Oxygen-Based Nucleophiles with Cyclopentadienyliron- η^2 -Alkyne Complexes. Crystal and Molecular Structure of a Diastereomeric Mixture of $\text{CpFeCO}[\text{P}(\text{OPh})_3][\eta^1\text{-CH}(\text{Me})\text{COMe}]$

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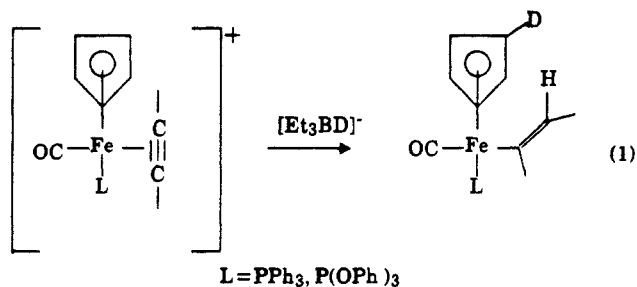
Reaction of $\{[\text{Fe}](\eta^2\text{-MeC}\equiv\text{CMe})\}^+$ ($[\text{Fe}] = \text{CpFeCO}[\text{P}(\text{OPh})_3]$) with PhNHLi or NH_2R ($\text{R} = \text{Ph}, \text{CH}_2\text{Ph}$) followed by base yields the respective $[\text{Fe}][\eta^1\text{-CH}(\text{Me})\text{C}(\text{NR})\text{Me}]$ complex. A similar reaction using Ph_2NLi yields $[\text{Fe}](\eta^1\text{-CH}_2\text{C}\equiv\text{CMe})$ whereas MeLi yields mainly the ring substitution product $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{-FeCO}[\text{P}(\text{OPh})_3][\eta^1\text{-}(E)\text{-C}(\text{Me})=\text{C}(\text{H})\text{Me}]$. The complex $[\text{Fe}][\eta^1\text{-CH}(\text{Me})\text{COMe}]$ forms by direct chromatography of the cationic η^2 -alkyne complex on alumina. X-ray analysis of a crystal composed of a ca. 7:3 mixture of the two diastereomerically related pairs of enantiomers has been carried out. The triclinic crystals are in the space group $P\bar{1}$ with $a = 12.358$ (2) Å, $b = 12.576$ (4) Å, $c = 8.289$ (2) Å, $\alpha = 96.54$ (2)°, $\beta = 95.66$ (2)°, $\gamma = 88.08$ (2)°, $V = 1273$ (1) Å³, and $Z = 2$. MeLi , PhNHLi , and Ph_2NLi react with $\{[\text{Fe}](\eta^2\text{-MeC}\equiv\text{CPh})\}^+$ at the cyclopentadienyl ring to yield mainly the respective $(\eta^5\text{-C}_5\text{H}_4\text{Nuc})\text{FeCO}[\text{P}(\text{OPh})_3][\eta^1\text{-}(E)\text{-C}(\text{Me})=\text{C}(\text{H})\text{Ph}]$ ($\text{Nuc} = \text{Me}, \text{PhNH}, \text{Ph}_2\text{N}$) complex. Reaction with $t\text{-BuOK}$ yields $[\text{Fe}](\eta^1\text{-CH}_2\text{C}\equiv\text{CPh})$ and with $\text{MeOH}/\text{Na}_2\text{CO}_3$ yields $[\text{Fe}][\eta^1\text{-}(E)\text{-C}(\text{Me})=\text{C}(\text{Ph})\text{OMe}]$, and treatment of the η^2 -alkyne complex with alumina yields $[\text{Fe}][\eta^1\text{-CH}(\text{Me})\text{COPh}]$. The complex $\{[\text{Fe}](\eta^2\text{-MeC}\equiv\text{CCO}_2\text{Me})\}^+$ reacts differently with each of the nucleophiles Et_2NLi , Ph_2NLi , and PhNHLi to yield respectively $[\text{Fe}][\eta^1\text{-C}(\text{CO}_2\text{Me})=\text{C}=\text{CH}_2]$, $[\text{Fe}][\eta^1\text{-}(E)\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{Me})\text{NPh}_2]$, and $(\eta^5\text{-C}_5\text{H}_4\text{NHPH})\text{FeCO}[\text{P}(\text{OPh})_3][\eta^1\text{-}(E)\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{H})\text{Me}]$. Reaction with $\text{MeOH}/\text{Na}_2\text{CO}_3$ yields $[\text{Fe}][\eta^1\text{-}(E)\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{Me})\text{OMe}]$ that upon treatment with alumina converts mainly to $[\text{Fe}][\eta^1\text{-CH}(\text{CO}_2\text{Me})\text{COMe}]$. Reaction with MeLi is indiscriminate, yielding four products that arise from attack at the ring, attack at the alkyne, deprotonation, and direct addition to the metal. The allene complex $\{[\text{Fe}](\eta^2\text{-CH}_2\text{C}=\text{C}=\text{CH}_2)\}^+$ reacts with Et_2NLi , Ph_2NLi , and MeLi by simple addition to the allene ligand to yield $[\text{Fe}][\eta^1\text{-C}(\text{CH}_2\text{Nuc})=\text{CH}_2]$ ($\text{Nuc} = \text{Et}_2\text{N}, \text{Ph}_2\text{N}, \text{Me}$). The complex $[\text{Fe}]$ undergoes ring substitution when treated with Et_2NLi to yield $(\eta^5\text{-C}_5\text{H}_4\text{NEt}_2)\text{FeCO}[\text{P}(\text{OPh})_3]\text{I}$.

Introduction

We have recently extensively developed the area of nucleophilic addition reactions with the complexes¹ $[\text{CpFeCO}(\text{L})(\eta^2\text{-alkyne})]\text{BF}_4$ ($\text{L} = \text{PPh}_3, \text{P}(\text{OPh})_3$). In this work, we have generally used reagents which are viewed as being "soft" nucleophiles² such as $\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$ and NaSPh . A number of our recent results caused us to decide to investigate the reactions of additional types of nucleophiles. First, we have observed that hydride (deuteride) generally does not add to the alkyne but adds to the cyclopentadienyl ring, followed by transfer to the alkyne of the endo hydrogen atom in the C_5H_6 ring thus formed (eq 1).³ This type of ring addition-substitution

reaction is unique for the η^2 -alkyne complexes and does not occur for similar η^2 -alkene or allene complexes. We wished to find out if nitrogen- or oxygen-based nucleophiles or RLi reagents would also react at the Cp ring. Second, we have now developed reaction conditions that will cleave the alkenyl group from iron and have prepared and isolated a series of alkenyl esters of potential use in organic syntheses.⁴ The ability to introduce heteroatom substituents was desired for this chemistry. Finally, for completeness in our nucleophilic addition studies, we wished to test hard nucleophiles. Hard nucleophiles generally react at the metal in other systems.⁵

We report here our studies on addition reactions of $[\text{NR}_2]^-$, $[\text{OR}]^-$, NR_3 , ROH , and RLi reagents with three iron complexes: $[\text{CpFeCO}[\text{P}(\text{OPh})_3](\eta^2\text{-alkyne})]\text{BF}_4$ (alkyne = $\text{MeC}\equiv\text{CMe}$, $\text{MeC}\equiv\text{CPh}$, $\text{MeC}\equiv\text{CCO}_2\text{Me}$). Although in certain cases straightforward alkyne addition chemistry is observed, in a number of cases we have discovered ring substitution reactions. A variety of other types of reactions, depending on metal complex and nucleophile, have been observed. In some cases, β -acyl complexes form. We have been able to grow single crystals of $\text{CpFeCO}[\text{P}(\text{OPh})_3][\eta^1\text{-CH}(\text{Me})\text{COMe}]$ in which both diastereomeric pairs have cocrystallized in unequal amounts and have solved the solid-state structure of the mixture by X-ray crystallography.



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Experimental Section

General Procedure. All operations on complexes in solution were carried out under an atmosphere of nitrogen using solvents that were dried and distilled before use. Chromatography was done by using Alcoa F-20 alumina. Proton NMR spectra were recorded at 60 or 90 MHz, with chemical shifts being reported as δ vs. Me₂Si. Carbon-13 NMR spectra were recorded at 20.13 MHz by using either CDCl₃ (δ 77.0), CD₂Cl₂ (δ 53.8), or C₆D₆ (δ 128.0) as solvent and internal standard and are reported as δ vs. Me₂Si. Elemental analyses were performed by Robertson Laboratory. Alkyl lithium reagents and (*n*-Bu)₄NOH were purchased from Aldrich. Preparations of [CpFeCO[P(OPh)₃](η^2 -MeC≡CMe)]BF₄, [CpFeCO[P(OPh)₃](η^2 -MeC≡CPh)]BF₄, [CpFeCO[P(OPh)₃](η^2 -MeC≡CCO₂Me)]BF₄, and [CpFeCO[P(OPh)₃](η^2 -CH₂=C=CH₂)]BF₄ have been reported previously.^{1,6} The known compound CpFeCO[P(OPh)₃]CH₃⁷ was prepared for use in assigning NMR spectra by reaction of CpFeCO[P(OPh)₃]I and MeLi.⁶ All lithium amides were prepared by addition of *n*-BuLi to a 10% excess of amine in THF at -78 °C and were added as solutions at this temperature.

CpFeCO[P(OPh)₃](η^1 -CH(Me)C(=NPh)Me) (1). **Method A.** [CpFeCO[P(OPh)₃](η^2 -MeC≡CMe)]BF₄ (1.68 g, 2.80 mmol) was stirred in THF (25 mL) at -78 °C. PhNHLi (2.80 mmol) was added via cannula, and the resulting solution was stirred for 1.5 h at -78 °C. The solution was allowed to warm to room temperature, and the solvent was evaporated. The residue was dissolved in CH₂Cl₂ (20 mL), filtered through alumina (7 cm), reduced in volume to 2 mL, and loaded onto an alumina column (30 cm). Elution with benzene, benzene/CH₂Cl₂ mixtures, and CH₂Cl₂ moved a broad orange band. The band was collected, and the solvent was evaporated to yield a 4:1 (A:B) mixture of diastereomers as a yellow-orange oil (1.03 g, 61%). **Method B.** A rapidly stirred CH₂Cl₂ solution (100 mL) of [CpFeCO[P(OPh)₃](η^2 -MeC≡CMe)]BF₄ (1.03 g, 1.71 mmol) was cooled to -78 °C and treated with PhNH₂ (0.16 mL, 1.8 mmol). The resulting solution was stirred 30 min at -78 °C and 1 h while being warmed to room temperature. The solution was then filtered through Celite, reduced in volume to 5 mL, and loaded onto an alumina column (30 cm). Elution with CH₂Cl₂ and CH₂Cl₂/THF mixtures moved a broad orange band. The band was collected, and the solvent was evaporated to yield a 5:1 (A:B) mixture of diastereomers as a yellow-orange oil (0.81 g, 78%): ¹H NMR (δ in CDCl₃) 7.21 (20, m, P(OPh)₃ and NPh), 4.22 (A), 4.17 (B) (total of 5, s, s, Cp), 2.66 (B), 2.37 (A) (total of 1, m, m, CH), 2.05 (B), 1.71 (A) (total of 3, s, s, NCMe), 1.60 (A), 1.45 (B) (total of 3, d, d, *J* = 6, 6 Hz, CHMe); IR (cm⁻¹ in C₆H₆) ν (CO) 1923; ¹³C NMR (δ in CDCl₃) 220.1 (d, *J* = 47 Hz, CO), 184.0 (d, *J* = 3 Hz, CN), 154.0, 128.6, 121.5, 120.1 (all s, NPh), 151.6, 129.5, 124.7, 121.3 (all d, *J* = 11, 1, 1, 4 Hz, P(OPh)₃), 85.1 (d, *J* = 2 Hz, Cp), 24.4 (d, *J* = 4 Hz, CHMe), 21.9 (s, NCMe), 21.8 (d, *J* = 22 Hz, FeC). Anal. (Mixture of diastereomers) Calcd for C₃₄H₃₂FeNO₅P: C, 67.45; H, 5.33; N, 2.31. Found: C, 68.03; H, 5.91; N, 2.28.

CpFeCO[P(OPh)₃](η^1 -CH(Me)C(=NCH₂Ph)Me) (2). [CpFeCO[P(OPh)₃](η^2 -MeC≡CMe)]BF₄ (1.03 g, 1.71 mmol) was dissolved in CH₂Cl₂ (50 mL), cooled to -78 °C, and treated with benzylamine (0.24 mL, 2.3 mmol). The resulting solution was stirred 40 min at -78 °C and 1.5 h while warming to room temperature. The solution was then filtered through Celite, reduced in volume to 2 mL, and loaded onto an alumina column (15 cm). Elution with CH₂Cl₂ and CH₂Cl₂/THF mixtures moved a broad orange band. The band was collected, and the solvent was evaporated to yield a 3:1 (A:B) mixture of diastereomers as a yellow oil (0.90 g, 85%): ¹H NMR (δ in CDCl₃) 7.26 (20, m, P(OPh)₃ and NCH₂Ph), 4.49 (2, br s, CH₂), 4.18 (A), 4.11 (B) (total of 5, s, s, Cp), 2.38 (1, m, CH), 2.18 (B), 1.87 (A) (total of 3, s, s, NCMe), 1.60 (3, br d, *J* = 7 Hz, CHMe); IR (cm⁻¹ in CH₂Cl₂) ν (CO) 1930; ¹³C NMR (δ in CDCl₃) 220.2 (d, *J* = 46 Hz, CO), 183.5 (m, CN), 151.5, 129.4, 124.5, 121.2 (d, s, s, d, *J* = 11, 4 Hz, P(OPh)₃), 142.1, 127.9, 127.8, 125.9 (all s, NCH₂Ph), 85.1 (d, *J* = 1 Hz, Cp), 54.8 (s, NCH₂), 24.3, 20.8 (s, s, Me's), 23.3 (d, *J* = 22 Hz, CH). Anal. Calcd for C₃₅H₃₄FeNO₅P: C, 67.86; H, 5.53; N, 2.26. Found: C, 67.87; H, 5.67; N, 2.24.

CpFeCO[P(OPh)₃](η^1 -CH₂C≡CMe) (3). **Method A.** [CpFeCO[P(OPh)₃](η^2 -MeC≡CMe)]BF₄ (1.03 g, 1.71 mmol) was stirred in THF (25 mL) at -78 °C. Ph₂NLi (1.71 mmol) was added, and the resulting solution was stirred 30 min at -78 °C and 30 min while being warmed to room temperature. The solvent was evaporated, and the dark residue was extracted with pentane (3 × 30 mL). The extracts were combined, and the solvent was evaporated to yield a yellow oil consisting primarily of Ph₂NH and 3. **Method B.** A stirred THF solution (12 mL) of CpFeCO[P(OPh)₃]I (2.00 g, 3.42 mmol) was cooled to -78 °C and treated dropwise with a 0 °C, THF solution of LiCH₂C≡CCH₃ (3.42 mmol).⁸ The resulting mixture was stirred for 2 h while slowly being warmed to room temperature. The THF was evaporated, and the dark residue was extracted with pentane (2 × 30 mL). The combined extracts were evaporated to dryness to yield a yellow oil consisting primarily of 3. Spectral properties of 3: ¹H NMR (δ in CDCl₃) 7.20 (m, P(OPh)₃), 4.05 (5, s, Cp), 1.84 (3, m, Me), 1.47, 1.30 (total of 2, m, m, CH₂); IR (cm⁻¹ in pentane) ν (CO) 1962; ¹³C NMR (δ in CDCl₃) 219.7 (d, *J* = 46 Hz, CO), 151.6, 129.8, 124.9, 121.5 (d, s, s, *J* = 8, 4 Hz, P(OPh)₃), 90.8, 74.8 (d, d, *J* = 5, 2 Hz, C≡C), 84.0 (d, *J* = 2 Hz, Cp), 4.5 (s, Me), -20.0 (d, *J* = 29 Hz, CH₂).

CpFeCO[P(OPh)₃](η^1 -CH(Me)COMe) (4). [CpFeCO[P(OPh)₃](η^2 -MeC≡CMe)]BF₄ (1.03 g, 1.71 mmol) was dissolved in CH₂Cl₂ (15 mL) and filtered through alumina (5 cm) using several CH₂Cl₂ rinses. The filtrate was evaporated to dryness leaving an orange oil. This was purified on alumina (20 cm) using benzene/THF (10:1) as eluant to yield a nearly 1:1 (A:B) mixture of diastereomers (0.25 g, 28%): ¹H NMR (δ in CDCl₃) 7.21 (15, m, P(OPh)₃), 4.22 (A), 4.16 (B) (total of 5, s, s, Cp), 2.38 (1, m, CH), 2.32 (B), 2.01 (A) (total of 3, s, s, COMe), 1.32 (A), 1.21 (B) (total of 3, d, d, *J* = 6, 7 Hz); IR (cm⁻¹, Nujol) ν (CO) 1930, 1632; ¹³C NMR (δ in CDCl₃) 219.3 (d, *J* = 46 Hz, CO), 215.0 (s, COMe), 151.3, 129.5, 124.8, 121.2, (121.1, other diastereoisomer) (d, s, s, d, *J* = 11, 4 Hz, P(OPh)₃), 84.5 (s, Cp), 29.4, 22.0 (s, m, Me's and FeC). Anal. Calcd for C₂₈H₂₇FeO₅P: C, 63.41; H, 5.13. Found: C, 63.41; H, 5.13.

Reaction of [CpFeCO[P(OPh)₃](η^2 -MeC≡CMe)]BF₄ and MeLi. [CpFeCO[P(OPh)₃](η^2 -MeC≡CMe)]BF₄ (1.03 g, 1.71 mmol) was stirred in THF (20 mL) at -78 °C and treated dropwise with MeLi (1.71 mmol). The resulting solution was stirred 30 min at -78 °C and 30 min while being warmed to room temperature. The solvent was evaporated and the dark residue was dissolved in CH₂Cl₂ (10 mL). This was filtered through alumina (3 cm), reduced in volume to 2 mL, and loaded onto an alumina column. Elution with pentane/benzene mixtures moved a single yellow band. The band was collected, and the solvent was evaporated to yield a yellow oil (0.45 g). ¹H NMR showed the oil to be (η^5 -C₅H₄Me)FeCO[P(OPh)₃][η^1 -(E)-C(Me)=C(H)Me] (5) contaminated with a small amount of CpFeCO[P(OPh)₃]Me (6). Spectral data for 5: ¹H NMR (δ in C₆D₆) 7.01 (20, m, P(OPh)₃), 5.79 (1, m, CH), 4.29, 4.17, 3.95 (total of 4, m, m, m, C₅H₄), 2.18 (3, s, FeCMe), 1.92 (3, d, *J* = 6 Hz, CHMe), 1.49 (3, s, C₅H₄Me); IR (cm⁻¹ in CH₂Cl₂) ν (CO) 1930; ¹³C NMR (δ in CD₂Cl₂) 220.4 (d, *J* = 39 Hz, CO), 151.9, 129.7, 124.8, 121.7 (d, s, s, d, *J* = 7, 5 Hz, P(OPh)₃), 142.3 (d, *J* = 39 Hz, FeC), 131.2 (d, *J* = 4 Hz, CHMe), 100.5, 86.6, 84.1, 81.7, 79.0 (d, s, s, d, s, *J* = 4, 2 Hz, Cp), 30.0, 16.6 (s, d, *J* = 2 Hz, vinyl Me's), 12.6 (s, C₅H₄Me).

(η^5 -C₅H₄NHPh)FeCO[P(OPh)₃][η^1 -(E)-C(Me)=C(H)Ph] (7). [CpFeCO[P(OPh)₃](η^2 -MeC≡CPh)]BF₄ (2.26 g, 3.42 mmol) was stirred in THF (40 mL) at -78 °C. PhNHLi (1.71 mmol) was added, and the resulting solution was stirred 15 min at -78 °C and 1 h while being warmed to room temperature. The solvent was evaporated, and the residue was dissolved in CH₂Cl₂ (15 mL). This was filtered through alumina, reduced in volume to 2 mL, and loaded onto an alumina column (25 cm). Elution with pentane/benzene (1:4) moved a yellow band well ahead of three faint dark colored bands. The yellow band was collected, and the solvent was evaporated to yield a yellow-orange oil (1.69 g, 74%): ¹H NMR (δ in CDCl₃) 7.05 (21, m, P(OPh)₃, NPh, and CH), 4.99, 4.20, 3.63 (1, 3, 1, m, m, m, C₅H₄ and NH), 2.11 (3, br s, Me); IR (cm⁻¹ in CH₂Cl₂) ν (CO) 1937; ¹³C NMR (δ in CD₂Cl₂) 219.4 (d, *J* = 45 Hz, CO), 166.5 (d, *J* = 39 Hz, FeC), 152.3, 130.1, 125.1,

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122.2 (d, s, s, d, $J = 9$, 4 Hz, P(OPh)₃), 143.9, 141.2, 131.9, 129.6, 128.3, 128.0, 124.5, 120.9, 117.7 (s, d, all s, $J = 2$ Hz, vinyl Ph and CNPh), 138.3 (d, $J = 5$ Hz, CHPh), 81.4, 75.0, 73.3, 70.2 (s, s, s, d, $J = 6$ Hz, Cp except CN), 34.3 (s, Me). Anal. Calcd for C₃₉H₃₄FeNO₄P: C, 70.17; H, 5.13; N, 2.10. Found: C, 70.46; H, 5.18; N, 1.98.

(η^5 -C₅H₄NPh₂)FeCO[P(OPh)₃][η^1 -(E)-C(Me)=C(H)Ph] (8). [CpFeCO[P(OPh)₃](η^2 -MeC≡CPh)]BF₄ (2.26 g, 3.42 mmol) was stirred in THF (40 mL) at -78 °C. Ph₂NLi (1.71 mmol) was added, and the resulting solution was stirred 15 min at -78 °C and 1 h while being warmed to room temperature. The solvent was evaporated, and the residue was dissolved in CH₂Cl₂ (15 mL). This was filtered through alumina, reduced in volume to 4 mL, and loaded onto an alumina column (25 cm). Elution with benzene moved a broad orange band. The band was collected, and the solvent was evaporated to yield an orange oil (2.08 g, 82%). ¹H NMR analysis showed this to be a mixture of 8, (η^5 -C₅H₄NPh₂)FeCO[P(OPh)₃][η^1 -C(=CH₂)CH₂Ph], and (η^5 -C₅H₄NPh₂)FeCO[P(OPh)₃][η^1 -C(Ph)=C(H)Me] (A, B, C) in a ratio of 6:3:2, respectively. Spectral data for the mixture: ¹H NMR (δ in CDCl₃) 7.12 (m, P(OPh)₃, NPh₂, and vinyl H of A), 5.81 (C) (m, CH), 5.51 (B) (br s, vinyl H), 4.31, 4.13 (m, m, C₅H₄), 3.80 (B) (br s, vinyl H), 2.91 (B) (m, PhCH₂), 2.36 (A) (br s, Me), 1.59 (C) (d, $J = 7$ Hz, Me); IR (cm⁻¹ in CH₂Cl₂) ν (CO) 1931; ¹³C NMR complexity of the spectrum precluded assignment of peaks to the minor isomers B and C. Hence, only peaks attributable to A are listed (δ in CD₂Cl₂): 219.6 (d, $J = 42$ Hz, CO), 158.1 (d, $J = 43$ Hz, FeC), 152.5, 129.8, 124.5, 122.1 (d, s, s, d, $J = 10$, 4 Hz, P(OPh)₃), 152.8, 145.9, 129.6, 128.9, 128.8, 128.2, 126.8, 125.2 (all s, NPh₂ and CPh), 141.6, 140.7 (d, d, $J = 3$, 3 Hz, Ph₂NC and PhC), 83.3, 81.4, 79.6, 64.0 (d, d, s, s, $J = 1$, 1 Hz, Cp except NC), 33.7 (s, Me). Anal. (mixture of isomers) Calcd for C₄₅H₃₈FeNO₄P: C, 72.69; H, 5.15; N, 1.88. Found: C, 72.55; H, 5.24; N, 1.81. A mixture of A and C, free of isomer B, can be obtained by extraction of the initial reaction mixture residue with pentane.

CpFeCO[P(OPh)₃](η^1 -CH₂C≡CPh) (9). [CpFeCO[P(OPh)₃](η^2 -MeC≡CPh)]BF₄ (1.13 g, 1.71 mmol) was stirred in -78 °C THF (20 mL), treated with solid *t*-BuOK (0.19 g, 1.7 mmol), and stirred 1.5 h while slowly being warmed to room temperature. The solvent was evaporated, and the residue was extracted with benzene (40 mL). This was filtered quickly through alumina (3 cm) and evaporated to dryness to yield a yellow oil (0.62 g, 63%). An analytical sample was obtained by recrystallization from hexane. Spectral data for 9: ¹H NMR (δ in CDCl₃) 7.26 (20, m, P(OPh)₃ and Ph), 4.13 (5, s, Cp), 1.70, 1.61 (1, 1, d, $J = 7$, 9 Hz, CH₂); IR (cm⁻¹, Nujol) ν (CO) 1940, ν (C≡C) 2178; ¹³C NMR (δ in CDCl₃) 218.9 (d, $J = 45$ Hz, CO), 151.3, 129.6, 124.7, 121.2 (d, s, s, d, $J = 8$, 5 Hz, P(OPh)₃), 130.7, 128.0, 126.2, 125.9 (all s, CPh), 103.8 (d, $J = 5$ Hz, CH₂C), 83.6 (d, $J = 2$ Hz, Cp), 81.4 (d, $J = 2$ Hz, PhC), -20.1 (d, $J = 28$ Hz, FeC). Anal. Calcd for C₃₃H₂₇FeO₄P: C, 69.01; H, 4.74. Found: C, 69.08; H, 4.77.

CpFeCO[P(OPh)₃][η^1 -(E)-C(Me)=C(Ph)OMe] (10). [CpFeCO[P(OPh)₃](η^2 -MeC≡CPh)]BF₄ (1.13 g, 1.71 mmol) was cooled to -78 °C, stirred in -78 °C MeOH (30 mL), and treated with Na₂CO₃ (1.8 g, 17 mmol). The resulting mixture was allowed to slowly (2.5 h) warm to room temperature with stirring. The solvent was evaporated, and the residue was extracted with benzene (30 mL). The extract was filtered and evaporated to dryness. ¹H NMR showed the remaining orange oil (1.08 g) to consist primarily of 10 and MeC≡CPh. Spectral data for 10: ¹H NMR (δ in CDCl₃) 7.20 (m, P(OPh)₃ and Ph), 4.23 (5, s, Cp), 3.15 (3, s, OMe), 2.31 (3, s, Me); IR (cm⁻¹, film) ν (CO) 1954; ¹³C NMR (δ in CDCl₃) 217.3 (d, $J = 50$ Hz, CO), 150.9, 129.1, 124.4, 121.2 (d, s, s, d, $J = 10$, 4 Hz, P(OPh)₃), 150.8 (s, CPh), 141.2 (s, =C(OMe)C), 84.2 (d, $J = 2$ Hz, Cp), 56.3 (s, OMe), 28.7 (d, $J = 6$ Hz, Me). The complexity of the phenyl region precluded definitive assignment of the ortho, meta, and para carbon atoms of the vinyl phenyl ring and the Fe-bound vinyl carbon atom. MS (CI-CH₃): base peak *m/e* 311 (P(OPh)₃ + H⁺), parent *m/e* 607 (10 + H⁺).

CpFeCO[P(OPh)₃][η^1 -CH(Me)COPh] (11). [CpFeCO[P(OPh)₃](η^2 -MeC≡CPh)]BF₄ (2.26 g, 3.42 mmol) was dissolved in CH₂Cl₂ (15 mL) and filtered through alumina using several CH₂Cl₂/THF (1:2) rinses. The filtrate was reduced in volume to 2 mL and loaded onto an alumina column (25 cm). Elution with benzene and benzene/THF moved a very faint yellow band (this was discarded) followed by an orange band. The orange band

was collected, and the solvent was evaporated to yield an orange oil (1.21 g, 60%): ¹H NMR (δ in CDCl₃) 7.34 (20, m, P(OPh)₃ and Ph), 4.23 (5, s, Cp), 3.11 (1, m, CH), 1.48 (3, d, $J = 7$ Hz, Me); IR (cm⁻¹, film) ν (CO) 1949; ¹³C NMR (δ in CDCl₃) 217.7 (d, $J = 45$ Hz, terminal CO), 208.2 (d, $J = 3$ Hz, COPh), 151.3, 129.7, 124.9, 121.2 (d, s, s, d, $J = 10$, 4 Hz, P(OPh)₃), 141.9, 130.1, 127.6, 126.3 (all s, Ph), 85.0 (d, $J = 2$ Hz, Cp), 20.7 (d, $J = 3$ Hz, Me), 16.5 (d, $J = 20$ Hz, FeC). Anal. Calcd for C₃₃H₂₉FeO₅P: C, 66.91; H, 4.93. Found: C, 67.20; H, 5.03.

Reaction of [CpFeCO[P(OPh)₃](η^2 -MeC≡CPh)]BF₄ and MeLi. [CpFeCO[P(OPh)₃](η^2 -MeC≡CPh)]BF₄ (2.26 g, 3.42 mmol) was stirred in THF (30 mL) at -78 °C and treated dropwise with MeLi (3.42 mmol). The resulting solution was stirred 5 min at -78 °C and 1 h while being warmed to room temperature. The solution was then concentrated to 2 mL and extracted with pentane (2 × 20 mL). The combined extracts were reduced in volume to 2 mL and loaded onto an alumina column (25 cm). Elution with pentane/benzene mixtures moved a yellow band slightly ahead of a very faint orange band. The yellow band was collected, and the solvent was evaporated to yield a yellow oil (1.15 g, 61% conversion of η^2 -alkyne complex). ¹H NMR showed the oil to be a mixture of (η^5 -C₅H₄Me)FeCO[P(OPh)₃][η^1 -(E)-C(Me)=C(H)Ph] (12), 6, and CpFeCO[P(OPh)₃][η^1 -(Z)-C(Me)=C(Ph)Me]^{1d} in a ratio of 4:3:3. Spectral data for 12: ¹H NMR (δ in C₆D₆) 7.05 (m, P(OPh)₃, Ph, and vinyl H), 4.74, 4.33, 4.20, 3.97 (all m, C₅H₄), 2.51 (s, vinyl Me), 1.52 (s, C₅H₄Me); IR (cm⁻¹, film) ν (CO) 1936; ¹³C NMR (δ in CDCl₃) 219.3 (d, $J = 45$ Hz, CO), 157.6 (d, $J = 40$ Hz, FeC), 151.5, 129.4, 124.5, 121.6 (d, s, s, d, $J = 9$, 4 Hz, P(OPh)₃), 140.3 (d, $J = 2$ Hz, =CHC), 138.4 (d, $J = 5$ Hz, CHPh), 101.1, 86.2, 84.4, 83.4, 81.6 (d, s, s, s, d, $J = 4$, 2 Hz, Cp), 33.3 (s, vinyl Me), 12.5 (s, C₅H₄Me). The complexity of the phenyl region precluded assignment of the ortho, meta, and para carbon atoms of the vinyl phenyl ring.

CpFeCO[P(OPh)₃][η^1 -C(CO₂Me)=C=CH₂] (13). [CpFeCO(P(OPh)₃)(η^2 -MeC≡CCO₂Me)]BF₄ (1.10 g, 1.71 mmol) was stirred in THF (25 mL) at -78 °C. Et₃NLi (1.71 mmol) was then dripped in over a 20-min period. The resulting solution was stirred 20 min at -78 °C and 45 min while being warmed to room temperature. The solvent was evaporated, and the residue was dissolved in benzene (20 mL). This was filtered through alumina (3 cm), reduced in volume to 2 mL, and loaded onto an alumina column (30 cm). Elution with benzene and benzene/CH₂Cl₂ mixtures moved a broad yellow band. The band was collected, and the solvent was evaporated to yield a yellow oil (0.79 g, 83%): ¹H NMR (δ in CDCl₃) 7.23 (15, m, P(OPh)₃), 4.27 (5, s, Cp), 4.25, 4.21 (1, 1, s, s, CH₂), 3.61 (3, s, Me); IR (cm⁻¹ thin film) ν (CO) 1967, 1693; ¹³C NMR (δ in CDCl₃) 217.9 (d, $J = 45$ Hz, CO), 208.1 (d, $J = 4$ Hz, CCH₂), 173.8 (s, CO₂), 151.4, 129.4, 124.7, 121.5 (d, d, d, $J = 10$, 1, 1, 4 Hz, P(OPh)₃), 83.8 (d, $J = 2$ Hz, Cp), 82.5 (d, $J = 39$ Hz, FeC), 63.0 (d, $J = 2$ Hz, CH₂), 51.7 (s, Me). Anal. Calcd for C₂₈H₂₅FeOP: C, 62.61; H, 4.53. Found: C, 62.31; H, 4.74. The same product is obtained in nearly identical yield (84%) by using (*n*-Bu)₄NOH in place of Et₃NLi.

CpFeCO[P(OPh)₃][η^1 -(E)-C(CO₂Me)=C(Me)NPh₂] (14). Method A. [CpFeCO[P(OPh)₃](η^2 -MeC≡CCO₂Me)]BF₄ (1.80 g, 2.80 mmol) was stirred at -78 °C in THF (35 mL). Ph₂NLi (2.80 mmol) was then added via cannula. The resulting mixture was stirred for 30 min at -78 °C and then allowed to warm slowly to room temperature with continued stirring. The THF was removed under vacuum leaving a dark oil that was dissolved in CH₂Cl₂ (20 mL) and filtered through an alumina plug using several CH₂Cl₂ rinses. Evaporation of the CH₂Cl₂ left a brown oil that was purified by chromatography on alumina (30 cm) using benzene and benzene/CH₂Cl₂ mixtures to yield a yellow-orange oil (1.13 g, 56%). Method B. [CpFeCO[P(OPh)₃](η^2 -MeC≡CCO₂Me)]BF₄ (1.10 g, 1.71 mmol) was stirred in CH₂Cl₂ (25 mL) at -78 °C and treated dropwise with a CH₂Cl₂ solution (25 mL) of Ph₂NH (0.289 g, 1.71 mmol). The resulting solution was stirred 30 min at -78 °C, stirred 30 min while being warmed to room temperature, filtered, and then reduced in volume to ca. 10 mL. This solution was treated with pentane (50 mL) to remove excess amine, stirred briefly, and allowed to settle. The solvent was decanted. The remaining orange-brown residue was dissolved in THF (20 mL) and dripped slowly into a rapidly stirred, -78 °C THF solution (20 mL) of lithium diisopropylamide (1.71 mmol). The resulting solution was stirred 30 min at -78 °C and

then warmed to room temperature. The solvent was evaporated, and the residue was dissolved in benzene (20 mL). This was filtered through alumina (3 cm), reduced in volume to 2 mL, and loaded onto an alumina column (30 cm). Elution with benzene and benzene/CH₂Cl₂ mixtures moved a broad yellow band. The band was collected, and the solvent was evaporated to yield a yellow-orange oil (0.97 g, 78%). The analytical sample was prepared by recrystallization from CH₂Cl₂/pentane (3:1). Spectral data for 14: ¹H NMR (δ in C₆D₆) 7.10 (25, m, P(OPh)₃ and NPh₂), 3.90 (5, s, Cp), 3.56 (3, s, OMe), 2.18 (3, s, Me); IR (cm⁻¹ in C₆H₆) ν (CO) 1948, ν (CO₂) 1698; ¹³C NMR (δ in CDCl₃) 218.9 (d, J = 48 Hz, CO), 179.1 (d, J = 6 Hz, CO₂), 151.7, 129.4, 124.7, 121.7 (d, d, d, J = 12, 1, 1, 4 Hz, P(OPh)₃), 146.5, 128.4, 120.6, 120.1 (d, s, s, J = 5 Hz, NPh₂), 144.1 (d, J = 2 Hz, =CN), 138.8 (d, J = 35 Hz, FeC), 82.8 (d, J = 2 Hz, Cp), 50.4 (s, OMe), 21.3 (d, J = 2 Hz, Me). Anal. Calcd for C₄₁H₃₆FeNO₆P: C, 67.87; H, 5.00; N, 1.93. Found: C, 67.59; H, 5.18; N, 1.68.

(η^5 -C₅H₄NHPh)FeCO[P(OPh)₃][η^1 -(E)-C(CO₂Me)=C(H)-Me] (15). [CpFeCO[P(OPh)₃](η^2 -MeC≡CCO₂Me)]BF₄ (2.20 g, 3.42 mmol) was stirred in THF (60 mL) at -78 °C. PhNHLi (3.42 mmol) was then added via cannula. The resulting solution was stirred 15 min at -78 °C and 30 min while being warmed to room temperature. The solvent was evaporated, and the residue was dissolved in CH₂Cl₂ (15 mL). This was filtered through alumina (3 cm), reduced in volume to 2 mL, and loaded onto an alumina column (30 cm). Elution with benzene and benzene/THF (25:1) moved a greenish brown band first (this was discarded) followed by a faint yellow band and then a broad yellow band. The faint yellow band was identified as 13 (0.045 g, 2%). The broad yellow band was collected to yield 15 as a yellow oil (1.05 g, 47%): ¹H NMR (δ in CDCl₃) 7.02 (20, m, P(OPh)₃ and NPh), 5.38 (1, q of d, J_{H-H} = 9 Hz, J_{H-P} = 2 Hz, CH), 4.15, 3.46 (3, 2, m, m, Cp and NH), 3.63 (3, s, OMe), 1.59 (3, d, J = 9 Hz, Me); IR (cm⁻¹ in C₆H₆) ν (CO) 1937, 1657; ¹³C NMR (δ in CD₂Cl₂) 218.8 (d, J = 43 Hz, CO), 181.5 (s, CO₂), 151.5, 129.7, 125.0, 122.0 (all d, J = 10, 1, 1, 4 Hz, P(OPh)₃), 143.3, 129.8, 120.9, 118.5 (all s, NPh), 139.8 (d, J = 34 Hz, FeC), 133.8 (d, J = 4 Hz, CHMe), 127.9, 78.5, 72.9, 70.4, 66.3 (d, s, s, s, d, J = 2, 7 Hz, Cp), 50.8 (s, OMe), 19.1 (d, J = 2 Hz, Me). Anal. Calcd for C₃₈H₃₂FeNO₆P: C, 64.73; H, 4.97; N, 2.16. Found: C, 64.70; H, 5.24; N, 1.94.

CpFeCO[P(OPh)₃][η^1 -(E)-C(CO₂Me)=C(Me)OMe] (16). [CpFeCO[P(OPh)₃](η^2 -MeC≡CCO₂Me)]BF₄ (1.10 g, 1.71 mmol) was stirred in MeOH at -78 °C and treated with Na₂CO₃ (1.8 g, 17 mmol). The resulting slurry was allowed to slowly warm to room temperature (2.5 h) with constant stirring. The solvent was removed, and the residue was extracted with benzene (30 mL). The extract was filtered through Celite, and the solvent was evaporated to yield a yellow-brown oil that was pure by ¹H NMR (0.76 g, 76%): ¹H NMR (δ in CDCl₃) 7.15 (15, m, P(OPh)₃), 4.38 (5, s, Cp), 3.57, 3.38 (3, 3, s, s, OMe's), 1.96 (3, s, Me); IR (cm⁻¹ in CH₂Cl₂) ν (CO) 1948, 1676; ¹³C NMR (δ in CDCl₃) 218.0 (d, J = 46 Hz, CO), 178.2 (s, CO₂), 150.9, 129.1, 124.5, 121.3 (d, s, s, d, J = 10, 4 Hz, P(OPh)₃), 149.6 (s, =CMe), 107.0 (d, J = 35 Hz, FeC), 83.5 (s, Cp), 56.7, 50.3 (s, s, OMe's), 17.1 (s, Me).

CpFeCO[P(OPh)₃][η^1 -CH(CO₂Me)COMe] (17). CpFeCO[P(OPh)₃][η^1 -(E)-C(CO₂Me)=C(Me)OMe] (0.78 g, 1.3 mmol) was loaded onto an alumina column (30 cm) and eluted with benzene and benzene/THF mixtures. A faint yellow band eluted first followed by a more intense yellow band. Both bands were collected, yielding two yellow oils. The initial band was formulated as (CpFeCO[P(OPh)₃][η^1 -C(CO₂Me)=C(Me)]₂O (18) (0.22, 29%) and the second band as nearly 1:1 (A:B) mixture of diastereomeric 17 (0.52 g, 53%). Spectral data for 17 (diastereomeric mixture): ¹H NMR (δ in CDCl₃) 7.26 (15, m, P(OPh)₃), 4.41 (A), 4.32 (B) (total of 5, s, s, Cp), 3.59 (A), 3.57 (B) (total of 3, s, s, OMe), 2.89 (B), 2.71 (A) (total of 1, d, d, J_{P-H} = 7, 7 Hz, CH), 2.35 (B), 2.01 (A) (total of 3, s, s, Me); IR (cm⁻¹ in C₆H₆) ν (CO) 1967, 1707; ¹³C NMR (δ in CDCl₃) 218.1 (d, J = 44 Hz, CO), 208.0 (B), 207.1 (A) (s, COMe), 177.1 (A), 176.7 (A) (s, CO₂), 150.2 (A), 150.1 (B) (d, d, J = 11, 10 Hz, POC), 129.1, 124.6, 120.6 (s, s, d, J = 3 Hz, o, m, and p of P(OPh)₃), 84.0 (A), 83.7 (B) (s, s, Cp), 49.9 (A), 49.7 (B) (s, s, OMe), 30.0 (B), 29.5 (A) (s, s, Me), 23.3 (m, FeC). Anal. Calcd for C₂₉H₂₇FeO₇P: C, 60.65; H, 4.74. Found: C, 60.71; H, 5.14. Spectral data for 18: ¹H NMR (δ in CDCl₃) 7.28 (15, m, P(OPh)₃), 4.52 (5, s, Cp), 3.70 (3, s, OMe), 2.12 (3, s, Me); IR (cm⁻¹, film) ν (CO) 1938, 1690; ¹³C NMR (δ in CDCl₃) 215.6 (d, J = 38

Hz, CO), 176.6 (s, CO₂), 153.2, 152.3 (s, s, diastereomeric CMe), 151.3, 151.0, 129.7, 129.4, 124.8, 120.9, 120.4 (d, d, s, s, d, d, J = 12, 7, 5, 5 Hz, diastereomeric P(OPh)₃), 112.4 (d, J = 28 Hz, FeC), 82.4 (d, J = 1 Hz, Cp), 51.5 (s, OMe), 17.3, 16.8 (s, s, diastereomeric Me).

Reaction of [CpFeCO[P(OPh)₃](η^2 -MeC≡CCO₂Me)]BF₄ and MeLi. [CpFeCO[P(OPh)₃](η^2 -MeC≡CCO₂Me)]BF₄ (1.10 g, 1.71 mmol) was stirred in THF (25 mL) at -78 °C and treated dropwise with MeLi (1.71 mmol). The resulting solution was stirred 15 min at -78 °C and 30 min while being warmed to room temperature. The solvent was evaporated, and the residue was dissolved in CH₂Cl₂ (15 mL). This was filtered through alumina (3 cm), reduced in volume to 2 mL, and loaded onto an alumina column (30 cm). Elution with benzene and benzene/THF mixtures yielded three distinct yellow bands that were collected. In order of elution, the bands were identified as 6 (0.10 g, 12%), (η^5 -C₅H₄Me)FeCO[P(OPh)₃][η^1 -(E)-C(CO₂Me)=C(H)Me] (19, 0.09 g, 9%), and lastly a mixture (0.47 g) of CpFeCO[P(OPh)₃][η^1 -C(CO₂Me)=C(Me)₂] and 13. Spectral data for 19: ¹H NMR (δ in CDCl₃) 7.31 (15, m, P(OPh)₃), 5.50 (1, q of d, J_{HH} = 6 Hz, J_{HP} = 3 Hz, CH), 4.49, 4.29, 4.16, 3.68 (1, 1, 1, 1, m, m, m, m, C₅H₄), 3.63 (3, s, OMe), 1.74 (3, d, J = 6 Hz, vinyl Me), 1.61 (3, s, C₅H₄Me); IR (cm⁻¹ in C₆H₆) ν (CO) 1940, 1693; ¹³C NMR (δ in CD₂Cl₂) 219.6 (d, J = 43 Hz, CO), 178.5 (s, CO₂), 152.2, 129.2, 125.1, 122.1 (all d, J = 10, 1, 1, 4 Hz, P(OPh)₃), 137.1 (d, J = 41 Hz, FeC), 134.2 (d, J = 3 Hz, CHMe), 100.3, 88.4, 85.5, 80.9, 80.3 (d, d, s, d, s, J = 4, 4, 1 Hz, Cp), 50.3 (s, OMe), 20.0 (d, J = 2 Hz, vinyl Me), 12.8 (s, C₅H₄Me); MS (CI-CH₄) parent *m/e* 572, base peak *m/e* 217. Anal. Calcd for C₃₀H₂₈FeO₆P: C, 62.95; H, 5.11. Found: C, 63.25; H, 5.11.

CpFeCO[P(OPh)₃][η^1 -C(=CH₂)CH₂NET₂] (21). [CpFeCO[P(OPh)₃](η^2 -CH₂=C=CH₂)]BF₄ (1.00 g, 1.71 mmol) was stirred at -78 °C in THF (35 mL). Et₂NLi (1.71 mmol) was then added via cannula. The resulting mixture was stirred for 5 min at -78 °C and then stirred for 30 min while being warmed to room temperature. Evaporation of the solvent left a dark oil that was dissolved in benzene (20 mL) and filtered through an alumina plug (3 cm) by using several benzene rinses. Evaporation of the benzene left a brown oil that was purified on alumina (30 cm) by using benzene/THF mixtures as eluant to yield a yellow oil (0.74 g, 76%): ¹H NMR (δ in CDCl₃) 7.18 (15, m, P(OPh)₃), 5.97, 5.22 (1, 1, br s, m, vinyl H's), 4.25 (5, s, Cp), 3.03 (2, br s, CH₂), 2.49 (4, q, J = 6 Hz, NCH₂), 0.96 (6, t, J = 6 Hz, Me); IR (cm⁻¹ in C₆H₆) ν (CO) 1928; ¹³C NMR (δ in C₆D₆) 220.0 (d, J = 47 Hz, CO), 158.9 (d, J = 42 Hz, FeC), 152.4, 129.6, 124.7, 122.1 (d, s, d, d, J = 10, 1, 4 Hz, P(OPh)₃), 126.0 (d, J = 6 Hz, =CH₂), 83.9 (d, J = 2 Hz, Cp), 73.2 (d, J = 3 Hz, =CCH₂), 47.0 (s, NCH₂), 12.4 (s, Me's). Anal. Calcd for C₃₁H₃₄FeNO₆P: C, 65.16; H, 6.00; N, 2.45. Found: C, 64.99; H, 5.87; N, 2.46.

CpFeCO[P(OPh)₃][η^1 -C(=CH₂)CH₂NPh₂] (22). [CpFeCO[P(OPh)₃](η^2 -CH₂=C=CH₂)]BF₄ (1.00 g, 1.71 mmol) was stirred at -78 °C in THF (40 mL). Ph₂NLi (1.71 mmol) was then added via cannula. The resulting mixture was stirred 5 min at -78 °C and then stirred 1 h while being warmed to room temperature. The solvent was evaporated, and the remaining dark oil was dissolved in CH₂Cl₂ (15 mL). This was filtered through alumina (3 cm) by using several CH₂Cl₂ rinses, then reduced in volume to 2 mL, and loaded onto an alumina column (30 cm). Elution with pentane/benzene mixtures moved a single yellow band. The band was collected, and the solvent was evaporated to yield a yellow oil (0.93 g, 81%): ¹H NMR (δ in CDCl₃) 7.14 (25, m, P(OPh)₃ and NPh₂), 6.01, 5.23 (1, 1, br s, br s, =CH₂), 4.58 (2, s, CH₂), 4.29 (5, s, Cp); IR (cm⁻¹ in C₆H₆) ν (CO) 1930; ¹³C NMR (δ in CDCl₃) 219.0 (d, J = 47 Hz, CO), 153.2 (d, J = 42 Hz, FeC), 151.7, 129.4, 124.6, 121.6 (d, d, d, d, J = 10, 1, 1, 4 Hz, P(OPh)₃), 148.3, 128.8, 120.1, 120.0 (s, s, s, s, NPh₂), 123.3 (d, J = 5 Hz, =CH₂), 83.4 (d, J = 2 Hz, Cp), 68.2 (d, J = 4 Hz, CH₂). Anal. Calcd for C₃₃H₃₄FeNO₆P: C, 70.17; H, 5.13; N, 2.10. Found: C, 69.89; H, 5.43; N, 2.18.

(η^5 -C₅H₄NEt₂)FeCO[P(OPh)₃]I (23). A THF solution (25 mL) of CpFeCO[P(OPh)₃]I (1.00 g, 1.71 mmol) was cooled to -78 °C and treated with a cold (-78 °C) THF solution (10 mL) of Et₂NLi (1.71 mmol). The resulting solution was stirred 30 min while being warmed to room temperature. The solvent was evaporated, and the residue was dissolved in benzene (20 mL). This was filtered through alumina (3 cm) and evaporated to

dryness to yield a dark red oil (0.82 g, 73%): ^1H NMR (δ in C_6D_6) 7.20 (15, m, P(OPh)₃), 4.14, 3.42, 3.27, 3.08 (1, 1, 1, 1, all m, C_5H_4), 2.67 (4, q, $J = 7$ Hz, CH_2 's), 0.82 (6, t, $J = 7$ Hz, Me's); IR (cm^{-1} in C_6H_6) $\nu(\text{CO})$ 1946; ^{13}C NMR 217.5 (d, $J = 40$ Hz, CO), 151.5, 129.4, 124.6, 121.7 (d, s, s, d, $J = 7$, 4 Hz, P(OPh)₃), 140.5, 77.9, 70.5, 60.5, 54.2 (s, s, s, s, d, $J = 7$ Hz, Cp), 46.7 (s, CH_2 's), 12.9 (s, Me's). Anal. Calcd for $\text{C}_{28}\text{H}_{23}\text{FeINO}_4\text{P}$: C, 51.17; H, 4.44; I, 19.31; N, 2.13. Found: C, 50.99; H, 4.61; I, 19.61; N, 1.97.

X-ray Structure Determination

The crystals grown from pentane/ CH_2Cl_2 (ca. 3:1) were in the form of plates bounded by {0,1,1}, {1,0,0}, {0,1,1}, {1,1,1}, and {1,0,1} with {0,1,1} being the most developed faces. They are triclinic of space group $P\bar{1}$ with unit-cell dimensions $a = 12.358$ (2) Å, $b = 12.576$ (4) Å, $c = 8.289$ (2) Å, $\alpha = 96.54$ (2)°, $\beta = 95.66$ (2)°, and $\gamma = 88.08$ (2)° and $V = 1273$ (1) Å³, $Z = 2$, $D_{\text{calcd}} = 1.305$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, linear absorption coefficient $\mu = 6.80$ cm^{-1} , $F(0,0,0) = 552$, and $T = 291$ K.

The data were collected with Enraf-Nonius CAD-4 diffractometer: graphite monochromator; ω - 2θ scan mode; $0.95^\circ + 0.35^\circ \tan \theta$ scan range; variable scan speed; orientation checked every 100 reflections; intensities of three reflections were monitored every 2.5 h of exposure time. The unit-cell dimensions were obtained from a least-squares fit to the setting angles ϕ , χ , ω , and θ for 25 general reflections. The crystal of dimensions $0.3 \times 0.2 \times 0.1$ mm sealed in a glass capillary showed little decay after 94 h of X-ray exposure time. Maximum decay correction was 1.015 (average 1.008). A total of 3826 reflections were measured in $2^\circ < \theta < 23^\circ$ range. Averaging of the data gave $R_{\text{int}} = 0.025$ for ($\pm h, \pm k, 0$) zone. Numerical absorption correction applied; maximum, minimum, and average transmission coefficients were 0.958, 0.921, and 0.945, respectively. Intensity statistics indicated the centrosymmetric space group. A total of 1754 reflections with $F \geq 4\sigma(F)$ were used in structure solution and refinement. The Fe position was determined from a Patterson map, and the rest of the structure was found in difference Fourier maps. The structure was refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma^2(F_o) + 0.0002F_o^2)^{-1}$, with anisotropic temperature factors for all non-hydrogen atoms. Phenyls and the cyclopentadienyl ring were treated as rigid bodies. Calculated positions for H atoms bonded to the rings were used. Refinement of this model with 274 parameters converged at $R = 0.060$ and $R_w = 0.058$. However, unsatisfactory bond lengths in the β -acyl ligand and residual electron density of $0.56\text{e}/\text{\AA}$ in this area of a difference Fourier map suggested some disorder.

At this point we returned to the isotropic temperature factors for the β -acyl ligand and introduced elastic restraints on the bond lengths ($\sigma = 0.005$ Å) and angles. Those last were restricted by restraining the distances between the second neighbors ($\sigma = 0.01$ Å). The target values were obtained from 1980 MM2 force field parameters.⁹ After further refinement, we were able to identify in a difference Fourier map a second position of the β -acyl moiety (for which we use index B) bonded to Fe with the opposite configuration at C(3). Further refinement was carried out with the sum of occupancies for the disordered acyl ligand constrained to 1.0. The isotropic temperature factors for the corresponding atoms of this ligand were constrained to be equal. The refinement of this model converged at virtually the same discrepancy factors $R = 0.060$ and $R_w = 0.059$ as for the fully anisotropic mode.¹⁰ The occupancies for the two configuromers A and B were 0.738 (8) and 0.262 (8), respectively. The maximum peak on the final difference Fourier map for this model was lower and equal to $0.45\text{e}/\text{\AA}^3$. The largest deviations from the restraints were 0.006 for the first neighbors and 0.021 for second neighbors. The disordered, isotropic model had formally 264 parameters, but 16 restraints made it effectively 248. Therefore, we accepted it as significantly better, and we present the results for it in Tables I-III. An Ortep drawing is shown in Figure 1.¹¹

(9) Allinger, N. L.; Yah, Y. H. MM2 Program from Quantum Chemistry Program Exchange.

(10) Calculations were carried out by using Enraf-Nonius Structure Determination Package: Frenz, B. A. (1983). Restraint refinement was carried out with: Sheldrick, G. M. Shelx-76, Program for Crystal Structure Determination, 1976; Cambridge University, Cambridge, England.

Table I. Fractional Atomic Coordinates with Esd's in Parentheses

	x/a	y/b	z/c	$B, \text{\AA}^2$
Fe(1)	0.1198 (1)	0.2280 (1)	0.1682 (2)	3.59
C(1)	0.1488 (7)	0.0997 (9)	0.0840 (12)	3.96
O(1)	0.1671 (6)	0.0143 (6)	0.0262 (9)	5.71
O(2A)	-0.0688 (7)	0.3188 (8)	-0.1571 (12)	6.51
C(4A)	0.0056 (7)	0.2534 (7)	-0.1512 (15)	4.97
C(5A)	-0.0120 (11)	0.1398 (7)	-0.2292 (20)	5.30
C(3A)	0.1161 (7)	0.2850 (7)	-0.0692 (14)	3.07
C(2A)	0.1323 (10)	0.4049 (7)	-0.0668 (16)	4.52
O(2B)	-0.0319 (17)	0.3809 (18)	-0.1424 (34)	6.51
C(4B)	0.0616 (16)	0.3506 (16)	-0.1172 (43)	4.97
C(5B)	0.1527 (21)	0.4277 (22)	-0.1161 (53)	5.30
C(3B)	0.0880 (20)	0.2344 (16)	-0.0982 (38)	3.07
C(2B)	-0.0026 (31)	0.1644 (19)	-0.1868 (58)	4.52
P(1)	0.2878 (2)	0.2622 (2)	0.2021 (3)	3.32
O(11)	0.3471 (4)	0.2192 (4)	0.0451 (7)	3.62
O(21)	0.3630 (4)	0.2169 (5)	0.3508 (7)	4.14
O(31)	0.3338 (5)	0.3813 (4)	0.2317 (7)	3.65
C(12)	0.4716 (5)	0.3311 (5)	-0.0580 (8)	4.85
C(13)	0.5757 (5)	0.3499 (5)	-0.0984 (8)	5.82
C(14)	0.6611 (5)	0.2783 (5)	-0.0632 (8)	5.12
C(15)	0.6424 (5)	0.1879 (5)	0.0124 (8)	5.03
C(16)	0.5383 (5)	0.1692 (5)	0.0528 (8)	3.94
C(11)	0.4529 (5)	0.2408 (5)	0.0176 (8)	3.37
C(22)	0.3527 (5)	0.0251 (6)	0.3385 (6)	4.89
C(23)	0.3392 (5)	-0.0651 (6)	0.4175 (6)	6.33
C(24)	0.3196 (5)	-0.0533 (6)	0.5815 (6)	6.60
C(25)	0.3134 (5)	0.0487 (6)	0.6666 (6)	6.52
C(26)	0.3269 (5)	0.1389 (6)	0.5876 (6)	5.26
C(21)	0.3465 (5)	0.1271 (6)	0.4236 (6)	3.76
C(32)	0.3780 (4)	0.4482 (5)	0.5145 (10)	4.29
C(33)	0.3641 (4)	0.5270 (5)	0.6439 (10)	5.51
C(34)	0.2892 (4)	0.6110 (5)	0.6233 (10)	5.87
C(35)	0.2283 (4)	0.6163 (5)	0.4734 (10)	5.59
C(36)	0.2423 (4)	0.5374 (5)	0.3440 (10)	3.95
C(31)	0.3172 (4)	0.4534 (5)	0.3645 (10)	3.30
C(41)	-0.0313 (8)	0.1890 (10)	0.2407 (15)	6.63
C(42)	-0.0372 (8)	0.2955 (10)	0.1983 (15)	6.23
C(43)	0.0414 (8)	0.3561 (10)	0.3035 (15)	6.48
C(44)	0.0959 (8)	0.2872 (10)	0.4108 (15)	6.44
C(45)	0.0510 (8)	0.1839 (10)	0.3720 (15)	6.59

Table II. Selected Interatomic Distances (Å) with Esd's in Parentheses

Fe(1)-C(1)	1.72 (1)	C(3A)-C(2A)	1.53 (1)
Fe(1)-C(3A)	2.17 (1)	C(3A)-C(4B)	1.13 (2)
Fe(1)-C(3B)	2.21 (3)	C(3A)-C(3B)	0.74 (2)
Fe(1)-P(1)	2.119 (3)	C(2A)-C(4B)	1.14 (2)
Fe(1)-C(41)	2.11 (1)	C(2A)-C(5B)	0.60 (4)
Fe(1)-C(42)	2.12 (1)	O(2B)-C(4B)	1.21 (3)
Fe(1)-C(43)	2.12 (1)	C(4B)-C(5B)	1.51 (3)
Fe(1)-C(44)	2.11 (1)	C(4B)-C(3B)	1.51 (2)
Fe(1)-C(45)	2.10 (1)	C(3B)-C(2B)	1.52 (4)
O(2A)-C(4A)	1.21 (1)	P(1)-O(11)	1.589 (6)
O(2A)-O(2B)	0.91 (2)	P(1)-O(21)	1.614 (6)
C(4A)-C(5A)	1.51 (1)	P(1)-O(31)	1.604 (5)
C(4A)-C(3A)	1.51 (1)	O(11)-C(11)	1.390 (7)
C(4A)-C(4B)	1.41 (2)	O(21)-C(21)	1.370 (9)
C(4A)-C(3B)	1.10 (3)	O(31)-C(31)	1.371 (9)
C(4A)-C(2B)	1.13 (2)	C(1)-O(1)	1.15 (1)
C(5A)-C(2B)	0.45 (4)		

Results

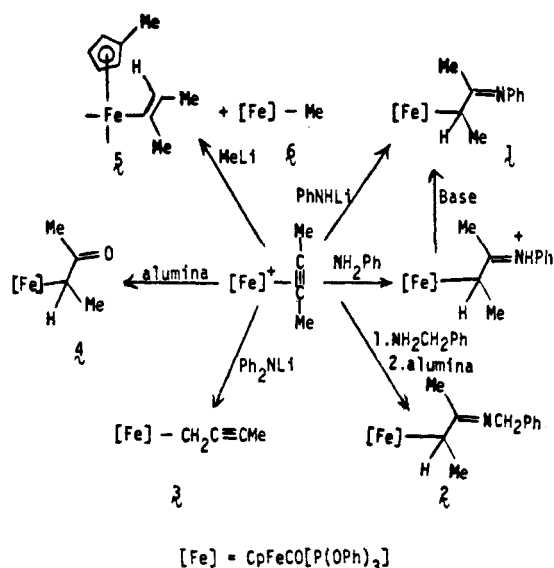
Scheme I shows the results of addition of a number of nucleophiles to the 2-butyne iron complex. PhNHLi adds normally to the alkyne, but the initial alkenyl complex rearranges, as expected, to give the imine product shown. This complex can also be prepared by addition of the neutral amine followed by deprotonation on alumina. In fact, this is clearly the better method of preparation for

(11) Johnson, C. K. Ortep II, Report ORNL-3794, 1970; Oak Ridge National Laboratory, Oak Ridge, TN.

Table III. Selected Bond Angles (deg) with Esd's in Parentheses

C(1)-Fe(1)-C(3A)	90.4 (4)	Fe(1)-C(41)-C(45)	70.0 (6)
C(1)-Fe(1)-C(3B)	75.7 (7)	Fe(1)-C(42)-C(41)	69.9 (6)
C(1)-Fe(1)-P(1)	90.5 (3)	Fe(1)-C(42)-C(43)	70.5 (6)
C(1)-Fe(1)-C(41)	94.4 (4)	Fe(1)-C(43)-C(42)	70.4 (6)
C(1)-Fe(1)-C(42)	126.1 (4)	Fe(1)-C(43)-C(44)	70.0 (6)
C(1)-Fe(1)-C(43)	159.8 (4)	Fe(1)-C(44)-C(43)	70.8 (6)
C(1)-Fe(1)-C(44)	130.2 (4)	C(41)-Fe(1)-C(44)	66.1 (4)
C(1)-Fe(1)-C(45)	96.4 (4)	C(41)-Fe(1)-C(45)	39.4 (4)
C(3A)-Fe(1)-C(3B)	19.4 (7)	C(42)-Fe(1)-C(43)	39.2 (4)
C(3A)-Fe(1)-P(1)	87.7 (2)	C(42)-Fe(1)-C(44)	65.9 (4)
C(3A)-Fe(1)-C(41)	116.2 (4)	C(42)-Fe(1)-C(45)	66.0 (4)
C(3A)-Fe(1)-C(42)	90.6 (4)	C(43)-Fe(1)-C(44)	39.2 (4)
C(3A)-Fe(1)-C(43)	101.9 (4)	C(43)-Fe(1)-C(45)	66.0 (4)
C(3A)-Fe(1)-C(44)	139.3 (4)	C(44)-Fe(1)-C(45)	39.4 (4)
C(3A)-Fe(1)-C(45)	155.0 (4)	Fe(1)-C(1)-O(1)	179.1 (9)
C(3B)-Fe(1)-P(1)	100.2 (6)	C(5A)-C(4A)-C(3A)	119.7 (8)
C(3B)-Fe(1)-C(41)	104.2 (7)	O(2A)-C(4A)-C(5A)	119.8 (9)
C(3B)-Fe(1)-C(42)	89.2 (6)	O(2A)-C(4A)-C(3A)	120.5 (9)
C(3B)-Fe(1)-C(43)	112.1 (7)	Fe(1)-C(3A)-C(4A)	103.8 (6)
C(3B)-Fe(1)-C(44)	151.2 (7)	Fe(1)-C(3A)-C(2A)	115.3 (6)
C(3B)-Fe(1)-C(45)	142.9 (7)	Fe(1)-C(3B)-C(4B)	105 (2)
P(1)-Fe(1)-C(41)	155.6 (3)	Fe(1)-C(3B)-C(2B)	117 (2)
P(1)-Fe(1)-C(42)	143.3 (3)	C(4A)-C(3A)-C(2A)	111.0 (8)
P(1)-Fe(1)-C(43)	105.7 (3)	C(4B)-C(3B)-C(2B)	110 (2)
P(1)-Fe(1)-C(44)	92.6 (3)	Fe(1)-P(1)-O(11)	111.3 (2)
P(1)-Fe(1)-C(45)	116.2 (3)	Fe(1)-P(1)-O(21)	119.5 (2)
C(41)-Fe(1)-C(42)	39.3 (4)	Fe(1)-P(1)-O(31)	123.6 (2)
C(41)-Fe(1)-C(43)	65.9 (4)	O(11)-P(1)-O(21)	104.1 (3)
O(2B)-C(4B)-C(5B)	120 (2)	O(11)-P(1)-O(31)	98.9 (3)
O(2B)-C(4B)-C(3B)	120 (2)	O(21)-P(1)-O(31)	96.0 (3)
C(5B)-C(4B)-C(3B)	120 (2)	P(1)-O(11)-C(11)	126.1 (4)
O(11)-C(11)-C(16)	120.8 (5)	P(1)-O(21)-C(21)	127.1 (5)
O(21)-C(21)-C(22)	121.3 (5)	P(1)-O(31)-C(31)	124.6 (5)
O(21)-C(21)-C(26)	118.7 (5)	O(11)-C(11)-C(12)	119.0 (5)
O(31)-C(31)-C(32)	121.6 (6)	Fe(1)-C(44)-C(45)	70.0 (6)
O(31)-C(31)-C(36)	118.3 (6)	Fe(1)-C(45)-C(44)	70.6 (6)
Fe(1)-C(41)-C(42)	70.8 (6)	Fe(1)-C(45)-C(41)	70.5 (6)

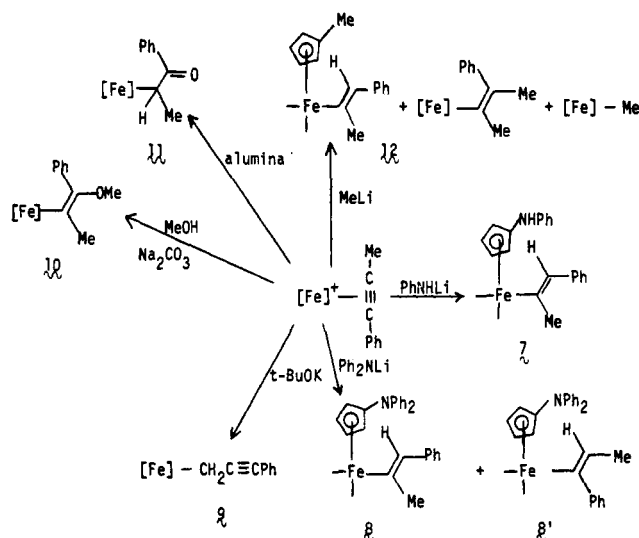
Scheme I



this complex and the analogous complex 2 starting from addition of benzylamine. A new chiral center is formed at the α -carbon atom in these reactions. Diastereomeric selectivity, as measured by NMR, ranging from 3:1 to 5:1 is observed.

Reaction with Ph_2NLi does not lead to addition but to deprotonation of the alkyne ligand to yield a propargyl complex. This somewhat unexpected complex was identified (contaminated by Ph_2NH) by its characteristic ^1H and ^{13}C NMR (CH_2 resonates at -20 ppm ($J_{\text{C-P}} = 29$ Hz)) spectra and by a direct preparation from the reaction of $\text{CpFeCO[P(OPh)}_3\text{]}_3$ with $\text{LiCH}_2\text{C}\equiv\text{CMe}$. It decomposes

Scheme II



upon attempted purification on alumina. The acyl analogue of 1 and 2 (characterized crystallographically, vide infra) can be prepared by treating the π -complex directly with alumina. An equal mixture of the two possible diastereomers forms in this reaction.

Reaction with MeLi yields mainly the product arising from exo addition to the Cp ring followed by transfer of the endo hydrogen atom (from the $\text{C}_5\text{H}_5\text{Me}$ ring thus formed) to the alkyne ligand. Also formed is a small amount of the alkyne displacement product 6. We also attempted to add alkoxides (or alcohols followed by deprotonation) and hydroxide, but characterizable products were not isolated.

As shown in Scheme II, the reaction of the phenylmethylacetylene π -complex with PhNHLi yields only the ring substitution product in good yield. The regiochemistry of the reaction is that which we have observed previously for both direct trans addition reactions at the alkyne^{10,d} and the hydride ring substitution chemistry.³ Ph_2NLi reacts in a similar fashion at the Cp ring, only in this case ca. 20% of the product mixture is the other regioisomer 8'. Attempted purification on alumina causes 8 to partially isomerize to $(\eta^5\text{-C}_5\text{H}_4\text{NPh}_2)\text{FeCO[P(OPh)}_3\text{][}\eta^1\text{-C(CH}_2\text{Ph)=CH}_2\text{]}$, a rearrangement type that we have observed previously.^{1d} All of these ring substitution products show very characteristic ^1H and ^{13}C spectra in which the Cp resonances are all separated, and the alkenyl ligands show resonances very similar to complexes of these same ligands that we have prepared earlier.¹

Reaction with $t\text{-BuOK}$ yields the deprotonated propargyl product. Addition of methanol in the presence of Na_2CO_3 yields the alkenyl ether complex. Although clearly characterized by NMR, attempted purification on alumina leads to decomposition. One of the expected products of this alumina chromatography, 11, does not form but can be prepared by direct chromatography of the starting π -complex. Reaction with MeLi yields three products in about equal amounts, the ring substitution product 12, the alkyne addition product,¹⁰ and the alkyne displacement product.

Scheme III shows analogous reactions for the case where the alkyne is substituted with an electron-withdrawing ester group. Et_2NLi yields an allenyl product by simple deprotonation of the alkyne ligand. In contrast, Ph_2NLi (or Ph_2NH addition followed by treatment with LDA) adds to the alkyne. A third type of product is observed with PhNHLi which mainly reacts at the Cp ring (trace amounts of 13 form).

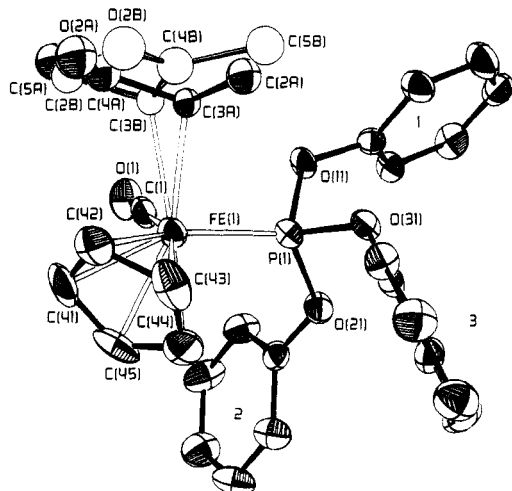
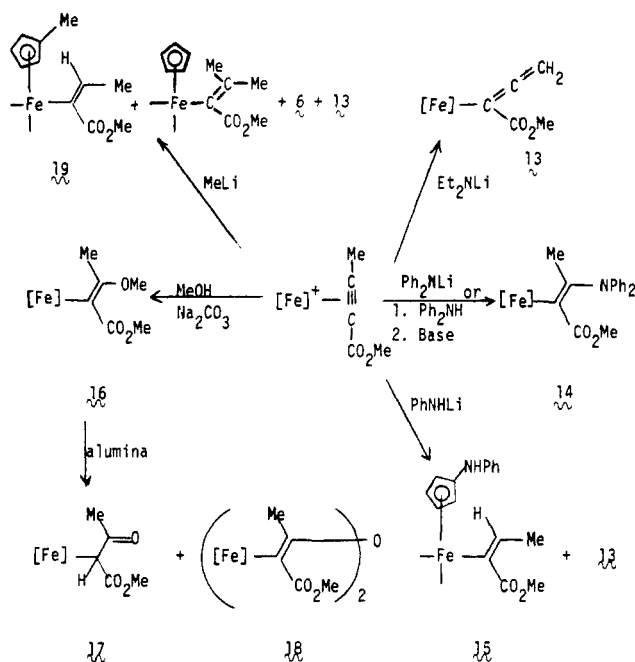


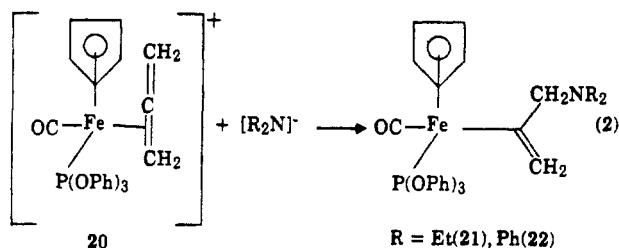
Figure 1. Ortep drawing of $\text{CpFeCO[P(OPh)}_3\text{][}\eta^1\text{-CH(Me)COMe]}$. The β -acyl ligand of the minor diastereomer is drawn with open circles and partially shaded bonds. The bond between C(4A) and C(5A) is obscured.

Scheme III



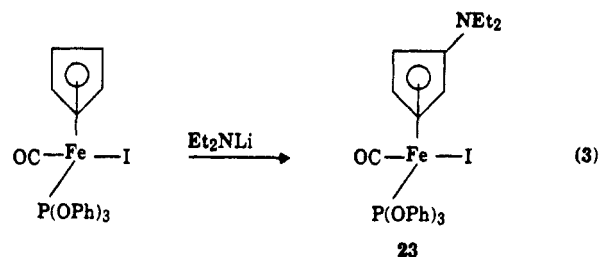
The reaction with $\text{MeOH/Na}_2\text{CO}_3$ yields the alkyne addition product. Chromatography of this complex yields the β -acyl complex 17 and an additional product tentatively formulated from NMR data as the dimeric complex 18. This product could arise from reaction of the intermediate vinyl alcohol formed in this hydrolysis reaction (stabilized by intramolecular hydrogen bonding with the ester group) with the starting material.¹² As observed with the other π -complexes, reaction with MeLi is indiscriminate. Four products are observed, one of which is the ring substitution product.

Amides will add normally to the π -allene complex 20 to yield terminal alkenyl products (eq 2). In contrast to our earlier work with carbon nucleophiles, these complexes do not rearrange to internal alkenyl complexes upon chromatography on alumina or exposure to CHCl_3 .¹³ MeLi also adds to the allene ligand to yield the same complex $\text{CpFeCO[P(OPh)}_3\text{][}\eta^1\text{-C(CH}_2\text{Me)=CH}_2\text{]}$ that we prepared



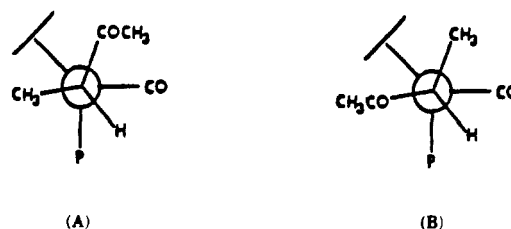
earlier by using cuprate reagents. There was no indication of ring substitution products.

Finally, eq 3 shows a very surprising reaction. Cp ring substitution is observed, with the product being isolated in good yield.



Description and Discussion of Structure

Crystals of $\text{CpFeCO[P(OPh)}_3\text{][}\eta^1\text{-CH(Me)COMe]}$ (4) were grown in which the two diastereomerically related pairs of enantiomers cocrystallize in a ratio of ca. 3:1. The two diastereomers (holding the iron configuration constant) are pictured together in Figure 1. The disorder introduced by the presence of the two diastereomeric pairs is only manifested in the β -acyl ligand. The partially shaded atoms (labeled A) are the structure of the major isomer. The open atoms (labeled B) are the minor isomer. Drawings A and B are Newman projections of each respective isomer.



The structure of both diastereomers is well described by the framework proposed by Seeman and Davies¹⁴ (from conformational analysis using extended Hückel calculations) in which the basic structure is an octahedron about the iron with the Cp group occupying three vertices of the octahedron. The model is especially accurate for A in that the angles formed by the CO, β -acyl, and P(OPh)_3 ligands are all nearly 90° . The (center of Cp)–Fe–CO and (center of Cp)–Fe–P(1) angles are $124.80(9)$ and $124.61(3)^\circ$, respectively, for both structures.

For $\text{CpFeCO(L)(}\eta^1\text{-CHR}_2\text{)}$ type molecules, such as described here, the structure predicted has the two R groups straddling the Cp ligand (or viewed another way, the structure that does not allow non-hydrogen atom substituents on the C(3) atom to dip very far below the C(3), Fe, CO plane). Both isomers conform to this theory. Isomer A places the larger C(3) substituent on the CO side of the molecule. Isomer B places it between the Cp and the large P(OPh)_3 ligand. Apparently to compensate for steric constraints, in isomer B the β -acyl ligand moves away

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from the $P(OPh)_3$ ligand causing the $C(3)-Fe-P$ angle to change from 87.66° in A to 100.24° in B. This movement causes a $C(3A)-Fe-C(3B)$ angle of 19.4° between the two structures and closes down the $C(3)-Fe-CO$ angle from 90.41° for A to 75.69° for B. This makes the $C(1)-C(3B)$ nonbonding contact rather close at 2.447 \AA .

Discussion

The results outlined in this study show that it is difficult to predict or control the type of products one obtains when η^2 -alkyne complexes react with the nucleophiles shown in the Schemes. For $MeLi$, the reactions are very indiscriminate with products in one case (Scheme III) arising from addition to the Cp or alkyne ligand, from deprotonation, and from displacement of the alkyne. These reactions are in sharp contrast to our earlier work with methylcuprate reagents ($Me_2Cu(CN)Li_2$ is best) where exclusive trans addition to the alkyne in high yield is observed, emphasizing the usefulness of these types of reagents in addition reactions with unsaturated hydrocarbons coordinated to metals.

Reactions with amides (or amines followed by deprotonation with base) generally yield a single product, but different types of complexes are prepared depending on which reagents are being used. For example, with Ph_2NLi , one observes deprotonation with the 2-butyne complex, reaction at the Cp ring for the phenylmethylacetylene complex, and "normal" addition to the alkyne for the methyltetrolate complex. Although Ph_2NLi adds to the alkyne in this last case, with the same π -complex, Et_2NLi yields a deprotonation product and $PhNHLi$ adds to the Cp ring. Watson and Bergman¹⁵ have previously noted two of the reaction types observed here with $[CpM(CO)(\eta^2-MeC\equiv CMe)_2]^+$ ($M = Mo, W$). Deuteration of the butyne ligand in a Et_3N /acetone- d_6 mixture led to the proposal that deprotonation of the alkyne by the amine was taking place to yield an unobserved allenyl intermediate similar to 13. Our isolation of 13 supports this proposal. Methoxide was shown to displace an alkyne ligand from Mo or W as we also observe with $MeLi$. For our systems, oxygen-based nucleophiles were not very successful, and in cases where alkenyl ethers were prepared, purification proved difficult due to decomposition of these complexes on alumina.

Thus, with the exception of complex 14, we have not prepared stable new alkenyl compounds from η^2 -alkyne complexes that are of synthetic use for conversion, via oxidative cleavage,⁴ to highly functionalized alkenyl esters. Addition reactions of amides with the allene complex 20 were successful, and we have converted 22 into $EtO_2CC(=CH_2)CH_2NPh_2$ in good yield.⁴

We have been successful in demonstrating that nucleophiles other than hydride will react preferentially at the Cp ring over the η^2 -alkyne ligand. Thus, ring substitution is noted for all three π -complexes with $MeLi$ and for three cases with amide nucleophiles. A somewhat similar case of ring substitution with a $CpCo$ complex and $MeLi$ has been recently reported.¹⁶ Davies, Green, and Mingos have

developed a series of rules for 18-electron cationic π -complexes that order the reactivity of unsaturated hydrocarbons in nucleophilic addition reactions.¹⁷ The rules predict that nucleophiles will react preferentially at even over odd polyenes. For the few exceptions to these rules noted from earlier work, it was proposed that generally the thermodynamic product formed by a rearrangement of the kinetic product predicted by the rules. The ring substitution reactions reported here violate these rules and are not of the type that would be expected to arise from rearrangement of the predicted products. Importantly, it is only these alkyne complexes that can react differently. We have noted here and in our earlier work that analogous ring substitution reactions with η^2 -alkene or allene complexes of the same system are not observed. The main difference for the alkyne complexes is the additional π -orbital (π_\perp) on the alkyne. This orbital has been shown to be very important in addition reactions with similar d^4 -molybdenum complexes in which the alkyne is a four-electron donor. In these cases, the LUMO is the antibonding combination of π_\perp and a metal π -type orbital¹⁸ and is the proposed reactive orbital for these complexes. This orbital is filled in these d^6 -iron complexes (alkyne is a two-electron donor), presumably leaving the LUMO^{18a} to be the antibonding combination of π_\perp^* and a metal π -orbital (possibly stabilized by "slippage" of the alkyne toward η^1 -coordination¹⁹), just as it is for alkene complexes. Of course, arguments of this type are based on assuming that the regiochemistry of these reactions is frontier orbital controlled whereas the above rules assume charge control.²⁰ In any case, the π_\perp orbital in the alkyne complexes perturbs the situation such that ring addition can be observed.

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Registry No. 1A, 101248-51-5; 1B, 101399-16-0; 2A, 101248-52-6; 2B, 101399-17-1; 3, 101248-53-7; 4A, 101248-54-8; 4B, 101399-18-2; 5, 92421-65-3; 6, 12290-98-1; 7, 101248-55-9; 8, 101248-56-0; 8', 101248-69-5; 9, 101248-57-1; 10, 101248-58-2; 11, 101248-59-3; 12, 101315-88-2; 13, 101248-60-6; 14, 101248-61-7; 15, 101248-62-8; 16, 101248-63-9; 17A, 101248-64-0; 17B, 101399-19-3; 18, 101315-89-3; 19, 101248-65-1; 20-BF₄, 71359-49-4; 21, 101248-66-2; 22, 100946-28-9; 23, 101248-67-3; [$CpFeCO[P(OPh)_3](\eta^2-MeC\equiv CMe)BF_4$], 87556-47-6; $CpFeCO[P(OPh)_3]I$, 31988-05-3; $LiCH_2C\equiv CCH_3$, 40276-89-9; [$CpFeCO[P(OPh)_3](\eta^2-MeC\equiv CPh)BF_4$], 101248-68-4; ($\eta^2-C_5H_4NPh_2$) $FeCO[P(OPh)_3][\eta^1-Cl=CH_2]CH_2Ph$], 101248-70-8; $CpFeCO[P(OPh)_3][\eta^1-(Z)-C(Me)=C(Ph)Me]$, 83149-30-8; [$CpFe(CO)[P(OPh)_3](\eta^2-MeC\equiv CCO_2Me)BF_4$], 87556-51-2.

Supplementary Material Available: Tables of positional parameters of H atoms, anisotropic thermal parameters, and structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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