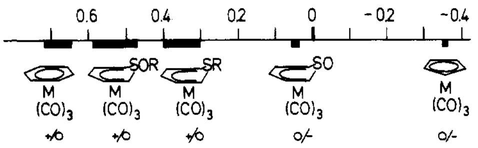

Figure 2. Comparison of redox potentials of group 6 metal tricarbonyl complexes in methylene chloride. The redox couple in each case represents an 18/17 valence electron change.

8 corresponds to the reversible change between the anion and the neutral radical. We found the same electrochemical characteristics for 8 in methylene chloride where the oxidation of the anion occurs with $E_{1/2}$ = -0.36 V vs. SCE, which is 0.92 V negative of 1 and 0.76 V negative of 4 (comparison is made with respect to the phenyl derivatives in view of the fact that phenyl and hydrogen as ligand substituents lead to nearly identical redox potentials).

We have further studied the oxidation of anions 9-11 in methylene chloride. It was found irreversible for 10 and 11 (peak potentials around 0.25 V) and partly reversible for 9 at scan rates >5 V/s, where $E_{1/2}$ is about -0.05 V, both values being more positive than the oxidation of the anion 8. The cyclovoltammograms for the oxidation of these anionic complexes are not consistent with a simple dimerization of the neutral radical but indicative of the formation of several electroactive follow-up products.

As depicted in Figure 2 λ^6-thiabenzene oxide and λ^4-thiabenzene complexes, with respect to their redox properties, lie between the neutral arene tricarbonyl and the anionic cyclopentadienyltricarbonyl complexes though closer to the former. The cathodic shift exhibited by the redox potentials of 1 and 4 with respect to 7 may in part be due to the lack of cyclic conjugation in the ylide complexes, which in general facilitates the oxidation.[16] The difference in redox potentials between 1 and 4, on the one hand, and within the syn/anti pairs **1a**/**1b** and **1d**/**1c**, on the other hand, demonstrates the importance of configuration and substitution at the sulfur center for the redox properties of the complex. Similar conclusions as drawn for the Cr complexes are valid for Mo and W homologues.

Due to the fact that second- and third-row transition-metal complexes are less prone to tolerate deviations from the 18-electron configuration, their redox transitions tend to be more irreversible and meaningful potential values are not easily obtained.

Acknowledgment. Support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is greatfully acknowledged.

Registry No. **1a**, 67179-22-0; **1b**, 67125-65-9; **1c**, 86286-68-2; **1d**, 85762-83-0; **1e**, 86225-37-8; **2a**, 69501-25-3; **2b**, 86225-30-1; **2c**, 86225-32-3; **3a**, 69501-26-4; **3b**, 86225-34-5; **3c**, 86225-36-7; **4a**, 76900-61-3; **4b**, 76900-60-2; **4c**, 93983-50-7; **4d**, 86228-68-4; **5**, 93983-51-8; **6**, 93983-52-9; *syn*-tricarbonyl(1,3,5-trimethylthiabenzene-1-oxide)chromium(I) hexafluorophosphate, 93895-79-5.

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[16] Cf. $Cr(C_6H_6)(CO)_3{}^{+/0}$ = 0.71 V/$Cr(C_7H_8)(CO)_3{}^{+/0}$ = 0.67 V;[14] $FeCp_2{}^{+/0}$ = 0.49 V/$Fe(\eta^5\text{-}C_7H_9)_2{}^{+/0}$ = 0.21 V; $CoCp(\eta^4\text{-}C_4H_4)^{+/0}$ = ~0.95 V/$CoCp(\eta^4\text{-}C_6H_8)^{+/0}$ = 0.32 V. Koelle, U., unpublished results; potentials in methylene chloride vs. SCE.

Synthesis and Investigation of Isomerization Reactions of Terminal Iron–Alkenyl Complexes

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The reaction of a variety of anionic nucleophiles (Nuc) with $[CpFeCO[P(OPh)_3](\eta^2\text{-}CH_2{=}C{=}CH_2)]BF_4$ leads to a new family of terminal alkenyl complexes, $CpFeCO[P(OPh)](\eta^1\text{-}C(CH_2Nuc){=}CH_2)$ (Nuc = H, Me, Ph, $CH{=}CH_2$, $C{\equiv}CMe$, SPh). Dissolving these complexes in $CHCl_3$ or other solvents in the presence of alumina (or upon alumina chromatography) causes a 1,3-hydrogen shift isomerization reaction that leads for the last four nucleophiles to $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(H)Nuc]$ derivatives. For Nuc = Me, an equilibrium mixture of the terminal alkenyl complex (21%), $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(H)Me]$ (72%), and $CpFeCO[P(OPh)_3](\eta^1\text{-}(Z)\text{-}C(Me){=}C(Me)H)$ (7%) is established. The (*E*)-2-butenyl isomer can also be prepared directly by the reaction of $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]BF_4$ with Li[HB(*sec*-Bu)$_3$]. Reaction of this same η^2-butyne complex with $Li[HBEt_3]$ leads to a mixture of *Z* (57%) and *E* (43%) isomers. A similar reaction using $Li[DBEt_3]$ shows that the *Z* isomer forms by direct trans addition to the alkyne whereas the *E* isomer forms from addition to the Cp ring followed by internal cis transfer from the ring to the alkyne. Both the pure *E* isomer and the mixture isomerize in $CHCl_3$ or upon chromatography to the same equilibrium mixture as the terminal butenyl isomer. A variety of deuterium labeling and protonation studies are reported that indicate that the intermediates in these isomerization reactions are the cationic carbene complexes formed by simple protonation of the alkenyl complexes.

Introduction

It has been recently shown that a wide variety of iron–alkenyl complexes can be prepared from the addition of anionic nucleophiles to cationic η^2-alkyne[1] or vinylidene complexes[2] (eq 1 and 2). Both reactions are generally regio- and/or stereoselective, and for reaction 1, trans addition of the nucleophile has been proven (the case where Nuc = H is an exception,[3] vide infra). Thus by

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[1] Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* **1984**, *3*, 134 and references therein.

[2] Reger, D. L.; Swift, C. A. *Organometallics* **1984**, *3*, 876.

[3] Reger, D. L.; Belmore, K. A.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 5710.

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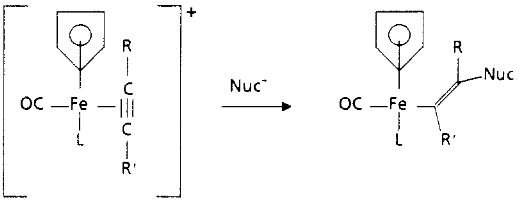
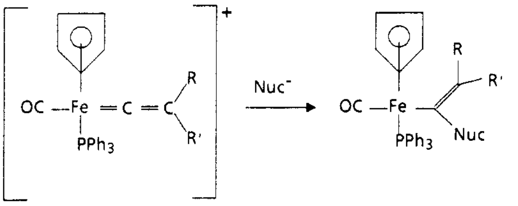


(1)

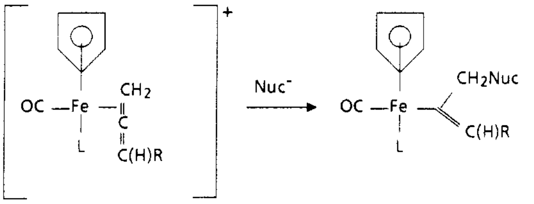
L = PPh3, P(OPh)3



(2)

proper choice of the cationic metal complex and the nucleophile, iron–alkenyl complexes with many different substituents can be prepared. In addition to being the first extensive family of metal–alkenyl complexes available for study, these complexes are of potential use in the synthesis of tri- and tetrasubstituted alkenes as selective cleavage reactions of the iron–carbon bond are developed.[4]

Another similar route to these iron–alkenyl complexes that potentially results in different types of products is the addition of nucleophiles to η^2-allene complexes (eq 3). For



(3)

the system where L = CO, this chemistry has previously been explored,[5] although not with the wide range of carbon nucleophiles used in the alkyne studies outlined above. In general, the nucleophiles have been shown to add to a terminal allene carbon atom. Frequently, yields were low due to the formation of $[CpFe(CO)_2]_2$ in the reactions.

Reported here is an investigation into the chemistry of reaction 3, for the case where L = $P(OPh)_3$ and R = H. As was anticipated from earlier work with alkyne addition reactions, the yields are very high in these reactions (no byproducts are observed). The products, each containing a terminal alkenyl group, readily isomerize stereoselectively to complexes containing an (*E*)-alkenyl group when stirred in $CDCl_3$ ($CHCl_3$) or with alumina. Thus two groups of new alkenyl complexes are prepared. In addition, reported here are further results on the location of addition of hydride to cationic iron η^2-unsaturated hydrocarbon complexes.

Experimental Section

General Procedure. All operations on complexes in solution were carried out under an atmosphere of nitrogen using solvents that were purified and degassed before use. Chromatography columns were 2.5 cm in diameter. The $AgBF_4$ (Ozark-Mahoning) was stored and weighed out in a drybox. Proton NMR spectra were recorded at 60 or 90 MHz, and chemical shifts are reported as δ vs. Me_4Si. Carbon-13 spectra were recorded at 20.13 MHz by using either $CDCl_3$ (δ 76.9), CD_2Cl_2 (δ 53.8), or C_6D_6 (δ 128.0) as the solvent and internal standard and are also reported as δ vs. Me_4Si. Hydrogen-2 NMR spectra were recorded, with proton decoupling, at 30.72 MHz by using C_6H_6 (δ 7.15) as the solvent and internal standard (natural abundance deuterium) and are reported as δ vs. Me_4Si. All resonances are singlets unless otherwise indicated. Proton NMR NOE experiments were carried out at 200 MHz using degassed solvents. Alkyllithium reagents, L-Selectride, Super-Hydride, and Super-Deuteride were purchased from Aldrich, CuCN was purchased from Fisher, and vinyllithium was purchased from Organometallics. Preparations of the organocuprates[1] and $[CpFeCO[P(OPh)_3](\eta^2\text{-allene})]BF_4$[6] have been reported previously. $CpFeCO[P(OPh)_3]I$ was prepared by the method of Brown et al.[7] Elemental analyses were performed by Robertson Laboratory.

$CpFeCO[P(OPh)_3][\eta^1\text{-}C(CH_3){=}CH_2]$ (1). $[CpFeCO[P(OPh)_3](\eta^2\text{-allene})]BF_4$ (1.24 g, 2.1 mmol) was stirred at −78 °C in THF (40 mL), and L-Selectride (2.5 mL, 2.5 mmol) was added. The solution was allowed to warm to room temperature and filtered through a Celite alumina (4 cm) plug. The plug was washed with benzene (20 mL), the filtrate collected, and the solvent evaporated, leaving a yellow oil (0.85 g, 80%): ^1H NMR (δ in C_6D_6) 7.2 (15, m, $P(OPh)_3$), 6.23, 5.55 (1, 1; s, s; vinyl H's), 4.22 (5, s, Cp), 2.51 (3, s, Me); IR spectrum (cm^{-1} in THF) ν(CO) 1930.

$CpFeCO[P(OPh)_3][\eta^1\text{-}C(CH_2Me){=}CH_2]$ (2). $[CpFeCO[P(OPh)_3](\eta^2\text{-allene})]BF_4$ (0.35 g, 0.60 mmol) was stirred at −78 °C in THF (40 mL), and $Li_2Cu(CN)Me_2$ (0.60 mmol) in THF at −78 °C was added by cannula. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 30 min. The solvent was evaporated. The oil was redissolved in benzene (40 mL) and filtered through a Celite plug (2 cm), and the plug was washed with benzene (25 mL). The solvent was evaporated from the filtrate to leave a yellow oil (0.26 g, 84%): ^1H NMR (δ in C_6D_6) 7.1 (15, m, $P(OPh)_3$), 6.13, 5.43 (1, 1; br s, br s; vinyl H's), 4.18 (5, s, Cp), 2.53 (2, q, J = 7 Hz, CH_2), 1.30 (3, t, J = 7 Hz, Me); IR spectrum (cm^{-1} in hexane) ν(CO) 1948. Anal. Calcd for $C_{28}H_{27}FeO_4P$: C, 65.39; H, 5.29. Found: C, 65.50; H, 5.64.

$CpFeCO[P(OPh)_3][\eta^1\text{-}C(CH_2Ph){=}CH_2]$ (3). $[CpFeCO[P(OPh)_3](\eta^2\text{-allene})]BF_4$ (0.50 g, 0.85 mmol) was stirred at −78 °C in THF (40 mL), and $Li_2Cu(CN)Ph_2$ (0.85 mmol) at −78 °C in THF was added by cannula. The reaction mixture was allowed to warm to room temperature, and the solvent was evaporated. The compound was redissolved in benzene (50 mL) and filtered through a Celite plug (2 cm). The plug was washed with 30 mL of benzene. The solvent was evaporated to leave a yellow oil (pure by NMR analysis, 0.45 g, 92%): ^1H NMR (δ in C_6D_6) 7.1 (20, m, $P(OPh)_3$, Ph), 6.00, 5.50 (1, 1; br s, br s; vinyl H's), 4.03 (5, s, Cp), 3.79 (2, m, CH_2); IR spectrum (cm^{-1} in hexane) ν(CO) 1945; ^{13}C NMR (δ in C_6D_6) 219.8 (d, J = 47.0 Hz, CO), 159.6 (d, J = 31.6 Hz, FeC), 152.3, 129.7, 124.8, 122.1 (d, d, d, d; J = 9.5, 1.1, 1.2, 4.3 Hz; $P(OPh)_3$), 143.0, 129.0, 128.0, 127.4 (d, s, s, s; J = 1.3 Hz, Ph), 128.5 (d, J = 5.5 Hz, $=CH_2$), 84.0 (d, J = 1.8 Hz, Cp), 58.7 (d, J = 1.3 Hz, CH_2).

$CpFeCO[P(OPh)_3][\eta^1\text{-}C(CH_2CH{=}CH_2){=}CH_2]$ (4). $[CpFeCO[P(OPh)_3](\eta^2\text{-allene})]BF_4$ (1.0 g, 1.7 mmol) was stirred at −78 °C in THF (40 mL), and $Li_2Cu(CN)(CH{=}CH_2)_2$ (1.7 mmol) at −78 °C in THF was added by cannula. The reaction mixture was allowed to warm to room temperature, and the solvent was evaporated. The oil was redissolved in benzene (40 mL) and filtered through a Celite plug (2 cm), and the plug was washed with benzene (30 mL). After evaporation of the solvent a ^1H NMR spectrum showed the oil to be 4, contaminated with some high boiling hydrocarbon introduced by the vinyllithium. An alumina column (20 cm) was used to purify 4. The mixture was placed on the column in hexane (10 mL). The column was first washed with hexanes (60 mL) to elute the hydrocarbon, and then elution with CH_2Cl_2 produced a single yellow band. The band was collected and the solvent evaporated (0.85 g, 95%). The remaining yellow oil proved to be a mixture of 4 and 8 (1:6.5). Spectral data for 4: ^1H NMR (δ in C_6D_6) 7.1 (15, m, $P(OPh)_3$), 6.1, 5.5, 5.3, 5.1

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[4] Reger, D. L.; Mintz, E., unpublished results.

[5] (a) Lichtenberg, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 8271. (b) Lichtenberg, D. W.; Wojcicki, A. *J. Organomet. Chem.* **1975**, *94*, 311. (c) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93. (d) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426.

[6] Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155.

[7] Brown, D. A.; Lyons, H. J.; Manning, A. R.; Rowley, J. M. *Inorg. Chem. Acta* **1969**, *3*, 346.

(5, all m, vinyl H's), 4.20 (5, s, Cp), 3.30 (2, d, *J* = 6 Hz, CH_2); ^{13}C NMR (δ in C_6D_6) 219.7 (d, *J* = 47.0 Hz, CO), 158.7 (d, *J* = 41.7 Hz, FeC), 152.3, 129.6, 124.8, 122.1 (d, d, d, d; *J* = 9.7, 1.0, 1.0, 4.1 Hz; $P(OPh)_3$), 140.8 (d, *J* = 1.1 Hz, CH=), 125.6 (d, *J* = 5.6 Hz, FeC=*C*H_2), 114.1 (CH=*C*H_2), 84.2 (d, *J* = 1.8 Hz, Cp), 56.7 (d, *J* = 2.4 Hz, CH_2).

CpFeCO[P(OPh)$_3$][η^1-C($CH_2C{\equiv}CMe$)=CH_2] (5). [CpFeCO[$P(OPh)_3$](η^2-allene)]BF_4 (1.0 g, 1.7 mmol) was stirred at −78 °C in THF (40 mL), and $Li_2Cu(CN)(C{\equiv}CMe)_2$ (1.7 mmol) at −20 °C in THF was added by cannula. The reaction mixture was allowed to warm to room temperature, and the solvent was evaporated. The compound was redissolved in benzene (50 mL) and filtered through a Celite plug (3 cm). The plug was washed with benzene (25 mL), and the solvent was evaporated from the filtrate to yield a yellow oil (pure by NMR analysis, 0.82 g, 89%): ^{1}H NMR (δ in C_6D_6) 7.1 (15, m, $P(OPh)_3$), 6.60, 5.60 (1, 1; m, m; vinyl H's), 4.20 (5, s, Cp), 3.40 (2, m, CH_2), 1.73 (3, t, *J* = 3 Hz, Me); IR spectrum (cm^{-1} in hexane) ν(C≡C) 2270, ν(CO) 1950; ^{13}C NMR (δ in C_6D_6) 219.5 (d, *J* = 46.5 Hz, CO), 154.4 (d, *J* = 42.1 Hz, FeC), 152.2, 129.8, 124.8, 122.1 (d, d, d, d; *J* = 9.4, 1.2, 1.4, 4.2 Hz; $P(OPh)_3$), 126.3 (d, *J* = 5.1 Hz, =CH_2), 84.2 (d, *J* = 2.0 Hz, Cp), 80.5 (d, *J* = 1.8 Hz, *C*≡CMe), 76.9 (s, C≡*C*Me), 40.9 (d, *J* = 2.4 Hz, CH_2), 3.7 (Me).

CpFeCO[P(OPh)$_3$][η^1-C(CH_2SPh)=CH_2] (6). [CpFeCO[P$(OPh)_3$](η^2-allene)]BF_4 (0.50 g, 0.85 mmol) was stirred in CH_2Cl_2 (30 mL) at 0 °C, and NaSPh (0.15 g, 1.1 mmol) was added as a solid. The reaction mixture was allowed to stir for 20 min, and then the solvent was evaporated. The oil was redissolved in benzene (40 mL) and filtered through a Celite plug (3 cm), and the plug was washed with an additional 30 mL of benzene. The solvent was evaporated to yield a yellow oil (0.44 g, 85%). The analytical sample was a yellow powder formed by trituration of this oil with hexane at 0 °C: ^{1}H NMR (δ in C_6D_6) 7.0 (20, m, $P(OPh)_3$, SPh), 6.50, 5.50 (1, 1; br s, s; vinyl H's), 4.13 (5, s, Cp), 4.05 (2, m, CH_2); IR spectrum (cm^{-1} in hexane) ν(CO) 1953; ^{13}C NMR (δ in C_6D_6) 219.5 (d, *J* = 46.4 Hz, CO), 153.3 (d, *J* = 42.1 Hz, FeC), 152.2, 129.8, 124.9, 122.1 (d, d, d, d; *J* = 9.7, 1.1, 1.2, 3.8 Hz; $P(OPh)_3$), 140.3, 128.8, 128.6, 127.4 (all s; SPh), 84.2 (d, *J* = 1.9 Hz, Cp), 53.5 (d, *J* = 3.4 Hz, CH_2). Anal. Calcd for $C_{33}H_{29}FeO_4PS$: C, 65.14; H, 4.80. Found: C, 65.58; H, 5.60.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(H)Ph] (7). CpFeCO-[$P(OPh)_3$][η^1-C(CH_2Ph)=CH_2] (3) (0.42 g, 0.73 mmol) was stirred at room temperature in $CHCl_3$ (30 mL) for 3.5 h. The solution was then filtered through Celite and the Celite washed with $CHCl_3$ (20 mL). The solvent was evaporated to leave a yellow oil (0.39 g, 93%). This compound may also be prepared by placing CpFeCO[$P(OPh)_3$][η^1-C(CH_2Ph)=CH_2] on an alumina column (10 cm) and eluting with CH_2Cl_2 to produce a single yellow band which, upon solvent evaporation, yields CpFeCO[$P(OPh)_3$][η^1-(*E*)-C(Me)=C(H)Ph] (93%) as a yellow oil: ^{1}H NMR (δ in $CDCl_3$) 7.2 (20, m, $P(OPh)_3$, Ph), 6.7 (1, br s, vinyl H), 4.30 (5, s, Cp), 2.20 (3, d, *J* = 3 Hz, Me); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1940; ^{13}C NMR (δ in CD_2Cl_2) 219.5 (d, *J* = 47.0 Hz, CO), 153.7 (d, *J* = 40.5 Hz, FeC), 152.1, 129.8, 125.0, 122.0 (d, d, d, d; *J* = 9.3, 0.7, 0.9, 4.1 Hz; $P(OPh)_3$), 141.0, 128.6, 128.1, 124.2 (d, s, s, s; *J* = 2.4 Hz, Ph), 139.7 (d, *J* = 4.9 Hz, =C(H)Ph), 84.6 (d, *J* = 1.8 Hz, Cp), 33.6 (Me). Anal. Calcd for $C_{33}H_{29}FeO_4P$: C, 68.76; H, 5.07. Found: C, 68.70; H, 5.28. Note that this compound has been prepared earlier by the reaction of Li[HB(*sec*-butyl)$_3$] and [CpFeCO[$P(OPh)_3$](η^2-MeC≡CPh)]BF_4.[3]

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(H)CH=CH_2] (8). The yellow oil mixture of 4 and 8 prepared as above was dissolved in $CHCl_3$ (40 mL) and stirred for 18 h. The solution was filtered through Celite, and the Celite was washed with $CHCl_3$ (20 mL). The solvent was evaporated from the filtrate to leave a yellow oil (92%): ^{1}H NMR (δ in $CDCl_3$) 7.2 (15, m, $P(OPh)_3$), 6.8–6.3, 4.9–4.4 (2, 2; m, m, vinyl H's), 4.27 (5, s, Cp), 2.05 (3, d, *J* = 2 Hz, Me); ^{13}C NMR (δ in $CDCl_3$) 218.6 (d, *J* = 46.8 Hz, CO), 156.5 (d, *J* = 41.7 Hz, FeC), 151.5, 129.1, 124.3, 121.5 (d, s, d, d; *J* = 9.4, 0.9, 3.8 Hz; $P(OPh)_3$), 148.1 (*C*H=CH_2), 141.8 (d, *J* = 4.8 Hz, FeC=*C*H), 106.5 (=CH_2), 83.7 (d, *J* = 1.7 Hz, Cp), 31.6 (Me). Anal. Calcd for $C_{29}H_{27}FeO_4P$: C, 66.18; H, 5.17. Found: C, 65.88; H, 5.46.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(H)C≡CMe] (9). CpFeCO[$P(OPh)_3$][η^1-C($CH_2C{\equiv}CMe$)=CH_2] (5) (0.40 g, 0.74 mmol) was stirred at room temperature in $CHCl_3$ (40 mL) for 13 h. The solution was then filtered through Celite, and the Celite was washed with $CHCl_3$ (20 mL). The solvent was evaporated to leave a yellow oil (0.38 g, 96%): ^{1}H NMR (δ in $CDCl_3$) 7.2 (15, m, $P(OPh)_3$), 5.60 (1, s, vinyl H), 4.22 (5, s, Cp), 2.20 (3, s, vinyl Me), 1.97 (3, d, *J* = 3 Hz, alkynyl Me); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1945; ^{13}C NMR (δ in $CDCl_3$) 218.4 (d, *J* = 45.7 Hz, CO), 171.2 (d, *J* = 42.0 Hz, FeC), 151.4, 129.2, 124.4, 121.5 (d, s, d, d; *J* = 9.4, 1.0, 4.0 Hz; $P(OPh)_3$), 117.1 (d, *J* = 4.5 Hz, =CH), 83.5 (d, *J* = 1.5 Hz, Cp), 81.8 (≡CMe), 79.7 (d, *J* = 3.6 Hz, *C*≡C), 34.5 (=C*Me*), 4.07 (≡C*Me*). Anal. Calcd for $C_{30}H_{27}FeO_4P$: C, 66.93; H, 5.06. Found: C, 66.64; H, 5.32.

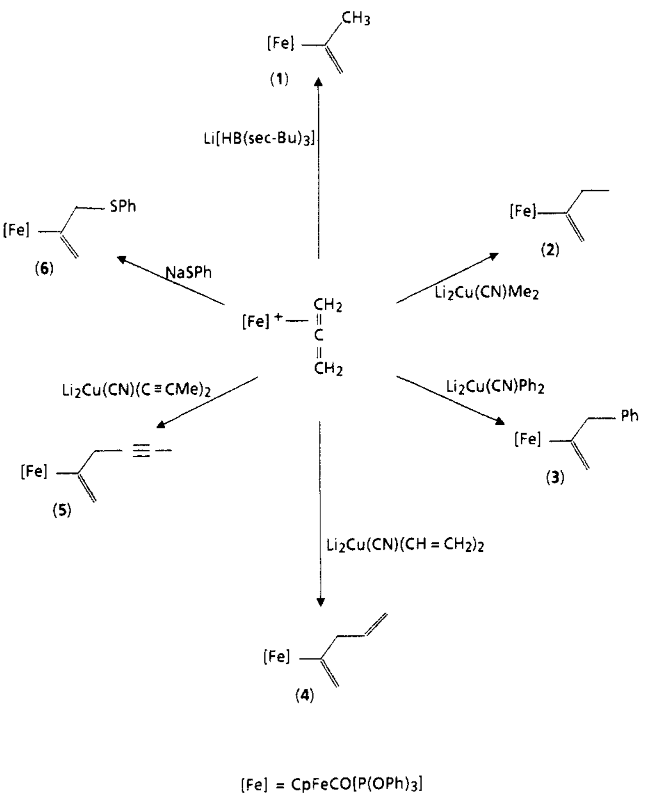
CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(H)SPh] (10). [CpFeCO[$P(OPh)_3$](η^2-allene)]BF_4 (0.50 g, 0.85 mmol) was stirred at 0 °C, and NaSPh (0.15 g, 1.10 mmol) was added as a solid. The reaction mixture was stirred for 20 min and the solvent evaporated. The oil was redissolved in $CHCl_3$ (30 mL) and filtered through a Celite plug (3 cm), and the plug was washed with $CHCl_3$ (20 mL). The solution was stirred for 18 h and then filtered through a Celite plug (3 cm), and the plug was washed with $CHCl_3$ (20 mL). The solvent was evaporated from the filtrate, and there remained a yellow oil (0.42 g, 82%): ^{1}H NMR (δ in $CDCl_3$) 7.2 (20, m, $P(OPh_3$, SPh), 6.00 (1, s, vinyl H), 4.27 (5, s, Cp), 2.20 (3, s, Me); IR spectrum (cm^{-1} in hexane) ν(CO) 1953; ^{13}C NMR (δ in $CDCl_3$) 218.4 (d, *J* = 46.3 Hz, CO), 158.1 (d, *J* = 39.6 Hz, FeC), 151.3, 129.3, 124.5, 121.4 (d, d, d, d,; *J* = 9.7, 0.8, 0.9, 4.2 Hz; $P(OPh)_3$), 140.5, 128.3, 126.4, 123.9 (SPh), 115.7 (d, *J* = 4.6 Hz, =CH), 83.5 (d, *J* = 1.6 Hz, Cp), 32.7 (Me). Anal. Calcd for $C_{33}H_{29}FeO_4PS$: C, 65.14; H, 4.80. Found: C, 64.95; H, 4.94.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(H)Me] (11). A mixture of CpFeCO[$P(OPh)_3$]I (1.64 g, 2.8 mmol) and $AgBF_4$ (0.58 g, 3.0 mmol) was stirred in CH_2Cl_2 (40 mL) at room temperature, and after 10 min MeC≡CMe (0.20 g, 0.30 mL, 3.7 mmol) was added. This solution was stirred for 20 min and then filtered through Celite. The filtrate was collected and the solvent evaporated, affording a reddish brown fluffy solid. This solid was dissolved in THF (40 mL) prechilled to −78 °C, and L-Selectride (3.0 mL, 3.0 mmol) was added by syringe. The solution was allowed to warm to room temperature and the solvent evaporated. At this point the black oil was extracted with benzene (40 mL) and filtered through Celite. The filtrate was collected and the solvent evaporated, leaving a yellow oil. A ^{1}H NMR spectrum indicated that 11 was present contaminated with a hydrocarbon. The yellow oil was redissolved in benzene (15 mL) and placed on an alumina column. The column was washed with hexane (30 mL), elution with a hexane–benzene (1:1, v/v) solution resulted in a single yellow band that was collected, and the solvent was evaporated to leave a yellow oil (0.74 g, 51%). A ^{1}H NMR spectrum showed there to be three products present: CpFeCO-[$P(OPh)_3$][η^1-(*E*)-C(Me)=C(H)Me] (11, 70%), CpFeCO[P-$(OPh)_3$][η^1-C(CH_2Me)=CH_2] (2, 23%), and CpFeCO[P-$(OPh)_3$][η^1-(**Z**)-C(Me)=C(Me)H] (12, 7%). Spectral data for 11: ^{1}H NMR (δ in C_6D_6) 7.1 (15, m, $P(OPh)_3$), 5.8 (1, m, vinyl H), 4.17 (5, s, Cp), 2.22, 1.95, (3, 3; s, d; *J* = 7 Hz, vinyl Me's); IR spectrum (cm^{-1} in hexane) ν(CO) 1945; ^{13}C NMR (δ in C_6D_6) 219.9 (d, *J* = 47.6 Hz, CO), 152.4, 129.6, 124.7, 122.1 (d, s, d, d; *J* = 9.7, 1.0, 4.2 Hz, $P(OPh)_3$), 139.1 (d, *J* = 41.5 Hz, FeC), 132.4 (d, *J* = 4.4 Hz, *C*(H)Me), 84.1 (d, *J* = 1.8 Hz, Cp), 30.7, 17.0 (s, d; *J* = 2.4 Hz, vinyl Me's). Anal. (of mixture) Calcd for $C_{28}H_{27}FeO_4P$: C, 65.39; H, 5.29. Found: C, 65.36; H, 5.43.

CpFeCO[P(OPh)$_3$][η^1-(*Z*)-C(Me)=C(H)Me] (12). A reaction as with 11 was carried out substituting Super Hydride (3.0 mL, 3.0 mmol) for L-Selectride. The benzene extraction step yielded 1.3 g of a yellow oil. A ^{1}H NMR spectrum indicated 12 and 11 were present in a 57:43 ratio along with a slight hydrocarbon impurity. Purification on alumina as above yielded the three products 11 (70%), 12 (8%), and 2 (22%). Spectral data for 12: ^{1}H NMR (δ in C_6D_6) 7.1 (15, m, $P(OPh)_3$), 6.4 (1, m, vinyl H), 4.20 (5, s, Cp), 2.53, 2.11 (3, 3; s, d; *J* = 7 Hz, vinyl Me's); IR spectrum (cm^{-1} in hexane) ν(CO) 1945; ^{13}C NMR (δ in C_6D_6) 219.7 (d, *J* = 47.5 Hz, CO), 152.1, 129.6, 124.8, 122.2 (d, s, d, d; *J* = 9.9, 2.0, 3.8 Hz, $P(OPh)_3$), 142.7 (d, *J* = 34.6 Hz, FeC), 120.4 (d, *J* = 5.0 Hz, =*C*(Me)H), 84.0 (d, *J* = 1.8 Hz, Cp), 40.9, 20.7 (d, s; *J* = 3.7 Hz, vinyl Me's).

(η^5-C_5H_4D)FeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(H)Me] (11-*d*$_1$) and CpFeCO[P(OPh)$_3$][η^1-(*Z*)-C(Me)=C(Me)D] (12-*d*$_1$). A reaction as with 12 was carried out by using Super Deuteride. A

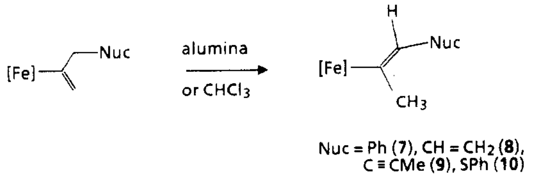
Scheme I



^{1}H NMR spectrum of the oil remaining after the benzene extraction step indicated two compounds: **11**-d_1 (40%) and **12**-d_1 (60%). Spectral data for **11**-d_1: ^{1}H NMR (δ in C_6D_6) 7.1 (15, m, $P(OPh)_3$), 5.8 (1, m, vinyl H), 4.17 (4, s, Cp), 2.21, 1.95 (3, 3; s, d; J = 7 Hz, vinyl Me's). Spectral data for **12**-d_1: ^{1}H NMR (δ in C_6D_6) 7.1 (15, m, $P(OPh)_3$), 4.20 (5, s, Cp), 2.51, 2.09 (s, s; vinyl Me's).

Results

Synthesis of Complexes. The reaction of a variety of nucleophiles with $[CpFeCO[P(OPh)_3](\eta^2\text{-}CH_2{=}C{=}CH_2)]BF_4$ yields new alkenyl complexes in high yield as shown in Scheme I. The nucleophile adds exclusively to a terminal allene carbon atom with the iron forming a σ bond with the internal carbon atom. In earlier work with η^2-alkyne complexes,[1] crude reaction products were generally purified on a short alumina column. In these reactions only filtration through Celite is possible because chromatography on alumina causes these terminal alkenyl complexes to rearrange to internal alkenyl complexes (eq 4). This conversion also takes place in $CHCl_3$ ($CDCl_3$) solutions but not in hexane, benzene, CH_2Cl_2, or EtOH. The reaction is virtually quantitative and goes to completion for complexes **3** through **6** (Nuc = Me, **2**, is a special case, vide infra). A single stereoisomer is produced in each case. For Nuc = Ph, the product **7** is identical with that formed from hydride addition to $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CPh)]BF_4$. We have previously conclusively shown that this product is the E isomer,[3] as pictured in eq 4. Also, for Nuc = Me, it has been shown that the major rearrangement product is the E isomer (vide infra). Extrapolation from these two cases coupled with the fact that the E isomer is clearly more stable for steric reasons leads to the assignment of the remaining complexes in eq 4 as the E isomers.



(4)

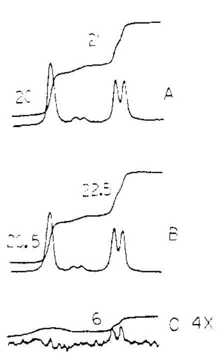
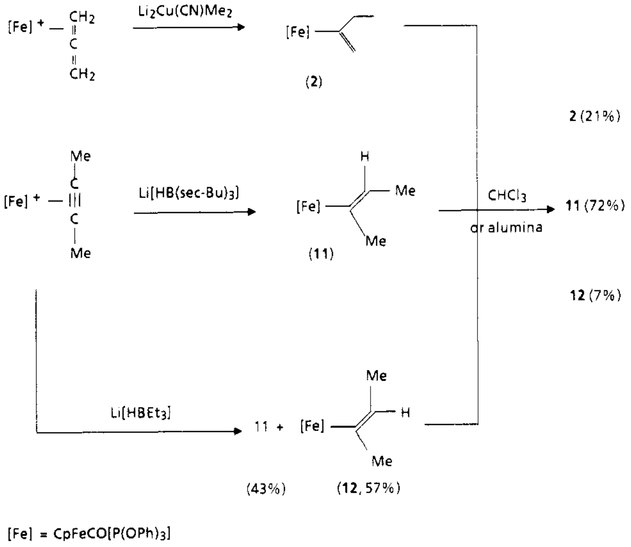


Figure 1. (A) Normal ^{1}H NMR spectrum of the methyl region of $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(H)Me]$. (B) Same spectrum as A run with irradiation of the vinyl hydrogen atom resonance (δ 5.8) run in the gated decoupled mode. (C) The difference spectrum (B − A) multiplied 4 times.

Scheme II



Three Isomers of $CpFeCO[P(OPh)_3](\eta^1\text{-}C_4H_7)$. As shown in Scheme II, three isomers of the butenyl group can be prepared. Complex **2** is prepared from the η^2-allene complex as in Scheme I. The E isomer of the 2-butenyl group forms in the reaction of L-Selectride with $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]BF_4$. About an even mixture of **11** and its Z isomer **12** forms in a similar reaction with Super Hydride. Stirring any of these products in $CHCl_3$ or in benzene containing a slurry of alumina leads to the same mixture of all three, as shown, with complex **11** being the main product of the final equilibrium mixture. Note that **12** does not isomerize to **11** in the absence of $CHCl_3$ or alumina.

That the product of the L-Selectride reaction is actually the E isomer is proven by three sets of experiments. A ^{1}H nuclear Overhauser effect (NOE) enhancement experiment was attempted initially.[8] In this experiment for the E isomer **11**, irradiation at the resonance position of the alkenyl hydrogen atom should cause an increase in the integrated intensity, vs. a standard, of the β-methyl group resonance (a doublet) with no change in the intensity of the α-Me singlet (only atoms in close proximity can show an enhancement). For the Z isomer **12**, both would show

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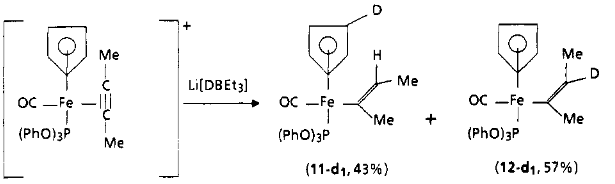
(8) (a) Noggle, J. H.; Schirmer, E. R. "The Nuclear Overhauser Effect"; Academic Press: New York, 1971. (b) Bell, R. A.; Saunders, J. K. *Top. Stereochem.* **1973**, *7*, 1–92.

some enhancement. Figure 1A shows the spectrum in the region of these two methyl groups. Figure 1B is the same spectrum with irradiation at the alkenyl hydrogen atom resonance, run in the gated decoupled mode to retain coupling. A very slight enhancement (2%) in the α-Me group is observed with a 7–8% enhancement of the β-Me group doublet. This 7–8% enhancement was observed on three different samples run at different times and with different decoupling modes. In these experiments, the resonance for the α-methyl group showed an enhancement of less than 2%. The enhancement is best observed in Figure 1C, the difference spectrum of B − A. Thus, these data are consistent with **11** being the *E* isomer. Although successful here, we have noted previously that this type of NOE experiment has not been generally successful with these iron–alkenyl complexes.[1]

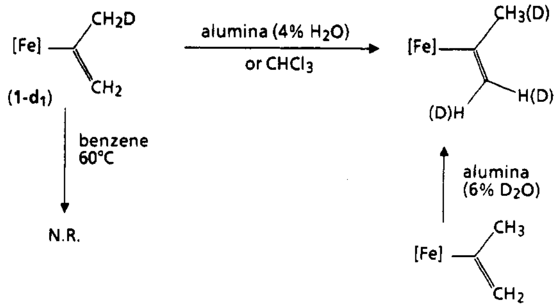
A second and more conclusive piece of evidence indicating that **11** is the *E* and **12** is the *Z* isomer comes from variable-temperature ^{1}H NMR data. We have shown previously[1] that complexes of the formula $\mathrm{CpFeCO[P(OPh)_3](\eta^1\text{-}(\mathit{E})\text{-}C(Me){=}C(Me)X)}$ show two rotamers about the Fe–C(alkenyl) bond in low temperature spectra (barriers to rotation are ca. 13 kcal/mol). Other complexes lacking the trans-methyl arrangement do not show rotamers. Cooling the **11**/**12** mixture formed in the $\mathrm{Li[HBEt_3]}$ reaction below −40 °C causes the α-methyl resonance for **12** to broaden and collapse (at −60 °C) into the base line, while the analogous resonance for **11** remains sharp. This indicates that **12** has trans-methyl groups but **11** does not.

Reaction of $\mathrm{Li[DBEt_3]}$ with η^2-Unsaturated Hydrocarbon Iron Complexes. The third piece of evidence on the stereochemistry of **11** and **12** is part of a larger study on deuteride addition to η^2-alkyne, allene, and alkene complexes. It has been previously communicated that deuteride addition to either the η^2-MeC≡CPh or MeC≡CCO$_2$Me iron complexes proceeds by initial exo attack at the Cp ring followed by intramolecular cis transfer of the endo hydrogen atom from the C_5H_5D ring thus formed to the alkyne to yield products such as $\mathrm{(\eta^5\text{-}C_5H_4D)FeCO[P(OPh)_3](\eta^1\text{-}(\mathit{E})\text{-}C(Me){=}C(H)Ph)}$.[3] The reaction of the η^2-MeC≡CMe complex proceeds as shown in eq 5 to yield a mixture of two products. This result was proven by a combination of ^{1}H and ^{2}H NMR experiments. In the ^{1}H NMR spectrum of the mixture, the doublet resonance for the β-Me group is normal for **11**-d_1 but has collapsed to a singlet as expected for **12**-d_1. Also the alkenyl hydrogen atom is normal for **11**-d_1 but is absent for **12**-d_1. In the ^{2}H NMR spectrum, a resonance at the correct location for the Cp ring of **11**-d_1 is observed and another of about equal intensity at the position expected for the alkenyl deuterium resonance for **12**-d_1. Clearly in this case two reaction pathways are operative. One is analogous to the ring addition reactions observed as outlined above with two unsymmetrical alkynes yielding the product arising from addition to the Cp ring followed by intramolecular cis hydrogen atom transfer to the alkyne to produce **11**-d_1. The other is normal trans addition (as observed with other nucleophiles[9]) of deuteride to produce **12**-d_1. These results confirm the stereochemical assignment.

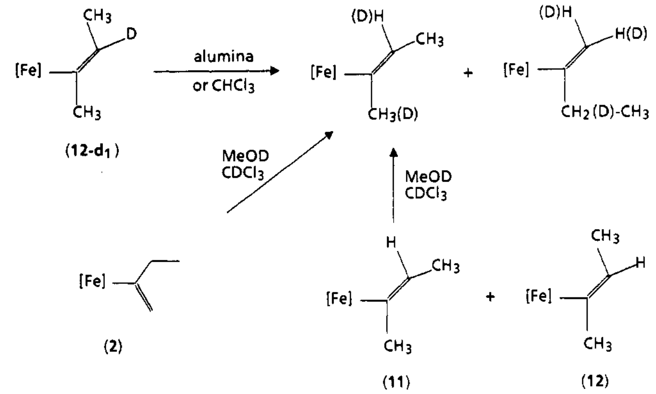


(5)

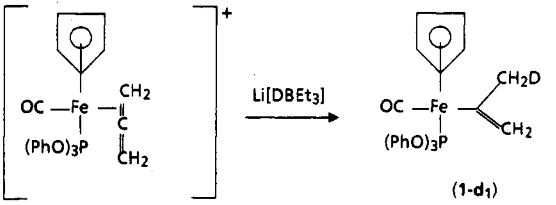
Scheme III



Scheme IV



Reaction of the η^2-allene complex with $\mathrm{Li[DBEt_3]}$ takes place at the allene ligand (eq 6). In a similar experiment with the analogous η^2-ethylene complex, we have shown that addition also takes place at the alkene.



(6)

Labeling Studies on Rearrangement Reactions. As shown in eq 4 and in Scheme II and as noted with similar complexes earlier,[1] many of these alkenyl complexes undergo a 1,3-hydrogen atom shift in either $CHCl_3$ ($CDCl_3$) or when purified with alumina. A number of deuterium labeling experiments have been carried out in order to obtain mechanistic information on these rearrangements. These studies were monitored by using ^{1}H and ^{2}H NMR. First, complex **1**-d_1 was studied as shown in Scheme III. Stirring **1**-d_1 with deactivated alumina causes scrambling of the deuterium label with some wash out (ca. 30%) of the label noted. Stirring **1**-d_1 in $CHCl_3$ (or $CDCl_3$) also causes scrambling of the label and no apparent loss (or gain for $CDCl_3$) of deuterium. Heating **1**-d_1 in benzene at 60 °C for 5 h causes no change. One can also form a product with the scrambled label by running undeuterated **1** through an alumina column previously deactivated with D_2O.

Studies with **11**-d_1 and **12**-d_1, as produced in eq 5, are complicated by the facts that they are prepared as a mixture, and, as shown in Scheme II, rearrangement of **2**, **11**, or **12** leads to a 21/72/7 mixture of each, respectively. The label in the Cp ring for **11**-d_1 is fixed, and none of the reaction conditions described below either increased or decreased the label even though **11**-d_1 does isomerize to the **2**/**11**/**12** mixture in $CHCl_3$ or when shown alumina. Scheme IV shows results similar to those observed in

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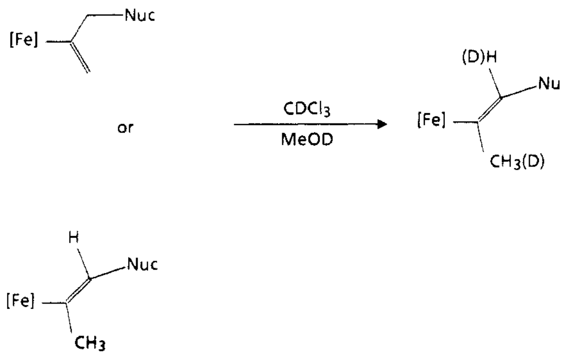
[9] Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101.

Scheme V



Scheme III. The amount of **12** in any final rearrangement mixture is not great enough to determine the position of deuterium labels and is thus omitted. From both ^{1}H and ^{2}H NMR data, it is clear that no deuterium is introduced into the β-methyl group for **11** or the methyl group in **2** in any of these reactions, but the label is scrambled among the other positions. Because these reactions are fairly slow, samples that have only partially rearranged can be studied. The closeness of the alkenyl methyl group resonances in the ^{1}H NMR and the vinyl deuterium resonances in the ^{2}H NMR prevents highly quantitative results, but certain trends can be observed. In the rearrangement of the **11**-d_1/**12**-d_1 mixture on a highly deactivated alumina column, essentially all of the original **12**-d_1 remains unchanged whereas the **11**-d_1 has isomerized to a normal equilibrium mixture with **2**. On a more active column where the **11** to **12** ratio had changed from 43–57 to 1.8–1 (about 1 half-life for the disappearance of **12**), the ratio of **2** to **11** is also about the same as in the equilibrium mixture. Essentially all of the **12** that remains is **12**-d_1 as the vinyl hydrogen atom resonance is not observed in the ^{1}H NMR spectrum (but a large resonance in the ^{2}H NMR spectrum) and the β-methyl group resonance is a singlet (still deuterium decoupled). For the **2** and **11** that form from **12**-d_1, the deuterium is located mainly in the methylene and vinyl position, respectively, and thus is mainly located on the same carbon atom that it is in **12**-d_1. Similar results are noted when the **11**-d_1/**12**-d_1 mixture is allowed to rearrange in $CDCl_3$ or $CHCl_3$.

When a mixture of **11** and **12** is allowed to rearrange in $CDCl_3$/MeOD extensive deuteration, as shown in Scheme IV, is noted. Again if the reaction is monitored after only about half of **12** has rearranged, the **12** that does remain is largely undeuterated. For **2** rearranging under similar conditions, the **11** that forms early in the reaction is mainly deuterated at the α-methyl group and as the reaction continues the vinyl position is also deuterated.

Treatment of complexes **3**–**10** with $CDCl_3$/MeOD leads to complexes **7**–**10** with deuterium incorporation at the α-methyl group and the β-vinyl position (Scheme V). Over a period of a week at room temperature, **7** is nearly completely perdeuterated at these two positions. It is important to note that no deuterium incorporation or the rearrangement shown in eq 4 takes place in pure EtOD.

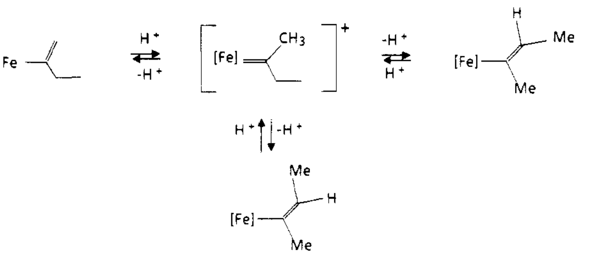
Protonation Studies. A series of NMR tube experiments were carried out to determine if these isomerization reactions could be initiated by acid. Addition of trace amounts of HBF_4 in Et_2O to a benzene solution of **3** causes the isomerization reaction producing **7**. Some sample decomposition is noted, and the reaction does not immediately go to completion but does overnight. Treating **6** under similar conditions slowly produces **10**. Increasing the ratio of acid to **6** from 1:250 to 1:50 increases the rate of the reaction. In CD_2Cl_2, addition of acid causes the conversion of **6** to **10** to be much faster than in benzene, but substantial sample decomposition also occurs. A similar reaction of acid with the **11**/**12** mixture in benzene causes conversion to the normal equilibrium mixture of **2**/**11**/**12** shown in Scheme II.

Finally, attempts to carry out meaningful kinetic experiments with any of these isomerization reactions has not been successful. Reaction rates are variable. Although the reasons for this are not clear, one important variable seems to be how recently the organometallic complex had been prepared. Thus samples that had aged two or three days seem to rearrange under identical conditions more rapidly than freshly prepared samples.

Discussion

Two new families of iron–alkenyl complexes can be prepared from nucleophilic addition reactions with $[CpFeCO[P(OPh)_3](\eta^2\text{-}CH_2{=}C{=}CH_2)]BF_4$. The initial products **1**–**6** are terminal alkenyl complexes. For **3**–**6**, they readily isomerize (eq 4) when dissolved in $CHCl_3$ or benzene containing alumina (or upon chromatography), a reaction that brings the double bond into conjugation with other functionality in the alkenyl substituent. The trisubstituted alkenyl complexes that form have *E* stereochemistry, presumably for steric reasons. The methyl addition product **2**, in which the isomerization reaction does not bring the double bond into conjugation, is the only one that yields a mixture of three possible isomers as shown in Scheme II. All three isomers can be prepared directly.

Although the driving force for these isomerization reactions seems obvious, the mechanism is not. In MeOD, no isomerization takes place unless $CHCl_3$ is also added. In the mixed solvent system, the hydrogen atom undergoing the 1,3 shift equilibrates with the alcohol deuterium atom of MeOD. The isomerization reaction can also be initiated in benzene or CD_2Cl_2 by addition of trace amounts of acid. A simple protonation type mechanism (eq 7), is reasonable in that examples of carbene intermediates such as that shown are well-known in this system[10] and have, in fact, been prepared in certain cases by the protonation of alkenyliron complexes.[11] If correct, this mechanism would explain the fact that in the isomerization of **12**-d_1 to **11** and **2**, the deuterium atom only slowly scrambles off the carbon atom to which it is originally bonded (for **12**-d_1 going to **2**, for example, the deuterium atom is not even involved and for **12**-d_1 going to **11**, it has at least a 50% chance of not moving). In reality, the situation is probably much more complicated as evidenced by the facts that the rate of the process is dependent on the age of the individual samples and that oxidizing



(7)

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[10] Brookhart, M.; Timmers, D.; Tucker, J. R.; Williams, G. D.; Husk, G. R.; Brunner, H.; Hammer, B. *J. Am. Chem. Soc.* **1983**, *105*, 6721 and references therein.

[11] (a) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (b) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (c) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *Ibid.* **1982**, *104*, 3761.

reagents also catalyze these and related reactions.[1,12]

As would be expected, deuteride delivered from Li[DBEt$_3$] adds to the η^2-allene complex at the allene ligand (the η^2-ethylene complex reacts in a similar fashion). This contrasts our earlier work[3] that shows that this same reagent adds to the η^5-C_5H_5 ring in [CpFeCO[P(OPh)$_3$](η^2-alkyne)]BF$_4$ for alkyne = PhC≡CMe and MeC≡CCO$_2$Me, an unexpected result.[13] A possible reason for this difference is the perturbation to the electronic levels of the iron-alkyne complexes by the unfavorable four-electron, two-center $d\pi$-$\pi_\perp$ interaction that has recently been invoked[14] to explain the fact that d^4 alkyne complexes are more stable than the d^6 alkyne complexes that are being used in this work. The situation is even further complicated by the facts (Scheme II) that Li[HB(*sec*-Bu)$_3$] also adds hydride to the η^5-C_5H_5 ring for alkyne = MeC≡CMe but Li[DBEt$_3$] (or Li[HBEt$_3$]) adds at both locations in about even amounts. Steric effects, the degree of distortion of the η^2-alkyne toward an η^1-geometry, and the nature of the transition state (whether reactant-like or product-like) have all been used to explain other trends in nucleophilic addition reactions[15] with π-coordinated unsaturated ligand complexes and could all have an effect on the above results. For example, steric differences in the two reagents used in Scheme II could explain the differing results for those two reactions, but in the absence of more detailed information about the probable reaction mechanism, such speculation seems unwarranted.

This work and our earlier work in this area clearly point out that nucleophilic addition reactions with alkynes do not simply parallel those with alkenes or allenes.[16] Also, one must be very careful in the study of metal-alkenyl complexes because of the possibility of rearrangement reactions that can be induced by standard purification techniques or typical NMR solvents.

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Registry No. 1, 92421-57-3; 2, 92421-58-4; 3, 92366-24-0; 4, 92421-59-5; 5, 92421-60-8; 6, 92421-61-9; 7, 86563-32-8; 8, 92421-62-0; 9, 92421-63-1; 10, 92421-64-2; 11, 92421-65-3; 11-d_1, 92421-66-4; 12, 92471-24-4; 12-d_1, 92421-67-5; [CpFe(CO)[P(OPh)$_3$][η^2-MeC≡CMe)]BF$_4$, 87556-47-6; [CpFeCO[P(OPh)$_3$](η^2-CH$_2$=C=CH$_2$)]BF$_4$, 71359-49-4; CpFeCO[P(OPh)$_3$]I, 31988-05-3.

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Transition Metal-Isocyanide Bonding: A Photoelectron Spectroscopic Study of Iron Tetracarbonyl Isocyanide Complexes

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The He I and X-ray photoelectron spectra of the iron tetracarbonyl complexes of methyl, *tert*-butyl, trimethylsilyl, and phenyl isocyanide have been obtained. The bonding properties of these isocyanides are compared with those of carbon monoxide by using the core-binding energy data to interpret the valence ionization energies. The data show that all the isocyanides have comparable σ-donor ability and that, in the Fe(CO)$_4$CNR complexes, they are significantly weaker σ donors than carbon monoxide. The stronger σ-donor character of the coordinated CO ligands is presumably due to the σ-π synergism of the Fe-CO bonding. The net interaction of an isocyanide ligand with the iron d orbitals leaves the energy of the d orbitals destabilized relative to Fe(CO)$_5$. The data indicate that the relative energies of interaction of the d orbitals with the filled ligand π orbitals and the empty ligand π^* orbitals are different in Fe-CO and Fe-CNR bonds, with the interactions of the filled ligand π orbitals being relatively more important in Fe-CNR bonds than in Fe-CO bonds. The net electron withdrawal by a coordinated isocyanide ligand, although significant, is much lower than that by a coordinated carbonyl ligand. It is clear that the interactions of transition metals with isocyanides (and probably also with other ligands with similar electronic structures) cannot be adequately described without considering the combined σ-donor, π-acceptor, and π-donor characters of the ligands.

Introduction

The study of transition-metal complexes containing isocyanide ligands has developed into an important area of organometallic chemistry that has been the subject of recent reviews.[2,3] However, the interactions of the isocyanide and metal orbitals in such complexes have received little attention. Because photoelectron spectroscopy is the most direct method for measuring orbital interactions of

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