

Synthesis and reactions of a chelated carbene-olefin complex of cyclopentadienyliron

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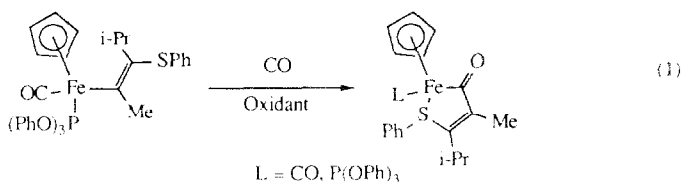
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Abstract

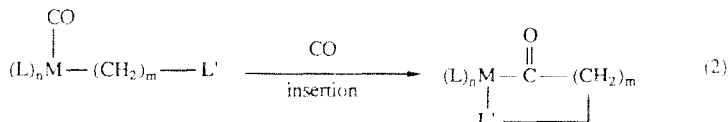
Heating $\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ in CH_3NO_2 yields $\text{CpFeCO}(\eta^1\text{-COCH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ in an approximate equimolar mixture with the starting material. Separation and recycling of starting material leads to isolation of the cyclic acyl in 83% yield. Alkylation of this acyl complex with Et_3OBF_4 yields the olefin-carbene complex $[\text{CpFeCO}(\eta^1\text{-C}(\text{OEt})\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{BF}_4$. Reduction of this carbene complex with NaBH_4 in the presence of base yields $\text{CpFeCO}(\eta^1\text{-CH}(\text{OEt})\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$. Treatment of this complex with trimethylsilyl triflate at -78°C yields an unstable complex tentatively assigned as the alkylidene-olefin complex $[\text{CpFeCO}(\eta^1\text{-CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{[CF}_3\text{SO}_3]$. Reaction of either PhLi or $\text{Ph}_2\text{CuCNLi}_2$ and $[\text{CpFeCO}(\eta^1\text{-C}(\text{OEt})\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{BF}_4$ yields $\text{CpFeCO}(\eta^1\text{-C}(\text{OEt})=\text{CHCH}_2\text{CH}=\text{CH}_2)$. It did not prove possible to form analogous cyclic complexes starting with $\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}_2\text{C}\equiv\text{CH})$, $\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-CH}_2\text{CH}_2\text{Un})$ or $\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-COCH}_2\text{CH}_2\text{Un})$ ($\text{Un} = \text{CH}=\text{CH}_2$, $\text{C}\equiv\text{CH}$). The reaction of the $\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-COCH}_2\text{CH}_2\text{Un})$ complexes with Et_3OBF_4 followed by reduction with NaBH_4 in the presence of base yields $\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-}(E)\text{-CH}=\text{CHCH}_2\text{Un})$.

Introduction

There is considerable interest in using CO insertion reactions with organotransition metal complexes as a means of elaborating the organic ligands bound to the metal [1]. A recently reported result from our laboratory [2] shows that during the oxidatively catalyzed insertion of CO in an alkenyliron complex to form an acyliron complex, isomerization of the double bond and coordination of sulfur also occurred (eq. 1). As shown, two products were isolated from this reaction.



A generalized version [3] of eq. 1 is shown below (eq. 2). The reaction has two notable features. First, an acylmetal complex is formed, that, in general, can be



elaborated in a number of ways. For example, acyls can be cleaved from the metal to form esters [4], reduced to hydrocarbons to yield alkylmetal complexes [5], or alkylated at oxygen to form alkoxy carbene complexes [6]. Second, the stabilizing effect of the chelate ring should allow coordination of ligands, L' , that otherwise would not coordinate to iron, if introduced as free ligands.

The goal of this work was to prepare new iron complexes that exploit these features of this general reaction (eq. 2). A large variety of alkenyliron complexes with appropriately placed, potential ligands (as in eq. 1) are available [2,4,7], but for the purposes of this initial study we decided to start with simpler alkyliron complexes.

Reported here is the synthesis of a chelated carbene-olefin complex that employs a CO insertion/olefin coordination rearrangement as the key step. Reactions of the carbene-olefin complex and related complexes are also reported, including ^1H NMR evidence for an unstable alkylidene-olefin complex.

Experimental

General procedure. All operations on complexes in solution were carried out under an atmosphere of nitrogen. All solvents except nitromethane were dried and distilled before use. Nitromethane (from Aldrich) was used as received. Chromatography was done on Alcoa F-20 alumina. ^1H NMR spectra were recorded at either 90 or 300 MHz and ^{13}C NMR spectra were recorded at either 20 or 75 MHz. Chemical shifts are reported as δ vs. Me_4Si with the solvent as internal reference. A refocused INEPT sequence [8] was used to aid in the assignment of all ^{13}C NMR spectra of the chelated complexes. Elemental analyses were performed by Robertson Laboratory. Published procedures were used in the preparation of $\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ [3], $\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}_2\text{C}\equiv\text{CH})$ [3], $\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-COCH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ [3], $\text{K}[\text{CpFe}(\text{CO})_2]$ [9], Et_3OBF_4 [10], and $\text{Ph}_2\text{CuCNLi}_2$ [11]. The trimethylsilyl triflate and the phenyllithium were obtained from Aldrich and used as received. A 450W Hanovia mercury vapor lamp was used for the photolyses.

$\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ (**1a**). ^{13}C NMR (δ in CDCl_3 at -13°C): 208.8 (s, CO's), 129.5, 112.1 (s, s, C=C), 85.1 (s, Cp), 41.8 (s, FeCH_2CH_2), 2.0 (s, FeCH_2).

$\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}_2\text{C}\equiv\text{CH})$ (**1b**). ^{13}C NMR (δ in CDCl_3 , all s): 216.8 (CO's), 87.4 (CH), 85.1 (Cp), 67.4 ($\text{C}\equiv\text{CH}$), 24.9 (FeCH_2CH_2), 0.5 (FeCH_2).

$Cp\overline{FeCO}(\eta^1-COCH_2CH_2CH=CH_2)$ (**2**). A CH_3NO_2 solution (70 ml) of **1a** (8.0 g, 34 mmol) was stirred overnight at $49^\circ C$. The solvent was removed under vacuum and the residue was placed on an alumina column with 15 ml CH_2Cl_2 . Elution with pentane moved unreacted **1a** and elution with CH_2Cl_2 moved **2**. Recovered **1a** was carried through this insertion and isolation procedure four more times. The combined yields of **2** were then recrystallized from hexane/ CH_2Cl_2 (10/1) to give a pure yellow powder (6.6 g, 83%). This compound has been briefly mentioned previously [12a]: 1H NMR (δ in $CDCl_3$): 4.89, 3.27, 2.62 (all 1, m, d, d, J 8, 12 Hz, $CH=CH_2$), 4.59 (5, s, Cp), 3.15, 2.73, 2.33, 0.63 (all 1, all m, CH_2CH_2); IR (cm^{-1} in CH_2Cl_2): $\nu(C=O)$ 1960, $\nu(C=O)$ 1645; ^{13}C NMR (δ in $CDCl_3$ at $-15^\circ C$): 271.2 (s, $C=O$), 218.2 (s, $C=O$), 86.2 (s, Cp), 75.3, 69.4 (s, s, $CH=CH_2$), 44.2, 28.6 (s, s, CH_2 's); MS (EI, 15 eV): m/e 232 (M^+), 204 ($M^+ - CO$). Anal. Found: C, 56.68; H, 5.01. $C_{11}H_{12}FeO_2$ calcd.: C, 56.93; H, 5.21%.

$[Cp\overline{FeCO}(\eta^1-C(OEt)CH_2CH_2CH=CH_2)]BF_4$ (**3**). Separate CH_2Cl_2 solutions of **2** (7.0 g, 30 mmol, 30 ml) and Et_3OBF_4 (5.7 g, 30 mmol, 30 ml) were cooled to $-78^\circ C$. The Et_3OBF_4 solution was transferred via cannula to the iron complex solution, the cold bath was removed, and the mixture was stirred for 90 min. The solvent was removed under vacuum and the orange oily residue was taken up in ca. 500 ml warm hexane/ CH_2Cl_2 (2/1). Upon cooling, **3** was obtained as an orange powder (9.7 g, 93%): 1H NMR (δ in $CDCl_3$): 5.68, 4.04, 3.56, 3.38, 3.17, 2.86, 1.08 (all 1, all m, $CH_2CH_2CH=CH_2$), 5.06 (5, s, Cp), 4.62 (2, m, OCH_2), 1.67 (3, t, J 7 Hz, Me); IR (cm^{-1} in CH_2Cl_2): $\nu(CO)$ 2010; ^{13}C NMR (δ in CD_2Cl_2 at $-15^\circ C$): 341.8 (s, $Fe=C$), 214.7 (s, $C=O$), 88.2 (s, Cp), 85.2 (s, CH), 78.3, 63.9, 54.2, 30.0 (all s, CH_2 's), 14.3 (s, Me). Anal. Found: C, 45.04; H, 4.74. $C_{13}H_{17}BF_4FeO_2$ calcd.: C, 44.88; H, 4.92%.

$Cp\overline{FeCO}(\eta^1-C(OEt)HCH_2CH_2CH=CH_2)$ (**4**). A solution of $NaBH_4$ (23 mmol) and $MeONa$ (47 mmol) was stirred in $MeOH$ (100 ml) for 2 h and complex **3** (2.03 g, 5.84 mmol in CH_2Cl_2 (25 ml)) was added dropwise [6a]. After 0.5 h, this mixture was diluted with H_2O (500 ml) and extracted with CH_2Cl_2 (3×35 ml). The combined CH_2Cl_2 portions were rinsed through an alumina plug and the solvent evaporated. Complex **4** was purified by dissolution in a minimum of pentane and filtration through Celite. Evaporation of the solvent yielded a spectroscopically pure, orange oil. This oil decomposes slowly at room temperature: 1H NMR (δ in $CDCl_3$): 5.96, 2.92, 1.83 (1, 1, 1, m, d, d, J 8, 12 Hz, $CH=CH_2$), 4.50 (5, s, Cp), 4.40 (1, m, $CH(OEt)$), 3.37 (2, q, J 7 Hz, OCH_2), 1.82, 1.56, 0.61 (1, 2, 1, all m, CH_2CH_2), 1.12 (3, t, J 7 Hz, Me); IR (cm^{-1} in CH_2Cl_2): $\nu(CO)$ 1949; ^{13}C NMR (δ in C_6D_6): 224.9 (s, CO), 86.9, 69.9 (s, s, CH's), 84.5 (s, Cp), 65.9 (vinyl CH_2), 42.3 (OCH_2), 38.3, 24.6 (CH_2CH_2), 16.2 (Me); MS (EI, 15 eV): m/e 262 (M^+), 234 ($M^+ - CO$).

Reaction of 4 and trimethylsilyl triflate. Complex **4** (10 mg, 38 μ mol) was dissolved in CD_2Cl_2 (0.3 ml) in an NMR tube, and the solution was frozen by submersing the tube in liquid nitrogen. Additional CD_2Cl_2 (0.2 ml) was added to the submersed tube, followed by trimethylsilyltriflate (8.5 mg, 7.4 μ l, 38 μ mol). The tube was then removed from the liquid nitrogen and placed in a dry ice/isopropanol bath. Upon thawing, the ether complex solution mixed with the trimethylsilyl triflate and turned deep red. After thawing, the tube was quickly transferred to an NMR spectrometer that was precooled to $-80^\circ C$.

$Cp\overline{FeCO}(\eta^1-(Z)-C(OEt)=CHCH_2CH=CH_2)$ (**5**). Complex **3** (0.93 g, 2.7 mmol)

was dissolved in CH_2Cl_2 (25 ml), cooled to -78°C , and treated dropwise with 1 equiv. of PhLi . The solution was stirred for 3 h while slowly warming to room temperature. The solvent was evaporated, and the residue was extracted with hexane (2×25 ml). The extracts were filtered through Celite, and the solvent was evaporated to yield an orange oil (0.65 g, 2.5 mmol, 93%). This oil decomposes slowly at room temperature and rapidly on an alumina column: $^1\text{H NMR}$ (δ in CDCl_3): 5.19, 3.20, 2.31 (all 1, m, d, d, J 8, 12 Hz, $\text{CH}=\text{CH}_2$), 4.76 (1, br s, $\text{C}(\text{OEt})=\text{CH}$), 4.61 (5, s, Cp), 3.78, 3.60 (1, 1, m, m, OCH_2), 2.69, 1.78 (1, 1, m, m, CH_2), 1.20 (3, t, J 7 Hz, CH_2Me); IR (cm^{-1} , thin film): $\nu(\text{CO})$ 1955; $^{13}\text{C NMR}$ (δ in CDCl_3 , all s): 223.5 ($\text{C}\equiv\text{O}$), 176.6 (COEt), 109.3 ($\text{FeC}=\text{C}$), 85.3 (Cp), 75.7, 64.5 ($\text{CH}_2=\text{CH}$), 45.2 (OCH_2), 33.5 (CH_2), 15.2 (Me). MS (EI, 15 eV): m/e 260 (M^+).

Reaction of 3 and $\text{Ph}_2\text{CuCNLi}_2$. Complex **3** (0.52 g, 1.5 mmol) was treated with 1 equiv. of $\text{Ph}_2\text{CuCNLi}_2$ in the same manner described for the preparation of **5**. The $^1\text{H NMR}$ spectrum of the product mixture indicated the presence of **5** contaminated by a second complex. Both complexes decomposed slowly at room temperature and could not be chromatographed on alumina or silica.

$\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ (6a**).** Complex **1a** (4.03 g, 17.4 mmol) and PPh_3 (13.6 g, 52 mmol) were dissolved in benzene and photolyzed at 0°C for 2.5 h. The solution was then reduced in volume to 15 ml and chromatographed on alumina with hexane/benzene (1/1). A broad orange band was collected, and the solvent was evaporated. The orange residue was recrystallized from hexane to give an orange powder (3.79 g, 47%): $^1\text{H NMR}$ (δ in C_6D_6): 7.2 (15, m, PPh_3), 6.03, 5.07, 4.93 (1, 1, 1, m, d, d, J 17, 9 Hz, $\text{CH}=\text{CH}_2$), 4.26 (5, s, Cp), 2.63, 2.35, 1.75, 1.01 (all 1, all m, FeCH_2CH_2); IR (cm^{-1} in hexane): $\nu(\text{CO})$ 1918; $^{13}\text{C NMR}$ (δ in CD_2Cl_2 at -15°C): 144.4, 110.4 (d, s, J 2 Hz, $\text{C}=\text{C}$), 136.9, 132.3, 129.6, 128.2 (all d, J 40, 10, 2, 9 Hz), 84.9 (d, J 1 Hz, Cp), 46.3, 3.9 (d, d, J 4, 18 Hz, FeCH_2CH_2). The CO resonance was not located. MS (EI, 15 eV): m/e 466 (M^+). Anal. Found: C, 71.95; H, 5.78. $\text{C}_{28}\text{H}_{27}\text{FeOP}$ calcd.: C, 72.12; H, 5.84%.

$\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-CH}_2\text{CH}_2\text{C}\equiv\text{CH})$ (6b**).** This complex was prepared from **1b** (3.28 g, 14.3 mmol) in a manner outlined for **6a**. Recrystallization of the crude product from hexane yielded an orange powder (2.11 g, 32%): $^1\text{H NMR}$ (δ in C_6D_6): 7.2 (15, m, PPh_3), 4.03 (5, s, Cp), 2.69, 2.41, 1.94, 1.16 (1, 1, 2, 1, all m, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$); IR (cm^{-1} in CH_2Cl_2): $\nu(\text{CO})$ 1907; $^{13}\text{C NMR}$ (δ in CDCl_3 at -15°C): 222.9 (d, J 33 Hz, CO), 136.4, 132.9, 129.4, 128.1 (all d, J 41, 10, 2, 9 Hz, PPh_3), 89.5, 65.7 (d, s, J 3 Hz, $\text{C}\equiv\text{C}$), 84.7 (s, Cp), 26.1, 2.2 (d, d, J 3, 19 Hz, FeCH_2CH_2); MS (EI, 15 eV): m/e 464 (M^+). Anal. Found: C, 72.30; H, 5.12. $\text{C}_{28}\text{H}_{25}\text{FeOP}$ calcd.: C, 72.43; H, 5.43%.

$\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-COCH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ (7a**).** This complex was prepared by a known procedure [3]. $^{13}\text{C NMR}$ (δ in CDCl_3 at -20°C): 276.6 (d, J 23 Hz, $\text{C}=\text{O}$), 220.4 (d, J 31 Hz, $\text{C}\equiv\text{O}$), 138.8, 113.8 (s, s, $\text{C}=\text{C}$), 137.9, 133.1, 129.6, 128.0 (all d, J 35, 10, 1, 10 Hz, PPh_3), 85.1 (s, Cp), 64.8, 29.5 (d, s, J 6 Hz, CH_2CH_2).

$\text{CpFeCO}(\text{PPh}_3)(\eta^1\text{-COCH}_2\text{CH}_2\text{C}\equiv\text{CH})$ (7b**).** This complex was prepared from **1b** (4.13 g, 18.0 mmol) in the same manner as **7a**. Yellow-orange crystals were obtained (2.70 g, 30%): The $^1\text{H NMR}$ matches that in the literature [13]. IR (cm^{-1} in CH_2Cl_2): $\nu(\text{C}\equiv\text{O})$ 1915, $\nu(\text{C}=\text{O})$ 1604; $^{13}\text{C NMR}$ (δ in CDCl_3 at -18°C): 274.8 (d, J 44 Hz, $\text{C}=\text{O}$), 220.2 (d, J 39 Hz, $\text{C}\equiv\text{O}$), 135.9, 133.1, 129.7, 129.0 (all d, J 43, 10, 2, 9 Hz, PPh_3), 85.1 (s, Cp), 67.8 (s, $\text{C}\equiv\text{CH}$), 62.8, 13.9 (d, s, J 6 Hz, CH_2CH_2). A resonance for CH was not found.

$CpFeCO(PPh_3)(\eta^1-(E)-CH=CHCH_2CH=CH_2)$ (**8a**). Complex **7a** (1.50 g, 3.04 mmol) was dissolved in CH_2Cl_2 (30 ml), added to a flask holding Et_3OBF_4 (587 mg, 3.04 mmol), and stirred for 2 h. The solvent was evaporated and the residue was extracted with benzene to remove any unreacted **7a**. The residue, presumed to be the ethoxycarbene complex, was then carried through the $NaBH_4/MeONa/MeOH$ reaction [6a] as described for the preparation of **4**. An orange oil was obtained (1.39 g, 96%): 1H NMR (δ in $CDCl_3$) 7.4 (15, m, PPh_3), 6.64, 5.41, 5.29, 4.78 (1, 1, 1, 2, all m, vinyl H's), 4.31 (5, s, Cp), 2.61 (2, m, CH_2); IR (cm^{-1} in CH_2Cl_2): $\nu(CO)$ 1919; ^{13}C NMR (δ in $CDCl_3$ at $-18^\circ C$): 221.8 (d, J 31 Hz, CO), 140.7, 140.0, 139.2 (d, s, d, J 32, 1 Hz, vinyl CH's), 135.9, 132.9, 129.3, 127.7 (all d, J 42, 10, 2, 10 Hz, PPh_3), 112.7 (s, $=CH_2$), 44.2 (d, J 3 Hz, CH_2), 84.5 (s, Cp); MS (EI, 15 eV): m/e 478 (M^+), 450 ($M^+ - CO$).

$CpFeCO(PPh_3)(\eta^1-(E)-CH=CHCH_2C\equiv CH)$ (**8b**). This complex was prepared from **7b** (1.16 g, 2.36 mmol) in a manner outlined for **7a**. An orange oil was obtained (1.03 g, 92%): 1H NMR (δ in $CDCl_3$): 7.3 (15, m, PPh_3), 6.91, 5.14 (1, 1, m, m, vinyl CH's), 4.33 (5, s, Cp), 2.79 (2, m, CH_2), 1.97 (1, m, alkynyl CH); IR (cm^{-1} in CH_2Cl_2): $\nu(CO)$ 1934; ^{13}C NMR (δ in $CDCl_3$ at $-18^\circ C$): 221.6 (d, J 31 Hz, CO), 143.2 (d, J 30 Hz, FeC), 136.0, 132.9, 129.4, 127.8 (all d, J 42, 10, 2, 10 Hz, PPh_3), 84.5 (d, J 1 Hz, Cp), 84.3, 68.8 (d, s, J 1 Hz, $C\equiv C$), 27.6 (d, J 3 Hz, CH_2); MS (EI, 15 eV): m/e 476 (M^+), 448 ($M^+ - CO$). Anal. Found: C, 72.81; H, 5.63. $C_{29}H_{25}FeOP$ calcd.: C, 73.12; H, 5.29%.

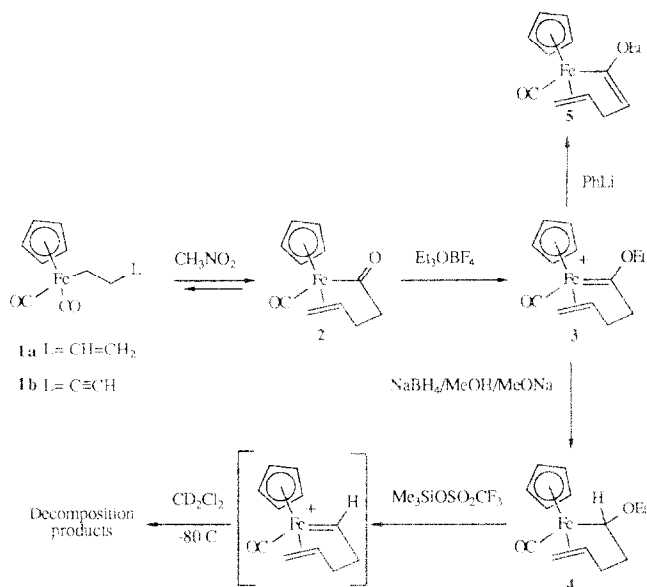
Results

The synthesis of the carbene-olefin complex **3** is outlined in Scheme 1. Attempts to oxidatively catalyze the CO insertion reaction of complexes **1a, 1b** analogous to the reaction shown in eq. 1 with $[Cp_2Fe]BF_4$ or Ce^{IV} did not appear successful. Heating **1a** in THF or CH_3CN was only marginally successful, yielding less than 10% of the cyclized product (as judged by IR analysis of the reaction mixture). Attempts to effect the same reaction using 1% HBF_4 in CH_2Cl_2 [14] resulted in isolated yields of 10–20% of complex **2a**. Finally, heating in CH_3NO_2 resulted in isolated yields of ca. 40%, with the starting material being recovered in 45–55% yields. Recycling of the starting material several times allowed an overall conversion of **1a** to **2** of 83%.

Complex **2** was obtained as yellow crystals that were stable indefinitely at $-20^\circ C$, but slowly reverted back to **1a** at room temperature. A sample of **2** was heated in CH_3NO_2 at $48^\circ C$ and monitored by IR. After 5 h, the equilibration with **1a** appeared complete. 1H NMR indicated the product ratio of **1a/2** as 56/44. Similar attempts to isolate the analogous cyclized acyl complex from the alkyne substituted complex **1b** were not successful.

The IR spectrum of **2** shows a band in the terminal CO region (1960 cm^{-1}) and in the acyl CO region (1645 cm^{-1}). NMR data clearly demonstrate the coordination of the olefin to iron [12]. The uncomplexed vinyl carbon resonances in the ^{13}C NMR for **1a** shift from δ 129.5 and 112.1 to δ 75.3 and 69.4 in **2**. An upfield shift in the 1H NMR is also seen for the vinylic protons upon coordination.

Complex **2** was readily alkylated with Et_3OBF_4 to afford the chelated carbene-olefin complex **3**. The reaction went cleanly at room temperature, in CH_2Cl_2 , with no starting material present after 2 h. As expected, the IR spectrum showed loss of



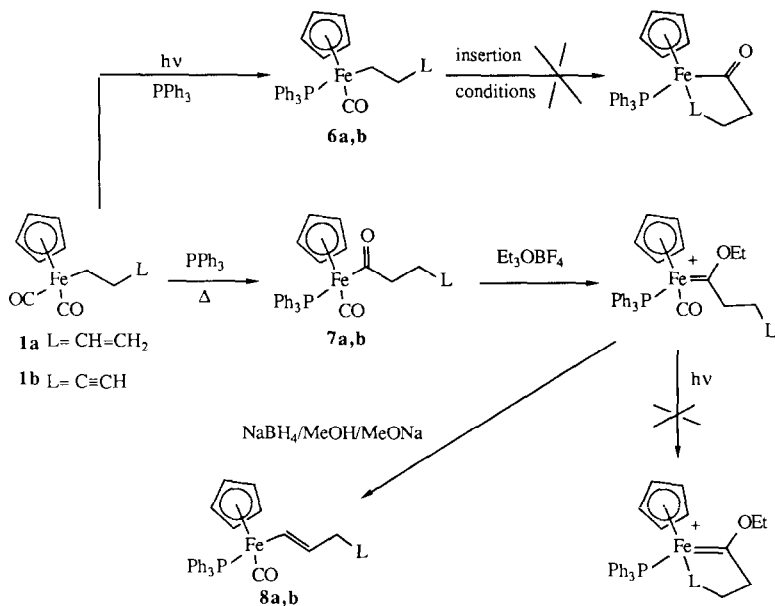
Scheme 1

the acyl CO band and the terminal CO band was shifted to a higher wave number (2010 cm^{-1}), typical for a cationic, monocarbonyl cyclopentadienyliron complex. The resonance at $\delta\ 341.8$ in the ^{13}C NMR spectrum of **3** conclusively shows formation of a carbene complex [6b]. The complex is soluble in polar organic solvents and was obtained, after recrystallization, as fine orange crystals that appear to be stable indefinitely at room temperature in an inert atmosphere.

Reduction of **3** to the α -ether **4** was effected by reaction with NaBH_4 in MeOH/MeONa [6a]. The ^{13}C NMR spectrum of **4** shows the loss of the carbene carbon resonance, and refocused INEPT experiments show the presence of a new resonance that is clearly assigned to the methine carbon atom. The upfield position of the vinylic carbon resonances indicate that the olefin is still coordinated to the iron. The α -ether was obtained as an orange oil that could be chromatographed on alumina, but decomposed over a period of several days at room temperature. The compound is stable at -20°C .

Complex **4** was treated with trimethylsilyl triflate in CD_2Cl_2 at -78°C . Upon mixing, the solution turned from light orange to deep red. Observation of the ^1H NMR spectrum showed a complicated alkyl region, but a clear resonance at $\delta\ 15.5$ was observed. This resonance slowly disappeared within 2–3 h while holding the sample at -80°C in the spectrometer. Proton substituted alkylideneiron complexes have been observed by other [6] to have highly deshielded alkylidene protons. It is most likely in this case that the low field resonance is due to the alkylidene proton from the alkylidene-olefin complex shown in Scheme 1.

The carbene-olefin complex **3** was deprotonated with PhLi to give the chelated alkenyl-olefin complex **5**. ^{13}C NMR again indicates olefin coordination as well as typical [2,7] alkenyliron vinyl carbon resonances. The complex decomposes on silica and alumina and was purified by filtration of a pentane solution through Celite.



Scheme 2

Reaction of **3** with $\text{Ph}_2\text{CuCNLi}_2$ results in mixtures of **5** and a second complex, that was seen by ^1H NMR to have added a phenyl group. Attempted purification and/or separation of the two complexes invariably resulted in decomposition of them both.

Efforts were also directed at the synthesis of PPh_3 complexes analogous to those in Scheme 1. This work is shown in Scheme 2. Complexes **1a,1b** were converted to the new complexes **6a,6b** by the general method of photolysis in the presence of PPh_3 [15]. All attempts to isolate CO insertion/olefin coordination products (analogous to **2**), however, were unsuccessful. Complexes **1a,1b** were then converted to the known acyl complexes **7a,7b** [3,13], by heating in CH_3NO_2 in the presence of PPh_3 . The acyliron complexes were then treated with Et_3OBF_4 to give, as yellow solids, the corresponding ethoxycarbene complexes. Photolysis of the carbene complexes at 0°C resulted in their decomposition to unidentifiable products. Finally, reaction of the ethoxycarbene complexes with a $\text{NaBH}_4/\text{MeOH}/\text{MeONa}$ mixture resulted in the isolation of alkenyliron complexes **8a,8b**.

Discussion

The rearrangement of **1a** to **2** was anticipated on the basis of results reported for similar complexes [3,12], but does not go to completion. In CH_3NO_2 , a solvent shown by Cutler to be particularly favorable for the CO insertion reaction [14], **1a** and **2** are in equilibrium in about equal amounts. By separation and recycling of **1a**, **2** can be prepared in high yield. The synthesis of "small amounts" of **2** has been reported [12a] previously. Complex **2** can exist (potentially) as two diastereomers

(each a racemic mixture of two enantiomers). However, because only one set of resonances is observed in ^1H and ^{13}C NMR spectra, only one diastereomer forms in the reaction. The isomer of **2** depicted in Scheme 1 is the diastereomer that minimizes interactions between the Cp ring and the olefin [12b]. As **1a** and **2** are equilibrating under the reaction conditions, the diastereomeric pair observed is the thermodynamically more stable one. It did not prove possible to cyclize the alkyne analog, **1b**.

Reaction of **2** with Et_3OBF_4 effects alkylation at oxygen to yield a chelated carbene-olefin complex. Carbene-olefin complexes have long been proposed as intermediates in olefin metathesis [16] and metal promoted cyclopropanation reactions [17]. There are still relatively few examples of these complexes [18]. The most closely related complex is $\{\text{CpFeCO}(\eta^2\text{-C}_3\text{H}_4)(\eta^1\text{-C(OMe)(OC}_6\text{H}_{11}))\}^+$ [18b]. As in complex **3**, the majority of these examples have heteroatom stabilized metal-carbene bonds. Examples of complexes without this mode of stabilization are rare. Schrock and Grevels have reported the isolation of tantalum and tungsten alkylidene-olefin complexes, respectively [19].

The reduction of **3** to the α -ether **4** is interesting in that the hydride adds exclusively to the carbene carbon rather than adding at the η^2 -olefin. Cationic η^2 -olefin complexes are known to react readily with hydride reagents to give alkyl complexes [20]. Hydride addition to carbene carbon atoms for a variety of complexes is also known [6a,21]. The carbene carbon atom is the more reactive site in **3**.

Treatment of **4** with trimethylsilyl triflate appears by ^1H NMR to yield the first example of a late transition metal alkylidene-olefin complex. This complex proved to be very unstable. Attempts were made to stabilize the alkylidene-olefin complex by substitution of the alkylidene proton with a π -donating phenyl group. Initial attempts to introduce a phenyl group at the carbene carbon, with PhLi, showed clean deprotonation at the β -carbon. Later attempts with phenylcuprates gave mixtures of products (including **5**) that could not be separated due to their instability.

Stabilization of the alkylidene-olefin complex was also attempted by replacing CO with the strong donor ligand PPh_3 [6]. Plans to repeat the chemistry in Scheme 1 with PPh_3 substituted analogues were thwarted, however, by the lack of success in isolating CO insertion/olefin coordination products from **6a,6b**. An alternative sequence to make the PPh_3 substituted carbene-olefin complex was tested. Initial formation of a carbene complex, followed by photolytic removal of a CO ligand, and olefin coordination did not yield the desired product. Reduction of this carbene complex and its alkynyl analog yielded the vinyl complexes **8a,8b** rather than the expected α -ether alkenyliron complexes. Casey [6b] has also reported that $\text{CpFe}(\text{CO})_2(\eta^1\text{-CMe}_2\text{OMe})$ is unstable and eliminates MeOH to yield $\text{CpFe}(\text{CO})_2(\eta^1\text{-C(Me)=CH}_2)$. The *E*-stereochemistry of **8a,8b** was assigned on the bases of our recently published empirical rules that state [2] for complexes of the type $\text{CpFeCOL}(\eta^1\text{-C(R)=CR}_2)$ ($\text{L} = \text{PPh}_3, \text{P(OPh)}_3$) that P-C coupling is observed into the α and *E*-position R groups and not the *Z*-position R group. For **8a** and **8b**, $J(\text{P-C})$ is 3 Hz.

In conclusion, a CO insertion/olefin coordination rearrangement was used as the key step in the synthesis of a stable, chelated carbene-olefin complex. We have obtained ^1H NMR evidence for an unstable alkylidene-olefin complex. Attempts to form stable analogues of the alkylidene-olefin complex were not successful.

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References

- 1 J.P. Collman, L.S. Hegedus, J.R. Norton, and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science, Mill Valley, CA, 1987.
- 2 D.L. Reger, S.A. Klaeren, J.E. Babin and R.D. Adams, *Organometallics*, in press.
- 3 J.L. Rouston, J.Y. Merour, C. Charrier, J. Benaim and P. Cadiot, *J. Organomet. Chem.*, 168 (1979) 61.
- 4 D.L. Reger, E. Mintz and L. Lebioda, *J. Am. Chem. Soc.*, 108 (1986) 1940.
- 5 J.A. Van Doorn, C. Masters and H.C. Volger, *J. Organomet. Chem.*, 105 (1976) 245.
- 6 (a) M. Brookhart, J.R. Tucker and G.R. Husk, *J. Am. Chem. Soc.*, 105 (1983) 258; (b) C.P. Casey, W.H. Miles and H. Tukada, *ibid.*, 107 (1985) 2924.
- 7 D.L. Reger, K.A. Belmore, E. Mintz and P.J. McElligott, *Organometallics*, 3 (1984) 134.
- 8 A.R. Garber, "INEPT", *NMR Spectroscopy Application Note 6*, 1983; IBM Instruments Inc., Danbury, CT.
- 9 J.S. Plotkin and S.G. Shore, *Inorg. Chem.*, 20 (1981) 284.
- 10 H. Meerwein, *Organic Syntheses*, 46 (1966) 113.
- 11 B.H. Lipshutz, J. Kozlowski and R.S. Wilhelm, *J. Am. Chem. Soc.*, 104 (1982) 2305.
- 12 (a) M.L.H. Green and M.J. Smith, *J. Chem. Soc., A*, (1971) 3220; (b) P. Lennon, W. Priester, A. Rosan, M. Madhavarao and M. Rosenblum, *J. Organomet. Chem.*, 139 (1977) C29.
- 13 N. Aktogu, H. Felkin, G.J. Baird, S.G. Davies and O. Watts, *J. Organomet. Chem.*, 262 (1984) 49.
- 14 T.C. Forschner and A.R. Cutler, *Organometallics*, 4 (1985) 1247.
- 15 P.M. Treichel, R.L. Shubkin, K.W. Barnett and D. Reichard, *Inorg. Chem.*, 5 (1966) 1177.
- 16 (a) R.H. Grubbs, *Prog. Inorg. Chem.*, 24 (1978) 1; (b) T.J. Katz, *Adv. Organomet. Chem.*, 16 (1977) 283.
- 17 (a) H. Nozaki, H. Takaya, S. Moriuti and R. Noyori, *Tetrahedron*, 24 (1968) 3655; (b) W.R. Moser, *J. Am. Chem. Soc.*, 91 (1969) 1135.
- 18 (a) M.J. McGeary, T.L. Tonker and J.L. Templeton, *Organometallics*, 4 (1985) 2102, and ref. therein; (b) W. Priester and M. Rosenblum, *J. Chem. Soc. Chem. Commun.*, (1978) 26; (c) C.P. Casey, N.W. Vollendorf and K.J. Haller, *J. Am. Chem. Soc.*, 106 (1984) 3754; (d) C.P. Casey, N.L. Hornung and W.P. Kosar, *ibid.*, 109 (1987) 4908.
- 19 (a) A.J. Schultz, R.K. Brown, J.M. Williams and R.R. Schrock, *J. Am. Chem. Soc.*, 103 (1981) 169; (b) K. Angermund, F.W. Grevels, C. Kruger and V. Skibbe, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 904.
- 20 (a) P. Lennon, M. Madhavarao, A. Rosan and M. Rosenblum, *J. Organomet. Chem.*, 108 (1976) 93; (b) D.L. Reger and C.J. Coleman, *Inorg. Chem.*, 18 (1979) 3155.
- 21 C.P. Casey, S.W. Polichnowski, A.J. Shuserman and C.R. Jones, *J. Am. Chem. Soc.*, 101 (1979) 7282.