

**A NEW SYNTHETIC METHOD FOR THE PREPARATION OF
 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{L})(\text{un})]\text{BF}_4$ (L = CO, PPh₃; un = UNSATURATED
 HYDROCARBON) COMPLEXES AND REDUCTION OF THE
 η^2 -ACETYLENE COMPLEXES ***

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Summary

The reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ with AgBF_4 in CH_2Cl_2 generates the reactive intermediate $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^+$ in solution which, when mixed with 2 or 3 equivalents of an olefinic or acetylene ligand produces η^2 -olefin and η^2 -acetylene complexes in ca. 70% yield. The analogous reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$ with AgBF_4 in CH_2Cl_2 produces $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)]^+$ in solution which also reacts readily with olefins and acetylenes to yield new π -complexes. The dicarbonyl complexes are generally more stable than the phosphine-substituted complexes. The η^2 -acetylene complexes in both systems can be reduced with hydride reagents to yield the corresponding neutral σ -vinyl compounds. Although unstable in the dicarbonyl system, these vinyl compounds in the phosphine system are quite stable and show no tendency to isomerize or thermally decompose to a metal hydride as previously established for the analogous alkyl derivatives. Attempts to prepare cyano-substituted olefin complexes lead instead to new complexes in which the iron bonds to these ligands through the nitrogen lone-pair.

Introduction

The synthesis and reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-olefin})]^+$ complexes have been an area of intense investigation over the past few years. Most notably, Rosenblum and coworkers have shown that these complexes can be useful intermediates for stoichiometric organic synthesis [1]. We have recently published a route for the synthesis of these complexes using the isolated solid

* No reprints available.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{THF})]\text{BF}_4$ (I) (THF = tetrahydrofuran) [2]. This complex is prepared by the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and AgBF_4 in THF and is useful for substitution reactions with olefins when used in non-coordinating solvents such as methylene chloride. A limitation of the reaction is that in certain cases the incoming olefin ligand can not readily displace the THF ligand leading to low yields in the exchange reaction. To overcome this problem, a modification of the procedure was reported in which gaseous BF_3 is introduced into the reaction mixture to coordinate the THF. This leads to rapid high yield reactions for even weakly coordinating ligands for this system such as cyclohexene [2]. Two negative aspects of introducing BF_3 are that it makes the reaction experimentally more difficult and some olefins such as norbornadiene polymerize in the presence of BF_3 .

The high reactivity of I in the presence of BF_3 led us to attempt to prepare new complexes with ligands that had not previously been used successfully in this system. During this effort, a new and clearly improved method of preparations for many of these complexes was developed. The new method, reported here for the preparation of new olefin and acetylene complexes is the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and AgBF_4 directly in CH_2Cl_2 followed by the desired ligand. This method is also successful for the preparation of a variety of new $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{ligand})]^+$ complexes, complexes that could not be prepared by other routes [2]. We also report some new reactions of these cationic complexes with hydride reagents.

Experimental

General data. All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen using solvents that were purified and degassed before use. Infrared spectra were recorded on a Perkin—Elmer Model 337 spectrometer. Proton NMR spectra were recorded on a Perkin—Elmer R32 spectrometer and chemical shifts are reported in δ (ppm) vs. TMS. Carbon-13 NMR spectra were recorded on a Varian CFT-20 spectrometer using CH_2Cl_2 , CHCl_3 or benzene as the solvent and internal standard. Chemical shifts are reported in δ (ppm) vs. TMS assigning the CH_2Cl_2 resonance to be at 54.00 ppm, the CHCl_3 resonance to be at 77.20 ppm and the benzene resonance to be at 128.70 ppm. All carbon-13 spectra were run with ^1H decoupling unless specified. The carbonyl resonance and the phenyl-carbon resonance were usually not observed because data was collected under conditions (0.5 second acquisition time, 41° pulse and no pulse delay) which tended to saturate these carbon atoms. The $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ [3] was recrystallized from a hot mixture of heptane/toluene (4/1, v/v, 20 ml/g). The $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$ was prepared by the procedure of Treichel [4]. The AgBF_4 was purchased from Ozark—Mahoning. The L-Selectride (lithium tri-sec-butylborohydride) was purchased from Aldrich as a 1.0 M solution in THF. All purchased reagents were used as received except for cycloheptatriene (Aldrich) which was passed through a plug of alumina (3×0.5 cm) immediately before use. Mixtures containing silver salts were filtered through a bed of filter-aid to insure a fast flow rate. This bed was washed with fresh reaction solvent, ca. 15 ml, until the washings were colorless. Unless specified, all reactions were carried out at room temperature. Melting

and decomposition points were determined in sealed evacuated capillaries and are uncorrected.

(Dicarbonyl)(1,2- η^2 -cycloheptatriene)(η^5 -cyclopentadienyl)iron(II) tetrafluoroborate. A mixture of (η^5 -C₅H₅)Fe(CO)₂I (1.5 g, 4.9 mmol) and AgBF₄ (1.05 g, 5.4 mmol) was stirred in CH₂Cl₂ (75 ml) for 30 minutes. This mixture was filtered using filter-aid and cycloheptatriene (0.45 g, 14.7 mmol) was added to the filtrate. This solution was stirred for 15 minutes until the color had turned from dark purple to yellow-orange. Stirring was stopped and diethyl ether (50 ml) was added dropwise to the solution. This precipitated yellow platelets which were collected and dried. Recrystallization from CH₂Cl₂/diethyl ether (2/1, v/v, 30 ml) yielded yellow crystals which were collected, washed with diethyl ether (10 ml), and dried in vacuo (0.77 g, 44%), dec. 82°C (Found: C, 46.94; H, 3.77. C₁₄H₁₃BF₄FeO₂ calcd.: C, 47.26; H, 3.65%). IR spectrum (cm⁻¹ in CH₂Cl₂): ν (CO) 2036, 2076. ¹³C NMR spectrum (-10°C in CH₂Cl₂): 133.93, 130.64, 129.17, 128.78 (free CH=), 88.84 (η^5 -C₅H₅), 73.67, 70.73 (complexed CH=), 31.90 (CH₂).

(η^2 -2-Butyne)(dicarbonyl)(η^5 -cyclopentadienyl)iron(II) tetrafluoroborate. A mixture of (η^5 -C₅H₅)Fe(CO)₂I (1.5 g, 4.9 mmol) and AgBF₄ (1.05 g, 5.4 mmol) was stirred in CH₂Cl₂ (75 ml) for 30 minutes. This mixture was filtered using filter-aid and 2-butyne was passed through the filtrate for ca. 4 minutes until the solution had turned yellow-orange. The solution was concentrated to 25 ml and diethyl ether (60 ml) added to precipitate a yellow-orange solid which was collected and dried. The solid was dissolved in a boiling mixture of CH₂Cl₂/diethyl ether (6/1, v/v, 70 ml) and filtered. Diethyl ether (10 ml) was then added and this solution cooled at -20°C overnight. The yellow crystals which formed were collected, washed with diethyl ether (10 ml), and dried in vacuo (1.1 g, 71%), dec 122–124°C (Found: C, 41.53; H, 3.53. C₁₁H₁₁BF₄FeO₂ calcd.: C, 41.57; H, 3.46%). ¹H NMR spectrum (acetone-*d*₆): 5.88 (5, singlet, η^5 -C₅H₅), 2.49 (6, singlet, CH₃). IR spectrum (cm⁻¹ in CH₂Cl₂): ν (CO) 2040, 2083. ¹³C NMR spectrum (CH₂Cl₂): 208.05 (CO), 89.15 (η^5 -C₅H₅), 43.76 (C≡C), 10.33 (CH₃).

(Dicarbonyl)(η^5 -cyclopentadienyl)(η^2 -3-hexyne)iron(II) tetrafluoroborate. A mixture of (η^5 -C₅H₅)Fe(CO)₂I (1.5 g, 4.9 mmol) and AgBF₄ (1.05 g, 5.4 mmol) was stirred in CH₂Cl₂ (75 ml) for 30 minutes. This mixture was filtered using filter-aid and 3-hexyne (0.40 g, 15 mmol) added to the filtrate. This solution was stirred for 15 minutes and then concentrated to 25 ml. Diethyl ether (50 ml) was added to this solution to precipitate yellow platelets which were collected, washed with diethyl ether (10 ml), and dried. This product was recrystallized from CH₂Cl₂/diethyl ether (1/2, v/v, 45 ml) to yield bright yellow platelets (1.19 g, 70%), dec. 126–128°C (Found: C, 44.86; H, 4.47. C₁₃H₁₅BF₄FeO₂ calcd.: C, 45.15; H, 4.62%). ¹H NMR spectrum (acetone-*d*₆): 5.87 (5, singlet, η^5 -C₅H₅), 2.81 (4, quartet, *J* 7.5 Hz, CH₂), 1.40 (6, triplet, *J* 7.5 Hz, CH₃). IR spectrum (cm⁻¹ in CH₂Cl₂): ν (CO) 1953, 1993. ¹³C NMR spectrum (CH₂Cl₂): 208.05 (CO), 89.22 (η^5 -C₅H₅), 50.31 (C≡C), 20.18 (CH₂), 15.08 (CH₃).

(Dicarbonyl)(η^5 -cyclopentadienyl)(η^2 -diphenylacetylene)iron(II) tetrafluoroborate. A mixture of (η^5 -C₅H₅)Fe(CO)₂I (1.0 g, 3.3 mmol) and AgBF₄ (0.70 g, 3.6 mmol) was stirred in CH₂Cl₂ (75 ml) for 30 minutes. This mixture was filtered

using filter-aid and diphenylacetylene (0.70 g, 3.9 mmol) was added to the filtrate. This solution was stirred for 15 minutes and then concentrated to 50 ml. Diethyl ether (60 ml) was added until the solution became cloudy and was then cooled at -20°C for 12 h. The yellow-orange crystals which formed were collected, washed with diethyl ether (10 ml), and dried in vacuo (0.98 g, 68%), dec. $107-110^{\circ}\text{C}$ (Found: C, 56.89; H, 3.36. $\text{C}_{21}\text{H}_{15}\text{BF}_4\text{FeO}_2$ calcd.: C, 57.07; H, 3.39%). ^1H NMR spectrum (CD_3NO_2): 7.85–8.05 (4, multiplet, *ortho*-phenyl protons), 7.55–7.75 (6, multiplet, *meta*- and *para*-phenyl protons), 5.94 (5, singlet, $\eta^5\text{-C}_5\text{H}_5$). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(\text{CO})$ 2085, 2050. ^{13}C NMR spectrum (CH_2Cl_2): 206.73 (CO), 132.61, 131.21, 129.89 (phenyl-carbons), 90.39 ($\eta^5\text{-C}_5\text{H}_5$), 57.99 ($\text{C}\equiv\text{C}$).

Hydride reduction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-acetylene})]\text{BF}_4$ complexes. A mixture of 3.0 g of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-acetylene})]\text{BF}_4$ complex and 1.25 equivalents of NaBH_3CN was stirred in THF (50 ml) at 0°C for 1 h. The solvent was then evaporated at 0°C , the residue extracted with benzene (three 10 ml portions), and these mixtures filtered. The filtrate was concentrated to 5 ml and placed on a chromatography column (alumina, 5×30 cm). Elution with benzene developed two bands. The first band to elute was a yellow band which upon evaporation of the solvent yielded a yellow oil (ca. 0.25 g) which was identified as the respective vinyl complex by IR and ^{13}C NMR spectroscopy. The second band was shown by IR to be $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (ca. 0.75 g).

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}(\text{CH}_3)\text{CHCH}_3)$. IR spectrum (cm^{-1} in hexane): $\nu(\text{CO})$ 2002, 1952. ^{13}C NMR spectrum (coupled spectrum in CH_2Cl_2): 216;53 (singlet CO), 138.46 (singlet, $\text{FeC}(\text{CH}_3)\text{CHCH}_3$), 130.02 (doublet, J 145.3 Hz, $\text{FeC}(\text{CH}_3)\text{CHCH}_3$), 85.66 (doublet, J 176.7, $\eta^5\text{-C}_5\text{H}_5$), 40.03 (quartet, J 124.5 Hz, $\text{FeC}(\text{CH}_3)\text{CHCH}_3$), 20.63 (quartet, J 123.1 Hz, $\text{FeC}(\text{CH}_3)\text{CHCH}_3$).

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3)$. ^1H NMR spectrum (CS_2): 5.82 (1, triplet, J 6.1 Hz, $\text{FeC}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$), 4.76 (5, singlet, $\eta^5\text{-C}_5\text{H}_5$), 2.18 (4, multiplet, $\text{FeC}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$), 0.98 (6, multiplet, $\text{FeC}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(\text{CO})$ 1950, 2004. ^{13}C NMR spectrum (CH_2Cl_2): 216.94 (CO), 142.90 ($\text{FeC}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$), 137.31 ($\text{FeC}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$), 86.76 ($\eta^5\text{-C}_5\text{H}_5$), 45.32 ($\text{FeC}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$), 28.65 ($\text{FeC}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$), 15.78, 14.88 ($\text{FeC}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$).

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}(\text{C}_6\text{H}_5)\text{CHC}_6\text{H}_5)$. IR spectrum (cm^{-1} in hexane): $\nu(\text{CO})$ 2025, 1982. ^{13}C NMR spectrum (CH_2Cl_2): 215.54 (CO), 149.60 ($\text{FeC}(\text{C}_6\text{H}_5)\text{CHC}_6\text{H}_5$), 141.90 ($\text{FeC}(\text{C}_6\text{H}_5)\text{CHC}_6\text{H}_5$), 136.71–124.29 (C_6H_5), 86.19 ($\eta^5\text{-C}_5\text{H}_5$).

$(\eta^2\text{-Allene})(\text{carbonyl})(\eta^5\text{-cyclopentadienyl})(\text{triphenylphosphine})\text{iron(II)}\text{tetrafluoroborate}$. CH_2Cl_2 (60 ml) was added to a mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$ (1.5 g, 2.8 mmol) and AgBF_4 (0.58 g, 3.0 mmol). Immediately after addition of the solvent, allene was passed through the mixture for 4 minutes until the solution had turned from a green to a yellow color. This mixture was filtered using filter-aid and then concentrated to 40 ml. Addition of diethyl ether (80 ml) precipitated yellow crystals which were collected, dried, and recrystallized from $\text{CH}_2\text{Cl}_2/\text{diethyl ether}$ (1/2, v/v, 60 ml) (1.15 g, 77%), m.p. $159-161^{\circ}\text{C}$ (Found: C, 59.95; H, 4.49. $\text{C}_{27}\text{H}_{24}\text{BF}_4\text{FeOP}$ calcd.: C, 60.28; H, 4.46%). ^1H NMR spectrum (CD_3NO_2): 7.62, 7.36 (15, multiplet, PPh_3), 7.44,

6.10 (1, 1, multiplets, free CH₂=), 5.24 (5, doublet, *J* 1.8 Hz, η^5 -C₅H₅), 3.27, 2.14 (1, 1, broad, complexed CH₂=). IR spectrum (cm⁻¹ in CH₂Cl₂): ν (CO) 2007. ¹³C NMR spectrum (coupled spectrum in CH₂Cl₂): 216.24 (doublet, *J* 32.9 Hz, CO), 160.79 (singlet, =C=), 136.54–125.31 (multiplet, phenyl carbons), 107.30 (triplet, *J* 167.4 Hz, free CH₂=), 89.95 (doublet, *J* 183.7 Hz, η^5 -C₅H₅), 17.02 (triplet, *J* 171.1 Hz, complexed CH₂=).

(η^2 -1-Butene)(carbonyl)(η^5 -cyclopentadienyl)(triphenylphosphine)iron(II) tetrafluoroborate. CH₂Cl₂ (60 ml) was cooled to 0° C and then added to a mixture of (η^5 -C₅H₅)Fe(CO)(PPh₃)I (1.0 g, 1.9 mmol) and AgBF₄ (0.40 g, 2.1 mmol). Into this mixture, 1-butene was passed until the color of the mixture turned orange. This mixture was filtered using filter-aid and the filtrate concentrated to 25 ml. Hexane (30 ml) was added slowly and this solution cooled at -20° C overnight. The orange crystals which formed were collected, washed with hexane (10 ml), and dried in vacuo. These crystals contained 1 equivalent of CH₂Cl₂ of crystallization (0.86 g, 72%), m.p. 116–118° C (Found: C, 54.79; H, 5.11; Cl, 11.43. C₂₈H₂₈BF₄FeOP · CH₂Cl₂ calcd.: C, 54.52; H, 4.70; Cl, 11.09%). IR spectrum (cm⁻¹ in CH₂Cl₂): ν (CO) 2002. ¹³C NMR spectrum (-10° C in CHCl₃, both diastereomers are observed, labelled A and B, the integration of A/B is 3/1): 220.48(A), 217.50(B) (pair of doublets, *J* 31.1 Hz, 32.7 Hz, CO), 132.50 (doublet, *J* 12.0 Hz, *ortho*-phenyl carbons), 131.55 (singlet, *para*-phenyl carbons), 129.15 (doublet, *J* 10.1 Hz, *meta*-phenyl carbons), 87.69(B), 86.98(A) (singlets, η^5 -C₅H₅), 83.77(A), 78.87(B) (singlets, CH=), 53.53(B) (singlet, CH₂= and CH₂Cl₂), 50.91(A) (singlet, CH₂=) 29.87(A), 28.00(B) (singlets, CH₂), 17.64(B), 17.09(A) (singlets, CH₃).

(Carbonyl)(η^2 -cyclooctene)(η^5 -cyclopentadienyl)(triphenylphosphine)iron(II) tetrafluoroborate. To a mixture of (η^5 -C₅H₅)Fe(CO)(PPh₃)I (1.0 g, 1.85 mmol) and AgBF₄ (0.40 g, 2.1 mmol) was added CH₂Cl₂ (40 ml) and cyclooctene (0.61 g, 5.6 mmol). This mixture was stirred for 10 minutes during which time the color turned orange. The mixture was then filtered using filter-aid and the filtrate concentrated to 30 ml. Benzene (60 ml) was added and this solution cooled overnight at 0° C. The orange crystals which formed were collected, washed with hexane (10 ml), and dried in vacuo. These crystals contained 1 equivalent of CH₂Cl₂ of crystallization (0.75 g, 59%), m.p. 107–109° C (Found: C, 56.90; H, 5.26; Cl, 10.75. C₃₂H₃₄BF₄FeOP · CH₂Cl₂ calcd.: C, 57.20; H, 5.19; Cl, 10.23%). ¹H NMR spectrum (CD₃NO₂): 7.54, 7.40 (15, multiplets, PPh₃), 5.55, 5.03 (1, 1, multiplets, CH=), 5.43 (2, singlet, CH₂Cl₂), 4.96 (5, singlet, η^5 -C₅H₅), 2.14, 1.49 (12, multiplets, CH₂). IR spectrum (cm⁻¹ in CH₂Cl₂): ν (CO) 2005. ¹³C NMR spectrum (CH₂Cl₂): 132.69 (doublet, *J* 9.4 Hz, *ortho*-phenyl carbons), 132.14 (singlet, *para*-phenyl carbons), 129.67 (doublet, *J* 10.0 Hz, *meta*-phenyl carbons), 87.11 (singlet, η^5 -C₅H₅), 79.34, 76.37 (singlets, CH=), 32.10, 31.12, 30.14, 25.85, 25.63 (singlets, CH₂).

(Carbonyl)(η^5 -cyclopentadienyl)(η^2 -3-hexyne)(triphenylphosphine)iron(II) tetrafluoroborate. A mixture of (η^5 -C₅H₅)Fe(CO)(PPh₃)I (1.0 g, 1.9 mmol), AgBF₄ (0.40 g, 2.1 mmol) and 3-hexyne (0.45 g, 5.6 mmol) was stirred in CH₂Cl₂ (40 ml) for 15 minutes. The resulting purple mixture was filtered using filter-aid and concentrated to 30 ml. Addition of benzene (80 ml) precipitated purple needles which were collected, dried, and recrystallized from a mixture of chloroform/benzene (1/3, v/v, 60 ml) to yield purple, cube-shaped crystals

(0.65 g, 60%), dec. 120–122°C (Found: C, 61.98; H, 5.23. $C_{30}H_{30}BF_4FeOP$ calcd.: C, 62.13; H, 5.17%). 1H NMR spectrum ($CDCl_3$): 7.56 (15, multiplet, PPh_3), 5.14 (5, singlet, $\eta^5-C_5H_5$), 2.67 (4, multiplet, CH_2), 1.13 (6, triplet, J 7.2 Hz, CH_3). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(CO)$ 2000. ^{13}C NMR spectrum ($-10^\circ C$ in $CHCl_3$): 132.55 (doublet, J 8.5 Hz, *ortho*-phenyl carbons), 131.62 (singlet, *para*-phenyl carbons), 129.23 (doublet, J 9.8 Hz, *meta*-phenyl carbons), 87.08 (singlet, $\eta^5-C_5H_5$), 56.74, 53.18 (doublet, J 5.1 Hz, singlet, $C\equiv C$) 21.46, 20.97 (singlets, CH_2), 16.50, 15.31 (singlets, CH_3).

(η^2 -2-Butyne)(carbonyl)(η^5 -cyclopentadienyl)(triphenylphosphine)iron(II) tetrafluoroborate. A mixture of ($\eta^5-C_5H_5$)Fe(CO)(PPh_3)I (1.0 g, 1.9 mmol), $AgBF_4$ (0.40 g, 2.1 mmol) and 2-butyne (0.30 g, 5.6 mmol) which had been condensed at $-20^\circ C$ was stirred in CH_2Cl_2 (40 ml) for 15 minutes. This mixture was then filtered and the filtrate concentrated to 35 ml. Addition of benzene (100 ml) and scratching precipitated small purple needles which were collected, dried, and recrystallized from CH_2Cl_2 /benzene (1/3, v/v, 60 ml) (0.64 g, 63%), m.p. 138–139°C (Found: C, 60.30; H, 4.69. $C_{28}H_{26}BF_4FeOP$ calcd.: C, 60.90; H, 4.75%). 1H NMR spectrum ($CDCl_3$): 7.42 (15, multiplet, PPh_3), 5.15 (5, doublet, J 1.1 Hz, $\eta^5-C_5H_5$), 2.08 (6, broad, CH_3). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(CO)$ 1998. ^{13}C NMR spectrum ($-35^\circ C$ in $CHCl_3$): 218.19 (doublet, J 32.0 Hz, CO), 132.87 (doublet, J 9.7 Hz, *ortho*-phenyl carbons), 131.88 (singlet, *para*-phenyl carbons), 129.51 (doublet, J 10.2 Hz, *meta*-phenyl carbons), 87.18 (singlet, $\eta^5-C_5H_5$), 48.84, 46.93 (doublet, J 6.0 Hz, singlet, $C\equiv C$), 11.78, 10.80 (singlets, CH_3).

(Carbonyl)(η^5 -cyclopentadienyl)(2- η^1 -propenyl)(triphenylphosphine)-iron(II). A suspension of [($\eta^5-C_5H_5$)Fe(CO)(η^2 -allene)(PPh_3)] BF_4 (1.2 g, 2.2 mmol) in THF (35 ml) was cooled to $0^\circ C$ and L -Selectride (2.2 ml of a 1.0 M solution in THF) added dropwise. The color of the solution immediately changed from the yellow color of the salt to an orange color. The solution was warmed to room temperature and stirred for an additional 20 minutes. The solvent was evaporated and the orange residue extracted with benzene (5 ml). This solution was placed on a chromatograph column (alumina, 2×15 cm). Elution with benzene/hexane (1/1, v/v) gave a single orange band. The solvent was evaporated from this band, the residue extracted with diethyl ether (10 ml), and this solution filtered. Slow evaporation of the solvent yielded small orange crystals (0.5 g, 50%), m.p. 129–130°C (Found: C, 72.08; H, 5.39. $C_{27}H_{25}FeOP$ calcd.: C, 71.72; H, 5.52%). 1H NMR spectrum ($CDCl_3$): 7.34 (15, multiplet, PPh_3), 5.54, 4.65 (1, 1, singlets, $CH_2=$), 4.43 (5, singlet, $\eta^5-C_5H_5$), 2.22 (3, singlet, CH_3). IR spectrum (cm^{-1} in hexane): $\nu(CO)$ 1918. ^{13}C NMR spectrum (CH_2Cl_2): 162.81 (doublet, J 25.5 Hz, Fe–C), 136.86 (doublet, J 39.9 Hz, P-bound phenyl carbons), 133.42 (doublet, J 9.6 Hz, *ortho*-phenyl carbons), 129.64 (singlet, *para*-phenyl carbons), 129.08 (doublet, J 9.7 Hz, *meta*-phenyl carbons), 124.10 (doublet, J 3.1 Hz, $CH_2=$), 84.65 (singlet, $\eta^5-C_5H_5$), 40.01 (singlet, CH_3).

Attempted isomerization of ($\eta^5-C_5H_5$)Fe(CO)($\eta^1-C(CH_3)CH_2$)(PPh_3). A solution of ($\eta^5-C_5H_5$)Fe(CO)($\eta^1-C(CH_3)CH_2$)(PPh_3) (0.4 g) in heptane (35 ml) was heated at $90^\circ C$ for 16 h. During this time there was no obvious color change in the solution. The solvent was evaporated to yield an orange powder. The 1H NMR spectrum of this powder confirmed that no isomerization had taken

place. The compound remaining in the flask was transferred to a Schlenk tube which was evacuated and immersed in a 140°C oil bath for 20 minutes. The substance which formed was mainly a brown insoluble tar along with a small amount of ferrocene. Prolonged heating at 140°C gave ferrocene as the predominant product.

(Carbonyl)(η⁵-cyclopentadienyl)(3-η¹-3-hexenyl)(triphenylphosphine)iron(II). To a suspension of [(η⁵-C₅H₅)Fe(CO)(η²-3-hexyne)(PPh₃)]BF₄ (2.0 g, 3.4 mmol) in THF (30 ml) at -78°C was added L-Selectride (3.6 ml of a 1.0 M solution in THF). This suspension was warmed to room temperature and the solvent was evaporated from the resulting red solution. The residue was extracted with benzene (6 ml) and placed on a chromatography column (alumina, 5 × 30 cm). Elution with hexane/benzene (2/1, v/v) gave an intense orange band which eluted ahead of a weaker green band. The orange band was collected and the solvent evaporated. The resulting red oil was extracted with boiling hexane (20 ml) and this solution filtered hot. Cooling overnight at -20°C yielded red crystals which were collected and dried in vacuo (0.89 g, 52%), m.p. 128–129°C (Found: C, 72.49; H, 6.39. C₃₀H₃₁FeOP calcd.: C, 72.88; H, 6.31%). ¹H NMR spectrum (CS₂): 7.23 (15, multiplet, PPh₃), 4.74 (1, triplet, *J* 6.2 Hz, FeC(CH₂CH₃)CHCH₂CH₃), 4.32 (5, singlet, η⁵-C₅H₅), multiplet centered at 1.43 (4, FeC(CH₂CH₃)CHCH₂CH₃), multiplet centered at 0.81 (6, FeC(CH₂-CH₃)CHCH₂CH₃). IR spectrum (cm⁻¹ in hexane): ν(CO) 1915. ¹³C NMR spectrum (benzene): 147.63 (doublet, *J* 28.0 Hz, FeC(CH₂CH₃)CHCH₂CH₃), 141.38 (doublet, *J* 7.3 Hz, FeC(CH₂CH₃)CHCH₂CH₃), 137.51 (doublet, *J* 40.8 Hz, P-bound phenyl carbons), 133.88 (doublet, *J* 9.7 Hz, *ortho*-phenyl carbons), 129.71 (singlet, *para*-phenyl carbons), 84.80 (singlet, η⁵-C₅H₅), 46.40 (singlet, FeC(CH₂-CH₃)CHCH₂CH₃), 37.30 (singlet, FeC(CH₂CH₃)CHCH₂CH₃), 23.41 (singlet, FeC(CH₂CH₃)CHCH₂CH₃), 15.32 (singlet, FeC(CH₂CH₃)CHCH₂CH₃); the *meta*-phenyl carbons were obscured by the benzene resonance.

(N-Acrylonitrile)(carbonyl)(η⁵-cyclopentadienyl)(triphenylphosphine)iron(II) tetrafluoroborate. A mixture of (η⁵-C₅H₅)Fe(CO)(PPh₃)I (1.0 g, 1.9 mmol), AgBF₄ (0.39 g, 2.0 mmol), and freshly distilled acrylonitrile (0.10 g, 1.9 mmol) was stirred in CH₂Cl₂ (30 ml) for 15 minutes. The mixture was filtered using filter-aid and the filtrate was concentrated to 10 ml. Slow addition of hexane (10 ml) yielded red crystals when stored at 0°C overnight (0.88 g, 84%), m.p. 168–170°C (Found: C, 58.76; H, 4.26. C₂₇H₂₃BF₄FeNOP calcd.: C, 58.82; H, 4.17%). ¹H NMR spectrum (acetone-*d*₆): 7.59 (15, broad with a high field shoulder, PPh₃), 6.03 (1, broad, CH), 5.90 (2, broad, CH₂), 5.10 (5, doublet, *J* 1.5 Hz, η⁵-C₅H₅). IR spectrum (cm⁻¹ in CH₂Cl₂): ν(CO) 1980. ¹³C NMR (CH₂Cl₂): 216.08 (doublet, *J* 28 Hz, CO), 140.79 (singlet, CH₂), 132.42 (doublet, 48.4 Hz, P-bound phenyl carbons), 133.14 (doublet, *J* 9.8 Hz, *ortho*-phenyl carbons), 131.62 (singlet, *para*-phenyl carbons), 130.62 (singlet, CN), 129.33 (doublet, *J* 10.3 Hz, *meta*-phenyl carbons), 106.69 (singlet, CH), 84.96 (singlet, η⁵-C₅H₅).

(N-1-Cyano-3-methyl-2-butene)(carbonyl)(η⁵-cyclopentadienyl)(triphenylphosphine)iron(II) tetrafluoroborate. A mixture of (η⁵-C₅H₅)Fe(CO)(PPh₃)I (1.0 g, 1.9 mmol), AgBF₄ (0.39 g, 2.0 mmol) and distilled 3-methyl-1-cyano-2-butene (0.18 g, 1.9 mmol) was stirred in CH₂Cl₂ (30 ml) for 30 minutes. The mixture was then filtered using filter-aid and the filtrate was concentrated to

10 ml. Slow addition of hexane (8 ml) yielded red crystals when stored overnight at -20°C (0.98 g, 87%), m.p. $156-157.5^{\circ}\text{C}$ (Found: C, 60.91; H, 4.86. $\text{C}_{30}\text{H}_{29}\text{BF}_4\text{FeNOP}$ calcd.: C, 60.73; H, 4.88%). ^1H NMR spectrum (acetone- d_6): 7.60 (15, broad with high field shoulder, PPh_3), 5.03 (5, doublet, J 1.8 Hz, $\eta^5\text{-C}_5\text{H}_5$), 3.25 (2, doublet, J 8.1 Hz, CH_2), 2.70 (1, triplet, J 7.2 Hz, CH), 1.58 (3, singlet, CH_3), 1.42 (3, singlet, CH_3). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(\text{CO})$ 1988. ^{13}C NMR spectrum (CH_2Cl_2): 210.00 (doublet, J 28.0 Hz, CO), 138.59 (doublet, J 48.4 Hz, P-bound phenyl carbons), 134.26 (doublet, J 9.6 Hz, *ortho*-phenyl carbons), 131.08 (doublet, J 9.4 Hz, *para*-bound phenyl carbons), 129.10 (doublet, J 9.8 Hz, *meta*-phenyl carbons), 121.70 (singlet, CN), 110.58 (singlet, CH), 109.53 (singlet, $\underline{\text{C}}(\text{CH}_3)_2$), 84.54 (singlet, $\eta^5\text{-C}_5\text{H}_5$), 25.53, 18.66 (singlets, CH_3), 17.58 (doublet, J 0.2 Hz, $\text{C}(\text{CH}_3)_2$).

(Carbonyl)(η^5 -cyclopentadienyl)(*N*-3-cyano-2-methylpropene)(triphenylphosphine)iron(II) tetrafluoroborate. A mixture of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh_3)I (1.0 g, 1.9 mmol), AgBF_4 (0.39 g, 2.0 mmol) and distilled 3-cyano-2-methylpropene (1.6 g, 2.0 mmol) was stirred in CH_2Cl_2 (30 ml) for 30 minutes. The mixture was filtered using filter-aid and the filtrate was concentrated to 10 ml. Slow addition of hexane (10 ml) yielded red crystals when stored at -20°C overnight (1.05 g, 95%), m.p. $176-177^{\circ}\text{C}$ (Found: C, 60.11; H, 5.00. $\text{C}_{29}\text{H}_{27}\text{BF}_4\text{FeNOP}$ calcd.: C, 60.12; H, 4.66%). ^1H NMR spectrum (acetone- d_6): 7.56 (15, broad with high field shoulder, PPh_3), 5.02 (5, doublet, J 1.8 Hz, $\eta^5\text{-C}_5\text{H}_5$), 4.82, 4.68 (2, singlet, $\text{CH}_2=$), 3.39 (2, singlet, CH_2CN), 1.54 (3, singlet, CH_3). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(\text{CO})$ 1988. ^{13}C NMR spectrum (CH_2Cl_2): 210.00 (doublet, J 28.0 Hz, CO), 134.78 (doublet, J 48.0 Hz, P-bound phenyl carbons), 132.26 (doublet, J 10.1 Hz, *ortho*-phenyl carbons), 131.62 (singlet, *para*-phenyl carbons), 131.28 (singlet, CN), 129.35 (doublet, J 10.3 Hz, *meta*-phenyl carbons), 115.75 (singlet, $\text{CH}_2=$), 100.21 (singlet, $\underline{\text{C}}(\text{CH}_3)$), 85.44 (singlet, $\eta^5\text{-C}_5\text{H}_5$), 28.04 (singlet, CH_3), 21.04 (singlet, $\underline{\text{CH}_2\text{CN}}$).

(Carbonyl)(η^5 -cyclopentadienyl)(*N*-3-cyanopropene)(triphenylphosphine)iron(II) tetrafluoroborate. A mixture of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh_3)I (0.75 g, 1.4 mmol), distilled 3-cyanopropene (0.10 g, 1.5 mmol) and AgBF_4 (0.40 g, 2.1 mmol) was stirred in CH_2Cl_2 (30 ml) for 30 minutes. The mixture was filtered using filter-aid and the filtrate concentrated (10 ml). Slow addition of hexane (8 ml) yielded red crystals when stored at -20°C overnight which were collected and dried (0.76 g, 96%), m.p. $180-182^{\circ}\text{C}$ (Found: C, 59.19; H, 4.49. $\text{C}_{28}\text{H}_{25}\text{BF}_4\text{FeNOP}$ calcd.: C, 59.48; H, 4.42%). ^1H NMR spectrum (acetone- d_6): 7.59 (15, broad with a high field shoulder, PPh_3), 5.60 (2, broad, $\text{CH}_2=$), 5.35 (1, multiplet, CH), 5.09 (5, doublet, J 1.5 Hz, $\eta^5\text{-C}_5\text{H}_5$), 3.38 (2, multiplet, CH_2). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(\text{CO})$ 1988. ^{13}C NMR spectrum (CH_2Cl_2): 218.19 (doublet, J 28.0 Hz, CO), 136.46 (doublet, J 49.0 Hz, P-bound phenyl carbons), 133.10 (doublet, J 10.0 Hz, *ortho*-phenyl carbons), 131.50 (singlet, *para*-phenyl carbons), 130.85 (singlet, CN), 128.26 (doublet, J 10.3, *meta*-phenyl carbons), 124.61 (singlet, CH), 121.71 (singlet $\text{CH}_2=$), 85.48 (singlet, $\eta^5\text{-C}_5\text{H}_5$), 23.71 (singlet, CH_2CN).

Results

Synthesis and characterization of new complexes. A red-brown CH_2Cl_2 solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ slowly turns purple over 30 minutes when treated with one equivalent of AgBF_4 . This generates in solution presumably the 16-electron species $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^+$ (II), probably solvated with CH_2Cl_2 [5]. This intermediate, which has carbonyl stretching bands at 2022 and 2065 cm^{-1} , only slowly decomposes in solution to $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$. Attempts to isolate II produced a purple solid which would not redissolve in CH_2Cl_2 . Addition of three equivalents of standard olefins such as cyclopentene to the $\text{CH}_2\text{-Cl}_2$ solution of II rapidly leads to the formation of known η^2 -olefin complexes which can be isolated in ca. 70% yield. Even cyclohexene, a ligand known to be rather poor in this system, will form a complex in 72% yield. The addition of cycloheptatriene produces $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(1,2\text{-}\eta^2\text{-C}_7\text{H}_8)]\text{BF}_4$, isolated in 44% yield. This new complex apparently also forms to some extent when the THF adduct I is mixed with cycloheptatriene in CH_2Cl_2 but it could not be isolated in pure form from this reaction. Although in acetone or nitromethane solution the solvent will displace the cycloheptatriene ligand, a high quality ^{13}C NMR spectrum was obtained in CH_2Cl_2 at -10°C . This spectrum has four resonances in the normal olefin region and two more around 72 ppm, the region typical for coordinated alkene carbon atoms [2]. Thus, the cycloheptatriene must be coordinated to the metal via the 1,2-carbon atoms.

Addition of the acetylenes 3-hexyne, 2-butyne, and 1,2-diphenylacetylene to a CH_2Cl_2 solution of II leads to the isolation of the respective $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-acetylene})]\text{BF}_4$ complexes in good yield. The 3-hexyne and 2-butyne ligands are not displaced by acetone in solution but diphenylacetylene is displaced rapidly. Although these complexes will form in the exchange reaction of I with the acetylene, the in situ reaction of II is a much cleaner procedure, especially for the weaker ligand diphenylacetylene.

The dark green CH_2Cl_2 solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$ immediately turns bright green when treated with AgBF_4 . In order to isolate new complexes from this solution, the incoming ligand must be present when the AgBF_4 is introduced or added to the solution within a couple of minutes. If not, the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)]^+$ (III) presumed intermediate rapidly decomposes to $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]^+$. The presence of an olefin such as 1-butene or cyclooctene in a CH_2Cl_2 solution of III leads readily to the isolation of the new η^2 -olefin complex in good yield. Also, the allene, 3-hexyne and 2-butyne complexes can be prepared by this route. Complexes with propene, *cis*-2-butene and diphenylacetylene form in solution but could not be isolated. Of the new isolated complexes, only the allene ligand is not displaced by the solvent in acetone solution. Only the allene and known ethene complexes [6] can be prepared from $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{THF})]\text{BF}_4$ in CH_2Cl_2 .

The cyanide-substituted olefins acrylonitrile, 3-cyanopropene, 1-cyano-3-methyl-2-butene and 3-cyano-2-methylpropene all rapidly turn the CH_2Cl_2 solution of III red. From these solutions, red, air stable crystals can be isolated in good yield. The ^{13}C { ^1H } NMR spectra of each of these complexes have resonances in the olefin region that are readily assigned [7] to a non-coordinated carbon-carbon double bond and also a resonance at ca. 130 ppm that can be

assigned to a N-bound nitrile carbon. Also, no sharp intense band around 2220 cm^{-1} is observed in the IR spectra of the complexes as would be expected for a non-coordinated cyanide group. Thus, all of these olefins bond in the metal through the nitrogen lone pair. Note that the ^{13}C NMR spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{-Fe}(\text{CO})_2(\text{acrylonitrile})]\text{BF}_4$ also shows resonances for the olefin ligand as described above for the analogous phosphine-substituted compound. This confirms an earlier suggestion made on the basis of ^1H NMR and IR that this complex also contains a N-bound acrylonitrile ligand [8].

Reactions of new complexes. The $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-acetylene})]\text{BF}_4$ complexes react with NaBH_3CN to yield new σ -vinyl complexes in low yield. The main product of these reactions is $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$. These complexes were isolated after chromatography purification as yellow, air-sensitive oils that thermally decompose at room temperature in two days and were characterized by ^{13}C and ^1H NMR and IR spectroscopy. More stable σ -vinyl complexes were prepared by the reduction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^2\text{-allene})]\text{BF}_4$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^2\text{-3-hexyne})]\text{BF}_4$ with $\text{LiB}(\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5)_3\text{H}$ (L-Selectride) to produce in good yield $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}(\text{CH}_3)\text{CH}_2)$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}(\text{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3)$, respectively. The hydride reagent NaBH_3CN is not successful in these reactions. These new complexes were completely characterized and were used to support the spectral characterization of the dicarbonyl- σ -vinyl complexes. Both of these complexes are thermally very stable and can be heated in solution at 90°C with no decomposition or isomerization of the σ -vinyl group. Although they do decompose at 140°C , no $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{H}$ was produced in the decomposition. Interestingly, in the reduction of the allene complex with NaBH_4 , some $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{CH}(\text{CH}_3)\text{CH}_3)$ is produced in addition to the expected σ -vinyl complex.

Discussion

A variety of methods are now available for the synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-olefin})]^+$ complexes. The most common method is an exchange reaction with the isobutylene [5a] or THF [2] complex in an inert solvent. These methods are quite successful for cases in which the incoming olefin coordinates strongly to the iron. For weaker ligands such as cyclohexene, yields are low. The THF adduct can be made more reactive by introducing gaseous BF_3 into the reaction. In this case the isolated yield with cyclohexene is 92% [2]. Although very useful, this method suffers the disadvantage of having to carefully handle the highly corrosive BF_3 gas and also some olefins are polymerized by BF_3 . Another method that is useful for preparing complexes of weakly coordinating olefins is to react an epoxide with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ followed by two equivalents of acid [9]. This method has been used to prepare complexes of weakly coordinating olefins in good yield, but it suffers the disadvantage of having to prepare the epoxide. Also, the iron anion is quite air-sensitive and must be handled carefully in an inert atmosphere. Another method of preparing these complexes is to oxidize $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ with the trityl cation in CH_2Cl_2 in the presence of the ligand [5b]. This reaction is useful for a number of simple olefins but cannot be readily used with ligands that are oxidized by the trityl cation. Also, the reactions are fairly slow. The reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{-}$

$\text{Fe}(\text{CO})_2\text{I}$ with AgBF_4 in CH_2Cl_2 reported here is rapid and the solution can be filtered to remove any excess silver salt before the olefin is added. This leads to the isolation of known olefin complexes, in particular the cyclohexene complex, in ca. 70% yield. Also the new complexes of cycloheptatriene and the internal acetylenes 3-hexyne, 2-butyne and diphenylacetylene have been prepared by this method. As this is a rapid one step reaction from a readily available starting material ($(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ can be prepared in better than 80% yield from the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ and I_2 on a large scale [3]), this is a very attractive method for preparing these complexes, especially if the ligand does not strongly coordinate to the iron. Because the reaction takes place rapidly after the ligand is added, gaseous olefins can simply be bubbled into the solution for a short time conserving the olefin. Also, although the reactions have been generally carried out in the presence of three equivalents of olefin, yields are not substantially lowered if only one equivalent of the olefin is used, thus also conserving the olefin.

This new method can be readily extended to the preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^2\text{-un})]\text{BF}_4$ (un = unsaturated hydrocarbon) complexes. In this system, the THF adduct can only be used to prepare the ethene [2] and allene adducts and the other general routes outlined above for the dicarbonyl system are not applicable because neither the appropriate anion nor dimer needed in the various preparations are known. These new triphenylphosphine derivatives are not as stable as the respective dicarbonyl complexes. Another difference in the two systems is that the 16-electron species generated in solution upon iodide extraction from the starting material by Ag^+ is much less stable in the phosphine system and must be mixed with the incoming ligand immediately. Although yields are optimum in the dicarbonyl system if the olefin is introduced 30 minutes after the AgBF_4 is added, they are not lowered substantially if the olefin addition is delayed by 2 h.

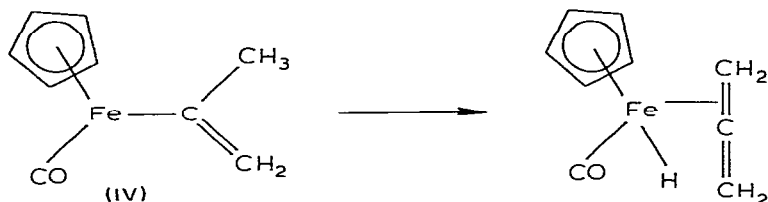
Attempts to prepare π -olefin complexes of cyano-substituted olefins failed because the nitrogen lone pair bonds preferentially to the iron. Carbon-13 NMR is very diagnostic for the mode of coordination because the olefin carbon atom resonances moved less than three ppm upon complex formation whereas they generally move upfield by 60 ppm when coordinated to the iron [2]. Also, the cyanide carbon moved downfield ca. 14 ppm.

Attempts to prepare σ -vinyl complexes by hydride addition to the η^2 -acetylene complexes in the dicarbonyl system met with limited success. Low yields were encountered and the complexes are not very stable. Hydride addition to the allene and 3-hexyne complexes in the phosphine system produced stable complexes in ca. 50% yield. The main difference in these reactions is that $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ forms in preference to a desired product in the dicarbonyl system whereas in the phosphine system there does not seem to be the analogous byproduct to lower isolated yields. This was particularly important in these reactions because the reagent L-Selectride was much more successful in the phosphine system than either NaBH_4 or NaBH_3CN whereas in the dicarbonyl system L-Selectride led only to the production of the iron dimer.

We have recently shown that $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{alkyl})$ complexes undergo a clean β -elimination reaction to form $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{H}$ and olefin at elevated temperatures [10]. Also, certain alkyl groups readily iso-

merize on the metal (e.g., the sec-butyl compound isomerizes to the n-butyl derivative [11]). Neither of these processes were observed for the new phosphine-substituted σ -vinyl complexes. They are stable in solution at 90°C, temperatures high enough to cause both the decomposition and isomerization reactions for alkyl complexes. They will pyrolyze at 140°C, but no $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{H}$ could be isolated. Previous results have shown that this hydride complex can survive these reaction conditions [10].

There are two obvious explanations for these differences in reactivity of the alkyl and vinyl derivatives. It has been shown that for either the decomposition [10] or isomerization [11] reaction to take place the phosphine ligand must first dissociate to form the intermediate IV shown below. This dissociation could be a higher energy process for the vinyl complexes. Because the spectral properties of the vinyl complexes match those of the alkyls, large differences in the bonding of the phosphine ligand to the iron seem unlikely. Alternatively, the β -elimination process shown below could be of higher energy for a vinyl complex such as IV than the analogous alkyls.



Schwartz has shown this to be the case in an iridium system [12]. Although further investigations on this point are necessary, this is a reasonable explanation in this case.

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