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Addition of nucleophiles to cationic diiron μ-vinylcarbyne complexes; synthesis of functionalized diiron μ-alkenylidene complexes

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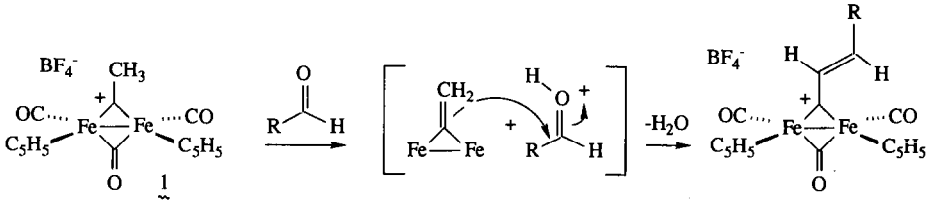
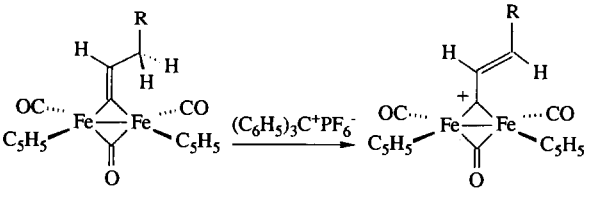
Abstract

The *p*-tolyl substituted vinylcarbyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}p\text{-}CH_3)^+ BF_4^-$ (**1**) reacts with sodio diethylmalonate by regioselective addition to the remote vinyl carbon to give neutral μ-alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}C{=}CHCH(C_6H_4\text{-}p\text{-}CH_3)[CH(CO_2CH_2CH_3)_2]\}$ (**3**) in 60% yield as a 1.2/1 mixture of diastereomers. Other nucleophiles, such as CH_3Li, $CH_3\text{-}p\text{-}C_6H_4\text{-}Li$, $P(CH_3)_3$, and $HFe(CO)_4^-$, also add regioselectively to vinylcarbyne complexes at the remote vinyl carbon to generate μ-alkenylidene complexes.



Recently we reported full synthetic details for two efficient methods for the preparation of cationic diiron μ-vinylcarbyne complexes [1]. One method involves a condensation reaction between μ-alkylidynediiron complexes and aldehydes, ketones, and orthoesters. This reaction involves nucleophilic attack of an intermediate μ-alkenylidene complex (in equilibrium with an alkylidyne complex) on a protonated aldehyde followed by dehydration to generate the vinylcarbyne complex.



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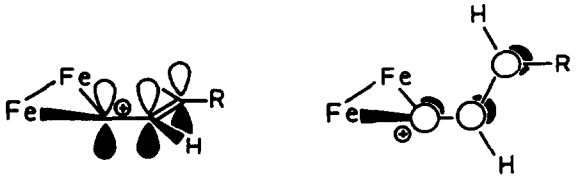
The other method involves allylic hydride abstraction from μ-alkenylidene complexes with $(C_6H_5)_3C^+ PF_6^-$. A wide range of vinylcarbyne complexes are readily available by these complementary procedures.

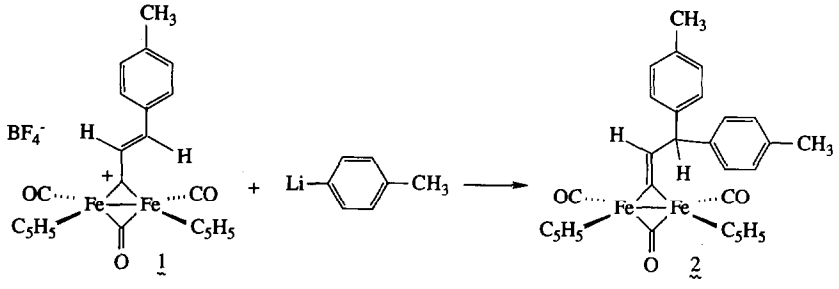


Vinylcarbyne complexes possess interesting electronic properties. The barrier to rotation of the vinylcarbyne ligand is unusually low [2]. Fenske–Hall molecular orbital calculations [3] reveal that the μ-alkylidyne carbon has perpendicular p-orbitals which can accept electron density from the vinyl group throughout rotation.

In this paper we report the reactions of vinylcarbyne complexes with nucleophiles. In all cases examined, adducts are formed in which the entering nucleophile has added regioselectively at the remote vinyl carbon atom to yield μ-alkenylidene complexes.

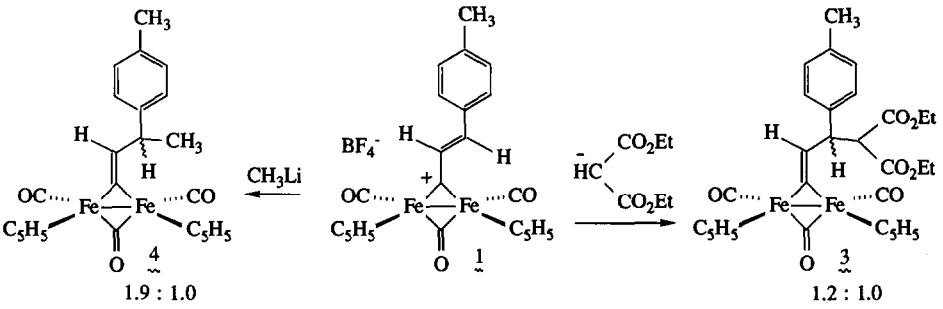
Results

When p-tolyllithium was added to a purple suspension of the p-tolyl substituted vinylcarbyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}p\text{-}CH_3)^+ BF_4^-$ (**1**) in THF at $-78°C$, **1** gradually dissolved to form a red solution from which the alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}C{=}CHCH(C_6H_4\text{-}p\text{-}CH_3)_2]$ (**2**) was isolated in 49% yield as a red-orange powder.

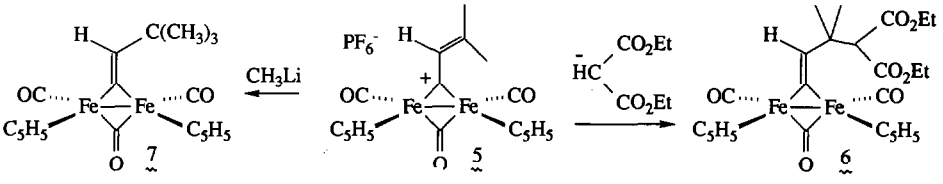


2 is formed by the regioselective addition of a p-tolyl group to the remote vinyl carbon of **1**. Its structure was readily established by spectroscopy. In the ^1H NMR of **2**, the vinyl proton appeared as a doublet at δ 7.59 ppm (d, J 9.6 Hz) coupled to the allylic hydrogen at δ 5.37 ppm (d, J 9.6 Hz). Four resonances were observed for the diastereotopic tolyl groups at δ 7.58 (d, J 8.2 Hz, 2H, C_6H_4), 7.23 (d, J 7.8 Hz, 2H, C_6H_4), 7.14 (d, J 8.1 Hz, 2H, C_6H_4), and 7.00 ppm (d, J 7.8 Hz, 2H, C_6H_4). Two cyclopentadienyl (η-C_5H_5, Cp) resonances were seen at δ 4.96 and 4.90 ppm while the diastereotopic p-tolyl methyl groups were observed at δ 2.34 and 2.22 ppm. The infrared spectrum indicates *cis* terminal carbonyls with symmetric and asymmetric stretches at 2002(vs) and 1911(m) cm^{-1}, while the bridging carbonyl gives rise to a band at 1800(s) cm^{-1} [4]. The high field ^1H NMR chemical shift of the Cp protons and low energy of the carbonyl infrared stretches are characteristics

of neutral diiron complexes. For cationic diiron complexes, the Cp protons in the ^1H NMR are typically observed at δ 5.5–5.7 ppm (δ 5.67 ppm for **1**) and the carbonyl bands in the infrared are of much higher energy (2033(vs), 2000(m), 1848(s) cm^{-1} for **1**).



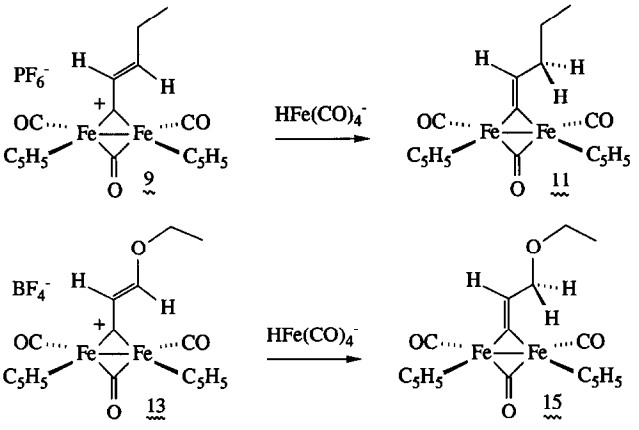
Other carbon nucleophiles added with complete regioselectivity to the remote vinyl carbon of **1** to give alkenylidene complexes. Sodio diethylmalonate reacted with **1** at −78°C to give alkenylidene complexes $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}C{=}CH\text{-}CH(C_6H_4\text{-}p\text{-}CH_3)[CH(CO_2CH_2CH_3)_2]\}$ (**3**) in 60% yield as a mixture of diastereomers. Methyllithium reacted rapidly with **1** at −78°C to give the alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}CHCH(C_6H_4\text{-}p\text{-}CH_3)(CH_3)]$ (**4**) in 60% yield as a mixture of diastereomers.



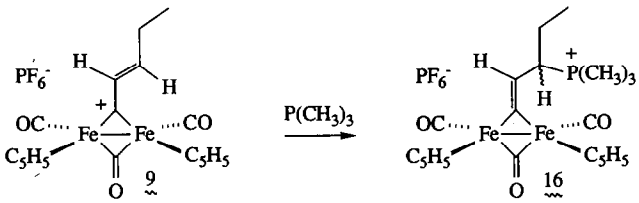
Sodio diethylmalonate reacted with the vinylcarbyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C\text{-}CH{=}C(CH_3)_2]^+ PF_6^-$ (**5**) to give the alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}C{=}CHC(CH_3)_2[CH(CO_2CH_2CH_3)_2]\}$ (**6**) in 46% yield. Methyllithium added to **5** to produce $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}CHC(CH_3)_3]$ (**7**) in 68% yield. Addition of basic nucleophiles to the vinylcarbyne complex **5** occurs in preference to deprotonation of an allylic proton which would have produced the alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}CHC(CH_3){=}CH_2]$ (**8**). Previously, we observed that deprotonation of the vinylcarbyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}(E)\text{-}CH{=}CHCH_2CH_3)^+ PF_6^-$ (**9**) with $LiN[Si(CH_3)_3]_2$ produced $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH{=}CHCH_3)$ (**10**) [5].

Heteroatom nucleophiles react regioselectively at the remote vinyl carbon of vinylcarbyne complexes to produce alkenylidene complexes. Hydride was added using $NEt_4^+ HFe(CO)_4^-$ as a hydride source. We have found this reagent to be a convenient, mild, nonbasic source of hydride. The addition of hydride to cationic diiron complexes gives ether soluble, neutral diiron complexes while the hydride by-product is ether insoluble anionic $HFe_3(CO)_{11}^-$ which is easily separated by filtration [6].

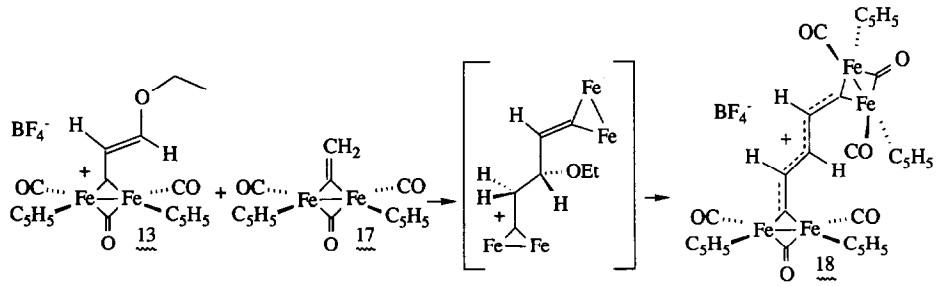
For example, reaction of $HFe(CO)_4^-$ with the ethyl substituted vinylcarbyne complex **9** gives the alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2\text{-}$



CH_2CH_3) (**11**) [4] in 89% yield. The reaction of $HFe(CO)_4^-$ with the vinylcarbyne complexes $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C\text{-}(E)\text{-}C(CH_3)=CHC_6H_4\text{-}p\text{-}CH_3]^+ PF_6^-$ (**12**) and $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}(E)\text{-}CH=CHOCH_2CH_3)^+ BF_4^-$ (**13**) produced the alkenylidene complexes $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C=C(CH_3)CH_2C_6H_4\text{-}p\text{-}CH_3]$ (**14**) in 44% yield and $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C=CHCH_2OCH_2CH_3)$ (**15**) in 81% yield.

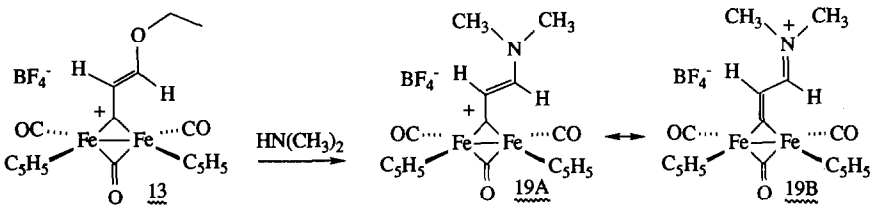


The reaction of the ethyl substituted vinylcarbyne complex **9** with $P(CH_3)_3$ led to the isolation of the phosphonium salt $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}C=CHCH\text{-}[P(CH_3)_3]CH_2CH_3\}^+ PF_6^-$ (**16**) in 88% yield as a mixture of diastereomers.

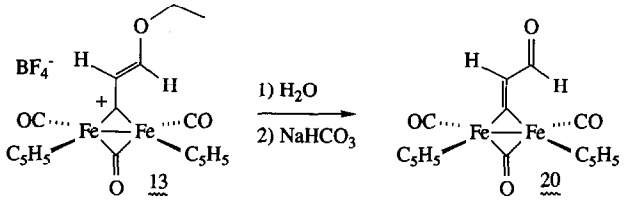


Vinyl ether carbyne complex **13** undergoes addition–elimination reactions with selected nucleophiles to give new vinylcarbyne complexes. Reaction of ethenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C=CH_2)$ (**17**) [7] with the vinyl ether carbyne complex **13** occurred rapidly at room temperature and led to the isolation of

tetrairon vinylcarbyne complex $\{[C_5H_5(CO)Fe]_2(\mu\text{-}CO)\}_2(\mu\text{-}C_5H_3)^+ BF_4^-$ (**18**) in 85% yield [8]. This reaction is thought to occur by nucleophilic attack of the remote ethenylidene carbon of **17** on the remote carbon of vinyl ether carbyne complex **13** followed by proton transfer to oxygen and elimination of ethanol.



Substitution of a dimethylamino group for the ethoxy group of vinyl ether carbyne complex **13** occurred under very mild conditions. When dimethylamine was added to a THF solution of **13** at $-78°C$ a color change from red-orange to orange occurred instantly. Orange, microcrystalline $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C\text{-}(E)\text{-}CH{=}CHN(CH_3)_2]^+ BF_4^-$ (**19**) precipitated from solution over several minutes and was isolated in 84% yield. **19** is the only vinylcarbyne complex to exhibit separate Cp resonances at room temperature in the ^1H and ^{13}C NMR and reflect the importance of resonance structures **19A** and **19B** [2]. Vinylcarbyne complexes **1**, **18**, and **19** have been examined in detail by single crystal X-ray crystallography; these results have been presented elsewhere [1,8,9].



Substitution of an oxo group for the ethoxy group in **13** also occurred under mild conditions. When H_2O and sodium bicarbonate were added to an acetone solution of the vinyl ether carbyne complex **13**, the formyl substituted alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCHO)$ (**20**) was isolated in 68% yield after extraction into ether and chromatography. The addition of water to the remote vinyl carbon of **13** followed by loss of ethanol and deprotonation produces **20**.

Conclusion

The synthesis of a variety of functionalized μ-alkenylidene complexes is readily achieved by the addition of nucleophiles to vinylcarbyne complexes. Previously, alkenylidene complexes were synthesized by deprotonation of alkylidyne complexes [4,6,7]. Alkylidyne complexes in turn can be prepared either by the addition of the C–H bond of the methylidyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}CH)^+PF_6^-$ (**21**), across the carbon–carbon double bond of alkenes in a hydrocarbation reaction [4], or by the reaction of selected lithium reagents with $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ followed by treatment with acid [10]. This new method greatly extends the range of functionalized alkenylidene complexes which can be synthesized. In order to realize

the full synthetic potential of these new reactions, synthetically useful procedures for cleaving the μ-alkenylidene ligand from the diiron center need to be developed. We are currently addressing this problem [11].

Experimental

The ^1H NMR spectra (δ, ppm) were obtained on a Bruker WP270, or AM500 spectrometer. The ^{13}C NMR spectra (δ, ppm) were obtained on a JEOL FX200 spectrometer operating at 50.1 MHz or an AM500 spectrometer operating at 126 MHz. The samples contained 0.07 *M* $Cr(acac)_3$ as a shiftless relaxation agent. Acetone-d_6 was dried over B_2O_3. NMR samples were prepared on a vacuum line in acetone-d_6 and sealed under a positive flow of N_2. IR spectra were recorded on a Beckman 4230 or 4250 spectrometer and calibrated with polystyrene film. Mass spectra were obtained on a Kratos MS-80 mass spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories or Galbraith Laboratories. Air sensitive compounds were handled using standard high vacuum line or Schlenk procedures and glovebox manipulations. Diethyl ether, THF, and hexane were distilled from degassed, purple solutions of sodium and benzophenone immediately prior to use.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}CHCH(C_6H_4\text{-}p\text{-}CH_3)_2]$ (2). *p*-Tolyllithium (1.4 ml, 0.95 *M* in diethyl ether, 1.33 mmol) was added to a stirred, purple suspension of **1** [1] (400 mg, 0.738 mmol) in THF (30 ml) at $-78°C$. **1** dissolved over 30 min to produce a red solution. Methanol (1 ml) was added to quench excess lithium reagent and the solvent was removed under reduced pressure. The residue was extracted into diethyl ether (50 ml), washed with 25 ml saturated aqueous $NaHCO_3$, and dried ($MgSO_4$). Column chromatography (silica gel, 1×20 cm, 49/1 hexane/diethyl ether) gave a red oil which was triturated in hexane (15 ml) and cooled to $-78°C$ to give **2** (197 mg, 49%) as a red-orange powder. ^1H NMR (270 MHz): δ 7.59 (d, *J* 9.6 Hz, μ-C=CH), 7.58 (d, *J* 8.2 Hz, 2H, C_6H_4), 7.23 (d, *J* 7.8 Hz, 2H, C_6H_4), 7.14 (d, *J* 8.1 Hz, 2H, C_6H_4), 7.00 (d, *J* 7.8 Hz, 2H, C_6H_4), 5.37 (d, *J* 9.6 Hz, μ-C=CHC*H*), 4.96 (s, C_5H_5), 4.90 (s, C_5H_5), 2.34 (s, CH_3), 2.22 (s, CH_3). $^{13}C\{^1H\}$ NMR (50.1 MHz): δ 271.4, 266.1 (μ-C, μ-CO); 212.9 (CO); 144.9 144.4, 142.9, 135.4, 134.9 (μ-C=*C*H, *ipso,p*-C_6H_4); 129.6, 129.0, 128.9, 128.3 (*o*-,*m*-C_6H_4); 88.7, 87.7 (C_5H_5); 58.7 (μ-C=CH*C*H); 20.9, 20.7 (CH_3). IR (THF): 2002 (vs), 1911 (m), 1800 (s) cm^{-1}. HRMS $C_{30}H_{26}Fe_2O_3$ calcd.: 546.0573. Found: 546.0579. Anal. Found: C, 65.66; H, 4.83. $C_{30}H_{26}Fe_2O_3$ calcd.: C, 65.97; H, 4.80%.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}C{=}CHCH(C_6H_4\text{-}p\text{-}CH_3)[CH(CO_2CH_2CH_3)_2]\}$ (3). A suspension of **1** (500 mg, 0.923 mmol) and $NaHC(CO_2CH_2CH_3)_2$ (336 mg, 1.84 mmol) were stirred in THF (25 ml) at $-78°C$ for 10 min. The solvent was evaporated under reduced pressure to give a red oil which was extracted into diethyl ether (60 ml), washed twice with 25 ml portions of saturated aqueous $NaHCO_3$, and dried ($MgSO_4$). Chromatography (alumina, 1×20 cm, 49/1 hexane/diethyl ether) gave a red oil which was triturated with hexane (20 ml) and cooled to $-45°C$ to give **3** (340 mg, 60%) as a red orange powder. ^1H NMR (500 MHz) indicated a 1.2/1 mixture of diastereomers of **3**. For the major isomer: δ 7.37 (d, *J* 9.9 Hz, μ-C=CH), 7.29 (d, *J* 8.0 Hz, 2H, C_6H_4), 6.99 (d, *J* 7.9 Hz, 2H, C_6H_4), 5.12 (s, C_5H_5), 4.883 (t, *J* 10.3 Hz, μ-C=CHC*H*), 4.79 (s, C_5H_5), 4.31 (dq, *J* 7.0, 1.0 Hz, CH_2), 4.02 (d, *J* 10.7 Hz, $CHCO_2$), 4.00 (m, CH_2), 2.18 (s, C_6H_4-*p*-CH_3), 1.36 (t, *J*

7.1 Hz, CH_2CH_3), 1.081 (t, *J* 7.1 Hz, CH_2CH_3). For the minor isomer: δ 7.64 (d, *J* 9.5 Hz, μ-C=CHC*H*), 7.60 (d, *J* 8.0 Hz, 2H, C_6H_4), 7.19 (d, *J* 7.9 Hz, 2 H, C_6H_4), 4.880 (s, C_5H_5), 4.79 (s, C_5H_5), 4.66 (t, *J* 9.6 Hz, μ-C=CHC*H*), 3.98 (m, CO_2CH_2), 3.87 (m, CO_2CH_2), 3.75 (d, *J* 9.6 Hz, $CHCO_2$), 2.31 (s, C_6H_4-*p*-CH_3), 1.078 (t, *J* = 7.1 Hz, CH_2CH_3), 1.02 (t, *J* 7.1 Hz, CH_2CH_3). ^{13}C NMR (126 MHz) for the major isomer: δ 270.8, 268.4 (μ-C, μ-CO); 212.5, 211.6 (CO), 169.4, 168.1 (CO_2); 141.0, 135.6 (*ipso*-,*p*-C_6H_4); 139.7 (d, *J* 157 Hz, μ-C=CH); 129.1, 128.0 (d, *J* 155, 155 Hz, *o*-,*m*-C_6H_4); 88.8, 88.1 (d, *J* 178, 177 Hz, C_5H_5); 61.8, 61.4, 59.8 ($CHCO_2$, CH_2); 53.1 (d, *J* 137 Hz, μ-C=CHCH); 20.8 (C_6H_4-*p*-CH_3); 14.4, 13.98 (CH_2CH_3); for the minor isomer: δ 270.8, 269.1 (μ-C,μ-CO); 212.7, 211.8 (CO); 168.0, 167.8 (CO_2); 142.5, 136.0 (*ipso*-,*p*-C_6H_4); 139.3 (d, *J* 157 Hz, μ-C=CH); 129.5, 128.9 (d, *J* 155, 155 Hz, *o*-,*m*-C_6H_4); 88.9, 87.6 (d, *J* 176, 179 Hz, C_5H_5); 61.2, 61.2, 61.1 ($CHCO_2$, CH_2); 52.4 (d, *J* 135 Hz, μ-C=CHCH); 21.0 (C_6H_4-*p*-CH_3), 14.04, 13.98 (CH_3). IR (CH_2Cl_2): 1999(vs), 1964(m), 1789(s), 1754(m), 1729(m) cm^{-1}, HRMS $C_{30}H_{30}Fe_2O_7$ calcd.: 614.0681. Found: 614.0697. Anal. Found: C, 58.55, H, 4.75. $C_{30}H_{30}Fe_2O_7$ calcd.: C, 58.66; H, 4.92%.

[C_5H_5(CO)Fe]$_2$(μ-CO)[μ-C=CHCH(C_6H_4-p-CH_3)(CH_3)] ***(4)***. CH_3Li (600 μl, 1.7 *M* in diethyl ether, 1.0 mmol) was added to a stirred suspension of **1** (400 mg, 0.738 mmol) in THF (30 ml) at −78 °C. Methanol (1 ml) was added to the resulting red solution and the solvent was evaporated under reduced pressure to give a red oil which was extracted into diethyl ether (40 ml) and washed with 25 ml saturated, aqueous $NaHCO_3$. Column chromatography (alumina, 1 × 20 cm, 19/1 hexane/diethyl ether) gave **4** (209 mg, 60%) as a red powder. ^1H NMR (270 MHz) indicated a 1.9/1.0 mixture of diastereomers of **3**. For the major isomer: δ 7.54 (d, *J* 7.9 Hz, 2H, C_6H_4), 7.38 (d, *J* 9.3 Hz, μ-C=CH), 7.20 (d, *J* 8.6 Hz, 2H, C_6H_4), 4.91 (s, C_5H_5), 4.89 (s, C_5H_5), 4.15 (m, $CHCH_3$), 2.33 (s, C_6H_4-*p*-CH_3), 1.43 (d, *J* 6.6 Hz, $CHCH_3$); for the minor isomer: 7.30 (d, *J* 7.8 Hz, 2H, C_6H_4), 7.20 (d, *J* 8.6 Hz, 1H, μ-C=CH), 7.02 (d, *J* 7.9 Hz, 2H, C_6H_4), 5.04 (s, C_5H_5), 4.91 (s, C_5H_5), 4.15 (m, $CHCH_3$), 2.23 (s, C_6H_4-*p*-CH_3), 1.69 (d, *J* 7.0 Hz, $CHCH_3$). $^{13}C\{^1H\}$ NMR (126 MHz) for the major isomer: δ 271.8, 264.3 (μ-C, μ-CO); 213.1, 213.1 (CO) 146.6, 144.7, 135.0 (μ-C=CH, *ipso*-,*p*-C_6H_4); 129.6, 127.3 (*o*-,*m*-C_6H_4); 88.6, 87.8 (C_5H_5); 48.2 ($CHCH_3$); 25.9, 20.9 (CH_3); for the minor isomer: 271.9, 263.7 (μ-C, μ-CO); 212.9, 212.8 (CO); 146.2, 145.3, 134.8 (μ-C=CH, *ipso*-, *p*-C_6H_4); 129.1, 127.2 (*o*-,*m*-C_6H_4); 88.7, 87.8 (C_5H_5); 47.8 ($CHCH_3$); 23.7, 20.8 (CH_3). IR (THF): 1996(vs), 1908(m), 1797(s) cm^{-1}. HRMS $C_{24}H_{22}Fe_2O_3$ calcd.: 470.0261. Found: 470.0245. Anal. Found: C, 61.57; H, 4.88. $C_{24}H_{22}Fe_2O_3$ calcd.: C, 61.32; H, 4.72%.

[C_5H_5(CO)Fe]$_2$(μ-CO)[μ-C=CHC(CH_3)$_2$CH($CO_2CH_2CH_3$)$_2$] ***(6)***. **5** [1] (200 mg, 0.372 mmol) and $NaHC(CO_2CH_2CH_3)_2$ (100 mg, 0.55 mmol) were stirred in CH_2Cl_2 (12 ml) for 1.5 h. The solvent was evaporated under reduced pressure to give a red oil which was extracted into diethyl ether (15 ml), filtered through alumina (1 g), and concentrated to 3 ml. Addition of hexane (5 ml) gave a red oil which was triturated with additional hexane (10 ml) to give **6** (96 mg, 46%) a red powder. ^1H NMR (270 MHz): δ 7.44 (s, μ-C=CH), 5.01 (s, C_5H_5), 4.90 (s, C_5H_5), 4.21 (m, 4H, CH_2), 3.37 (s, $CHCO_2$), 1.65 (s, $C(CH_3)$), 1.43 (s, $C(CH_3)$), 1.29 (t, *J* 7.5 Hz, CH_2CH_3), 1.29 (t, *J* 7.5 Hz, CH_2CH_3). ^{13}C NMR (50.1 MHz): δ 269.8, 262.8 (μ-C, μ-CO); 213.5, 213.1 (CO), 168.9 (CO_2); 150.3 (d, *J* 152 Hz, μ-C=CH); 88.6, 88.4 (d, *J* 180, 176 Hz, C_5H_5); 63.3 (d, *J* 132 Hz, CH); 61.1, 61.1 (t, *J* 144 Hz, CH_2); 41.7 [$C(CH_3)_2$]; 26.5 (q, *J* 128 Hz, $C(CH_3)_2$); 14.5 (q, *J* 128 Hz,

CH_2CH_3). IR (CH_2Cl_2): 2000(s), 1960(m), 1790(m), 1755(m), 1730(m) cm^{-1}. HRMS $C_{25}H_{28}Fe_2O_7$ calcd.: 552.0532. Found: 552.0532.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}CHC(CH_3)_3]$ (7). CH_3Li (400 μL, 1.4 *M* in diethyl ether, 0.56 mmol) was added to a suspension of **5** (205 mg, 0.381 mmol) in CH_2Cl_2 (8 ml) at $-78°C$. The solution was stirred for 2 h, warmed to ambient temperature and the solvent was evaporated under reduced pressure to give a red solid which was extracted into diethyl ether (25 ml) and filtered through alumina (4 g). The alumina was extracted with additional diethyl ether (30 ml) and hexane (35 ml). Solvent was evaporated from the combined extracts to give 7 (105 mg, 68%) as red crystals. ^1H NMR (270 MHz): δ 7.39 (s, μ-C=CH), 4.96 (s, C_5H_5), 4.89 (s, C_5H_5), 1.32 (s, 9 H, CH_3). $^{13}C\{^1H\}$ NMR (50.1 MHz): δ 271.8, 260.7 (μ-C, μ-CO); 213.8, 213.3 (CO); 153.6 (CH); 89.3, 88.5 (C_5H_5), 36.6 [$C(CH_3)_3$]; 32.3 (CH_3). IR (CH_2Cl_2): 1990(s), 1952(m), 1785(m) cm^{-1}. HRMS $C_{19}H_{20}Fe_2O_3$: calcd. 408.0110. Found: 408.0117.

*Reaction of **9** with $N(CH_2CH_3)_4^+HFe(CO)_4^-$.* **9** [1] (125 mg, 0.323 mmol) and $N(CH_2CH_3)_4^+$ $HFe(CO)_4^-$ (103 mg, 0.344 mmol) were stirred in THF (20 ml) at $-78°C$ for 1 h. The solvent was evaporated under reduced pressure and the resulting red solid was extracted into diethyl ether (5×5 ml). The combined extracts were filtered through alumina (2 g) and concentrated to 2 ml under reduced pressure. The alumina was extracted with additional diethyl ether (4 ml) and hexane (20 ml). Solvent was evaporated from the combined extracts under reduced pressure to give **11** [4] (81 mg, 89%).

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CH_3)CH_2C_6H_4\text{-}p\text{-}CH_3]$ (14). **13** [1] (250 mg, 0.407 mmol) and $N(CH_2CH_3)_4^+$ $HFe(CO)_4^-$ (185 mg, 0.611 mmol) were stirred in THF (30 ml) at 25 °C for 30 min. Solvent was removed under reduced pressure. The residue was chromatographed (alumina, diethyl ether) to give pure **14** (84 mg, 44%). ^1H NMR (270 MHz): δ 7.36 (d, *J* 7.9 Hz, 2H, C_6H_4), 7.13 (d, *J* 7.9 Hz, 2H, C_6H_4), 5.03 (s, C_5H_5), 4.96 (s, C_5H_5), 4.25 (d, *J* 15.2 Hz, C*H*H), 4.06 (d, *J* 14.9 Hz, CH*H*), 2.32 (s, CH_3), 2.30 (s, CH_3). $^{13}C\{^1H\}$ (126 MHz); δ 271.2, 261.7 (μ-C, μ-CO); 213.4, 213.2 (CO); 140.6, 139.7, 135.3 (*ipso-*, *p*-C_6H_4, and μ-C=*C*); 129.5, 128.9 (*o*-,*m*-C_6H_4); 88.2, 88.1 (C_5H_5); 48.7 (CH_2); 25.3, 20.9 (CH_3). IR (CH_2Cl_2); 1997(s), 1956(m), 1785(m) cm^{-1}. HRMS $C_{24}H_{22}Fe_2O_3$ calcd.: 470.0261. Found: 470.0265.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2OCH_2CH_3)$ (15). **13** [1] (310 mg of 0.5 acetone solvate, 0.590 mmol) and $N(CH_2CH_3)_4^+$ $HFe(CO)_4^-$ (265 mg, 0.886 mmol) were stirred in THF (50 ml) at $-78°C$ for 1.5 h. Solvent was evaporated under reduced pressure, diethyl ether (25 ml) and hexane (5 ml) were added, and the solution was filtered. The solution was concentrated to 5 ml and additional hexane (70 ml) was added to precipitate a bright orange-red solid which was collected by filtration at $-78°C$ and dried under vacuum to give **15** (196 mg, 81%). ^1H NMR (270 MHz); δ 7.33 (t, *J* 7.2 Hz, μ-C=CH), 5.02 (s, C_5H_5), 4.94 (s, C_5H_5), 4.57 (dd, *J* 10.6, 7.2 Hz, μ-C=CHC*H*H), 4.35 (dd, *J* 10.6, 7.2 Hz, μ-C=CHCH*H*), 3.67 (dq, *J* 9.3, 7.0 Hz, OC*H*H), 3.55 (dq, *J* 9.3, 7.0 Hz, OCH*H*), 1.21 (t, *J* 7.0 Hz, CH_3). $^{13}C\{^1H\}$ NMR (50.1 MHz): δ 274.0, 270.3 (μ-C, μ-CO); 212.7 (CO); 137.8 (μ-C=*C*H); 89.0, 88.2 (C_5H_5); 75.3 (μ-C=CH*C*H_2); 64.9 (OCH_2); 15.9 (CH_3). IR (THF): 2003 (vs), 1958(m), 1798(s) cm^{-1}. HRMS $C_{18}H_{18}Fe_2O_4$ calcd.: 409.9898. Found: 409.9909.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}C{=}CHCH[P(CH_3)_3]CH_2CH_3\}^+$ PF_6^- (16). $P(CH_3)_3$

(88 mmHg, 100 ml, 24°C, 0.48 mmol) was condensed onto a frozen solution of **9** (200 mg, 0.372 mmol) in acetone (8 ml) at −196°C. The solution was warmed to ambient temperature and stirred for 40 min. The volume of the solution was reduced to 4 ml and diethyl ether (10 ml) was added. An orange precipitate formed which was isolated by filtration, washed with diethyl ether (3 ml), and dried under reduced pressure to give **16** (200 mg, 88%). ^{1}H NMR (270 MHz) indicated a 2/1 mixture of diastereomers of **16**. For the major isomer: δ 7.58 (dd, J 10.7, 6.2 Hz, μ-C=CH), 5.11 (s, C_5H_5), 5.07 (s, C_5H_5), 3.89 (m, μ-C=CHC*H*), 2.00 (d, J 13.9 Hz, $P(CH_3)_3$), 1.48 (t, J 7.3 Hz, CH_2CH_3) (CH_2 obscured by phosphine methyls). For the minor isomer: δ 6.97 (dd, J 10.8, 6.6 Hz, μ-C=CH), 5.11 (s, C_5H_5), 5.08 (s, C_5H_5), 3.89 (m, μ-C=CHC*H*), 2.26 (d, J 13.8 Hz, $P(CH_3)_3$), 1.06 (t, J 7.3 Hz, CH_2CH_3) (CH_2 obscured by phosphine methyls). ^{13}C{^{1}H} NMR (50.1 MHz) for the major isomer: δ 277.7, 267.0 (μ-C, μ-CO); 212.7 (CO), 130.0 (μ-C=*C*H); 89.9, 88.9 (C_5H_5); 44.5 (d, J 51 Hz, *C*HP$(CH_3)_3$); 23.4 (CH_2); 13.2 (CH_2CH_3); 7.4 (d, J 55 Hz, $P(CH_3)_3$); for the minor isomer: δ 277.5, 267.3 (μ-C, μ-CO); 213.5 (CO); 130.0 (μ-C=*C*H), 89.6, 88.5 (C_5H_5), 44.9 (d, J 47 Hz, *C*HP$(CH_3)_3$]; 23.8 (CH_2); 13.2 (CH_2CH_3), 7.6 (d, J 55 Hz, $P(CH_3)_3$). ^{31}P{^{1}H} NMR (80.8 MHz, 0.07 *M* $Cr(acac)_3$) δ 32.8 (major isomer), 3.7 (minor isomer), −141.0 (septet, J 708 Hz, PF_6^-). IR (nujol): 1996(s), 1954(m), 1813(m), 1800(m) cm^{-1}. Anal. Found: C, 41.32; H, 4.57. $C_{21}H_{26}F_6Fe_2O_3P_2$ calcd.: C, 41.08; H, 4.27%.

*{[C_5H_5(CO)Fe]$_2$(μ-CO)}$_2$(μ-C_5H_3)$^+$ BF_4^- (**18**).* A mixture of **13** (100 mg, 0.202 mmol) and **17** [7] (77 mg, 0.22 mmol) was stirred in CH_2Cl_2 (5 ml) for 5 min at ambient temperature. A rapid color change from red to deep purple was observed and microcrystals precipitated from solution. The volume of solvent was reduced to 2 ml and diethyl ether (20 ml) was added. Pink-brown microcrystals were isolated by filtration, washed twice with 2 ml portions of solvent, and dried under vacuum to give **18** (138 mg, 85%). ^{1}H NMR (270 MHz) δ 9.10 (d, J 12.6 Hz, 2 H, μ-C–CH), 7.73 (t, J 12.6 Hz, μ-C–CH=C*H*), 5.44 (s, 20 H, C_5H_5). ^{13}C{^{1}H} (50.1 MHz): δ 379.1 (μ-C), 259.4 (μ-CO), 210.4 (CO), 156.2 (μ-CCH=*C*H), 148.5 (μ-C*C*H), 91.2 (C_5H_5). IR (CH_2Cl_2): 2010(vs), 1990(sh), 1830(s), 1822(s) cm^{-1}. Anal. Found: C, 46.30; H, 2.79. $C_{31}H_{23}BF_4Fe_4O_6$ calcd.: C, 46.44; H, 2.89%.

*[C_5H_5(CO)Fe]$_2$(μ-CO)[μ-C-(E)-CH=CHN$(CH_3)_2$]$^+$ BF_4^- (**19**).* **13** (100 mg, 0.202 mmol) was dissolved in THF (15 ml) at −78°C. $HN(CH_3)_2$ (350 ml, 0.13 atm, 23°C, 1.9 mmol) was condensed in at −78°C. An instant color change from red-orange to orange was observed. After 2 min orange microcrystals precipitated from solution. The crystals were isolated by filtration, washed three times with 2 ml portions of solvent and dried under vacuum to give **19** (84 mg, 84%). ^{1}H NMR (270 MHz): δ 8.85 (d, J 11.1 Hz, μ-C-CH), 8.41 (d septets, J 11.1, 0.7 Hz, μ-CCH=C*H*), 5.35 (s, C_5H_5), 5.31 (s, C_5H_5), 3.71 (d, J 0.7 Hz, CH_3), 3.56 (d, J 0.8 Hz, CH_3). ^{13}C{^{1}H} NMR (50.1 MHz): δ 355.7 (μ-C), 261.1 (μ-CO), 210.9 (CO), 164.6 (μ-CCH=*C*H), 137.0 (μ-C*C*H), 91.1 (C_5H_5), 90.5 (C_5H_5), 47.7 (CH_3), 40.4 (CH_3). IR (Nujol): 2001 (vs), 1964(m), 1828(s) cm^{-1}. Anal. Found: C, 43.46; H, 3.81, N, 2.68. $C_{18}H_{18}BF_4Fe_2O_3N$ calcd.: C, 43.69; H, 3.67; N, 2.83%.

*[C_5H_5(CO)Fe]$_2$(μ-CO)(μ-C=CHCHO) (**20**).* **13** (200 mg, of 0.5 acetone solvate, 0.381 mmol) and H_2O (5 ml) were stirred in acetone (10 ml) for 1 min. $NaHCO_3$ (150 mg, 1.8 mmol) was added and the solution was extracted with diethyl ether (3 × 25 ml). The combined extracts were washed with saturated, aqueous $NaHCO_3$ solution (25 ml) and dried ($MgSO_4$). Column chromatography (alumina, 3/1 diethyl

ether/acetone) gave **20** (98 mg, 68%) as a red-orange powder. ^{1}H NMR (270 MHz): δ 9.74 (d, J 7.0 Hz, CHO), 8.06 (d, J 7.0 Hz, μ-C=CH), 5.18 (s, C_5H_5), 5.13 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (50.1 MHz): δ 319.5 (μ-C), 265.7 (μ-CO), 211.9 (CO), 211.3 (CO), 191.0 (CHO), 148.8 (CH), 89.9 (C_5H_5), 89.4 (C_5H_5). IR (CH_2Cl_2): 2004(vs), 1975(m), 1813(s), 1636(s) cm^{-1}. HRMS $C_{16}H_{12}Fe_2O_4$ calcd.: 379.9430. Found. 379.9427.

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