Synthesis and Characterization of Cationic Iron Vinylidene Compounds. Formation of C–H, C–N, and C–P Bonds and the X-ray Crystal Structure of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3)=CH_2\}]^+BF_4^-$

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Received November 23, 1981

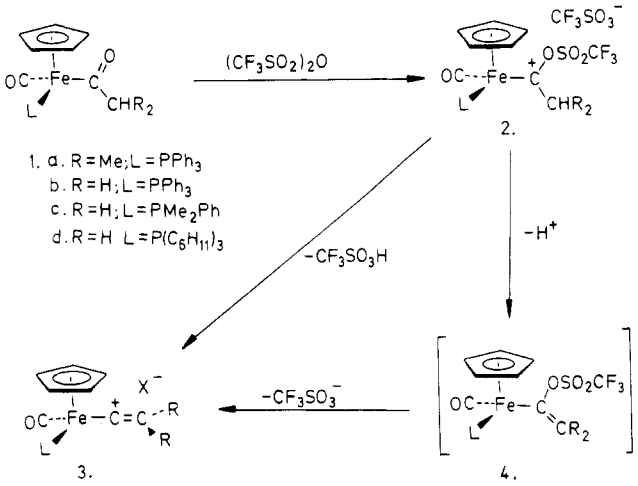
The syntheses and spectroscopic characterization of the vinylidene complexes $[Fe(\eta\text{-}C_5H_5)(CO)(L)(C{=}CR_2)]^+BF_4^-$ {L = PPh_3, R = Me, H; L = PMe_2Ph, $P(C_6H_{11})_3$, R = H}, from the acyl precursors $[Fe(\eta\text{-}C_5H_5)(CO)(L)\{C(O)CHR_2\}]$ and trifluoromethanesulfonic anhydride in the presence of $HBF_4{\cdot}Et_2O$, are described. An upper limit to the barrier for rotation about the Fe–C bond in $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CMe_2)]^+$ of 8.6 kcal·mol^{-1} is calculated. Reaction of $Li^+[Mn(\eta\text{-}C_5H_5)(CO)_2\{C(O)CH_3\}]^-$ with $(CF_3SO_2)_2O$ and 1,8-bis(dimethylamino)naphthalene affords $[Mn_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}C{=}CH_2)]$. Thermal decomposition of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ in CH_2Cl_2 solution affords the vinyl phosphonium compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3){=}CH_2\}]^+BF_4^-$, whose molecular structure has been determined by X-ray crystallography (space group C_i^1—$P\bar{1}$, a = 9.517 (4) Å, b = 11.038 (3) Å, c = 18.965 (4) Å, α = 99.81 (2)°, β = 94.41 (3)°, γ = 102.54 (3)°, Z = 2). Other vinyl derivatives $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(Y){=}CH_2\}]^+BF_4^-$ (Y = PMe_2Ph, pyridine, 4-methylpyridine) have also been characterized. Deprotonation of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ with t-BuO$^-$ affords $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$, while reduction with BH_4^- leads to $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(CH{=}CH_2)]$.

Introduction

The stabilization of carbene ligands by coordination to a transition-metal center is a well-established phenomenon in organometallic chemistry. While numerous examples of neutral and cationic complexes containing carbene ligands with stabilizing heteroatoms α to the carbene carbon atom were synthesized after Fischer's pioneering work,[2] it was not until the discovery of $Ta(\eta\text{-}C_5H_5)_2(CH_3)(CH_2)$[3] and $W(CO)_5(CPh_2)$[4] that carbenes without such heteroatom stabilization became recognized as viable ligands. An even more recent development has seen the synthesis and characterization of a number of complexes containing unsaturated carbene, or vinylidene, ligands.

Chisholm and Clark initially proposed the intermediacy of a reactive cationic vinylidene complex of Pt, obtained by rearrangement of a coordinated terminal alkyne,[5] and almost concurrently the first reports of stable neutral complexes of Fe, Mo, and W containing bridging and terminal dicyanovinylidene ligands appeared.[6,7] Since that time a series of neutral and cationic mononuclear complexes of Cr,[7] Mn,[8–11,24] Re,[12] Fe,[13–17] Ru,[18–21] and Os[20–22] containing terminal vinylidene ligands has been reported; almost invariably the vinylidene ligand results either from

Scheme I



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A. B.

Figure 1. Canonical forms representing (A) a cationic metal vinylidene complex and (B) a metal-substituted vinyl cation.

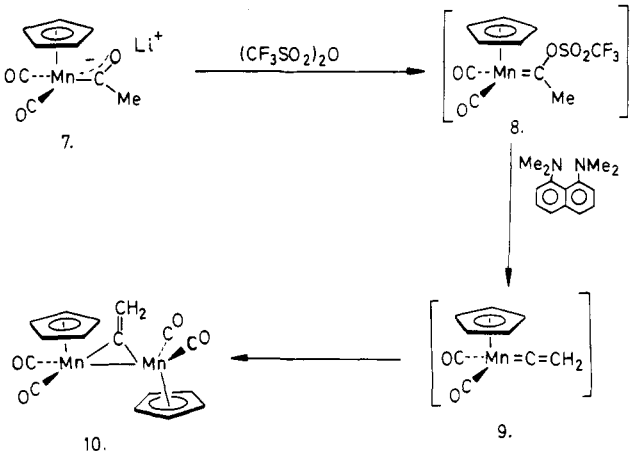
the rearrangement of a coordinated terminal alkyne or by the electrophilic protonation or alkylation of the β-carbon atom of an alkynylmetal complex. Examples of substituted allenylidene complexes of Cr,[7,23] W,[23] Ru,[24] and Mn[25] have also been reported.

Cationic transition-metal vinylidene complexes can be regarded as metal stabilized vinyl cations (Figure 1). A particularly useful route to organic vinyl cations has involved dissociation of the super leaving group triflate ($CF_3SO_3^-$, OTf^-) from vinyl triflates; the vinyl triflate precursors are readily available by the reaction of the oxygen atom of enolate anions with triflic anhydride [$(CF_3SO_2)_2O$, Tf_2O].[26,27] The known nucleophilicity of the acyl oxygen atom in neutral[28,29] and anionic[2] transition-metal acyl complexes suggested a similar route to cationic and neutral organometallic vinylidene complexes. This paper presents the results of our synthetic and spectroscopic studies, together with some characteristic reaction chemistry. A preliminary account of some of these results has already appeared,[30a] and further reaction chemistry of cationic vinylidene complexes of Fe is presented in the following paper.[30b]

Results and Discussion

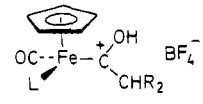
Synthesis and Spectroscopic Characterization of Vinylidene Complexes. In a preliminary communication[30a] we reported IR and ^1H NMR observations of the reactions of the acyl complexes **1a–c** with Tf_2O in either CH_2Cl_2 or $CDCl_3$ solution. The spectroscopic evidence clearly indicated the clean, quantitative and rapid formation of the cationic carbene complexes **2**, followed by a relatively slow, spontaneous elimination of the elements of triflic acid to produce the vinylidene complexes **3**. Analogous observations have since been made by using the tricyclohexylphosphine complex **1d**. It is not known whether the elimination of HOTf from **2** occurs by sequential loss of H^+, to give the vinyl triflates **4**, followed by loss of triflate anion to give the final product, or whether a concerted elimination occurs. Generation of **3b** by this route in $CDCl_3$ solution allowed a $^{13}C\{^1H\}$ NMR spectrum of this complex to be recorded. The α-vinylidene carbon resonance was observed as a doublet at δ 372.38 (J_{P-C} = 29.3 Hz), corresponding well with the reported chemical

Scheme II



shifts of δ 363.0 (t, J_{P-C} = 33.3 Hz) and δ 358.9 (t, J_{P-C} = 24 Hz) for the corresponding α-carbon resonances in $[Fe(\eta\text{-}C_5H_5)(dppe)(C{=}CMe_2)]^+$ [15] and $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2(C{=}CHPh)]^+$ [20], respectively.

While the methodology outlined in Scheme I allowed the characterization of the vinylidene complexes **3** (X = $CF_3SO_3^-$) as stable solution species, it proved impossible to obtain crystalline materials upon evaporation of solutions of these triflate salts; only oily solids were obtained. However, a modification of the reaction procedure did allow for the isolation of clean tetrafluoroborate salts **3** (X = BF_4^-). Addition of excess $HBF_4{\cdot}Et_2O$ to diethyl ether solutions of the acyl precursors **1** caused immediate precipitation of oils, which are presumably the hydroxycarbene complexes **5**;[28] subsequent addition of triflic an-



5.

hydride to these reaction mixtures effected slow dissolution of the oils and subsequent precipitation of the vinylidene complexes **3a–d** (X = BF_4^-) as microcrystalline solids. These compounds were spectroscopically identical with those previously characterized in solution, except for the presence of strong IR bands at 1050–1100 cm^{-1} and ^{19}F NMR singlet resonances at ca. δ 154 (upfield from internal $CFCl_3$), characteristic of the BF_4^- anion.[31] No ^{19}F NMR resonances at δ 78 due to the $CF_3SO_3^-$ anion were observed.[32]

A low-temperature ^1H NMR study of complex **3a** failed to freeze out rotation of the dimethylvinylidene ligand around the Fe–C bond axis at −100 °C, the lowest temperature which could be reached before freezing of the solution or crystallization of the solute occurred. Theoretical calculations[33] indicate that the ground state of the cationic vinylidene complexes **3** should be as depicted in Scheme I, with nonequivalent R substituents. The observation of a single sharp methyl resonance for **3a** at −100 °C can only mean that rotation is fast even at this tem-

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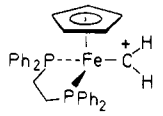
(32) A ^{19}F NMR spectrum of $HBF_4{\cdot}Et_2O$ exhibited a singlet resonance at δ 153.1 upfield from $CFCl_3$; that of $(CF_3SO_2)_2O$ gave a singlet peak at δ 78.8.
(33) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585–590. The solid-state structure of the isoelectronic complex $[Mn(\eta\text{-}C_5H_5)(CO)_2(C{=}CHPh)]$ also defines this as the ground-state conformation of the vinylidene ligand.[8]

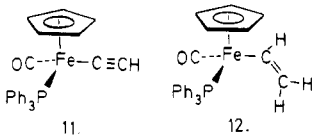
perature, in accord with the predictions of theory.[33] An upper limit to the free energy of activation for vinylidene rotation of between 8 and 9 kcal·mol^{-1} can be calculated.[34] In comparison, $\Delta G^{\ddagger}$ for methylene rotation in cation **6** has been observed to be 10.4 ± 0.1 kcal·mol^{-1}.[35,36]



6.

Modification of the synthetic methodology already outlined provided a useful new route to a neutral vinylidene complex as shown in Scheme II. An ether suspension of the anionic manganese acyl **7**[37] reacted with triflic anhydride to give an orange solution of a compound presumed to have structure **8**, on the basis of two strong IR bands at 1960 and 1897 cm^{-1} characteristic of alkoxycarbene complexes of manganese.[37] This compound was too unstable to be isolated but reacted in situ with the non-nucleophilic base 1,8-bis(dimethylamino)naphthalene[40] to eliminate CF_3SO_3H and produce as the final product the μ-vinylidene complex **10**, presumably via the intermediacy of the mononuclear complex **9**. The facile thermal conversion of terminal vinylidene complexes of manganese to the corresponding μ-vinylidene compounds has already been documented.[9,11] Complex **10** produced in this manner was spectroscopically identical (IR, ^{1}H NMR) with that reported in the literature.[11]

Deprotonation and Reduction of [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$)(C=CH$_2$)]$^+$BF$_4^-$. The unsubstituted vinylidene ligand of complex **3b** was readily deprotonated by treatment with a solution of *t*-BuOK in *t*-BuOH to afford good yields of the previously unknown alkynyl complex **11**.[41] This compound exhibited a medium intensity IR



11. 12.

band at 1933 cm^{-1} ($\nu_{C\equiv C}$) and a doublet resonance in the ^{1}H NMR spectrum at δ 2.35 (J_{P-H} = 2.7 Hz); these data are entirely compatible with those reported for the closely related compound [Fe(η-C$_5$H$_5$)(dppe)(C≡CH)].[15] A similar deprotonation of [Ru(η-C$_5$H$_5$)(PPh$_3$)$_2$(C=CHPh)]$^+$ to afford the corresponding alkynylruthenium complex has been reported.[20] In our particular system the overall conversion of the acyl complex **1b** to **11** represents the net dehydration of a ketone.

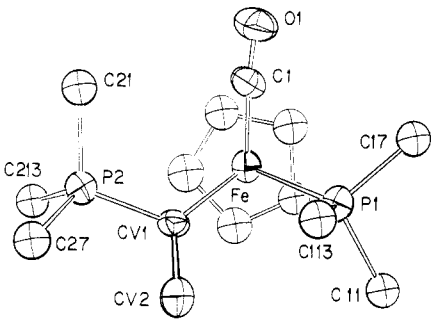
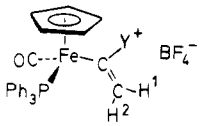


Figure 2. View of the structure of the cation [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(PPh$_3$)=CH$_2$}]$^+$ with numbering scheme.

Treatment of **2b** with $NaBH_4$ in CH_2Cl_2 solution at −78 °C afforded the known vinyl complex **12**[42] resulting from hydride addition to the cationic α-carbon atom.[43] Notably the related cationic compound [Fe(η-C$_5$H$_5$)(dppe)(C=CMe$_2$)]$^+$ is reported to be reactive toward BH_4^-[44] although cleaner reduction to give the corresponding substituted vinyl derivative was achieved by using $BH(OMe)_3^-$.[44,45]

Thermal Decomposition of [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$)(C=CH$_2$)]$^+$BF$_4^-$ and Formation of Tertiary Phosphine and Pyridine Adducts. Gentle warming (40 °C) of CH_2Cl_2 solutions of **3b** led to partial decomposition and formation of the vinylphosphonium compound **13**; the



13. Y = PPh$_3$
14. Y = PMe$_2$Ph
15. Y = N⬡
16. Y = N⬡-Me

molecular structure of this complex was verified by an X-ray crystallographic investigation described below. Analogous adducts **14–16** were prepared in high yields by the reaction of **3b** with the appropriate donor molecule. Notably the ^{1}H NMR spectra of the adducts **13** and **14** exhibited vinylic proton signals, coupled to a single phosphorus center, with coupling constants very similar to those reported for the vinylphosphonium derivative (Ph$_3$PCD=CH$_2$)$^+$Br$^-$.[46] Clearly, compound **3b** is thermally labile in solution and decomposes to release PPh_3 which is trapped by the carbonium ion center of a further molecule of **3b**. The observed reactions of PMe_2Ph, pyridine, and 4-methylpyridine add credence to this hypothesis. Reactions of **3b** with other amines are described separately.[30b]

A compound [Fe(η-C$_5$H$_5$)(CO)$_2${C(PPh$_3$)=CHPh}]$^+$BF$_4^-$, analogous to **13**, has been synthesized by the low-temperature protonation of [Fe(η-C$_5$H$_5$)(CO)$_2$(C≡CPh)] in the presence of PPh_3.[47] The authors proposed that an intermediate vinylidene compound [Fe(η-C$_5$H$_5$)(CO)$_2$(C=CHPh)]$^+$ was formed and was trapped with PPh_3 at the α-carbon atom; our results clearly substantiate this proposal.

(34) For the coalescence formula used see: Anet, F. A. L.; Brown, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760. The coalescence temperature was assumed to be 173 K, the separation of methyl resonances at the slow exchange limit was assumed to be 53 Hz (the methyl resonance separation in the acyl complex **1a**) and the frequency factor *A* was taken as 10^{12} (see ref 35).

(35) Brookhart, M.; Tucker, J.; Flood, T. C.; Jensen, T. *J. Am. Chem. Soc.* **1980**, *102*, 1203–1205.

(36) Theory predicts a lower $\Delta G^{\ddagger}$ for vinylidene rotation than for methylene rotation in analogous systems.[33]

(37) Fischer, E. O. *Chem. Ber.* **1967**, *100*, 2445–2456.

(38) The alternative formulation of **8** as the triflate salt of the cationic carbyne complex [Mn(η-C$_5$H$_5$)(CO)$_2$(CMe)]$^+$ was discounted due to its solubility in Et$_2$O and the absence of ν_{CO} bands above 2000 cm^{-1} which are characteristic of cationic carbyne complexes of this type.[39]

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(41) This deprotonation can also be carried out cleanly by using Me$_3$N.[30b]

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(43) This reduction cannot be carried out in THF solution since **2b** reacts with this solvent.[30b]

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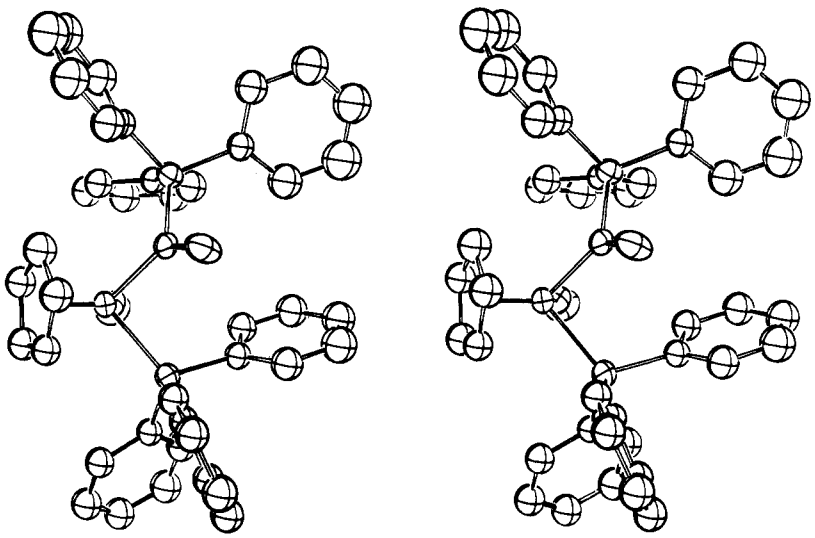

Figure 3. Stereoview of the structure of the cation $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3)=CH_2\}]^+$.

Molecular Structure of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3)=CH_2\}]^+BF_4^-$ (13). Final positional parameters appear in Table I, and final anisotropic thermal parameters are listed in Table II. Interatomic distances and their estimated standard deviations (esd's) are shown in Table III, and interatomic angles are presented in Table IV. The labeling scheme and stereoviews of the cation $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3)=CH_2\}]^+$ are shown in Figures 2 and 3, respectively.

The structure of the cation $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3)=CH_2\}]^+$ is similar in most respects to that determined by Kolobova et al. for $[Fe(\eta\text{-}C_5H_5)(CO)_2\{C(PPh_3)=CHPh\}]^+$ [47] and differs significantly only in the absence of the 2-vinylphenyl group and the replacement of one of the CO ligands by PPh_3. These differences do not result in any major changes in the molecular framework. In both structures the vinyl group is exclusively σ bonded; for the present structure, Fe–CV(1) = 2.014 (7) and Fe···CV(2) = 2.992 (8) Å. Neither structure reveals clear indication for localization of positive charge at a site other than the phosphonium phosphorus atom. In both structures the average P–C distance in the phosphonium group is 1.800 (8) Å, a value similar to that found in simpler phosphonium salts (e.g., $[Ph_3PCH_2Ph]^+Cl^-$, P–C(av) = 1.790 Å)[48] and 0.04 Å shorter than normally found in tertiary phosphines.[49]

Experimental Section

General Remarks. Infrared spectra were recorded on a Perkin-Elmer 257 instrument and calibrated against the 1601-cm^{-1} band of polystyrene. ^1H NMR (59.75 MHz), ^{13}C NMR (15.00 MHz) and ^{19}F NMR (56.20 MHz) spectra were recorded on a JEOL FX-60Q Fourier Transform spectrometer. Certain ^1H NMR spectra (270 MHz) were recorded on a Brüker HX-270 instrument at the NSF-NMR Regional Facility at Yale University. All NMR spectra were run in $CDCl_3$ solution. Cation mass spectra of organometallic salts were obtained by field desorption or fast atom bombardment techniques at the Middle Atlantic Mass Spectrometry Regional Facility at Johns Hopkins University School of Medicine. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI, or Atlantic Microlab, Inc., Atlanta, GA.

Reaction solvents were distilled from sodium benzophenone ketyl, except for CH_2Cl_2 and $CDCl_3$ which were distilled from P_4O_{10}. All reactions were performed under an atmosphere of dry nitrogen.

Trifluoromethanesulfonic anhydride (Tf_2O) were prepared by the method of Stang and Duebner.[50] $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)CHMe_2\}]$ (**1a**), $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ (**1b**), $[Fe(\eta\text{-}C_5H_5)(CO)(PMe_2Ph)\{C(O)Me\}]$ (**1c**), and $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}\{C(O)Me\}]$ (**1d**) were prepared by literature procedures.[51]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C=CMe_2)]^+BF_4^-$ (3a). To a stirring solution of **1a** (0.10 g, 0.21 mmol) in Et_2O (25 mL) was added $HBF_4\cdot Et_2O$ (Aldrich, 0.06 mL, 0.53 mmol) in a dropwise fashion. A yellow oil precipitated. Dropwise addition of Tf_2O (0.10 mL, 0.62 mmol) caused the oil to slowly redissolve and a peach-colored solid to precipitate. After the solution was stirred (3 h, 20 °C), the solid was allowed to settle and the supernatant liquid was removed by using a cannula. The solid was washed with Et_2O (2 × 20 mL), the washings being removed by cannula, and dried under vacuum to give pure product: 0.104 g 90%; mp 135–136 °C dec; IR (Nujol) ν_{CO} 2030 (vs), $\nu_{C=C}$ 1621 (m), $\nu_{BF_4^-}$ 1030–1100 (vs) cm^{-1}; ^1H NMR δ 5.30 (d, J_{PH} = 1.2 Hz, C_5H_5), 7.50 (m, PPh_3), 1.66 (s, CMe_2); ^{19}F NMR δ 153.3 (s, BF_4^-). Anal. C, H. The ^1H NMR spectrum of **3a** was invariant down to −100 °C in a 1:1 $CDCl_3/Tf_2O$ solution.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C=CH_2)]^+BF_4^-$ (3b) was prepared similarly from **1b** (0.10 g, 0.22 mmol), $HBF_4\cdot Et_2O$ (0.07 mL, 0.55 mmol), and Tf_2O (0.11 mL, 0.66 mmol) in Et_2O (25 mL), as a yellow-gold solid: 0.10 g, 90%; mp 154–155 °C dec; IR (Nujol) ν_{CO} 2035 (vs), $\nu_{C=C}$ 1630 (m), $\nu_{BF_4^-}$ 1035–1110 (vs) cm^{-1}; ^1H NMR δ 5.25 (d, J_{PH} = 2.0 Hz, C_5H_5), 7.50 (m, PPh_3), 5.30 (s, CH_2); ^{19}F NMR δ 149.5 (BF_4^-); ^{13}C NMR δ 92.03 (C_5H_5), 107.14 ($C=CH_2$), 128–134 (Ph), 209.40 (d, J_{PC} = 26.9 Hz, CO), 372.38 (d, J_{PC} = 29.3 Hz, $C=CH_2$). Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PMe_2Ph)(C=CH_2)]^+BF_4^-$ (3c) was prepared similarly from **1c** (0.10 g, 0.30 mmol), $HBF_4\cdot Et_2O$ (0.10 mL, 0.75 mmol), and Tf_2O (0.15 mL, 0.90 mmol) in Et_2O (25 mL), as a lime-green solid: 0.09 g, 70%; mp 130–134 °C dec; IR (Nujol) ν_{CO} 2030 (vs), $\nu_{C=C}$ 1633 (m), $\nu_{BF_4^-}$ 1030–1100 (vs) cm^{-1}; ^1H NMR δ 5.20 (d, J_{PH} = 2.0 Hz, C_5H_5), 7.40 (m, Ph), 2.08 (d, J_{PH} = 11.0 Hz, P-Me), 1.98 (d, J_{PH} = 11.0 Hz, P-Me), 5.41 (s, CH_2); ^{19}F NMR δ 154.0 (BF_4^-). Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C=CH_2)]^+BF_4^-$ (3d) was prepared similarly from **1d** (0.10 g, 0.18 mmol), $HBF_4\cdot Et_2O$ (0.06 mL, 0.45 mmol), and Tf_2O (0.09 mL, 0.54 mmol) in Et_2O (30 mL), as a lime-green solid: 0.09 g, 88%; mp 170 °C dec; IR (Nujol) ν_{CO} 2020 (vs), $\nu_{C=C}$ 1629 (m), $\nu_{BF_4^-}$ 1020–1110 (vs) cm^{-1}; ^1H NMR δ 5.46 (d, J_{PH} = 2.0 Hz, C_5H_5), 1.50 (m, C_6H_{11}), 5.36 (s, CH_2); ^{19}F NMR δ 153.5 (BF_4^-). Anal. C, H.

$[Mn_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}C=CH_2)]$ (10). A suspension of Li$[Mn(\eta\text{-}C_5H_5)(CO)_2\{C(O)Me\}]$[37] (3.16 g, 14 mmol) in Et_2O (50 mL) was cooled to −78 °C, and Tf_2O (3.70 mL, 21 mmol) was added dropwise. The resultant mixture was warmed to 20 °C to afford

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Table I. Positional Parameters (and Esd's) for $Fe(CP)(CO)PPh_3\{C(PPh_3)=CH_2\}^2$

atom	x	y	z	B, Å²
Fe	0.763 92 (11)	0.289 23 (10)	0.315 49 (6)	
P1	0.869 56 (21)	0.192 73 (19)	0.391 76 (11)	
P2	0.705 02 (20)	0.118 92 (20)	0.145 91 (11)	
C1	0.598 27 (91)	0.191 22 (78)	0.325 68 (41)	
O1	0.490 49 (64)	0.139 14 (59)	0.340 05 (31)	
Cp1	0.725 08 (94)	0.455 60 (77)	0.377 33 (46)	
Cp2	0.654 97 (89)	0.434 74 (76)	0.306 54 (52)	
Cp3	0.758 4 (10)	0.435 98 (72)	0.258 59 (42)	
Cp4	0.896 24 (90)	0.460 29 (74)	0.299 36 (56)	
Cp5	0.874 22 (89)	0.470 81 (72)	0.371 66 (46)	
CV1	0.821 90 (74)	0.184 35 (69)	0.229 84 (37)	
CV2	0.954 92 (88)	0.170 43 (84)	0.221 29 (41)	
C11	1.063 46 (74)	0.255 23 (70)	0.427 99 (39)	2.86 (15)
C12	1.157 20 (77)	0.327 17 (72)	0.391 61 (40)	3.25 (16)
C13	1.305 78 (82)	0.363 19 (78)	0.415 76 (43)	3.76 (17)
C14	1.356 15 (85)	0.325 77 (80)	0.476 47 (45)	4.05 (18)
C15	1.264 54 (84)	0.268 27 (78)	0.513 79 (44)	3.85 (17)
C16	1.116 26 (81)	0.220 99 (76)	0.490 42 (42)	3.57 (17)
C17	0.786 30 (76)	0.189 31 (71)	0.474 79 (39)	3.01 (15)
C18	0.786 70 (83)	0.304 60 (78)	0.520 53 (43)	3.73 (17)
C19	0.728 04 (87)	0.305 80 (83)	0.585 77 (46)	4.39 (19)
C110	0.666 85 (91)	0.196 68 (88)	0.605 54 (48)	4.60 (19)
C111	0.663 66 (93)	0.081 98 (91)	0.562 57 (50)	5.07 (20)
C112	0.724 75 (89)	0.079 39 (84)	0.497 32 (47)	4.42 (19)
C113	0.860 91 (77)	0.025 00 (72)	0.356 86 (39)	3.05 (15)
C114	0.726 64 (84)	−0.057 12 (80)	0.330 01 (44)	3.93 (17)
C115	0.715 76 (92)	−0.184 31 (87)	0.301 10 (48)	4.63 (19)
C116	0.841 0 (10)	−0.225 74 (91)	0.296 99 (50)	5.08 (20)
C117	0.974 4 (10)	−0.147 68 (94)	0.321 07 (52)	5.34 (21)
C118	0.985 94 (86)	−0.019 96 (82)	0.351 31 (45)	4.27 (19)
C21	0.519 04 (77)	0.065 68 (74)	0.159 67 (48)	3.18 (16)
C22	0.461 18 (93)	−0.058 88 (88)	0.162 13 (48)	4.76 (20)
C23	0.316 6 (11)	−0.093 6 (10)	0.179 39 (55)	6.11 (24)
C24	0.240 1 (10)	−0.004 0 (10)	0.193 49 (52)	5.47 (22)
C25	0.296 1 (10)	0.118 55 (92)	0.191 58 (50)	5.11 (20)
C26	0.437 47 (85)	0.155 46 (80)	0.174 41 (43)	3.98 (18)
C27	0.762 41 (77)	−0.013 22 (74)	0.095 87 (41)	3.25 (16)
C28	0.794 14 (95)	−0.104 29 (92)	0.131 35 (50)	4.95 (20)
C29	0.840 0 (11)	−0.208 0 (10)	0.094 30 (59)	6.55 (25)
C210	0.853 7 (10)	−0.214 9 (10)	0.023 49 (55)	5.92 (23)
C211	0.829 3 (10)	−0.125 43 (94)	−0.011 98 (52)	5.40 (21)
C212	0.780 39 (87)	−0.022 10 (83)	0.023 86 (46)	4.22 (18)
C213	0.714 78 (80)	0.235 11 (74)	0.089 82 (40)	3.33 (16)
C214	0.596 73 (93)	0.233 17 (88)	0.040 29 (40)	4.83 (20)
C215	0.609 7 (11)	0.322 7 (10)	−0.004 56 (55)	5.99 (23)
C216	0.735 9 (11)	0.410 8 (10)	−0.000 16 (57)	6.26 (24)
C217	0.852 5 (10)	0.414 71 (94)	0.048 33 (52)	5.44 (21)
C218	0.842 00 (88)	0.325 90 (83)	0.092 50 (46)	4.38 (19)
F1	0.382 7 (14)	0.604 9 (12)	0.206 45 (81)	
F2	0.282 5 (10)	0.456 3 (10)	0.258 34 (42)	
F3	0.202 8 (16)	0.435 3 (14)	0.149 54 (67)	
F4	0.180 9 (14)	0.574 2 (12)	0.202 87 (94)	
F5	0.384 1 (21)	0.451 1 (21)	0.163 6 (10)	
B	0.285 64 (0)	0.510 89 (0)	0.191 22 (0)	7.64 (62)
HCV21	1.029 78 (0)	0.200 00 (0)	0.260 52 (0)	6.0000 (0)
HCV22	0.975 32 (0)	0.130 90 (0)	0.175 93 (0)	6.0000 (0)
HCp1	0.680 28 (0)	0.458 76 (0)	0.420 47 (0)	6.0000 (0)
HCp2	0.553 61 (0)	0.421 95 (0)	0.293 74 (0)	6.0000 (0)
HCp3	0.740 02 (0)	0.422 88 (0)	0.207 58 (0)	6.0000 (0)
HCp4	0.986 97 (0)	0.467 98 (0)	0.280 74 (0)	6.0000 (0)
HCp5	0.948 08 (0)	0.485 85 (0)	0.410 91 (0)	6.0000 (0)
HC12	1.121 26 (0)	0.352 77 (0)	0.349 79 (0)	6.0000 (0)
HC13	1.370 94 (0)	0.412 88 (0)	0.390 50 (0)	6.0000 (0)
HC14	1.457 15 (0)	0.347 91 (0)	0.492 31 (0)	6.0000 (0)
HC15	1.301 16 (0)	0.235 73 (0)	0.556 50 (0)	6.0000 (0)
HC16	1.052 06 (0)	0.172 82 (0)	0.516 78 (0)	6.0000 (0)
HC18	0.827 41 (0)	0.382 31 (0)	0.506 71 (0)	6.0000 (0)
HC19	0.731 29 (0)	0.384 18 (0)	0.616 47 (0)	6.0000 (0)
HC110	0.625 44 (0)	0.198 87 (0)	0.649 62 (0)	6.0000 (0)
HC111	0.620 60 (0)	0.005 33 (0)	0.576 89 (0)	6.0000 (0)
HC112	0.723 64 (0)	0.000 17 (0)	0.468 06 (0)	6.0000 (0)
HC114	0.641 27 (0)	−0.025 81 (0)	0.331 45 (0)	6.0000 (0)
HC115	0.623 97 (0)	−0.240 58 (0)	0.284 73 (0)	6.0000 (0)
HC116	0.834 86 (0)	−0.311 82 (0)	0.276 66 (0)	6.0000 (0)
HC117	1.059 16 (0)	−0.179 56 (0)	0.317 41 (0)	6.0000 (0)
HC118	1.078 29 (0)	0.035 14 (0)	0.367 81 (0)	6.0000 (0)
HC22	0.516 57 (0)	−0.120 52 (0)	0.152 49 (0)	6.0000 (0)

Table I (*Continued*)

atom	x	y	z	B, Å^2
HC23	0.274 19 (0)	−0.179 27 (0)	0.180 99 (0)	6.0000 (0)
HC24	0.143 86 (0)	−0.028 14 (0)	0.205 10 (0)	6.0000 (0)
HC25	0.239 90 (0)	0.179 37 (0)	0.201 85 (0)	6.0000 (0)
HC26	0.477 60 (0)	0.241 48 (0)	0.172 80 (0)	6.0000 (0)
HC28	0.785 07 (0)	−0.097 30 (0)	0.181 33 (0)	6.0000 (0)
HC29	0.860 90 (0)	−0.271 66 (0)	0.118 61 (0)	6.0000 (0)
HC210	0.881 71 (0)	−0.285 94 (0)	−0.002 05 (0)	6.0000 (0)
HC211	0.844 74 (0)	−0.131 31 (0)	−0.061 22 (0)	6.0000 (0)
HC212	0.760 12 (0)	0.040 63 (0)	−0.001 37 (0)	6.0000 (0)
HC214	0.508 45 (0)	0.171 54 (0)	0.037 15 (0)	6.0000 (0)
HC215	0.529 94 (0)	0.321 72 (0)	−0.038 16 (0)	6.0000 (0)
HC216	0.743 70 (0)	0.470 54 (0)	−0.031 10 (0)	6.0000 (0)
HC217	0.939 59 (0)	0.477 77 (0)	0.051 58 (0)	6.0000 (0)
HC218	0.923 46 (0)	0.327 34 (0)	0.125 16 (0)	6.0000 (0)

[a] Esd's are right-justified to the least significant figure of the parameter.

Table III. Selected Interatomic Distances (Å) with Esd's for $[Cp(CO)(PPh_3)FeC(PPh_3)=CH_2]^+BF_4^-$

(A) $[Cp(CO)(PPh_3)FeC(PPh_3)=CH_2]^+$

Fe-P (1)	2.237 (2)	P(1)-C(17)	1.819 (8)
Fe-C(1)	1.752 (9)	P(1)-C(113)	1.839 (8)
Fe-Cp(av)	2.112 (9)	P(2)-CV(1)	1.811 (7)
Fe-CV(1)	2.014 (7)	P(2)-C(21)	1.794 (8)
Fe···CV(2)	2.992 (8)	R(2)-C(27)	1.811 (8)
C(1)-O(1)	1.139 (11)	P(2)-C(213)	1.793 (8)
P(1)-C(11)	1.856 (8)	CV(1)-CV(2)	1.327 (11)

(B) BF_4^-

B-F(1)	1.206 (13)	B-F(4)	1.346 (14)
B-F(2)	1.498 (9)	B-F(5)	1.347 (21)
B-F(3)	1.156 (14)	B-F(av)	1.311 (14)

Table IV. Selected Interatomic Angles (Deg) with Esd's for $[Cp(CO)(PPh_3)FeC(PPh_3)=CH_2]^+BF_4^-$

(A) $[Cp(CO)(PPh_3)Fe\text{-}C(PPh_3)=CH_2]^+$

P(1)-Fe-CV(1)	91.6 (2)	Fe-CV(1)-P(2)	123.8 (4)
C(1)-Fe-CV(1)	100.9 (4)	Fe-CV(1)-CV(2)	125.9 (6)
P(1)-Fe-C(1)	87.4 (3)	P(2)-CV(1)-CV(2)	109.4 (6)
Fe-C(1)-O(1)	171.0 (8)		

(B) BF_4^-

F(1)-B-F(2)	104.2 (8)	F(2)-B-F(4)	97.6 (7)
F(1)-B-F(3)	151 (1)	F(2)-B-F(5)	95 (1)
F(1)-B-F(4)	94.1 (9)	F(3)-B-F(4)	88 (1)
F(1)-B-F(5)	86.7 (1)	F(3)-B-F(5)	85 (1)
F(2)-B-F(3)	103.8 (8)	F(4)-B-F(5)	167 (1)

an orange, homogeneous solution. This solution was recooled to −78 °C, a solution of 1,8-bis(dimethylamino)naphthalene (2.98 g, 14 mmol) in Et_2O (10 mL) was added dropwise, and the resultant mixture was warmed slowly to 20 °C. After being stirred for 1 h, the mixture was filtered by using filter aid to give a solid, characterized as the hydrotriflate salt of 1,8-bis(dimethylamino)naphthalene by IR comparison with an authentic sample prepared from the naphthalene derivative and HOTf. Ether was removed from the filtrate under vacuum, to afford a red-purple residue which was chromatographed on a 150 × 2 cm alumina (activity III)/hexane column. Hexane eluted $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ (0.85 g) and a 1:1 hexane/Et_2O mixture eluted a purple band, which upon removal of the solvent yielded **10** (1.11 g, 42%). The IR and ^1H NMR data for **10** corresponded exactly with those reported in the literature.[11]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$ (11). A suspension of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (0.350 g, 0.66 mmol) in *t*-BuOH (10 mL) was treated with a solution of $t\text{-}BuO^-K^+$ (0.230 g, 1.98 mmol) in *t*-BuOH (16 mL), and the resultant mixture was stirred for 0.5 h to give an orange solution. The solvent was removed under vacuum, and the residue was extracted with toluene (3 × 50 mL). The extracts were filtered and concentrated to ca. 20 mL under vacuum. Hexane (50 mL) was added, and the solution was set aside overnight at −20 °C to afford red-brown crystals of **11**: 0.19 g, 65%; mp 160 °C dec; IR (CCl_4) ν_{CO} 1957 (s), $\nu_{C=C}$ 1933 (m) cm^{-1}; ^1H NMR δ 7.40 (m, Ph), 4.38 (d, J_{PH} = 1.2 Hz, C_5H_5), 2.35 (d, J_{PH} = 2.7 Hz, C≡CH). Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(CH{=}CH_2)]$ (12). A solution of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (1.15 g, 2.2 mmol) in CH_2Cl_2 (25 mL) was cooled to −78 °C and solid $NaBH_4$ (0.50 g, 13.8 mmol) was added. The yellow slurry was stirred at −78 °C for 2 h and then allowed to warm to 20 °C, at which point gas evolution was observed and the solution became yellow-orange. The solvent was removed under vacuum, and the residue was extracted with benzene (20 mL) and filtered. The filtrate was reduced in volume to ca. 5 mL and applied to a 40 × 3 cm silica gel/hexane column. Hexane produced a yellow eluate, which was concentrated to ca. 15 mL and cooled to −50 °C to afford **12** as a yellow solid (0.38 g, 40%). The IR and ^1H NMR spectra of **12** were identical with those reported in the literature.[42]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3){=}CH_2\}]^+BF_4^-$ (13). A solution of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (1.15 g, 2.2 mmol) in CH_2Cl_2 (50 mL) was refluxed for 24 h, cooled, and filtered. The resultant orange solution was reduced in volume to ca. 5 mL and applied to a 50 × 6 cm deactivated silica gel/Et_2O column. Elution with Et_2O produced traces of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$, and subsequent elution with CH_2Cl_2 developed a bright orange band, which afforded a dark orange residue on evaporation. Recrystallization from CH_2Cl_2/Et_2O gave **13** as large, bright orange crystals: 0.34 g, 40%; mp 174 °C dec; IR (CH_2Cl_2) ν_{CO} 1937 (s) cm^{-1}; ^1H NMR (numbering shown in text) δ 7.40 (m, Ph), 4.33 (d, J_{PH} = 1.2 Hz, C_5H_5), 6.47 (d, J_{PH} = 23.0 Hz, H^1), 6.63 (d, J_{PH} = 45.8 Hz, H^2); ^{13}C NMR δ 125–135 (Ph), 84.70 (C_5H_5), 120.18 ($C{=}CH_2$), 158.00 ($C{=}CH_2$), 215.60 (CO); mass spectrum (field desorption) *m/e* 671 $[Fe(\eta\text{-}C_5H_5)(PPh_3)\{C(PPh_3){=}CH_2\}]^+$. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(PMe_2Ph){=}CH_2\}]^+BF_4^-$ (14). A solution of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (1.15 g, 2.2 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C, and PMe_2Ph (0.31 mL, 2.2 mmol) was added. The resultant red-orange solution was warmed to 20 °C and treated with Et_2O (100 mL) to precipitate an orange solid. The supernatant liquid was decanted off, and the solid was washed with Et_2O (2 × 20 mL). The product was purified by chromatography on a deactivated silica gel column, eluting with CH_2Cl_2, followed by recrystallization from CH_2Cl_2/Et_2O to give **14** as red orange crystals: 1.12 g, 80%; mp 165 °C dec; IR (CH_2Cl_2) ν_{CO} 1937 (s) cm^{-1}; ^1H NMR δ 7.40 (m, Ph), 4.38 (d, J_{PH} = 1.2 Hz, C_5H_5), 6.27 (d, J_{PH} = 23.2 Hz, H^1), 6.47 (d, J_{PH} = 53.0 Hz, H^2), 1.83 (d, J_{PH} = 11.0 Hz, PMe), 1.79 (d, J_{PH} = 11.0 Hz, PMe); ^{13}C NMR δ 125–135 (Ph), 85.10 (C_5H_5), 121.00 ($C{=}CH_2$), 150.80 ($C{=}CH_2$), 200.85 (CO), 10.17 (PMe), 9.53 (PMe). Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NC_5H_5){=}CH_2\}]^+BF_4^-$ (15). Pyridine (15 mL) was added to $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ (1.15 g, 2.2 mmol), and the resultant dark orange solution was stirred for 3 h. Excess pyridine was removed under vacuum, and the residue was chromatographed on deactivated silica gel. A 1/1 mixture of $CH_2Cl_2/(CH_3)_2CO$ eluted an orange band. Removal of the solvents under vacuum and recrystallization of the residue twice from CH_2Cl_2/Et_2O afforded **15** as orange crystals: 1.04 g, 79%; mp 165 °C dec; IR (CH_2Cl_2) ν_{CO} 1937 (s)

Table V. Crystal and Refinement Data

formula	$FeP_2F_4OC_{45}BH_{37}$
fw	798.40
space group	C_i^1–$P\bar{1}$
a, Å	9.517 (4)
b, Å	11.038 (3)
c, Å	18.965 (4)
α, deg	99.81 (2)
β, deg	94.41 (3)
γ, deg	102.54 (3)
V, Å^3	1902.9
Z	2
ρ(obsd), ρ(calcd)[a]	1.37, 1.39 g·cm^{-3}
temp.	23 °C
crystal dimension	0.26 × 0.30 × 0.35 mm
radiation	graphite-monochromated Mo $K\bar{\alpha}$ (λ = 0.710 73 Å)
diffractometer	Syntex $P2_1$
abs coeff, cm^{-1}	μ = 5.5
scan speed	3.0° in 2θ/min (fixed)
scan range, deg	3.0 < 2θ < 42
scan technique	θ–2θ
data collected	$h,\pm k,\pm l$
scan width, deg	[2θ (Mo K$\bar{\alpha}_1$) − 0.9] to [2θ(Mo K$\bar{\alpha}_2$) + 0.9]
ignorance factor	0.02
unique data	4107 rflns (4426 collected)
unique data with $(F_o)^2 > 3\sigma(F_o)^2$	3269

[a] By flotation, CH_2I_2/cyclohexane.

cm^{-1}; ^{1}H NMR δ 7.50 (m, Ph, meta and para protons of C_5H_5N), 4.79 (d, J_{PH} = 1.3 Hz, C_5H_5), 5.50 (m, br, CH_2), 8.20 (m, ortho protons of C_5H_5N); ^{13}C NMR δ 130–133 (Ph), 87.9 (C_5H_5), 125.0 (C=*C*H$_2$), 162.0 (d, J_{PC} = 19.0, *C*=CH$_2$), 210.0 (CO), 127.5, 135.0, 141.0 (C_5H_5N). Anal. C, H, N (the molecules crystallize with 0.25 molecules CH_2Cl_2 of crystallization).

[Fe(η-C_5H_5)(CO)(PPh$_3$){C(4-MeC_5H_4N)=CH$_2$}]$^+$BF$_4^-$ (16) was prepared similarly from [Fe(η-C_5H_5)(CO)(PPh$_3$)(C=CH$_2$)]$^+$BF$_4^-$ (1.15 g, 2.2 mmol) and 4-methylpyridine (10 mL), as orange crystals: 1.11 g, 82%; mp 104 °C dec; IR (CH_2Cl_2) ν_{CO} 1937 (s) cm^{-1}; ^{1}H NMR δ 7.50 (m, Ph, meta protons of 4-MeC_5H_4N), 4.73 (d, J_{PH} = 1.3 Hz, C_5H_5), 5.43 (m, br, CH_2), 8.00 (m, ortho protons of 4-MeC_5H_4N), 2.48 (s, Me); ^{13}C NMR δ 132–134 (Ph), 85.5 (C_5H_5), 131.2 (d, J_{PC} = 4.0 Hz, C=*C*H$_2$), 155.1 (d, J_{PC} = 19.0 Hz, *C*=CH$_2$), 21.6, 127.6, 139.4, 141.0 (4-MeC_5H_4N). Anal. C, H, N (the molecules contain 0.75 molecules CH_2Cl_2 of crystallization).

X-ray Diffraction Measurements. Collection and Reduction. Specific details concerning crystal characteristics and X-ray diffraction methodology are shown in Table V. The crystal selected for study was an irregularly shaped fragment cleaved from a larger crystal and mounted on a glass fiber with "Crazy Glue". The crystal was centered on the diffractometer using 25 Friedel-related reflections with 20° < 2θ < 30°, and the cell dimensions were refined on these reflections to give the values shown in Table V.

Data were placed on an approximately absolute scale via a Wilson plot which provided the average overall thermal parameter ($\bar{B}$ = 2.95 Å^2).

Intensity data were collected and corrected for *Lp* effects and absorption as previously described.[52] The intensities of three reflections located along the reciprocal lattice axes were measured every 97 reflections to check crystal stability and alignment. No decay correction was required. Diffractometer examination of the reciprocal lattice revealed no systematic absences.

Solution and Refinement of the Structure. The structure was solved by the SHELEX direct methods routine and the heavy atoms located from the *E* map based on the phase solution of highest internal consistency. The remaining nonhydrogen atoms with the exception of the boron atom were located from a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. All nonhydrogen atoms with the exceptions of the phenyl carbon atoms and the boron atom were refined with anisotropic thermal parameters.[53] Neutral atom scattering factors were used, and anomalous dispersion corrections were applied to all nonhydrogen atoms.[54]

Full-matrix least-squares refinement for all nonhydrogen atoms, except boron, of the scale factor and positional and thermal parameters led to convergence with R = 12.5% and R_w = 14.3%. A difference-Fourier map at this stage of refinement revealed a peak in the vicinity of the anion which was located in a position inconsistent with its identity being the still unlocated boron atom and more consistent with its being a "fifth" fluorine atom. Further refinement of all "five" fluorine atoms with variable occupancy led to the postulation of a model for the apparent disorder in the anion: two BF$_4^-$ tetrahedra are oriented with parallel, shared interpenetrating bases and eclipsed vertices. Incorporation of this model in which the shared fluorine atoms, F(1)–F(3), were refined at unit occupancy, the apical fluorines, F(4) and F(5), at half occupancy, and the boron atom in an idealized, centered and fixed position (see Figure 4) lowered the discrepancy indices to R = 8.0% and R_w = 8.3%. The final refinement cycles included all hydrogen atoms at calculated positions with the C–H bond lengths fixed at 0.95 Å, the H–CV(1)–H bond angle fixed at 120°, and B = 6.0 Å^2.[55] At convergence, R = 7.4%, R_w = 7.6%, and GOF = 2.157. A final difference map showed a general background of approximately 0.2 e/Å^3 and a peak (0.84 e/Å^3) associated with the anion, and the residual $\sum w(|F_o| - |F_c|)^2$ showed no significant variation against $|F_o|$, (sin θ)/λ, or identity or parity of index or sequence number.

Acknowledgment. R.P.H. is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Alfred P. Sloan Foundation for support of this research. The assistance of the Middle Atlantic Mass Spectrometry Facility at Johns Hopkins University School of Medicine and the Northeast NSF Regional NMR Facility at Yale University, supported by Grant CHE 7916210 from the Chemistry Division, is also gratefully acknowledged. We also thank J. Zubieta for assistance in obtaining the SHELX structure solution.

Registry No. 1a, 32661-71-5; **1b**, 12101-02-9; **1c**, 32993-87-6; **1d**, 32610-55-2; **3a**, 80642-54-2; **3b**, 80642-55-3; **3c**, 80642-56-4; **3d**, 80642-58-6; **10**, 71616-07-4; **11**, 80642-59-7; **12**, 79292-33-4; **13**, 80658-43-1; **14**, 80642-61-1; **15**, 80642-63-3; **16**, 80642-65-5; Li[Mn(η-C_5H_5)(CO)$_2$\{C(O)Me\}], 12082-24-5.

Supplementary Material Available: Observed and calculated structure factor tables, Table II, anisotropic thermal parameters, a full list of bond lengths, and Figure 4, the disordered BF$_4^-$ ion (35 pages). Ordering information is given on any current masthead page.

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