468 *Organometallics* **1996,** *15,* 468−471

Synthesis of a Zwitterionic P-Coordinated Complex with Bis(diphenylphosphino)acetylene

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Received June 29, 1995[⊗]

Summary: New cationic, $[(Fp)Ph_2PC{\equiv}CPPh_2(Fp)]^{2+}$ (**1**) *and* $[(Fp)Ph_2PC{\equiv}CPPh_2]^{+}$(**2**), *and anionic,* $[Fe_3(CO)_9(\mu_3\text{-}CCH_3)(Ph_2PC{\equiv}CPPh_2)]^{-}$ (**3**) *and* $[\{Fe_3(CO)_9(\mu_3\text{-}CCH_3)\}_2(Ph_2PC{\equiv}CPPh_2)]^{2-}$ (**4**), *P-coordinate complexes with bis(diphenylphosphino)acetylene have been prepared. The zwitterionic P-coordinated iron complex* $[\{Fe_3(CO)_9(\mu_3\text{-}CCH_3)\}Ph_2PC{\equiv}CPPh_2(Fp)]$ (**5**) *has been synthesized in two different ways and characterized by X-ray crystallography.*

The reactivity of phosphinoalkynes $Ph_2PC{\equiv}CR$ with polynuclear transition metal compounds has been studied extensively. The reaction through the phosphine and the alkyne function is usually observed,[1] but some P-coordinated complexes have been reported where the alkyne function is uncoordinated.[2] In a recent study,[3] we reported the synthesis of the cationic P-coordinated complexes $[(Fp)Ph_2PC{\equiv}CR]^{+}$ (Fp = $CpFe(CO)_2$), in which significant π(C≡C) bond polarization was postulated to be a consequence of the phosphorus atom charge. In an earlier paper,[4] we also reported the synthesis of the anionic P-coordinated complexes $[Fe_3(CO)_9(\mu_3\text{-}CCH_3)(Ph_2PC{\equiv}CR)]^{-}$. These results prompted an attempt to prepare a zwitterionic complex by means of the bis(diphenylphosphino)acetylene ($Ph_2PC{\equiv}CPPh_2$). To our knowledge, this diphosphine has been used to prepare symmetrical binuclear and polynuclear P-coordinated complexes,[5] but in no case did the groups bonded to phosphorus atoms have different charges, and the only related zwitterionic compounds reported are the phosphonioboratoalkynes $[Ph_2(CH_3)PC{\equiv}CBR_3]$[6] and the complex $[Br(CO)_4MnC{\equiv}CPPh_3]$.[7] Furthermore, the preparation of the ionic complexes $[(Fp)Ph_2PC{\equiv}CPPh_2]^{+}$ and $[Fe_3(CO)_9(\mu_3\text{-}CCH_3)(Ph_2PC{\equiv}CPPh_2)]^{-}$ seemed of interest due to their potential in synthesizing $Ph_2PC{\equiv}CPPh_2$ bridged mixed polynuclear compounds.

The reactions performed in the synthesis of the reported complexes are presented in Scheme 1. All prepared complexes were identified by the usual analytical and spectroscopic techniques. The cationic complexes $[(Fp)Ph_2PC{\equiv}CPPh_2(Fp)]^{2+}$ (**1**) and $[(Fp)Ph_2PC{\equiv}CPPh_2]^{+}$ (**2**) were prepared[3] by the simple expedient of oxidizing 1 or 0.5 mol of $[Fe_2(CO)_4Cp_2]$ with ferrocenium in the presence of the diphosphine. The symmetry and asymmetry around the C≡C bond in complexes **1** and **2** are shown clearly by the IR and ^{31}P NMR spectra of both complexes. The infrared spectrum of **2** shows one band assigned to ν(C≡C) at 2104 cm^{-1}, which is absent from complex **1**. The ^{31}P NMR spectrum of **2** shows a signal at 46.5 ppm that is assigned to the phosphorus atom coordinated to an iron atom,[3] and another signal at −27.3 ppm is assigned to the uncoordinated phosphorus atom. In contrast, only one signal assigned to the coordinated phosphorus atoms at 46.1 ppm is observed in the ^{31}P NMR spectrum of **1**.

The anionic complexes $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}CCH_3)(Ph_2PC{\equiv}CPPh_2)]$ (**3**) and $[PPh_4]_2[\{Fe_3(CO)_9(\mu_3\text{-}CCH_3)\}_2(Ph_2PC{\equiv}CPPh_2)]$ (**4**) were also prepared[4] by the simple method of adding 1 or 2 mol of the cluster $[HFe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]^{-}$ to 1 mol of the diphosphine. Like complexes **1** and **2**, the symmetry and asymmetry of complexes **3** and **4** are shown clearly by their IR and ^{31}P NMR spectra. In the IR spectra, the characteristic band assigned to ν(C≡C) is observed only in complex **3** (2124 cm^{-1}); in the ^{31}P NMR spectra, two signals (δ = −31.2, 43.9 ppm) and one signal (δ = 43.0 ppm) are observed for complexes **3** and **4**, respectively.

The zwitterionic complex $[\{Fe_3(CO)_9(\mu_3\text{-}CCH_3)\}Ph_2PC{\equiv}CPPh_2(Fp)]$ (**5**) was prepared in two different ways (Scheme 1): by reaction between the cationic complex **2** and the anionic cluster $[HFe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]^{-}$ or by reaction between the anionic complex **3** and $[Fe_2(CO)_4Cp_2]$ in the presence of ferrocenium cation. Spectroscopic methods show that the products obtained by either method are identical, and their formulations agree with the title complex **5**. However, the yields from

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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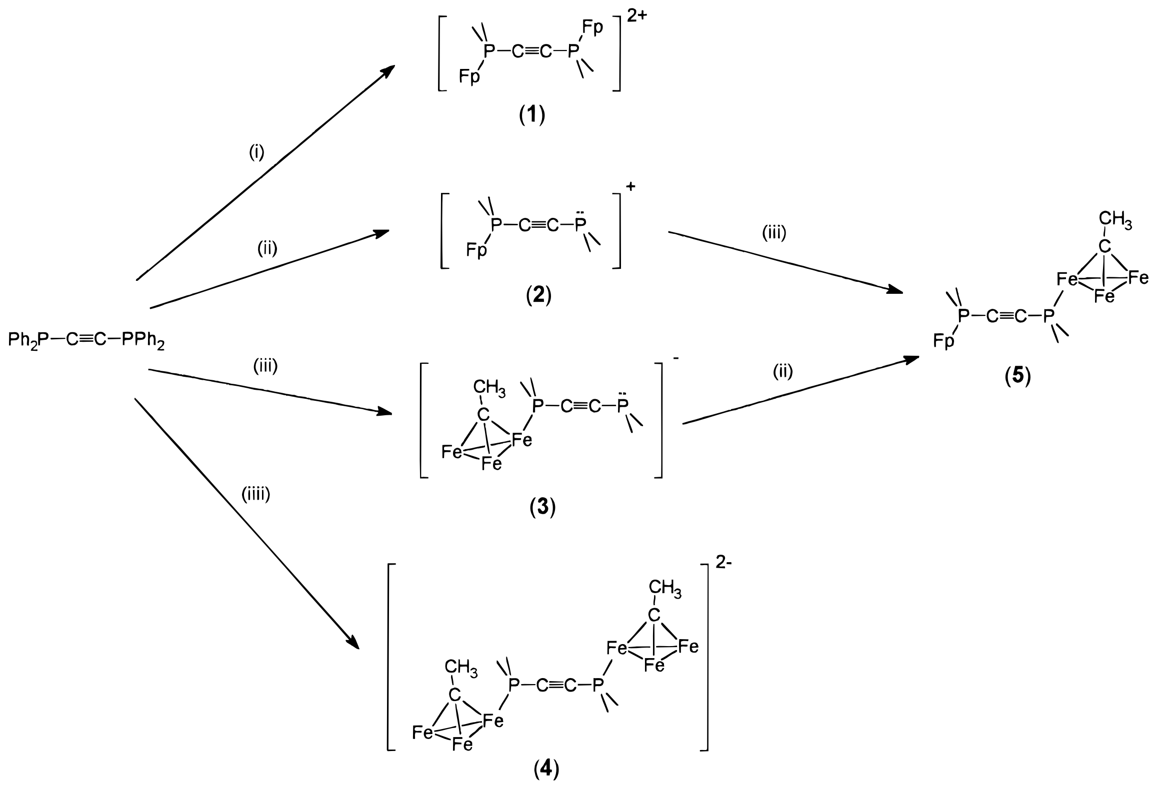
Scheme 1



(i)=+$(Fp)_2$, +2$[FeCp_2]^+$; (ii)=+1/2$(Fp)_2$, +$[FeCp_2]^+$; (iii)=+$[HFe_3(CO)_9(C{=}CH_2)]^-$; (iiii)=+2$[HFe_3(CO)_9(C{=}CH_2)]^-$

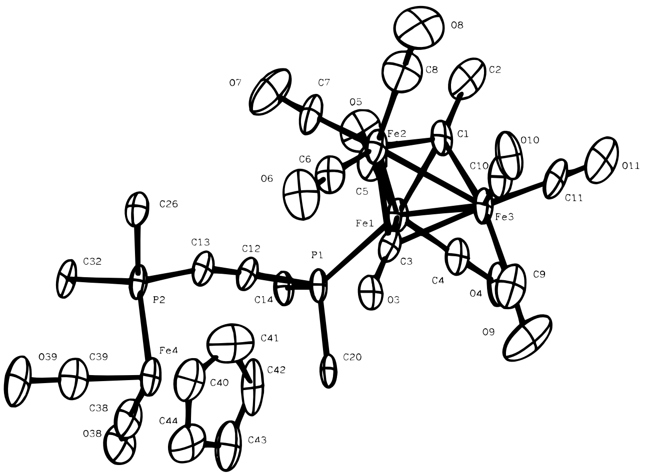


Figure 1. View of the molecular structure of complex **5a** together with the atomic numbering scheme. The phenyl rings have been omitted.

the two methods were very different: 85% in the first and 15% in the second. The very low yield in the synthesis of **5** from complex **3** may be related with to competitive oxidation of the anionic complexes by means of the ferrocenium cation.

In the crystals of complex **5**, there are two crystallographically independent complexes (even if very similar labeled as **5a** and **5b**) and two independent water molecules. The structure of **5a**, with the atom numbering system adopted, is shown in Figure 1, and selected bond distances and angles are shown in Table 1 .

The structures of **5a** and **5b** consist of a diphosphine ligand $Ph_2PC{\equiv}CPPh_2$ simultaneously bonded to the fragments {Fp} and $\{Fe_3(CO)_9(CCH_3)\}$ by two Fe−P bonds. The structure of the fragment $\{Ph_2PFe(CO)_2Cp\}$ is very similar to that reported in the cationic complex $[(Fp)Ph_2PC{\equiv}CPh][BF_4]$[3] [Fe−P = 2.207(1) Å; P−C(sp) = 1.746(3) Å; Fe−C(CO) = 1.785(3) Å; Fe−C(CO) = 1.787(4) Å]. Furthermore, the IR spectrum of **5** shows two intense bands at 2056 and 2029 cm^{-1}, which are assigned to the ν_{CO} stretching vibrations of the {Fp} fragment, and similar values are observed in the IR spectra of the cationic complexes $[(Fp)Ph_2PC{\equiv}CPh][BF_4]$ (2061, 2020 cm^{-1})[3] and $[(Fp)PPh_3]^+$ (2070, 2025 cm^{-1}).[8] For comparison, the positions of the ν_{CO} bands in the neutral Fe(0) complexes $[(\eta^4\text{-}C_8H_8)Fe(CO)_2(PPh_3)]$ (1970, 1920 cm^{-1}) show a decrease of 80−100 cm^{-1}, with respect to the cationic complexes, in agreement with the charge influence on the metal to carbonyl back-bonding.[8] This result agrees with the description of complex **5** as a zwitterionic compound in which the diphosphine is bonded to a cationic $\{Fp\}^+$ fragment. In addition, the anionic nature of the fragment $\{Fe_3(CO)_9(CCH_3)\}$ is supported by the spectroscopic and structural parameters of **5**. The Fe−C bond distances of the ethylidyne ligand μ_3-CCH_3 and the triple-bridging CO ligand are very similar to those found in the related anionic complex $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CCH_3)]$.[9] Furthermore, similar ^1H and ^{13}C NMR resonances are observed in the related complexes $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CCH_3)]$ [δ(ppm): ^1H 4.18 (CH_3); ^{13}C 44.3 (CH_3), 221.8 (CO), 289.0 (Fe_3C)][9] and $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}CCH_3)Ph_2PC{\equiv}CPh]$ [δ(ppm): ^1H 4.2 (CH_3); ^{13}C 43.3 (CH_3), 225.1 (CO), 283.6 (Fe_3C)].[4]

It is interesting to note that the fragment P−C(12)−C(13)−P(2) is not linear, since the angles P(1)−C-

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Table 1. Selected X-ray Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for 5a and 5b

	5a	5b
Fe(1)−Fe(2)	2.522(1)	2.535(1)
Fe(1)−Fe(3)	2.554(1)	2.540(1)
Fe(2)−Fe(3)	2.533(1)	2.550(1)
Fe(1)−C(1)	1.968(2)	1.963(3)
Fe(2)−C(1)	1.964(4)	1.934(4)
Fe(3)−C(1)	1.932(3)	1.927(5)
Fe(1)−C(3)	1.983(3)	1.992(5)
Fe(2)−C(3)	2.100(3)	2.044(5)
Fe(3)−C(3)	2.076(3)	2.087(3)
Fe−C(COterminal)a,b	1.779(6)	1.761(8)
C(1)−C(2)	1.488(6)	1.503(7)
C(3)−O(3)	1.192(4)	1.195(6)
C−O(COterminal)a,b	1.135(7)	1.15(1)
Fe(4)−C(38)	1.795(3)	1.800(5)
Fe(4)−C(39)	1.709(5)	1.796(4)
Fe−C(Cp)a	2.097(8)	2.06(1)
C(38)−O(38)	1.094(4)	1.086(6)
C(39)−O(39)	1.214(6)	1.095(4)
Fe(1)−P(1)	2.211(1)	2.195(1)
Fe(4)−P(2)	2.210(1)	2.198(1)
P(1)−C(12)	1.779(3)	1.747(3)
P(2)−C(13)	1.750(3)	1.724(3)
P(1)−C(14)	1.815(3)	1.831(4)
P(1)−C(20)	1.815(4)	1.816(5)
P(2)−C(26)	1.822(3)	1.795(4)
P(2)−C(32)	1.790(4)	1.782(4)
C(12)−C(13)	1.210(4)	1.250(5)
Fe(1)−Fe(2)−Fe(3)	60.7(1)	59.9(1)
Fe(2)−Fe(1)−Fe(3)	59.9(1)	60.3(1)
Fe(1)−Fe(3)−Fe(2)	59.5(1)	59.7(1)
Fe(1)−C(1)−C(2)	130.8(2)	128.5(3)
Fe(2)−C(1)−C(2)	133.4(3)	129.8(3)
Fe(3)−C(1)−C(2)	130.2(3)	134.1(2)
Fe(1)−C(3)−O(3)	138.0(2)	136.3(3)
Fe(2)−C(3)−O(3)	129.7(3)	133.7(4)
Fe(3)−C(3)−O(3)	135.2(2)	131.9(3)
C(38)−Fe(4)−C(39)	93.1(2)	95.2(2)
C(38)−Fe(4)−P(2)	91.1(2)	90.3(2)
C(39)−Fe(4)−P(2)	94.3(2)	92.6(2)
Fe(1)−P(1)−C(12)	114.9(1)	113.5(1)
Fe(1)−P(1)−C(14)	117.8(1)	115.0(1)
Fe(1)−P(1)−C(20)	121.6(1)	122.9(1)
C(14)−P(1)−C(20)	101.0(1)	101.7(2)
Fe(4)−P(2)−C(13)	109.8(1)	109.1(2)
Fe(4)−P(2)−C(26)	118.4(1)	119.2(1)
Fe(4)−P(2)−C(32)	112.6(1)	115.7(1)
C(26)−P(2)−C(32)	106.5(2)	103.0(2)
P(1)−C(12)−C(13)	172.1(3)	175.2(4)
P(2)−C(13)−C(12)	166.2(3)	169.1(3)

[a] Mean value. [b] {$Fe_3(CO)_9(CCH_3)$} fragment.

Table 2. Crystallographic Data for 5

formula	$C_{44}H_{28}Fe_4O_{11}P_2 \cdot H_2O$
FW	1036.04
space group	$P\bar{1}$
a (Å)	12.776(2)
b (Å)	12.856(2)
c (Å)	32.463(4)
α (deg)	87.76(3)
β (deg)	86.86(2)
γ (deg)	63.57(2)
V (Å^3)	4767(2)
Z	4
D_{calcd} (g cm^{-3})	1.443
μ(Mo Kα) (cm^{-1})	13.46
T (K)	298
λ (Å)	0.710 69

(12)−C(13) and P(2)−C(13)−C(12) are bent by 6.4° and 12.4°, respectively. Similar distortions have been observed in phosphinoalkynes[10] and P-coordinated phosphinoalkynes,[3] which have been related to nonbonding interactions between the alkyne and the groups bonded to the phosphorus atom,[5e,10a] crystal packing effects,[10b] or a resonance form with a lone pair in the α-acetylenic carbon atom.[7] We emphasize that some of the more bent P−C≡C angles have just been reported in the zwitterionic complexes [$Br(CO)_4MnC{\equiv}CPPh_3$][7] (164°) and [$Ph_2(CH_3)PC{\equiv}CBPh_3$][6] (168.9°). These results suggest that a resonance form with a nonbonding pair of electrons on the acetylenic carbon atom bonded to the "cationic phosphorus" could be considered. However, we believe that the differences between the distortion observed in the zwitterionic complexes and other compounds with the {P−C≡C} fragment are too small to justify any conclusions.

Experimental Section

All reactions were performed under nitrogen by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 1710 FT spectrometer using dichloromethane or acetonitrile solutions. The NMR spectra were recorded by the Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona on a Bruker AM400 instrument. The ^{31}P chemical shifts are reported in ppm upfield from external 85% H_3PO_4. The ^1H and ^{13}C chemical shifts are expressed in ppm upfield from TMS.

The diphosphine $Ph_2PC{\equiv}CPPh_2$ was prepared by published procedures.[11] Microanalyses were performed by Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

Synthesis of [(Fp)$Ph_2PC{\equiv}PPh_2$(Fp)][BF_4]$_2$ (1). A solution of [$Fe(C_5H_5)_2$][BF_4] (0.74 g, 2.7 mmol) in dichloromethane (10 mL) was added to a solution of [$Fe_2(CO)_4Cp_2$] (0.50 g, 1.4 mmol) and $Ph_2PC{\equiv}CPPh_2$ (0.55 g, 1.4 mmol) in dichloromethane (20 mL). After 2 h of stirring, the solution was filtered from the precipitated ferrocene and then evaporated to dryness. The residual oil was washed in light petroleum (2 × 10 mL) and recrystallized from acetonitrile/diethyl ether at −20 °C. The yellow crystals that separated were collected, washed in diethyl ether, and dried *in vacuo*. Yield: 84%. Anal. Calcd for $C_{40}H_{30}B_2F_8Fe_2O_4P_2$: C, 52.11; H, 3.28. Found: C, 52.33; H, 3.26. IR (CH_3CN, cm^{-1}): 2066 (s), 2025 (s) (ν_{CO}). ^{31}P NMR (CD_3CN): δ 46.1. ^1H NMR (CD_3CN): δ 5.7 (s, Cp), 7.7 (m, Ph). ^{13}C NMR (CD_3CN; except phenyl resonances): δ 89.4 (s, Cp), 105.1 (dd, $J_1 = 6.1$ Hz, $J_2 = 67.1$ Hz, ≡CP), 208.2 (d, $J = 24.6$ Hz, CO).

Synthesis of [(Fp)$Ph_2PC{\equiv}CPPh_2$][BF_4] (2). A solution of [$Fe(C_5H_5)_2$][BF_4] (0.74 g, 2.7 mmol) in dichloromethane (10 mL) was added to a solution of [$Fe_2(CO)_4Cp_2$] (0.50 g, 1.4 mmol) and $Ph_2PC{\equiv}CPPh_2$ (1.10 g, 2.8 mmol) in dichloromethane (20 mL). After 2 h of stirring, the solution was filtered from the precipitated ferrocene and then evaporated to dryness. The residual oil was washed in light petroleum (2 × 10 mL) and recrystallized from dichloromethane/diethyl ether at −20 °C. The yellow crystals that separated were collected, washed in diethyl ether, and dried *in vacuo*. Yield: 79%. Anal. Calcd for $C_{33}H_{25}BF_4FeO_2P_2$: C, 60.22; H, 3.83. Found: C, 60.23; H, 3.95. IR (CH_2Cl_2, cm^{-1}): 2062 (s), 2025 (s) (ν_{CO}), 2109 (w) ($\nu_{C\equiv C}$). ^{31}P NMR ($(CD_3)_2CO$): δ −27.3 (s, PPh_2), 46.5 (s, $FePPh_2$). ^1H NMR ($(CD_3)_2CO$): δ 5.7 (s, Cp), 7.7 (m, Ph). ^{13}C NMR ($(CD_3)_2CO$; except phenyl resonances): δ 89.0 (s, Cp), 99.3 (d, $J = 91.6$ Hz, ≡CPFe), 117.1 (dd, $J_1 = 34.3$ Hz, $J_2 = 7.8$ Hz, ≡CP), 209.1 (d, $J = 20.0$ Hz, CO).

Synthesis of [PPh_4][$Fe_3(CO)_9(\mu_3\text{-}CCH_3)(Ph_2PC{\equiv}CPPh_2)$] (3). A solution of $Ph_2PC{\equiv}CPPh_2$ (0.26 g, 0.66 mmol) in acetone (10 mL) was added to a solution of [PPh_4][$HFe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$] (0.50 g, 0.64 mmol) in acetone (20 mL). The resulting solution was stirred for 16 h, filtered, and evaporated to

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dryness. The residual oil was crystallized in dichloromethane/methanol at −20 °C. The red-brown crystals that separated were collected, washed in cold methanol, and dried *in vacuo*. Yield: 75%. Anal. Calcd for $C_{61}H_{43}Fe_3O_9P_3$: C, 62.07; H, 3.67. Found: C, 62.14; H, 3.52. IR (CH_2Cl_2, cm^{-1}): 2023 (m), 1972 (s), 1954 (s) (ν_{CO}), 2124 (w) ($\nu_{C\equiv C}$). ^{31}P NMR ($(CD_3)_2CO$): δ −31.2 (s, PPh_2), 24.1 (s, PPh_4), 43.9 (s, $FePPh_2$). ^{1}H NMR ($(CD_3)_2CO$): δ 4.2 (s, CH_3), 7.7 (m, Ph). ^{13}C NMR ($(CD_3)_2CO$; except phenyl resonances): δ 43.1 (s, CH_3), 224.6 (b, CO), 282.1 (s, Fe_3C) (the signals for acetylenic carbons could not be identified).

Synthesis of $[PPh_4]_2[\{Fe_3(CO)_9(\mu_3\text{-}CCH_3)\}_2(Ph_2PC\equiv CPPh_2)]$ (4). A solution of $Ph_2PC\equiv CPPh_2$ (0.25 g, 0.63 mmol) in acetone (10 mL) was added to a solution of $[PPh_4][HFe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (1.00 g, 1.27 mmol) in acetone (20 mL). The resulting solution was stirred for 16 h, filtered, and evaporated to dryness. The residual oil was crystallized in dichloromethane/methanol at −20 °C. The red-brown crystals that separated were collected, washed in cold methanol, and dried *in vacuo*. Yield: 65%. Anal. Calcd for $C_{96}H_{66}Fe_6O_{18}P_4$: C, 58.63; H, 3.38. Found: C, 57.52; H, 3.43. IR (CH_2Cl_2, cm^{-1}): 2027 (m), 1981 (s), 1963 (s) (ν_{CO}). ^{31}P NMR ($(CD_3)_2CO$): δ 23.9 (s, PPh_4), 43.0 (s, $FePPh_2$). ^{1}H NMR ($(CD_3)_2CO$): δ 4.1 (s, CH_3), 7.7 (m, Ph). ^{13}C NMR ($(CD_3)_2CO$; except phenyl resonances): δ 42.8 (s, CH_3), 224.4 (b, CO), 282.8 (s, Fe_3C) (the signals for acetylenic carbons could not be identified).

Synthesis of $[\{Fe_3(CO)_9(\mu_3\text{-}CCH_3)\}Ph_2PC\equiv PPh_2(Fp)]$ (5). Method a. A solution of **2** (0.25 g, 0.4 mmol) in dichloromethane (20 mL) was added to a solution of $[PPh_4][HFe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (0.30 g, 0.4 mmol) in dichloromethane (15 mL). The resulting solution was stirred for 24 h, filtered, and evaporated to dryness. The residual oil was dissolved in dichloromethane, and after the addition of diethyl ether, a white precipitate of $[PPh_4][BF_4]$ was formed. The filtered solution was cooled to −20 °C and red-brown crystals were obtained, which were collected, washed in diethyl ether, and dried *in vacuo*. Yield: 85%.

Method b. A solution of $[Fe(C_5H_5)_2][BF_4]$ (0.110 g, 0.4 mmol) in dichloromethane (10 mL) was added to a solution of $[Fe_2(CO)_4Cp_2]$ (0.071 g, 0.2 mmol) and (**3**) (0.500 g, 0.4 mmol) in dichloromethane (20 mL). After 2 h of stirring, the solution was filtered from the precipitated ferrocene and then evaporated to dryness. The residual oil was washed in light petroleum (2 × 10 mL) and dissolved in dichloromethane, and after the addition of diethyl ether, a white precipitate of $[PPh_4][BF_4]$ was formed. The filtered solution was cooled to −20 °C and red-brown crystals were obtained, which were collected, washed in diethyl ether, and dried *in vacuo*. Yield: 15%.

Anal. Calcd for $C_{44}H_{28}Fe_4O_{11}P_2$: C, 51.91; H, 2.77. Found: C, 51.30; H, 3.17. IR (CH_2Cl_2, cm^{-1}): 2056 (s), 2029 (s), 1983 (s), 1960 (s), 1956 (s) (ν_{CO}), 2125 (w) ($\nu_{C\equiv C}$). ^{31}P NMR ($(CD_3)_2CO$): δ 47.2 (b, $PFe(CO)_2Cp$), 56.4 (b, $P\{Fe_3(CO)_9(\mu_3\text{-}CCH_3)\}$). ^{1}H NMR ($(CD_3)_2CO$): δ 4.1 (d, J = 2.3 Hz, CH_3), 5.6 (d, J = 1.6 Hz, Cp), 7.7 (m, Ph). ^{13}C NMR ($(CD_3)_2CO$; except phenyl resonances): δ 43.3 (s, CH_3), 90.0 (s, Cp), 209.3 (d, J = 23.5 Hz, $Fe(CO)_2$), 220.2 (b, $Fe_3(CO)_9$), 281.4 (s, Fe_3C) (the signals for acetylenic carbons could not be identified).

X-ray Structure Determination. A summary of the crystal data is given in Table 2 . A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12 \le \theta \le 16°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation using the $\omega{-}2\theta$ scan technique. A total of 12 816 reflections was measured in the range $2 \le \theta \le 30°$, 10 000 of which were assumed as observed by applying the condition $I \ge 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz polarization but not absorption corrections made.

The structure was solved by Patterson synthesis, using the SHELXS computer program,[12] and refined by the full-matrix least-squares method with the SHELX76 computer program.[13] The function minimized was $\sum w|\,|F_o|^2 - |F_c|^2\,|^2$, where $w = \sigma^{-2}(F_o)$. f, f', and f'' were taken from *International Tables of X-ray Crystallography*. The final R factor was 0.036 (R_w = 0.044) for all observed reflections. The number of refined parameters was 1119. Maximum shift/esd = 0.1; maximum and minimum peaks in final difference synthesis were 0.4 and −0.4 $eÅ^{-3}$, respectively.

Acknowledgment. We thank the DGICYT (Projects PB89-0306 and PB92-0621, Programa de Promoción General del Conocimiento) for financial support.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compound **5** (11 pages). Ordering information is given on any current masthead page.

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[12] SHELXS. Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

[13] SHELX 76. Program for Crystal Structure Determination; Sheldrik, G. M., Ed.; University of Cambridge: Cambridge, England, 1976.