Organometallics **1990**, *9*, 2933–2937 2933

representing diverse regions of reciprocal space were monitored every 100 reflections during data collection. Little deviation in peak intensities was observed during data collection, and no absorption corrections were applied.

The structures were solved by direct methods with the SHELXTL software package. In all three structures, most of the atoms were located in the E maps; the remaining atoms were found in subsequent difference electron density maps. Blocked-cascade least-squares refinements of the structures used the reflections with $F_o > 3\sigma(F_o)$. Atomic form factors were taken from standard sources.[22] In the final refinement cycles the non-hydrogen atoms were assumed to vibrate anisotropically while the hydrogen atoms were included as idealized isotropic fixed contributors (C–H bond length 0.96 Å, U(hydrogen) = 1.2[U(carbon)]. The final discrepancy indices R_1 and R_2 are given in Table II.

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Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters for **2a**, **2c**, and **6** (8 pages); listings of observed and calculated structure factor amplitudes for **2a**, **2c**, and **6** (72 pages). Ordering information is given on any current masthead page.

[22] Atomic form factors from: Cromer, D.; Waber, J. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, Table 2.2B. Atomic form factor for hydrogen from: Stewart, R.; Davidson, E.; Simpson, W. *J. Chem. Phys.* **1985**, *42*, 3175. Anomalous scattering components from: Cromer, D.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1981.

Further Illustration of the Versatility of the Alkynylphosphines $Ph_2P(C\equiv CR)$ toward $[PPh_4][HFe_3(CO)_{11}]$ When R = H, C(O)OMe

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The alkynylphosphines $Ph_2P(C\equiv CR)$ (R = H, C(O)OMe) react with $[PPh_4][HFe_3(CO)_{11}]$ to give, in a first step, complexes containing the $Ph_2PC{=}CHR$ ligands. When R = C(O)OMe, the structure of the complex **3** isolated was determined by a single-crystal X-ray diffraction study. The anionic part consists of a $Ph_2PC{=}CHC(O)OMe$ ligand in which the phosphorus atom is bonded to an $Fe(CO)_4$ group and in which the $C{=}CHC(O)OMe$ fragment is η^1,η^2-bonded and η^1(O)-bonded to an anionic $Fe_2(CO)_6$ unit. When R = H, the structure of complex **5** was deduced from spectroscopic data. It consists of a Ph_2PCCH_2 ligand bonded to each iron atom of an $[Fe_3(CO)_9]^-$ triangle through the P, C, and $C{=}CH_2$ atoms, respectively. Complexes **3** and **5** evolved in boiling acetone and ethyl acetate, respectively, to $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}CCHR)]$ compounds, resulting from the breaking of the phosphorous–carbon bond.

Introduction

Previous studies by Carty[1] and Sappa[2] have shown the great reactivity of alkynylphosphines toward polynuclear complexes. The reactions observed generally imply the breaking of the phosphorus–alkynyl bond and, in some cases, the reaction of the acetylide fragment generated with either hydride[3] or hydrocarbon ligands bonded on the polymetallic frames.[2] The backformation of a PPh_2–carbon bond has even been observed.[2,4]

We have recently shown that the reactivity of alkynylphosphines $Ph_2PC\equiv CR$ with $[PPh_4][HFe_3(CO)_{11}]$ (**1**) is also very versatile and dependent on the R group. For instance, when R = Me, Ph, we have observed the transformation of the phosphine into the PhPC(R)CH(Ph) μ^3-η^1,η^2-bonded phosphido ligand.[5] When R = t-Bu, one product of the reaction, $[PPh_4][Fe_3(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(\mu\text{-}CCH(t\text{-}Bu))]$ (A), results from the breaking of the phosphorus–alkynyl bond and transformation of the acetylide into a μ^3-η^2-bonded vinylidene ligand. As for the other product of the reaction, there is formation of the $Ph_2PCH{=}C(CMe_3)C(O)$ ligand[6] bonded to a $Fe_2(CO)_6$ unit. This dependence of the reactivity on the R group has led us to increase the field of this study to the case when R = H and R = electron-withdrawing group.

For this reason we have synthesized the phosphine $Ph_2PC\equiv CC(O)OMe$, which, to our knowledge, has never been described before. Reaction with $[PPh_4][HFe_3(CO)_{11}]$

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[1] Nucciarone, D.; McLauglin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 106 and references therein.

[2] Sappa, E.; Pasquinelli, G.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Dalton Trans.* **1989**, 601 and references therein.

[3] Van Gastel, F.; McLaughlin, S. A.; Lynch, M.; Carty, A. J.; Sappa, E.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organomet. Chem.* **1987**, *326*, C65.

[4] Fogg, D. E.; McLaughlin, S. A.; Kwek, K.; Cherkas, A. A.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1988**, *352*, C17.

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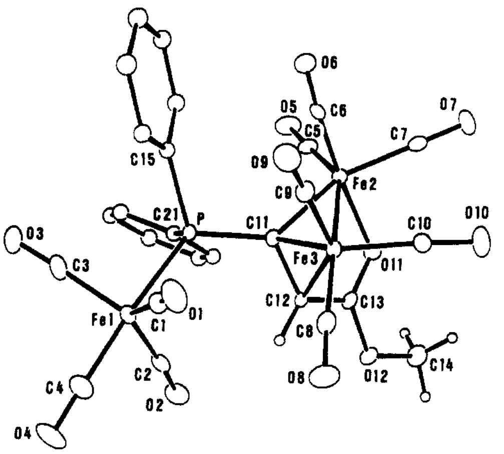

Figure 1. ORTEP view of the anionic part of 3, showing the atomic numbering scheme.

has allowed us to isolate in both cases the intermediates prior to formation of complexes of type A. In these intermediates, breaking of the phosphorous–alkynyl bond did not occur and migration of the hydride ligand onto the C_β carbon of the C≡CR group was observed. Furthermore, when R = C(O)OMe, the coordination of the C(O) group to iron stabilized a structure in which two Fe–Fe bonds have been broken.

Results and Discussion

Reactivity of $Ph_2PC{\equiv}CC(O)OMe$. The phosphine $Ph_2PC{\equiv}CC(O)OMe$ (2) has been synthesized in 60% yield by the most general procedure used for the synthesis of alkynylphosphines,[7] i.e. by the reaction of Ph_2PCl with the lithium salt of the alkyne. This salt has been synthesized by the reaction of $LiN(SiMe_3)_2$ at -60° C with the alkyne. The phosphine has been isolated as a white solid, which slowly darkened even at −20 °C under a nitrogen atmosphere. Phosphine 2 reacts readily at room temperature with $[PPh_4][HFe_3(CO)_{11}]$ to give a new complex, 3, in nearly quantitative yield, for which chemical analysis is consistent with the $[PPh_4][Fe_3(CO)_{10}Ph_2PCCH(C(O)CH_3)]$ formulation.

Infrared spectroscopy gives evidence of terminal carbonyl groups only, while the presence of two absorptions at high frequencies suggests the presence either of isomers or of different types of $Fe(CO)_n$ groups.

Proton NMR data are consistent with the presence of PPh_4, PPh_2, and OCH_3 groups, and a doublet (J = 11.1 Hz) is observed at 3.19 ppm, suggesting that the hydride ligand has migrated onto the acetylide fragment.

The ^{13}C NMR spectrum is not very informative but shows that the CH group is coupled with the phosphorus nucleus (J = 12.2 Hz), which presumably precludes the breaking of the phosphorus–alkyne bond during the reaction. This hypothesis seems consistent with the phosphorus chemical shift of 91.1 ppm, even though this value cannot exclude the presence of a diphenylphosphido group bridging two metals at a nonbonding distance.[8]

All these spectroscopic data are not fully informative about the structure of 3. An X-ray structure determination was therefore carried out. The structure of the anionic part of 3 is shown in Figure 1. Bond distances and bond angles of interest are gathered in Table I.

Table I. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for 3

Fe(1)–P(1)	2.383 (2)	Fe(2)–C(7)	1.803 (5)
Fe(1)–C(1)	1.776 (6)	Fe(2)–Fe(3)	2.578 (1)
Fe(1)–C(2)	1.795 (6)	Fe(2)–C(11)	2.024 (4)
Fe(1)–C(3)	1.776 (7)	Fe(2)–O(11)	2.044 (3)
Fe(1)–C(4)	1.779 (6)	Fe(3)–C(8)	1.739 (7)
Fe(2)–C(5)	1.790 (7)	Fe(3)–C(9)	1.796 (6)
Fe(2)–C(6)	1.740 (6)		
Fe(3)–C(10)	1.767 (5)	C(11)–C(12)	1.435 (8)
Fe(3)–C(11)	1.965 (5)	C(12)–C(13)	1.412 (7)
Fe(3)–C(12)	2.066 (5)	C(12)–H(C12)	0.97 (3)
P(1)–C(11)	1.785 (5)	C(13)–O(11)	1.253 (7)
P(1)–C(15)	1.827 (3)	C(13)–O(12)	1.336 (7)
P(1)–C(21)	1.829 (3)	O(12)–C(14)	1.454 (6)
C(1)–O(1)	1.157 (7)	C(6)–O(6)	1.158 (7)
C(2)–O(2)	1.136 (8)	C(7)–O(7)	1.143 (6)
C(3)–O(3)	1.138 (8)	C(8)–O(8)	1.161 (8)
C(4)–O(4)	1.139 (8)	C(9)–O(9)	1.127 (7)
C(5)–O(5)	1.141 (8)	C(10)–O(10)	1.168 (7)
Fe(1)–C(1)–O(1)	174.2 (4)	Fe(2)–C(6)–O(6)	175.1 (4)
Fe(1)–C(2)–O(2)	175.9 (5)	Fe(2)–C(7)–O(7)	179.7 (5)
Fe(1)–C(3)–O(3)	177.0 (5)	Fe(3)–C(8)–O(8)	176.9 (5)
Fe(1)–C(4)–O(4)	179.2 (6)	Fe(3)–C(9)–O(9)	173.2 (6)
Fe(2)–C(5)–O(5)	174.9 (5)	Fe(3)–C(10)–O(10)	175.6 (6)
P(1)–Fe(1)–C(1)	92.8 (2)	C(5)–Fe(2)–C(7)	101.6 (3)
P(1)–Fe(1)–C(2)	87.3 (2)	C(5)–Fe(2)–C(11)	103.6 (2)
P(1)–Fe(1)–C(3)	89.7 (2)	C(5)–Fe(2)–O(11)	94.3 (2)
P(1)–Fe(1)–C(4)	175.3 (2)	C(6)–Fe(3)–C(7)	88.9 (2)
C(1)–Fe(1)–C(2)	128.0 (3)	Fe(1)–P(1)–C(11)	117.8 (2)
C(1)–Fe(1)–C(3)	111.8 (3)	Fe(1)–P(1)–C(15)	114.9 (1)
C(1)–Fe(1)–C(4)	89.4 (3)	Fe(1)–P(1)–C(21)	107.4 (1)
C(2)–Fe(1)–C(3)	120.2 (3)	Fe(2)–C(11)–Fe(3)	80.5 (2)
C(2)–Fe(1)–C(4)	88.1 (3)	Fe(2)–C(11)–P(1)	131.9 (3)
C(3)–Fe(1)–C(4)	93.4 (3)	Fe(2)–C(11)–C(12)	103.9 (3)
Fe(3)–Fe(2)–C(5)	152.1 (2)	Fe(3)–C(11)–P(1)	129.8 (3)
Fe(3)–Fe(2)–C(6)	85.6 (2)	Fe(3)–C(11)–C(12)	73.0 (3)
Fe(3)–Fe(2)–C(7)	106.2 (2)	P(1)–C(11)–C(12)	119.3 (3)
Fe(3)–Fe(2)–C(11)	48.7 (1)	C(12)–C(13)–O(11)	122.6 (5)
Fe(3)–Fe(2)–O(11)	87.0 (1)	C(12)–C(13)–O(12)	116.7 (5)
C(5)–Fe(2)–C(6)	94.9 (3)	O(11)–C(13)–O(12)	120.8 (4)
C(6)–Fe(2)–C(11)	95.3 (2)	C(9)–Fe(3)–C(12)	142.3 (2)
C(6)–Fe(2)–O(11)	170.6 (2)	C(10)–Fe(3)–C(11)	128.5 (2)
C(7)–Fe(2)–C(11)	153.9 (3)	C(10)–Fe(3)–C(12)	109.8 (2)
C(7)–Fe(2)–O(11)	87.6 (2)	C(11)–Fe(3)–C(12)	41.6 (2)
C(11)–Fe(2)–O(11)	84.1 (2)	C(11)–P(1)–C(15)	107.3 (2)
Fe(2)–Fe(3)–C(8)	164.0 (2)	C(11)–P(1)–C(21)	105.6 (2)
Fe(2)–Fe(3)–C(9)	104.4 (2)	C(15)–P(1)–C(21)	102.5 (2)
Fe(2)–Fe(3)–C(10)	83.1 (2)	Fe(3)–C(12)–C(11)	65.4 (3)
Fe(2)–Fe(3)–C(11)	50.7 (1)	Fe(3)–C(12)–C(13)	107.7 (3)
Fe(2)–Fe(3)–C(12)	71.6 (1)	Fe(3)–C(12)–H(C12)	115 (2)
C(8)–Fe(3)–C(9)	90.2 (3)	C(11)–C(12)–C(13)	115.6 (5)
C(8)–Fe(3)–C(10)	98.9 (2)	C(11)–C(12)–H(C12)	123 (3)
C(8)–Fe(3)–C(11)	119.6 (2)	C(13)–C(12)–H(C12)	117 (3)
C(8)–Fe(3)–C(12)	93.0 (2)	Fe(2)–O(11)–C(13)	107.6 (3)
C(9)–Fe(3)–C(10)	106.8 (2)	C(13)–O(12)–C(14)	116.9 (4)
C(9)–Fe(3)–C(11)	106.0 (2)		

The anionic part of 3 consists of a $Ph_2PC{=}CHC(O)OMe$ ligand in which the phosphorus is bonded to an $Fe(CO)_4$ group and in which the C=CHC(O)OMe group (which results from migration of the hydride ligand of 1 on the C_β carbon of the alkynyl group) is η^1,η^2(C)-bonded and η^1(O)-bonded to an $Fe_2(CO)_6$ unit through the oxygen atom of the ester group.

This result shows that the reaction has occurred with the rupture of two Fe–Fe bonds and that the stabilization of the dinuclear unit is allowed by coordination of the oxygen of the ester group. Indeed, each iron atom in 3 is surrounded by 18 valence electrons if we consider that the negative charge is localized on the Fe(3) atom.

The geometry around Fe(1) is a distorted trigonal bipyramid with the phosphorus atom in an axial position. The Fe(1)–C distances are equal even for the Fe(1)–C(4)

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[7] Carty, A. J.; Hota, N. K.; Ng, T. W.; Patel, M. A.; O'Connor, T. J. *Can. J. Chem.* **1971**, *49*, 2706.

[8] McLauglin, S. A.; Nucciarone, D.; Carty, A. J. In *Phosphrus-31 NMR Spectroscopy in Stereochemical Analysis, Organic Compounds and Metal Complexes*; Verkade, J. G., Quinn, L. D., Eds.; VCH: New York, 1987; Chapter 16.

bond, which is trans to Fe(1)–P(1). The Fe(1)–P(1) distance is very long for an iron–phosphine bond,[9] being 0.09 Å longer than in the $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ complex, in which the phosphines are bonded through phosphorus to one iron atom and π-bonded to the other iron through the carbon–carbon triple bond.[10] The origin of this lengthening is not clearly evident but may be due to the steric effect of the dinuclear iron complex bonded to phosphorus.

In the dinuclear unit, the CC(H)C(O)OMe group forms a metallacycle, a situation closely resembling that found for the $FeCo(CO)_6(\mu\text{-}MeOC(O)C{=}CHC(O)OMe)$ complex.[11] The O-coordination induces the shortening of the Fe(2)–C(6) bond, which is trans to the oxygen group.

Refluxing 3 in boiling acetone or directly reacting 1 with 2 at the same temperature leads to the formation of a new product, 4, which is analyzed as $[PPh_4][Fe_3(CO)_8PPh_2CCHC(O)OMe]$. Spectroscopic data are consistent with the structure $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}CCHC(O)OMe)]$ by comparison with the analogous product (A) obtained with the phosphine $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$.[6] Indeed, the infrared spectra are very similar in the ν_{CO} stretching region, and particularly, absorptions consistent with the presence of the ν_{CO} bridges are observed. The phosphorus resonance at 267.4 ppm is also consistent with the presence of a phosphido bridge, and the doublet observed at 4.47 ppm (J = 3.5 Hz) in the proton NMR spectrum is in agreement with the presence of the C=CHC(O)OMe group.

Thus, the formation of 4 successively implies the migration of the hydride ligand onto the C_β carbon of the alkynyl group, such a reaction occurring with the opening of two metal–metal bonds and departure of one CO group and then the breaking of the phosphorus–carbon bond and the reformation of two metal–metal bonds with departure of two carbonyl groups. In these transformations, the $PPh_2CCHC(O)OMe$ group remains a seven-electron ligand. This constitutes a further example of the transformation of the alkynyl part of an alkynylphosphine into a vinylidene ligand and gives convenient access to the relatively rare class of homonuclear clusters containing this ligand.[12] The literature provides another example of the formation of a vinylidene ligand from an alkynylphosphine, but in this case the vinylidene group is provided by the $Ph_2PC{\equiv}CR$ to $C{=}CR(PPh_2)$ isomerization on a trinuclear iron or ruthenium unit.[15]

Reactivity of $Ph_2PC{\equiv}CH$ toward 1. This phosphine reacts slowly at room temperature with 1 to give, after 2 days, a mixture of two products, 5 and 6, which can be separated by fractional crystallization. These two products can be obtained more selectively by operating at higher temperature. Indeed, 5 is obtained as the only isolable product after 1 h in refluxing acetone and 6 is produced in quite good yield in boiling ethyl acetate. Moreover, 5 evolves to 6 in boiling ethyl acetate.

The infrared spectrum of 5 in the ν_{CO} stretching region gives only evidence of terminal carbonyl groups, while the ^{31}P NMR spectrum shows a signal at 29.4 ppm which is not consistent with the presence of a phosphido bridge. More precise information about the structure of 5 comes from proton and ^{13}C NMR data.

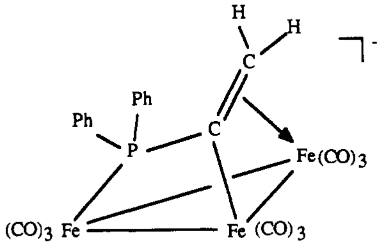

Figure 2. Proposed structure for complex 5.

In the proton NMR spectrum, two double doublets in a 1/1 ratio are observed which are characteristic of two hydrogen atoms coupled to each other (J = 1.6 Hz) and with the phosphorus atom (J_1 = 18.4 Hz, J_2 = 35.1 Hz). Similar data are found for the CH_2 proton resonances of the $HOs_3(Et_2PC{=}CH_2)(CO)_9$ complex, a compound obtained by transformation of the $Os_3(CO)_{11}PEt_3$ compound.[14] In this complex, the CCH_2 group is σ-bonded through carbon to phosphorus and osmium atoms and π-bonded through the $C{=}CH_2$ double bond to another osmium center. The presence of a CH_2 group in 5 is confirmed by the observation of a triplet at 57.7 ppm (J = 164 Hz) in the ^{13}C NMR spectrum. The resonance of the carbon directly bonded to phosphorus has not been detected, being perhaps obscured by the phenyl resonances, an area where it is expected.[15]

Complex 5 is analyzed as $[PPh_4][Fe_3(CO)_9(Ph_2PCCH_2)]$, and consequently, we propose the structure shown in Figure 2.

As for 3, the reaction of the alkynylphosphine with 1 occurred with migration of the hydride ligand onto the C_β carbon of the alkynyl group and without breaking of the phosphorus–carbon. However, in this case there is no breaking of metal–metal bonds.

The compound 6 has the same spectroscopic characteristics as 4, viz. the presence of bridging carbonyl groups in the infrared spectrum and of a diphenylphosphido bridge ($\delta^{31}P$ = 270.7 ppm) in the ^{31}P NMR spectrum. The presence of a CCH_2 ligand is ascertained from the ^1H NMR spectrum, which shows a doublet (J = 2.3 Hz) at 3.69 ppm. Thus, we propose for 6 the structure that corresponds to the $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}CCH_2)]$ formulation.

To conclude, the study of the reactivity of the $Ph_2PC{\equiv}CR$ ligands (R = C(O)OMe, H) toward $[PPh_4][HFe_3(CO)_{11}]$ has given further evidence of the great versatility of these alkynylphosphines toward polymetallic complexes. Indeed, with these two phosphines, we have observed the migration of the hydride ligand onto the C_β carbon of the alkynyl group without breaking of the phosphorus–C_α carbon bond in a first step. The breaking of this P–C bond then occurred at higher temperature.

Furthermore, in the case when R = C(O)OMe, the coordination of the ester group has allowed the stabilization of an intermediate in which the breaking of two metal–metal bonds has occurred. In the 3 → 4 transformation, the ligand and its transformation fragments remain seven-electron-donating ligands, allowing the departure of two CO groups and back-formation of two metal–metal bonds. All these observations are summarized in Scheme I.

Experimental Section

All reactions were performed under a nitrogen atmosphere by using standard Schlenk-tube techniques. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer in dichloro-

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[9] Krüger, C.; Barnett, B. L.; Brauer, D. In *The Organic Chemistry of Iron*; Koerner von Gustorf, E. A., Grevels, F. W., Fischer, I., Eds.; Academic Press: New York, 1978; p 1.

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[13] Reference deleted in revision.

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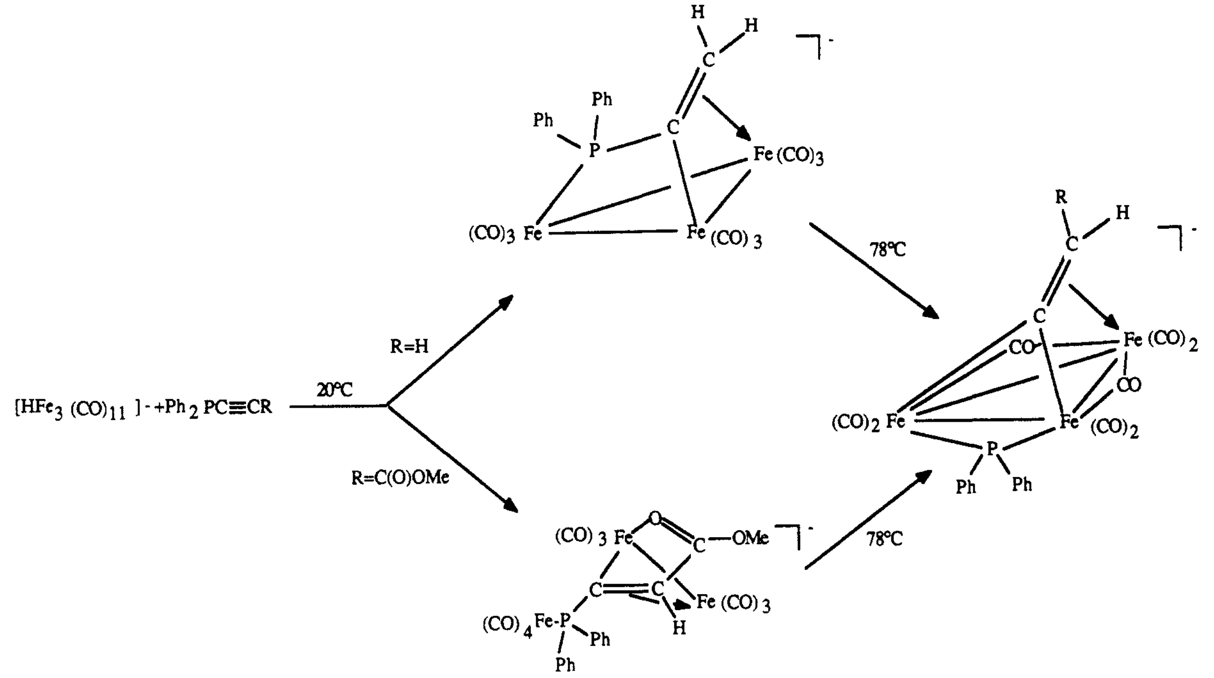
Scheme I



methane solution. ^{1}H and ^{31}P NMR spectra were obtained on a Bruker WH 90 spectrometer and ^{13}C CMR spectra on Bruker AC 200 and WM 250 instruments. $[PPh_4][HFe_3(CO)_{11}]$[16] and $Ph_2PC{\equiv}CH$[17] were prepared by published procedures.

Synthesis of $Ph_2PC{\equiv}CC(O)OMe$. To a solution of methyl propiolate (2 mL, 22.5 mmol) in 20 mL of ether maintained at −61 °C was added a 1 M solution of lithium bis(trimethylsilyl)amide (23 mL) in tetrahydrofuran. The solution was stirred for 15 min; then Ph_2PCl (4 mL) in solution in 20 mL of ether was slowly added at −60 °C. This mixture was slowly raised to room temperature, and the solution was stirred for 1 h. After filtration through Celite to remove LiCl, the solution was evaporated to dryness. Crystallization in methanol gave 3.6 g (60% yield) of $Ph_2PC{\equiv}CC(O)OMe$ as white crystals. Anal. Calcd for $C_{16}H_{13}O_2P$: C, 71.64; H, 4.85. Found: C, 71.38; H, 4.44. ^{1}H NMR ($(CD_3)_2CO$): 7.57 (m), C_6H_5), 3.92 (s, OCH_3) ppm. ^{31}P NMR ($CDCl_3$): 34.7 ppm.

Synthesis of $[PPh_4][Fe_3(CO)_{10}Ph_2PC{=}CH(C(O)OMe)]$ (3). To $[PPh_4][HFe_3(CO)_{11}]$ (1 g) dissolved in 10 mL of acetone was added $Ph_2PC{\equiv}CC(O)OMe$ (0.35 g). The brown solution was stirred for 2 h at room temperature and then evaporated to dryness. Crystallization in dichloromethane/ethanol afforded 1 g of **3** (80% yield) as brown crystals. Anal. Calcd for $C_{50}H_{34}Fe_3O_{12}P_2$: C, 56.81; H, 3.21; P, 5.87. Found: C, 56.31; H, 3.12; P, 5.62. IR (ν_{CO}), CH_2Cl_2): 2035 (sh), 2025 (s), 1965 (s), 1960 (sh), 1917 (m), 1900 (sh) cm^{-1}. ^{1}H NMR ($(CD_3)_2(CO)$: 7.96 (m, PPh_4), 7.47 (m, Ph), 3.63 (OCH_3), 3.19 (d, J = 11.1 Hz, H) ppm. ^{31}P NMR ($(CD_3)_2CO$): 91.1, 28.5 (PPh_4) ppm. ^{13}C NMR (CD_2Cl_2; except phenyl resonances): 222, 215.9 (d, J = 16.6 Hz, CO), 47.1 (dd, J_1 = 162 Hz, J_2 = 12.2 Hz) (the OCH_3 resonance is obscured by the solvent).

Synthesis of $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_3\text{-}C{=}CHC(O)OMe)]$ (4). A solution of $[PPh_4][HFe_3(CO)_{11}]$ (1 g) and $Ph_2PC{\equiv}CC(O)OMe$ (0.35 g) in 30 mL of acetone was refluxed for 2 h. Evaporation of the green solution and crystallization in dichloromethane/ethanol afforded 0.7 g of **4** (60% yield) as green crystals. The complex **4** could also be obtained by refluxing **3** in acetone solution in nearly quantitative yield. Anal. Calcd for $C_{48}H_{34}Fe_3O_{10}P_2$: C, 57.60; H, 3.40; P, 6.20. Found: C, 57.48; H, 3.22; P, 6.42. IR (ν_{CO}, CH_2Cl_2): 2005 (m), 1955 (s), 1925 (m), 1905 (sh), 1815 (sh), 1780 (w) cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$): 7.96 (m, PPh_4), 7.45 (m, Ph), 4.47 (d, J = 3.5 Hz, H), 3.59 (OCH_3) ppm. ^{31}P NMR ($(CD_3)_2CO$): 267.4, 28.5 (PPh_4) ppm.

Table II. Crystal Data and Data Collection Details

	Crystal Data		
formula	$C_{50}Fe_3H_{34}O_{12}P_2$	α, deg	96.54 (1)
fw	1056.3	β, deg	97.95 (1)
cryst syst	triclinic	γ, deg	73.33 (1)
space group	$P\bar{1}$	V, Å^3	2368.0 (9)
a, Å	14.618 (2)	Z	2
b, Å	16.229 (2)	F(000)	1076
c, Å	10.553 (1)	D_{calcd}, g cm^{-3}	1.481
		μ(Mo Kα), cm^{-1}	10.3

	Data Collection
temp, °C	20
radiation	Mo Kα (λ = 0.71073 Å) from graphite monochromator
θ(min–max), deg	1.5–23.5
scan mode	ω–2θ
scan range, deg	0.80 + 0.35 tan θ
scan speed, deg min^{-1}	1.1–5.5

Synthesis of $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}Ph_2PC{\equiv}CH_2)]$ (5). $[PPh_4][HFe_3(CO)_{11}]$ (1 g) and $Ph_2PC{\equiv}CH$ (0.26 g) dissolved in 20 mL of acetone were refluxed for 1 h. After evaporation of the solvent, crystallization in dichloromethane/ethanol gave 0.3 g of **5** (25% yield) as brown crystals. Anal. Calcd for $C_{47}H_{32}Fe_3O_9P_2$: C, 58.18; H, 3.32. Found: C, 57.85; H, 3.32. IR (ν_{CO}, CH_2Cl_2): 2028 (m), 1970 (s), 1949 (m) cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$): 7.97 m (PPh_4), 7.46 m (Ph), 2.99 (dd, J_1) = 35.1 Hz, J_2 = 1.6 Hz, 1 H), 2.56 (dd, J_1 = 18.4 Hz, J_2 = 1.6 Hz, 1 H) ppm. ^{31}P NMR ((CD_3CO): 29.4, 28.5 (PPh_4) ppm. ^{13}C NMR (CD_2Cl_2; except phenyl resonances): 221.1 (CO), 57.7 (t, J = 164 Hz, CH_2).

Synthesis of $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH_2)]$ (6). An ethyl acetate solution of $[PPh_4][Fe_3(CO)_{11}]$(1 g) and Ph_2PCCH (0.3) was refluxed for 2 h. The green solution then was evaporated to dryness. Recrystallization in dichloromethane/methanol afforded 0.3 g of **6** (24% yield) as dark green crystals. Refluxing **5** in ethyl acetate also gave **6** in quantitative yield. Anal. Calcd for $C_{46}H_{32}Fe_2O_8P_2$: C, 58.64; H, 3.42. Found: C, 58.32; H, 3.57. IR (ν_{CO}, CH_2Cl_2): 2011 (m), 1960 (s), 1932 (m), 1820 (sh), 1791 (w) cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$): 7.9 (m, PPh_4), 7.43 (m, Ph), 3.69 (d, J = 2.3 Hz, 2 H) ppm. ^{31}P NMR ($(CD_3)_2CO$): 270.7, 28.5 (PPh_4) ppm.

X-ray Structure Analysis of $[PPh_4][Fe_3(CO)_{10}Ph_2PC{=}C(H)(C(O)OMe)]$ (3). Collection and Reduction of X-ray Data. A red parallelepipedic crystal with dimensions 0.25 × 0.15 × 0.075 mm was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Crystals belong to the triclinic system, space group $P\bar{1}$. Cell constants were obtained from the least-squares

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Table III. Fractional Atomic Coordinates with Esd's in Parentheses

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Fe(1)	0.45693 (6)	0.12772 (5)	0.17909 (8)	C(18)	0.4164 (2)	0.3668 (2)	−0.2278 (3)
C(1)	0.3567 (4)	0.1124 (4)	0.0730 (6)	C(19)	0.3982 (2)	0.2878 (2)	−0.2202 (3)
O(1)	0.2966 (3)	0.0960 (3)	−0.0001 (4)	C(20)	0.3977 (2)	0.2591 (2)	−0.1006 (3)
C(2)	0.4655 (4)	0.1486 (4)	0.3505 (6)	C(21)	0.4958 (2)	0.3186 (2)	0.2728 (3)
O(2)	0.4743 (3)	0.1568 (3)	0.4594 (4)	C(22)	0.4737 (2)	0.3611 (2)	0.3919 (3)
C(3)	0.5566 (4)	0.1211 (4)	0.0956 (6)	C(23)	0.5428 (2)	0.3912 (2)	0.4735 (3)
O(3)	0.6212 (3)	0.1130 (3)	0.0416 (4)	C(24)	0.6339 (2)	0.3789 (2)	0.4359 (3)
C(4)	0.4933 (5)	0.0156 (4)	0.2023 (6)	C(25)	0.6560 (2)	0.3364 (2)	0.3168 (3)
O(4)	0.5158 (4)	−0.0560 (3)	0.2183 (4)	C(26)	0.5869 (2)	0.3063 (2)	0.2352 (3)
Fe(2)	0.21501 (5)	0.45546 (5)	0.20173 (7)	P(2)	0.1063 (1)	0.87408 (9)	0.2896 (1)
C(5)	0.3025 (4)	0.5152 (4)	0.2355 (5)	C(27)	0.1880 (3)	0.9236 (2)	0.3881 (4)
O(5)	0.3587 (3)	0.5526 (3)	0.2475 (4)	C(28)	0.2059 (3)	0.9151 (2)	0.5200 (4)
C(6)	0.2114 (3)	0.4523 (3)	0.0358 (5)	C(29)	0.2662 (3)	0.9584 (2)	0.5962 (4)
O(6)	0.2058 (3)	0.4565 (3)	−0.0740 (4)	C(30)	0.3086 (3)	1.0101 (2)	0.5405 (4)
C(7)	0.1043 (4)	0.5409 (4)	0.1930 (5)	C(31)	0.2908 (3)	1.0185 (2)	0.4086 (4)
O(7)	0.0340 (3)	0.5949 (3)	0.1869 (5)	C(32)	0.2305 (3)	0.9753 (2)	0.3324 (4)
Fe(3)	0.16711 (5)	0.31292 (5)	0.15963 (7)	C(33)	0.1682 (2)	0.7986 (2)	0.1730 (3)
C(8)	0.1486 (4)	0.2136 (4)	0.1753 (5)	C(34)	0.2663 (2)	0.7857 (2)	0.1692 (3)
O(8)	0.1342 (3)	0.1489 (3)	0.1905 (4)	C(35)	0.3155 (2)	0.7220 (2)	0.0834 (3)
C(9)	0.1619 (4)	0.2904 (4)	−0.0114 (5)	C(36)	0.2665 (2)	0.6712 (2)	0.0013 (3)
O(9)	0.1548 (3)	0.2698 (3)	−0.1172 (4)	C(37)	0.1684 (2)	0.6841 (2)	0.0052 (3)
C(10)	0.0530 (4)	0.3803 (3)	0.1924 (5)	C(38)	0.1192 (2)	0.7478 (2)	0.0910 (3)
O(10)	−0.0242 (3)	0.4200 (3)	0.2140 (4)	C(39)	0.0581 (2)	0.8144 (2)	0.3803 (4)
C(11)	0.2941 (3)	0.3314 (3)	0.2160 (4)	C(40)	0.1188 (2)	0.7372 (2)	0.4235 (4)
C(12)	0.2625 (3)	0.3059 (3)	0.3245 (5)	C(41)	0.0848 (2)	0.6880 (2)	0.4962 (4)
H(C12)	0.288 (3)	0.249 (1)	0.355 (4)	C(42)	−0.0099 (2)	0.7160 (2)	0.5257 (4)
C(13)	0.2215 (4)	0.3738 (4)	0.4134 (5)	C(43)	−0.0706 (2)	0.7933 (2)	0.4825 (4)
O(11)	0.1999 (2)	0.4516 (2)	0.3905 (3)	C(44)	−0.0366 (2)	0.8425 (2)	0.4098 (4)
O(12)	0.2065 (3)	0.3514 (2)	0.5250 (3)	C(45)	0.0108 (2)	0.9579 (2)	0.2194 (3)
C(14)	0.1595 (4)	0.4206 (4)	0.6141 (5)	C(46)	0.0010 (2)	1.0432 (2)	0.2681 (3)
P(1)	0.40884 (9)	0.27371 (8)	0.1670 (1)	C(47)	−0.0749 (2)	1.1092 (2)	0.2177 (3)
C(15)	0.4155 (2)	0.3094 (2)	0.0113 (3)	C(48)	−0.1410 (2)	1.0898 (2)	0.1186 (3)
C(16)	0.4337 (2)	0.3884 (2)	0.0037 (3)	C(49)	−0.1313 (2)	1.0045 (2)	0.0699 (3)
C(17)	0.4341 (2)	0.4171 (2)	−0.1159 (3)	C(50)	−0.0553 (2)	0.9386 (2)	0.1203 (3)

fit of the setting angles of 25 reflections in the range 9–11°. A summary of crystal and intensity collection data is given in Table II. Intensity standards, monitored every 2 h, showed only random, statistical fluctuations. After data reduction[18] of the 6870 recorded reflections ($\pm h,\pm k,l$), empirical absorption corrections[19] were applied ($\mu = 10.3\ \mathrm{cm}^{-1}$; calculated transmission range 0.93–1.00).

Structure Solution and Refinement. Fe atoms were located from a Patterson map. The full-matrix least-squares refinement and difference Fourier synthesis were achieved with the SHELX-76 program[20] with 3475 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. Phenyl rings were refined as isotropic rigid groups (C–C = 1.395 Å). All hydrogen atoms, except for the one bonded to C(12), were introduced in calculations in a constrained geometry (C–H = 0.97 Å) with isotropic thermal parameters kept fixed. H(C12) was allowed to vary with a fixed U value of 0.065 Å^2. All other atoms were refined anisotropically. The atomic scattering factors used were those proposed by Cromer and Waber.[21] with anomalous dispersion effects[22] and by Stewart et al.[23] for H atoms. The final full-matrix least-squares refinement converged to $R = \sum(|F_o|-|F_c|)/\sum|F_o| = 0.029$ and $R_w = [\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.028$ with $w = 1/\sigma^2(F_o)$. The error in an observation of unit weight was $S = [\sum w(|F_o|-|F_c|^2/(n-m)]^{1/2} = 0.98$ with $n = 3475$ observations and $m = 355$ variables. An analysis of variance showed no unusual trends. In the last cycle of refinement, the maximum parameter shift was 0.17σ on a H parameter (mean value 0.02σ). A final difference Fourier map showed a residual electron density of 0.4 e/Å^3. The final fractional atomic coordinates are listed in Table III.

Registry No. 1, 40806-49-3; 2, 51105-92-1; 3, 129467-24-9; 4, 129467-26-1; 5, 129467-28-3; 6, 129467-30-7; Ph_2PCl, 1079-66-9; $Ph_2PC{\equiv}CH$, 6104-47-8; methyl propiolate, 922-67-8.

Supplementary Material Available: Tables of hydrogen atomic coordinates, thermal parameters, and bond lengths and angles (5 pages); a listing of structure factors (17 pages). Ordering information is given on any current masthead page.

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