in this species should be possible, and the structural characterization[15] of the metal–metal bonded species [Ir$_2$(CO)$_4$(I)(CH$_2$I)(μ-SC$_5$H$_4$N)$_2$] offers unambiguous proof that metal–metal bond formation is possible, at least with small carbonyl groups as the terminal ligands. The feasibility of metal–metal bond making in our complexes is currently under investigation.

Michael-Type Addition Reactions of Bis(phenylphosphido)bis(tricarbonyliron) with Acetylenic α,β-Unsaturated Carbonyl Compounds: Multiple Reaction Pathways

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The piperidine-catalyzed addition of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ to acetylenic α,β-unsaturated esters and ketones has been studied. The type of product obtained depended on the organic substrate used. Of special interest were those products in which addition of both P–H bonds to the substrate gave complexes with a one-, two-, or three-carbon bridge between the PhP units.

Introduction

In earlier work, we investigated base-catalyzed Michael-type addition reactions of (μ-HS)$_2$Fe$_2$(CO)$_6$ with acetylenic α,β-unsaturated carbonyl compounds.[1] In all cases, the initial 1:1 adduct, 1, underwent intramolecular

1
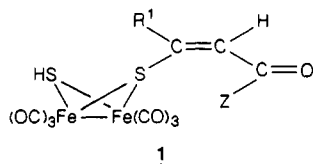
SH addition to the C=C bond of the alkenethiolate ligand to give products of type 2 when R^1 was H or alkyl. When


2
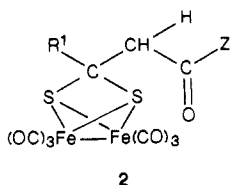
R^1 was CO$_2$CH$_3$ and Z = OCH$_3$ (i.e., when dimethyl acetylenedicarboxylate was used), addition to either carbon atom of the C=C bond was activated by an ester function and the less strained 3 was formed.

3
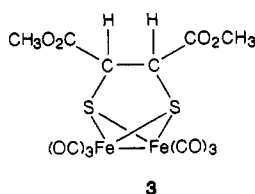
We have also been studying the chemical reactivity of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ (4) and during the course of this work have examined its base-catalyzed addition reactions with olefinic α,β-unsaturated carbonyl compounds.[2c] A comparison with the reactions of (μ-HS)$_2$Fe$_2$(CO)$_6$ with the same α,β-unsaturated substrates showed some interesting differences, and, for this reason, we have investigated base-catalyzed reactions of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ with acetylenic α,β-unsaturated carbonyl compounds.

In comparison to olefinic α,β-unsaturated carbonyl compounds, the acetylenic analogs present a somewhat more complicated and perhaps, therefore, more interesting problem in terms of reaction mechanism than do the olefins. In the olefin case, essentially only two different types of products, the unbridged and the three-carbon-bridged compounds, are possible, and this makes structural assignments fairly straightfoward. Such products are, for instance, in the case of the 1:1 piperidine-catalyzed reaction of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ with methyl vinyl ketone, the complexes 5 and 6.

5   6
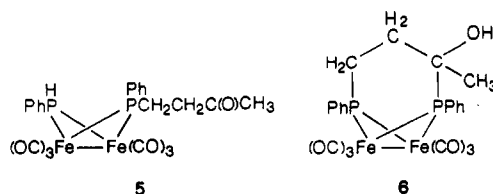
With the acetylene reactions, however, four distinct reaction pathways are possible, leading to products 7, 8, 9, and 10. First, the trivial unbridged product, 7, which

(1) Seyferth, D.; Womack, G. B.; Henderson, R. S.; Cowie, M.; Hames, B. W. *Organometallics* 1986, 5, 1568.

(2) (a) Seyferth, D.; Wood, T. G.; Henderson, R. S. *J. Organomet. Chem.*, 1987, 336, 163. (b) Seyferth, D.; Henderson, R. S.; Wood, T. G. *Recl. J. R. Neth. Chem. Soc.*, in press. (c) Seyferth, D.; Wood, T. G., in press.

7

8

9

10
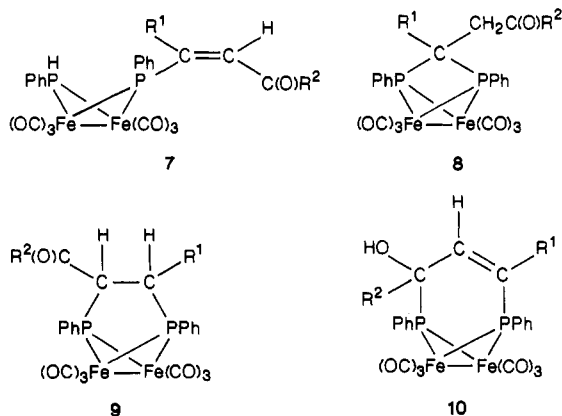
now retains a carbon–carbon double bond is, of course, possible. Also possible are the one- and two-carbon-bridged products **8** and **9**, which are analogous to those obtained in the $(\mu\text{-HS})_2Fe_2(CO)_6$ reactions. The fourth possibility is the three-carbon-bridged product **10**. Although products of this type were not observed in reactions of $(\mu\text{-HS})_2Fe_2(CO)_6$ with acetylenic α,β-unsaturated carbonyl compounds, they are analogous to the three-carbon-bridged products obtained in reactions of $(\mu\text{-HS})_2Fe_2(CO)_6$ as well as $(\mu\text{-PhPH})_2Fe_2(CO)_6$ with olefinic α,β-unsaturated ketones and, therefore, cannot be excluded from consideration. As reported here, we have obtained all four of these product types and have delineated the factors that lead to each of them.

Results and Discussion

The reactions reported here were carried out with $(\mu\text{-PhPH})_2Fe_2(CO)_6$ prepared by the method of Stelzer and his co-workers.[3] This procedure gives a mixture of three isomers, **4a**, **4b**, and **4c**, in ca. 50:45:5 ratio. This isomer mixture was used in all reactions.


4a   4b   4c
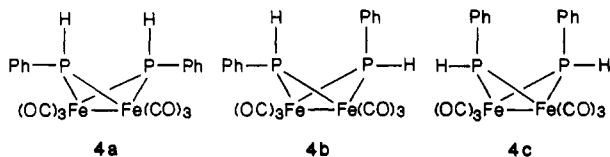
Reaction of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ with 1 equiv of methyl propiolate was carried out by using the standard reaction conditions: a THF solution of the iron complex was cooled to −78 °C; the acetylene and then slightly less than 2 molar equiv of piperidine (based on **4**) were added. The resulting red solution was stirred at −78 °C for 30 min and then for 12–16 h at room temperature. Two products were obtained, **11** and **12**, in yields of 27% and 33%, respectively (eq 1). The ^{31}P NMR spectrum of **11** showed an AX


4

11   12   (1)
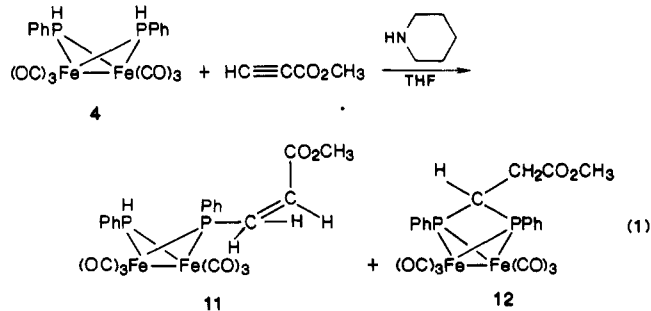
quartet (δ_P 81.5, 113.8 (J(P-P) = 146.5 Hz)), the ^1H

spectrum a P–H resonance (J(P$_1$–H) = 385.2 Hz, J(P$_2$–H) = 22.0 Hz), and the IR spectrum a medium intensity C=O stretch at 1722 cm^{-1}, indicating that it is the unbridged isomer shown. The ^1H NMR spectrum showed a doublet of doublets at 6.41 ppm (J(H–H) = 12.7 Hz, J(P–H) = 32.4 Hz) for the vinylic proton β to phosphorus. The large value of J(P–H) is characteristic of trans P–H coupling[4] and indicates that trans addition of P–H to the C≡C bond had occurred. The ^{31}P NMR spectrum of complex **12** showed a singlet at 89.4 ppm, and in its ^1H NMR spectrum multiplets were seen at 3.09 and 5.79 ppm for the methylene and methine protons, respectively. These data are consistent only with the one-carbon-bridged structure indicated. This product is analogous to that obtained from the reaction of $(\mu\text{-HS})_2Fe_2(CO)_6$ with methyl propiolate.[1]

Reaction of $(\mu\text{-PhPH})_2Fe_2(CO)_6$ with 3-butyn-2-one also gave two products, but the reaction did not proceed in the same manner as that with methyl propiolate (eq 2). In-

13   14
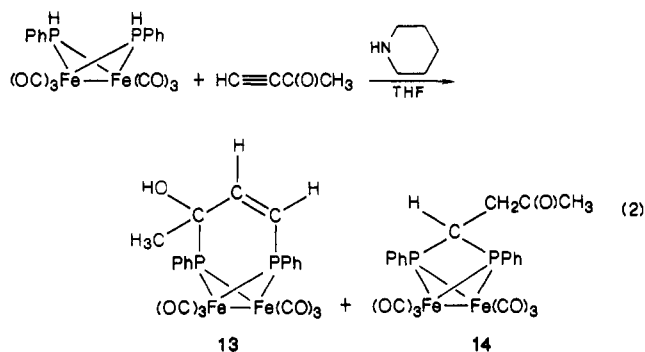
stead, product **13**, the three-carbon-bridged species, was obtained in 56% yield. This complex showed no ketone C=O stretch in the IR spectrum but did show a broad OH absorption at 3400 cm^{-1}. The ^1H NMR spectrum showed an OH resonance at 1.64 ppm, and no P–H resonances were observed. The ^{31}P NMR spectrum exhibited an AX quartet (δ_P 101.8, 146.5 (J(P-P) = 186.0 Hz)), with a large J(P-P) value very similar to those observed for the three-carbon-bridged complexes obtained in the olefin reactions.[2c] The one-carbon-bridged product **14** also was obtained in 14% yield in this reaction. This complex did show a C=O stretch at 1712 cm^{-1} in the IR spectrum and exhibited ^1H and ^{31}P NMR spectra that were nearly identical with those obtained for complex **12** from the methyl propiolate reaction. None of the unbridged product analogous to **11** was obtained from this reaction in several attempts. We lack a good explanation for this difference. A possible explanation for the formation of two different bridged products is that the intermediate complex which contains the axially bound vinylic group may be formed by either cis or trans addition of P–H and exists as a mixture of cis and trans isomers, **15** and **16**. Isomer **15**

15   16
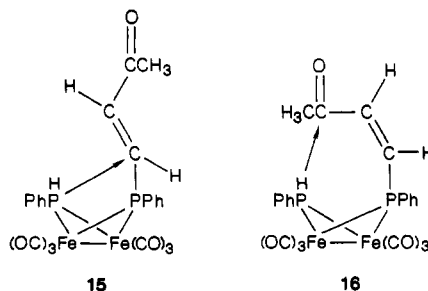
may then lead exclusively to the one-carbon-bridged

(3) Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. *J. Organomet. Chem.* **1981**, *222*, 263.

(4) Grim, S. O.; Molenda, R. P.; Mitchell, J. D. *J. Org. Chem.* **1980**, *45*, 250.

species, while 16 leads to the three-carbon-bridged complex. On the other hand, both products may arise from the same intermediate, but via two transition states which are not very different in energy.

The reaction with 3-butyn-2-one also was carried out using a fivefold excess of the acetylene, and, in this case, three products were obtained (eq 3). Complexes 13 and

$$13 + 14 + \quad (3)$$
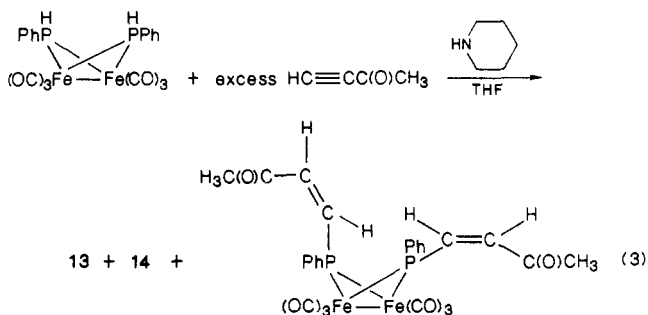
14 were isolated as a mixture, in 44% combined yield. The disubstituted complex 15 also was obtained as a single, asymmetric isomer in 49% yield. This complex was identified on the basis of its IR spectrum, which showed a strong C=O stretch at 1690 cm^{-1}, and its ^{1}H NMR spectrum, which clearly showed resonances for two inequivalent organic substituents. This asymmetric species gave rise to a singlet (δ_P 118.0) in the ^{31}P NMR spectrum, behavior similar to that which we had observed for (μ-PhPCH$_3$)$_2$Fe$_2$(CO)$_6$ and (μ-PhPCH$_2$CH$_2$CO$_2$CH$_3$)$_2$Fe$_2$-(CO)$_6$.[2] The isolation of complex 15 would seem to indicate that the monosubstituted, unbridged isomer which we expected to obtain from the 1:1 reaction should not be inherently unstable and, indeed, is probably present in solution at some point during the reaction.

Reaction of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ with 1 equiv of 3-pentyn-2-one again yielded two products. In this case, complexes 18 and 19 were obtained in 13 and 41% yield, respectively (eq 4). Complex 18 showed spectral data typical

$$18 \qquad 19 \qquad (4)$$
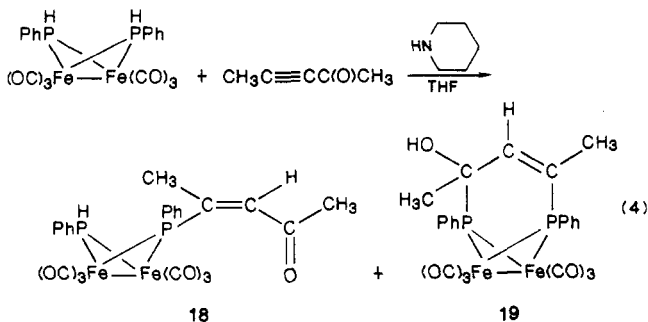
for these unbridged species, including a P–H resonance in the ^{1}H NMR spectrum at 3.47 ppm ($J(P_1$–H) = 386.0 Hz, $J(P_2$–H) = 24.3 Hz). The ^{1}H NMR spectrum also showed that trans addition of P–H to the C≡C bond had again occurred (J(P–H) = 30.0 Hz). The spectral data for complex 19 also were in line with those obtained for the other three-carbon-bridged species. Although species 18 was isolated in poor yield, it is quite stable and shows that these (β-oxovinyl)phosphido products are viable species.

Reactions with acetylenes that contain two electron-withdrawing groups proceed differently from those discussed above. Reaction of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ with 1 equiv of ethyl phenylpropiolate yielded two products, 20 and 21, in 24 and 44% yield, respectively (eq 5). The structure of the unbridged complex 20 is easily assigned on the basis of the spectroscopic data, and the ^{1}H NMR spectrum again showed that the isomer resulting from trans addition is obtained exclusively (J(P–H) = 28.1 Hz). The structure

$$20 \qquad 21 \qquad (5)$$
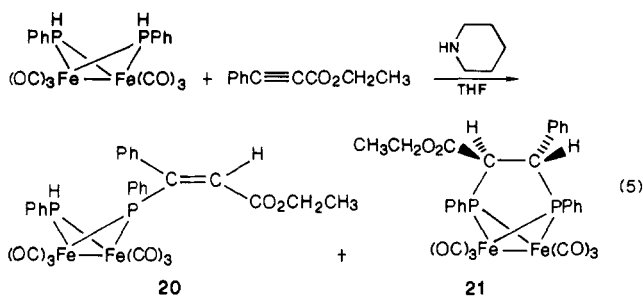
of the two-carbon-bridged complex 21 was confirmed by its ^{31}P and ^{1}H NMR spectra. The ^{31}P spectrum showed an AX pattern (δ_P 174.3, 182.0 (J(P–P) = 134.7 Hz)) in which both resonances are shifted downfield relative to those of the one- and three-carbon-bridged products and in which the J(P–P) value has been significantly decreased from the 175–185 Hz range observed in the three-carbon-bridge case. The ^{1}H NMR spectrum showed two doublets of doublets (3.54, 4.00 ppm) for the bridge protons that are coupled to each other and to both phosphorus nuclei. There are two possible isomers of this product, corresponding to cis or trans orientations of the bridge protons with respect to the cluster framework, but only one of these is obtained. Unfortunately, ^{1}H NMR data for similar types of compounds are not available, so that no correlation between the magnitude of the vicinal coupling constant and the orientation of these protons can be made. Although we cannot make a conclusive assignment based on the spectral data, we have depicted this product as the trans isomer, since this isomer minimizes the steric interactions between the large groups in the alkylene bridge.

In a similar manner, reaction of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ with dimethyl acetylenedicarboxylate gave the unbridged and bridged products 22 and 23, in 37 and 54% yields, respectively (eq 6). Complex 22 is a new type of product

$$22 \qquad 23 \qquad (6)$$
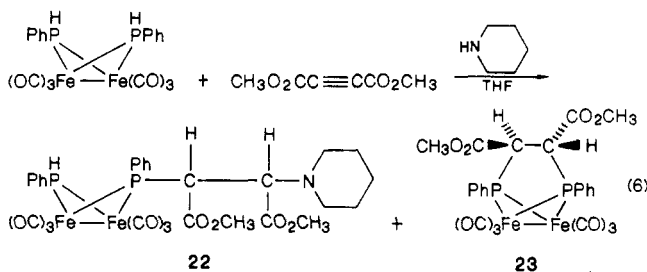
and results from addition of piperidine to the C=C bond of the more usual unbridged species. The resonances of the saturated ring protons are easily observed in the ^{1}H NMR spectrum, and all other data are in accord with the structure shown. This secondary reaction with piperidine probably occurs because the typical unsaturated, unbridged species in this case would still be very electrophilic (since the carbon atoms of the C=C bond bear two carbomethoxy groups and the electron-withdrawing phosphido group) and thus the vinyl intermediate is activated toward further nucleophilic attack. The two-carbon-bridged product 23 also is obtained in this reaction. This complex showed a singlet at 179.1 ppm in the ^{31}P NMR spectrum and a doublet of doublets for the two equivalent bridge protons at 3.66 ppm in the ^{1}H NMR spectrum. Again we depict this species as the trans isomer, although we have no conclusive evidence for this assignment.

Thus, we have identified four distinct reaction pathways in the reactions of electrophilic acetylenes with (μ-PhPH)$_2$Fe$_2$(CO)$_6$. First, as in the case of the olefin reactions, the unbridged, monosubstituted product 7 can be obtained, and we have observed this product in all of the

reactions except for that with 3-butyn-2-one. In all cases, we isolated a single isomer of this product, and we feel that this is due to the fact that, as in the olefin case, the initial attack of the phosphorus nucleophile can occur to give either the axially or equatorially substituted product and that the axially substituted species reacts completely and irreversibly to give the appropriate bridged species. We have also obtained one-carbon-bridged species, analogous to those observed in the addition of (μ-HS)₂Fe₂(CO)₆ to electrophilic acetylenes. These products were obtained only with the terminal acetylenes HC≡CC(O)CH₃ and HC≡CCO₂CH₃, i.e., where R = hydrogen, and we suggest that this is due to simple steric effects. When two activating groups are present in the acetylene, as with PhC≡CCO₂CH₂CH₃ and CH₃O₂CC≡CCO₂CH₃, two-carbon-bridged products of type 9 are obtained. This may be understood by considering the intermediate formed by addition of the P–H to the C≡C bond, 24. Addition of
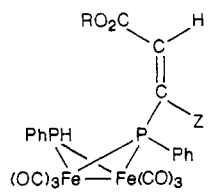
24a, Z = CO₂CH₃; R = CH₃
  b, Z = Ph; R = C₂H₅

the second P–H to the C=C bond could take place so that a one-carbon bridge is formed (25a) or a two-carbon bridge (25b). In either mode of addition, the intermediate anion
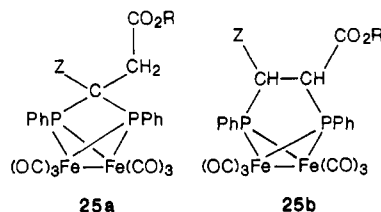
25a   **25b**

will be stabilized. That being the case, the direction of addition of the second P–H will be the one that gives the less strained product, 25b. Finally, three-carbon-bridged products 10 are obtained in the case where R is neither electron-withdrawing enough to favor formation of 9 nor small enough to favor formation of 8. A product of type 10 is formed in the reaction with CH₃C≡CC(O)CH₃, since the other reaction pathways are less favorable for this acetylene. The three-carbon-bridged species is also the major product of the reaction of (μ-PhPH)₂Fe₂(CO)₆ with HC≡CC(O)CH₃, indicating that, when it can be formed, the larger ring size product is favored, for either steric or electronic reasons.

Experimental Section

General Comments. The "general comments" of our initial paper on the reactivity of (μ-PhPH)₂Fe₂(CO)₆ and (μ-PhPLi)₂Fe₂(CO)₆²ᵃ are applicable. All reactions were carried out under an atmosphere of prepurified nitrogen.

Reaction between Bis(μ-phenylphosphido)bis(tricarbonyliron) and Methyl Acrylate. In a drybox, a 200-mL Schlenk flask equipped with a stir bar and a serum cap was charged with 0.622 g (1.25 mmol) of (μ-PhPH)₂Fe₂(CO)₆. THF (50 mL) was added, and the resulting solution was cooled to –78 °C. Next, 0.108 mL (1.25 mol) of HC≡CCO₂Me (Aldrich) and 0.20 mL (2.02 mmol) of piperidine were added by syringe, causing a yellow-to-orange-red color change. After it had been stirred for 0.5 h at –78 °C and overnight at room temperature, the solution was orange. Solvent was removed on a rotary evaporator to give a dark red, gummy residue which was extracted with 30% dichloromethane/pentane until the washings were colorless. After

filtration of the extracts and evaporation of solvent, the orange-red residue was chromatographed on a 2.5 × 30 cm Florisil column. Elution with 25% CH₂Cl₂/hexane separated two yellow bands and with 70% CH₂Cl₂/hexane separated a third. (This is the "standard workup" in all subsequent experiments.)

(1) (μ-PhPH)₂Fe₂(CO)₆ (0.04 g, 0.08 mmol, 6% recovery), identified by comparison of its ³¹P NMR spectrum and melting point with those of an authentic sample, and (2) 0.196 g (0.34 mmol, 27%) of orange crystals of (μ-PhPH)(μ-cis-CH₃O₂CCH=CHPPh)Fe₂(CO)₆ (11), which were recrystallized from pentane (mp 73–74 °C): IR (CHCl₃) ν(C=O) 1722 (vs), terminal carbonyl region, 2075 (s), 2035 (s), 1995 (s), 1982 (sh) cm⁻¹; 250-MHz ¹H NMR (CDCl₃) δ 3.65 (dd, J(P₁–H) = 385.2 Hz, J(P₂–H) = 22.0 Hz, PH, 1 H), 3.65 (s, CO₂CH₃, 3 H), 6.41 (dd, J(H–H) = 12.7 Hz, J(P–H) = 32.4 Hz, (H)C=C(H)CO₂CH₃, 1 H), 7.25–7.67 (PhP and (H)C=C(H)CO₂CH₃, 11 H); ³¹P NMR (CHCl₃) δ_P 81.5, 113.8 (AX quartet, J(P–P) = 146.5 Hz, one diastereomer), 73.8, 135.5 (AX quartet, J(P–P) = 146.5 Hz). Anal. Calcd for C₂₂H₁₆O₈P₂Fe₂: C, 45.40; H, 2.77. Found: C, 45.26; H, 2.84.

(3) Orange crystals of (μ-CH₃O₂CCH₂CH(PPh)₂)Fe₂(CO)₆ (12), (0.238 g, 0.41 mmol, 33%) which were recrystallized from pentane: mp 108–110 °C; IR (CHCl₃) ν(OH) 3400 (br), ν(C=O) 1723 (s), terminal carbonyl region, 2078 (s), 2040 (vs), 1998 (s), 1980 (sh) cm⁻¹; 250-MHz ¹H NMR (CDCl₃) δ 3.09 (td, J(H–H) = 6.9 Hz, J(P–H) = 16.4 Hz, CH₂CO₂CH₃, 2 H), 3.22 (s, CO₂CH₃, 3 H), 5.79 (m, C(H)CH₂, 1 H), 7.42–7.59 (complex m, PhP, 10 H); ³¹P NMR (CHCl₃) δ_P 89.4 (s). Anal. Calcd for C₂₂H₁₆O₈P₂Fe₂: C, 45.40; H, 2.77. Found: C, 45.53; H, 2.87.

Reaction between Bis(μ-phenylphosphido)bis(tricarbonyliron) and 3-Butyn-2-one. (a) 1:1 Molar Ratio. The standard apparatus was charged with 0.538 g (1.08 mmol) of (μ-PhPH)₂Fe₂(CO)₆ and THF (50 mL). The resulting solution was cooled to –78 °C. Next, 0.085 mL (1.08 mmol) of HC≡CC(O)Me (Farchan) and 0.20 mL (2.02 mmol) of piperidine were added by syringe, causing a yellow-to-orange-red color change. After it had been stirred for 0.5 h at –78 °C and overnight at room temperature, the solution was orange. The standard workup left an orange-red residue that was chromatographed on a 2.5 × 30 cm Forisil column. Elution with 30% CH₂Cl₂/hexane separated two bright yellow bands.

(1) Yellow crystals of (μ-HC=CHC(OH)(CH₃)PPh)(PPh))Fe₂(CO)₆ (13) (0.342 g, 0.60 mmol, 56%), which were recrystallized from pentane: mp 153–155 °C; IR (CHCl₃) ν(OH) 3580 (m), 3400 (br), terminal carbonyl region, 2075 (s), 2039 (vs), 2000 (m), 1979 (m) cm⁻¹; 250-MHz ¹H NMR (CDCl₃) δ 1.32 (d, J(P–H) = 11.7 Hz, CH₃, 3 H), 1.64 (s, OH, 1 H), 5.84 (ddd, J(H–H) = 12.1 Hz, J(P₁–H) = 35.9 Hz, J(P₂–H) = 19.9 Hz, =C(H)C(OH), 1 H), 6.26 (dd, J(P–H) ≃ J(H–H) = 12.1 Hz, PC(H)=, 1 H), 7.41–7.76 (complex m, PhP, 10 H); ³¹P NMR (CHCl₃) δ_P 101.8, 146.5 (AX quartet, J(P–P) = 186.0 Hz).

(2) Orange crystals of (μ-CH₃C(O)CH₂CH(PPh)₂)Fe₂(CO₆) (14) (0.080 g, 0.14 mmol, 14%), which were recrystallized from pentane: mp 176–178 °C; IR (CHCl₃) ν(C=O) 1720, terminal carbonyl region, 2047 (s), 2005 (vs), 1983 (s), 1960 (s), 1930 (sh) cm⁻¹; 250-MHz ¹H NMR (CDCl₃) δ 1.92 (s, CH₃, 3 H), 3.20 (td, J(P–H) = 16.8 Hz, J(H–H) = 6.0 Hz, CH₂, 2 H), 5.58 (tt, J(P–H) = 14.1 Hz, J(H–H) = 6.0 Hz, C(H)CH₂, 1 H), 7.38–7.54 (complex m, PhP, 10 H); ³¹P NMR (CHCl₃) δ_P 88.3 (s). Satisfactory analytical data were obtained on a mixture of 13 and 14. Anal. Calcd for C₂₂H₁₆O₇P₂Fe₂: C, 46.69; H, 2.85. Found: C, 46.43; H, 2.94.

(b) Excess of 3-Butyn-2-one. The reaction was carried out as in (a) using 1.17 mmol of (μ-PhPH)₂Fe₂(CO)₆ and 5.84 mmol of HC≡CC(O)CH₃ (0.2 mL of piperidine, 50 mL of THF). Standard workup gave an orange-red residue that was chromatographed on a 2.5 × 30 cm Florisil column. Elution with 20% CH₂Cl₂/hexane separated one yellow band and with 70% CH₂Cl₂/hexane separated another.

(1) A mixture of 13 and 14 (0.290 g, 0.51 mmol, 44%), identified by comparison of its ³¹P NMR spectrum with those of authentic samples (from (a)), and (2) 0.362 g (0.57 mmol, 49%) of orange crystals of (a,e-μ-cis-CH₃C(O)CH=CHPPh)₂Fe₂(CO)₆ (17), which were recrystallized from pentane (mp 122–124 °C): IR (CHCl₃) ν(C=O) 1690, terminal carbonyl region, 2057 (s), 2022 (vs), 1985 (vs), 1963 (sh) cm⁻¹; 250-MHz ¹H NMR (CDCl₃) δ 1.88, 2.16 (both s, CH₃, 6 H), 5.66, 5.95, 6.58, 7.01 (all m, J(H–H) ≃ 12 Hz,

P(H)C=C(H)C(O)CH$_3$, 4 H), 7.22–7.86 (complex m, PhP, 10 H); ^{31}P NMR (CDCl$_3$) δ_P 118.0 (s). Anal. Calcd for C$_{26}$H$_{20}$O$_8$P$_2$Fe$_2$: C, 49.25; H, 3.18. Found: C, 49.15; H, 3.22.

Reaction between Bis(μ-phenylphosphido)bis(tricarbonyliron) and 3-Pentyn-2-one. To a solution of 0.703 g (1.41 mmol) of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ in 50 mL of THF at –78 °C was added 0.13 mL (1.41 mmol) of CH$_3$C≡CC(O)CH$_3$[5] and 0.20 ml (2.02 mmol) of piperidine, causing a yellow-to-orange-red color change. After it had been stirred for 0.5 h at –78 °C and overnight at room temperature, the solution was orange. Standard workup gave an orange-red solid that was chromatographed on a 2.5 × 30 cm Florisil column. Elution with 30% CH$_2$Cl$_2$/hexane separated one yellow band and with 40% CH$_2$Cl$_2$/hexane separated another.

(1) Orange crystals of (μ-PhPH)(μ-cis-CH$_3$C(O)CH=C(CH$_3$)-PPh)Fe$_2$(CO)$_6$ (18) (0.105 g, 0.18 mmol, 13%), which were recrystallized from dichloromethane/pentane: mp 167–169 °C; IR (CHCl$_3$) ν(C=O) 1690 (s), terminal carbonyl region, 2050 (s), 2012 (vs), 1982 (vs), 1955 (sh) cm^{-1}; 250-MHz ^{1}H NMR (CDCl$_3$) δ 2.28 (s, C(O)CH$_3$, 3 H), 2.30 (dd, J(P$_1$-H) ≃ 13.5 Hz, J(P$_2$-H) = 2.5 Hz, PC(CH$_3$), 3 H, partially obscured by C(O)CH$_3$ resonance), 3.47 (dd, J(P$_1$-H) = 386.0 Hz, J(P$_2$-H) = 24.3 Hz, PH, 1 H), 6.50 (d, J(P–H)$_{trans}$ = 30.0 Hz, =C(H)CO$_2$CH$_3$, 1 H), 7.28–8.04 (complex m, PhP, 10 H); ^{31}P NMR (CDCl$_3$) δ_P 80.2, 133.1 (AX quartet, J(P-P) = 142 Hz). Anal. Calcd for C$_{23}$H$_{18}$Fe$_2$P$_2$O$_7$: C, 47.63; H, 3.13. Found: C, 47.82; H, 3.35.

(2) Orange crystals of (μ-CH$_3$C=C(H)C(OH)(CH$_3$)(PPh)-(PPh))Fe$_2$(CO)$_6$ (19) (0.405 g, 0.7 mmol, 41%), which were recrystallized from dichloromethane/pentane: mp 139–140 °C; IR (CHCl$_3$) ν(OH) 3400 (vs, br), ν(C=C) 1618 (s), terminal carbonyl region, 2053 (vs), 2015 (vs), 1993 (s), 1920 (s) cm^{-1}; 250-MHz ^{1}H NMR (CDCl$_3$) δ 1.29 (d, J(P-H) = 11.8 Hz, CH$_3$, 3 H), 1.46 (d, J(P-H) = 11.8 Hz, CH$_3$, 3 H), 1.62 (s, OH, 1 H), 5.66 (dd, J(P$_1$-H) = 21.9 Hz, J(P$_2$-H) = 33.7 Hz, =C(H), 1 H), 7.44–7.77 (complex m, PhP, 10 H); ^{31}P NMR (CHCl$_3$) δ_P 113.4, 150.4 (AX quartet, J(P-P) = 185.5 Hz). Anal. Calcd for C$_{23}$H$_{18}$Fe$_2$P$_2$O$_7$: C, 47.63; H, 3.13. Found: C, 47.77; H, 3.20.

Reaction between Bis(μ-phenylphosphido)bis(tricarbonyliron) and Ethyl Phenylpropiolate. The standard apparatus was charged with 0.69 g (1.39 mmol) of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ and THF (50 mL) and the resulting solution cooled to –78 °C. Next, 0.23 mL (1.39 mmol) of PhC≡CCO$_2$Et (Aldrich) and 0.20 mL (2.02 mmol) of piperidine were added, causing a yellow-to-orange-red color change. After it had been stirred for 0.5 h at –78 °C and overnight at room temperature, the solution was orange. Standard workup gave an orange-red residue that was chromatographed on a 2.5 × 30 cm Florisil column. Elution with 15% CH$_2$Cl$_2$/hexane separated one yellow band and with 40% CH$_2$Cl$_2$/hexane separated another.

(1) Yellow-orange crystals of (μ-PhPH)(μ-cis-(CH$_3$CH$_2$O$_2$CCH=C(Ph)PPh))Fe$_2$(CO)$_6$ (20) (0.221 g, 0.33 mmol, 24%), which were recrystallized from dichloromethane/pentane: mp 172–174 °C; IR (CHCl$_3$) ν(C=O) 1712 (vs), terminal carbonyl region, 2071 (s), 2040 (vs), 1987 (vs) cm^{-1}; 250-MHz ^{1}H NMR (CDCl$_3$) δ 1.31 (t, J(H-H) = 7.2 Hz, CH$_3$, 3 H), 3.65 (dd, J(P$_1$-H) = 386.0 Hz, J(P$_2$-H) = 21.0 Hz, PH, 1 H), 4.29 (q, J(H-H) = 7.1 Hz, CH$_2$, 2 H), 6.45 (d, J(P–H)$_{trans}$ = 28.1 Hz, C=C(H), 1 H),

7.28–8.13 (complex m, arene H, 15 H); ^{31}P NMR (CDCl$_3$) δ_P 81.6, 127.0 (AX quartet, J(P-P) = 136.7 Hz). Anal. Calcd for C$_{29}$H$_{22}$O$_8$Fe$_2$P$_2$: C, 51.82; H, 3.30. Found: C, 51.68; H, 3.39.

(2) Orange crystals of (μ-PhCHCH(CO$_2$CH$_2$CH$_3$)(PPh)-(PPh))Fe$_2$(CO)$_6$ (21) (0.411 g, 0.61 mmol, 44%), which were recrystallized from dichloromethane/pentane: mp 155–156 °C; IR (CHCl$_3$) ν(C=O) 1712 (vs), terminal carbonyl region, 2057 (s), 2018 (vs), 1998 (s), 1975 (m) cm^{-1}; 250-MHz ^{1}H NMR (CDCl$_3$) δ 0.73 (t, J = 7 Hz, CH$_3$, 3 H), 3.54 (ddd, J(H-H) = 5.8 Hz, J(P$_1$-H) = 14.5 Hz, J(P$_2$-H) = 1.3 Hz, (H)CCO$_2$C-H$_2$CH$_3$, 1 H), 3.67 and 3.74 (both d of q, J(H-H)$_{vic}$ = 7.0 Hz, diastereotopic H's of CH_2CH$_3$, 2 H; 3.67 and 3.74 ppm resonances collapse to an AB quartet upon irradiation of t at 0.73 ppm (J(H-H)$_{gem}$ = 10.8 Hz)), 4.0 (ddd, J(H-H) = 5.8 Hz, J(P$_1$-H) = 15.5 Hz, J(P$_2$-H) = 2.1 Hz, (H)CPh or (H)CCO$_2$CH$_2$CH$_3$, 1 H), 6.89–7.85 (complex m, arene H, 15 H). ^{31}P NMR (CHCl$_3$) δ_P 174.3, 182.0 (AB quartet, J(P-P) = 134.7 Hz). Anal. Calcd for C$_{29}$H$_{22}$O$_8$Fe$_2$P$_2$: C, 51.82; H, 3.30. Found: C, 51.96; H, 3.38.

Reaction between Bis(μ-phenylphosphido)bis(tricarbonyliron) and Dimethyl Acetylenedicarboxylate. Using the standard procedure, a reaction was carried out between 0.720 g (1.44 mmol) of (μ-PhPH)$_2$Fe$_2$(CO)$_6$ and 0.177 mL (1.44 mmol) of CH$_3$O$_2$CC≡CCO$_2$CH$_3$ in the presence of 0.2 mL of piperidine in 50 mL of THF, initially at –78 °C (30 min) and then at room temperature overnight. The usual workup gave an orange-red residue that was chromatographed on a 2.5 × 30 cm Florisil column. Elution with 25% CH$_2$Cl$_2$/hexane separated one yellow band and with 65% CH$_2$Cl$_2$/hexane separated another.

(1) Orange crystals of (μ-PhPH)(μ-C$_5$H$_{10}$N(H)C(CO$_2$CH$_3$)C-(H)(CO$_2$CH$_3$)PPh)Fe$_2$(CO)$_6$ (22) (0.345 g, 0.5 mmol, 37%), which were recrystallized from dichloromethane/pentane: mp 156–158 °C; IR (CHCl$_3$) ν(C=O) 1725 (vs), terminal carbonyl region, 2078 (s), 2040 (vs), 1998 (s), 1982 (s) cm^{-1}; 250-MHz ^{1}H NMR (CDCl$_3$) δ 1.30–1.57 (m, CH$_2$(CH_2)$_3$CH$_2$, 6 H), 2.01–2.05 and 2.54–2.61 (m, CH_2NCH_2, 4 H), 3.05 (dd, J(P$_1$-H) = 389.2 Hz, J(P$_2$-H) = 22.7 Hz, P-H, 1 H), 2.87 (dd, J(H-H) = 11.7 Hz, J(P-H) = 8.6 Hz, PC(H)CO$_2$CH$_3$, 1 H), 3.65 (d, J(H-H) = 11.7 Hz, C(H)N, 1 H), 3.78 (s, CO$_2$CH$_3$, PhP, 10 H); ^{31}P NMR (CHCl$_3$) δ_P 81.5, 122.5 (AX quartet, J(P-P) = 141.6 Hz). Anal. Calcd for C$_{29}$H$_{29}$Fe$_2$P$_2$O$_{10}$N: C, 48.03; H, 4.03. Found: C, 47.85; H, 4.06.

(2) Orange crystals of (μ-HC(CO$_2$CH$_3$)CH(CO$_2$CH$_3$)(PPh)-(PPh))Fe$_2$(CO)$_6$ (23) 0.502 g, 0.78 mmol, 54%), which were recrystallized from dichloromethane/pentane: mp 175–177 °C; IR (CHCl$_3$) ν(C=O) 1722 (vs), terminal carbonyl region, 2075 (s), 2045 (vs), 2000 (vs), 1990 (s) cm^{-1}; 250-MHz ^{1}H NMR (CDCl$_3$) δ 3.29 (s, CO$_2$CH$_3$, 6 H), 3.66 (dd, J(P$_1$-H) = 5.6 Hz, J(P$_2$-H) = 4.7 Hz, C(H)C(H), 2 H), 7.45–7.78 (complex m, PhP, 10 H); ^{31}P NMR (CHCl$_3$) δ_P 179.1 (s). Anal. Calcd for C$_{24}$H$_{18}$O$_{10}$P$_2$Fe$_2$: C, 45.04; H, 2.83. Found: C, 45.04; H, 2.87.

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