in idealized postions with group isotropic dfc's. The final $R$ and $R_w$ values were 0.064 and 0.059, respectively, with 386 parameters and weights = $1/[\sigma^2(F_o) + 0.0005F_o^2]$. The maximum and minimum values on the final difference electron density map were +0.6 and −0.4 e Å$^{-3}$, respectively. The non-hydrogen atom coordinates are listed in Table V.

**Acknowledgment.** We are grateful to the Science and Engineering Research Council for support (to L.M.W.) and for the provision of X-ray facilities.

**Registry No.** 1, 109630-83-3; 2, 109630-95-7; 3, 110613-17-7; 4, 109631-03-0; 5, 109631-01-8; 6, 109631-07-4; 7, 109631-05-2; 8, 110589-64-5; 9, 110589-66-7; 10, 110589-68-9; 11, 110589-70-3; 12, 109631-37-0; 13, 109631-09-6; 14, 110589-72-5; 15, 110589-74-7; 16, 109630-97-9; 17, 110589-76-9; 18, 110589-79-2; [$Cp_2Ti\{\eta^2$-C(Me)N-$t$-Bu$\}$(CN-$t$-Bu)]$BPh_4$, 110589-78-1; $Cp_2TiMe_2$, 1271-66-5; $Cp_2TiMeCl$, 1278-83-7; $Ind_2TiMeCl$, 109630-87-7; [$Cp_2TiMe(NH_3)$]$ClO_4$, 109630-84-4; $Cp_2TiCl_2$, 1271-19-8; $t$-BuNC, 7188-38-7; carbon monoxide, 630-08-0.

**Supplementary Material Available:** Tables of fractional coordinates of hydrogen atoms, $U_{ij}$ values for non-hydrogen atoms, bond lengths and angles (4 pages); lists of $F_o/F_c$ values (26 pages). Ordering information is given on any current masthead page.

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# Michael-Type Addition Reactions of Bis($\mu$-phenylphosphido)bis(tricarbonyliron) with Olefinic $\alpha,\beta$-Unsaturated Carbonyl Compounds. Construction of Chelating Bis(phosphido) Ligands

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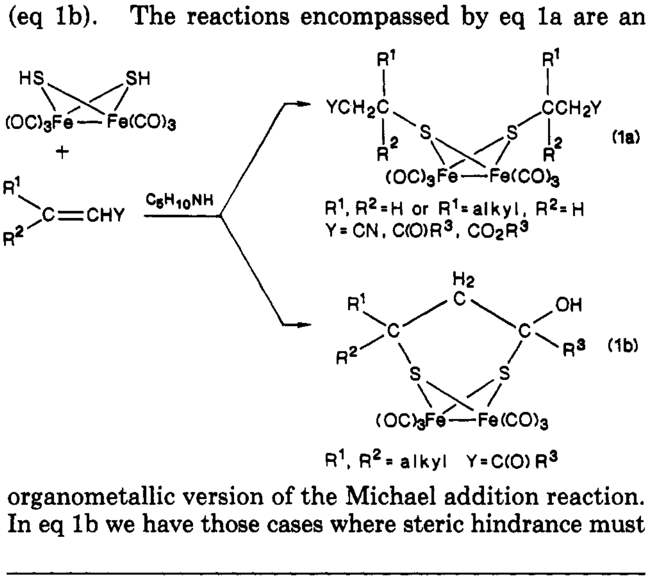
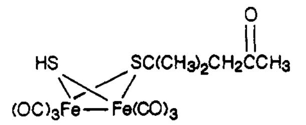
The piperidine-catalyzed addition of ($\mu$-PhPH)$_2Fe_2(CO)_6$ to olefinic $\alpha,\beta$-unsaturated esters and ketones has been studied. With esters, 1:1 and 2:1 adducts were obtained. With terminally unsubstituted or monosubstituted ketones, two types of products were obtained in 1:1 reactions: the simple 1:1 addition product of a PH unit to the C=C bond and a bridged product in which one PH unit had added to the C=C bond and the other to the C=O bond of the $\alpha,\beta$-unsaturated ketone. In the case of mesityl oxide, a terminally disubstituted $\alpha,\beta$-unsaturated ketone, only the product of PH addition to the C=C bond was formed.

## Introduction

In earlier studies, we investigated base-catalyzed addition of the SH units of ($\mu$-HS)$_2Fe_2(CO)_6$ to $\alpha,\beta$-unsaturated carbonyl compounds and nitriles.[1] In the case of olefinic $\alpha,\beta$-unsaturated substrates, two types of behavior were encountered: independent addition of the two SH units to two molecules of the $\alpha,\beta$-unsaturated compound (eq 1a) and addition of both SH units to one molecule of the olefin, one SH to the C=C bond and the other to the C=O bond (eq 1b). The reactions encompassed by eq 1a are an organometallic version of the Michael addition reaction. In eq 1b we have those cases where steric hindrance must be operative.

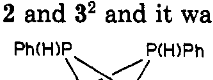


The initial 1:1 adduct (e.g., 1 in the case of mesityl oxide) is too hindered to permit attack on a second $(CH_3)_2C{=}CHC(O)CH_3$ molecule.

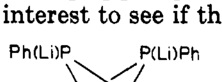


1

(Most likely, both isomers in which the $SC(CH_3)_2CH_2C(O)CH_3$ group is axial or equatorial are present.[1] As a consequence, the second SH adds to the C=O bond of the newly introduced organic group, giving a chelating 1,3-propanedithiolato unit, which contains an alcohol function. Similar base-catalyzed addition reactions of ($\mu$-HS)$_2Fe_2(CO)_6$ to acetylenic $\alpha,\beta$-unsaturated carbonyl compounds were observed. In parallel studies we have been investigating the chemistry of a phosphorus analogue of ($\mu$-HS)$_2Fe_2(CO)_6$ and its derived dianion, [($\mu$-S)$_2Fe_2(CO)_6$]$^{2-}$, the bridging phosphido complexes 2 and 3[2] and it was of interest to see if the base-catalyzed additions of 2 to $\alpha,\beta$-unsaturated substrates would proceed similarly to such reactions of ($\mu$-HS)$_2Fe_2(CO)_6$.



2



3

In the present paper we report our results of

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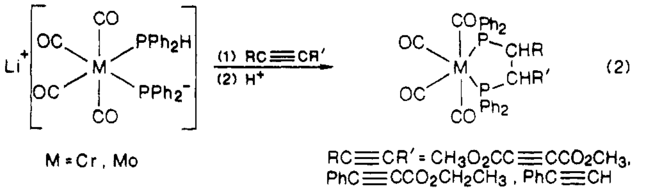
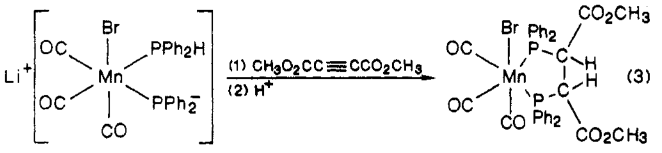
(1) Seyferth, D.; Womack, G. B.; Henderson, R. S.; Cowie, M.; Hames, B. W. *Organometallics* **1986**, *5*, 1568.

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

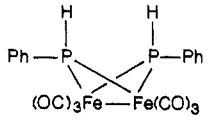
base-catalyzed reactions of complex **2** with olefinic $\alpha,\beta$-unsaturated carbonyl compounds. Although base-catalyzed addition of $RPH_2$ and $R_2PH$ or of phosphide anions (e.g., $R_2P^-$) to electrophilic olefins is well-known,[3] very few examples of such additions involving metal-coordinated RPH or $RP^-$ reactants have been recorded. Two examples of such reactions have been described by Treichel and Wong[4] (eq 2 and 3).

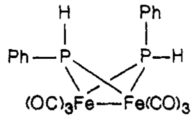


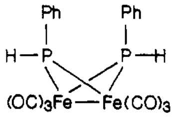


In the case of complex **2** and its derived dianion, **3**, we hoped that the close proximity of the two phenyl-phosphido units might lead to some cooperative reactivity between the phosphorus centers and thus allow us to prepare "linked" bis(phosphido) ligands. We also hoped that the different steric requirements of the PhP and S units, as well as the increased stability of the metal-bonded PhPH unit, relative to its SH counterpart, might allow us to isolate species that were postulated as intermediates in the reactions of the thiol complex.

Bis($\mu$-phenylphosphido)bis(tricarbonyliron) is readily prepared by the reaction of $PhPH_2$ with $Fe(CO)_5$,[5] and in this preparation a mixture of three isomers, **2a**, **2b**, and **2c** (~50:45:5 ratio) is obtained. This isomer mixture was used during the course of this study.


**2a**

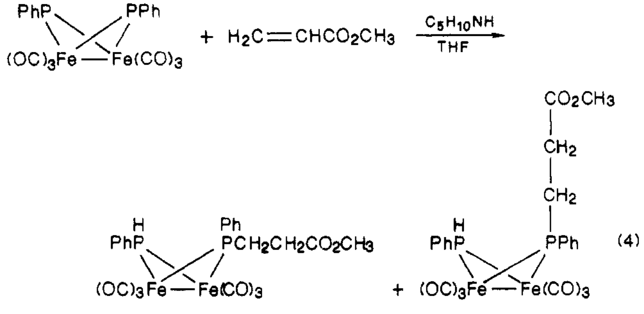

**2b**


**2c**

## Results and Discussion

Our previous work on the addition reactions of ($\mu$-HS)$_2$Fe$_2$(CO)$_6$ to $\alpha,\beta$-unsaturated substrates showed that these reactions proceed smoothly at relatively low temperature in the presence of a secondary amine base such as piperidine in tetrahydrofuran (THF) solvent. In the present work we chose to employ similar reaction conditions, rather than the lithiation route used by Treichel.[4] The piperidine-induced reactions with ($\mu$-HS)$_2$Fe$_2$(CO)$_6$ had been found to be catalytic in base, thus obviating the need to employ larger quantities of lithium reagents. Secondly, in the piperidine system, a separate reprotonation step is not required, the system being reprotonated internally as the reaction proceeds. Thirdly, the piperidine method does not involve high concentrations of very nucleophilic carbanion species, which in the lithium case might undergo undesirable side reactions. Thus, all reactions of ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$ with electrophilic olefins and acetylenes were carried out under the same set of reaction conditions: A solution of the iron complex **1** in THF (1–1.5 mmol), under nitrogen, was cooled to −78 °C, and the desired quantity of the $\alpha,\beta$-unsaturated substrate was added. Addition of piperidine (slightly less than 2 equiv, based on starting iron complex) caused a color change from orange to red. The solution was stirred for 0.5 h at −78 °C and 12–16 h at room temperature, after which time the color had changed back to orange. Workup involved evaporation of solvent, extraction into $CH_2Cl_2$/hexanes, chromatography on Florisil or silicic acid, and recrystallization. All of the products obtained were reasonably air-stable, and most are isolated as yellow or yellow-orange crystalline solids.

In our first attempt we chose an $\alpha,\beta$-unsaturated substrate which, based on the known chemistry of ($\mu$-HS)$_2$Fe$_2$(CO)$_6$, should react with ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$ via a single addition of a P–H bond to the carbon–carbon double bond. Reaction of the iron complex with 1 equiv of methyl acrylate under the conditions described above did lead to the expected monosubstituted product, **4**, in 74% yield (eq 4). This complex showed a strong C═O stretch at 1738 cm$^{-1}$ in the IR spectrum, indicating that the ester carbonyl group had been retained but that it was no longer in conjugation with a C═C bond. The IR spectrum also showed a four-band pattern for the C≡O ligands, the center of gravity of which was shifted slightly to lower energy relative to that of the starting complex, indicating that the incorporation of the organic moiety had increased the electron density at the iron centers. The $^{31}$P NMR spectrum of **4** showed two sets of AX quartets ($\delta_P$ 83.2, 132.4 ($J$(P–P) = 146.5 Hz), 71% abundance, and 73.8, 135.5 ($J$(P–P) = 166.0 Hz), 29% abundance), indicating that two isomers were present in solution. In all, four isomers are possible for this complex. Two are depicted in eq 4 and the other two are the analogous species, which have an axially bound phenyl group on the PhPH unit. For all practical purposes, the latter two isomers can be ignored since, in this and all of the subsequent reactions that we have attempted, we have never seen evidence for more than two isomers of an unbridged product. This observation is not surprising if we consider the model case of ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$, the axial, axial-diphenyl isomer of which accounts for only 5% of the total isomer distribution.[5]



**4a** **4b**

Upon recrystallization of the mixture of isomers of **4**, the isomer with $\delta_P$ 83.1, 132.4 was obtained in pure form. The 250-MHz $^1$H NMR spectrum of this isomer showed multiplets at 2.34 and 2.61 for the $CH_2CH_2$ protons, a singlet at 3.57 for the $CH_3$ group, and a complex multiplet at 7.32–7.64 ppm for the protons of the phenyl rings. The most notable feature of the spectrum, however, was the doublet of doublets ($J$(P$_1$–H) = 388.9 Hz, $J$(P$_2$–H) = 23.4 Hz) at 3.51 ppm for the P–H proton. This pattern is characteristic of all of the unbridged, monosubstituted complexes that we have prepared and, in addition to a characteristic $^{31}$P NMR shift in the range 80–90 ppm for

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(3) *Organophosphorus Compounds*, Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1972; Vol. 1, Chapter 1, Section C.1.XII.

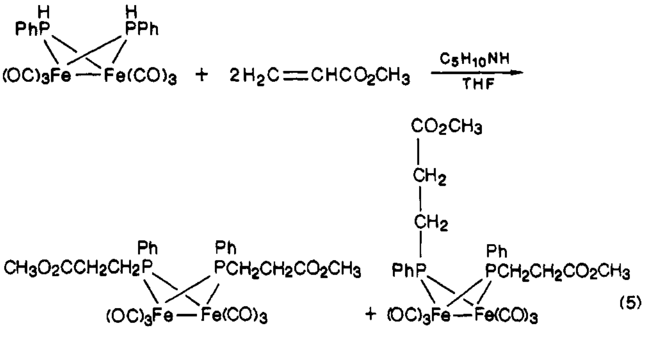
(4) Treichel, P. M.; Wong, W. K. *J. Organomet. Chem.* **1978**, *157*, C5.

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

the PhPH unit, it is diagnostic in assigning the structures of these species.

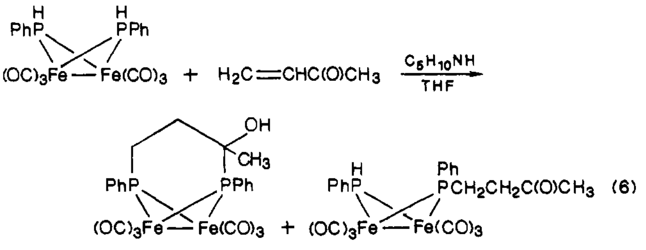
Finally, it is interesting to note that **4** is completely air- and moisture-stable, in contrast to the monoalkyl derivatives of $(HS)_2Fe_2(CO)_6$, which are quite air-sensitive. Although species containing an alkylthio and a thiol group most certainly are intermediates in the reactions of ($\mu$-HS)$_2$Fe$_2$(CO)$_6$ with alkenes and alkynes, no sulfur analogue of species **4** has been isolated from these reactions.

In a similar manner, reaction of ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$ with *2 equiv* of methyl acrylate yielded the expected disubstituted derivatives **5a,b** (eq 5). These isomeric complexes were separable by column chromatography and were obtained in 45% and 51% yields, respectively. Curiously, both **5a** and **5b** exhibit singlets in their $^{31}$P NMR spectra, although the asymmetric isomer **5b** contains nonequivalent organic residues (as determined conclusively by its $^1$H NMR spectrum, which showed resonances for two different $CH_2CH_2CO_2CH_3$ groups). Similar behavior was exhibited by the asymmetric isomer of ($\mu$-PhPMe)$_2$Fe$_2$(CO$_6$.[2a] The assignment of **5a** as the e,e isomer is also based on its similarity to ($\mu$-PhPMe)$_2$Fe$_2$(CO)$_6$ in terms of its simpler $^1$H NMR spectrum, the symmetric isomer of which was shown by X-ray crystallography to contain equatorially bound methyl groups.[6]



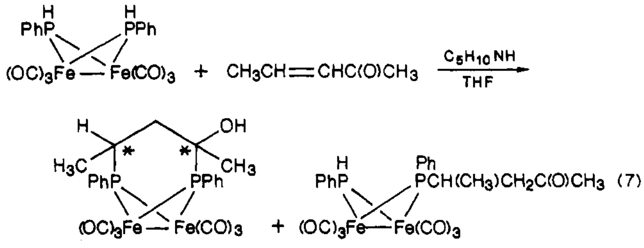
**5a** (e,e) **5b** (a,e)

We were more interested in finding routes to alkylene-bridged phosphido systems than in these simple alkyl-substituted complexes, so we turned to $\alpha,\beta$-unsaturated ketones as our substrates. In the case of ($\mu$-HS)$_2$Fe$_2$(CO)$_6$, terminally disubstituted $\alpha,\beta$-unsaturated ketones were the only olefins that yielded alkylene-bridged products. The phosphido complex has very different steric requirements than the dithiol analogue, however, and we therefore carried out a general survey of reactions with $\alpha,\beta$-unsaturated ketones of varying degrees of substitution at the terminal carbon. Reaction of **2** with methyl vinyl ketone, using the usual reaction conditions, gave two products, **6** and **7**, in 41% and 42% yields, respectively (eq 6). Complex **7** is the trivial monosubstituted alkyl derivative, arising from addition of a P-H bond to the C=C bond. The $^{31}$P NMR spectrum of this complex exhibited the expected AX quartet ($\delta_P$ 83.9, 133.4 ($J$(P-P) = 146.5 Hz) in the $^{31}$P NMR spectrum and clearly showed a P-H resonance ($J$(P$_1$-H) = 387.1 Hz, $J$(P$_2$-H) = 23.2 Hz) in the $^1$H NMR spectrum as well as a medium intensity C=O stretch at 1708 cm$^{-1}$ in the IR spectrum. It is significant that, in contrast to the case of $CH_2{=}CHCO_2CH_3$, only one of the two possible isomers of this complex was obtained and this point will be discussed in detail later. Complex **6** also exhibited an AX quartet ($\delta_P$ 129.2, 154.3) in the $^{31}$P NMR spectrum, but the resonances were shifted to lower field relative to **7**. For comparison, the simple three-carbon-bridged species ($\mu$-PhP(CH$_2$)$_3$PPh)Fe$_2$(CO)$_6$ shows a singlet at 130.0 ppm in the $^{31}$P NMR spectrum.[2a] The $J$(P-P) coupling constant also increases from 146.5 to 185.5 Hz on going from **7** to **6**. The $^1$H NMR spectrum of **6** contained no P-H resonances but clearly showed an OH resonance ($J$(P-H) = 1.5 Hz) at 1.65 ppm. The IR spectrum of **6** also showed the presence of OH and the absence of any organic carbonyl groups.



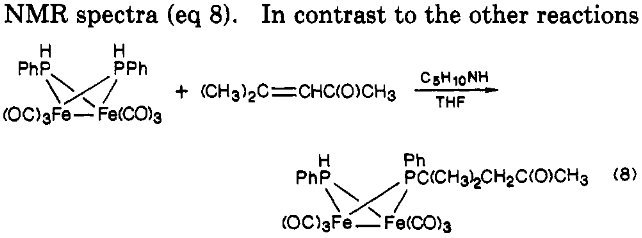
**6** **7**

Thus, in contrast to what was observed in the ($\mu$-HS)$_2$Fe$_2$(CO)$_6$ chemistry, terminally unsubstituted olefins can react with ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$ to give alkylene-bridged complexes. Olefins with terminal monosubstitution gave similar results as evidenced by the reaction of **2** with methyl propenyl ketone, in which **8** and **9** were formed in 44% and 33% yield, respectively (eq 7). The $^{31}$P NMR data from complex **9** were very similar to those obtained for **7**, and $^1$H NMR and IR spectra again provided evidence for the presence of P-H and for an organic carbonyl group. The three-carbon-bridged complex **8** was isolated as a 50:50 mixture of two diastereomers (since the two carbon atoms indicated are chiral) as evidenced by its $^{31}$P and $^1$H NMR spectra. The $^{31}$P spectrum showed $J$(P-P) couplings of 175.7 and 185.6 Hz for the two diastereomers, values very close to the 185.5 value obtained for complex **6**. The $^1$H NMR and IR spectra again were consistent with a species containing OH but no organic carbonyls.



**8** **9**

Finally, the base-catalyzed reaction was carried out with a terminally disubstituted olefinic $\alpha,\beta$-unsaturated ketone as substrate. Reaction of **2** with mesityl oxide gave, in addition to a 35% recovery of the starting iron complex, a single product, in 62% yield. This was identified as the simple monoalkylated species **10** by its IR and $^1$H and $^{31}$P NMR spectra (eq 8). In contrast to the other reactions with $\alpha,\beta$-unsaturated ketones and to the ($\mu$-HS)$_2$Fe$_2$(CO)$_6$ chemistry, none of the three-carbon-bridged product was obtained.



**10**

Our explanation for the observed reactivity of ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$ with electrophilic olefins is as follows.

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[6] Dahl, L. F.; Huntsman, J. J., cited in: Treichel, P. M.; Douglas, W. M.; Dean, W. K. *Inorg. Chem.* **1972**, *11*, 1615.

First, we feel that the initial attack of the phosphorus nucleophile at the olefinic carbon $\beta$ to the carbonyl group can either place the organic fragment in the equatorial position relative to the cluster or in the axial position. The attack of the second P–H at the carbonyl group can now occur, but *only* if the organic residue is in the axial position, where it is in close proximity to the second phosphorus atom. This conclusion is supported by the fact that in each of the $\alpha,\beta$-unsaturated ketone reactions, as well as in reactions of acetylenic $\alpha,\beta$-unsaturated ketones to be described later,[7] only one of the two possible isomers of the unbridged, monosubstituted compound was isolated. There is no compelling reason why the unbridged isomer with the organic residue in the axial position should not be isolable, other than that it reacts further to give the bridged product. We can isolate both isomers in the case of methyl acrylate because the ester group is stable toward attack by P–H. Furthermore, we have shown that the unbridged isomer of the methyl propenyl ketone adduct does not isomerize either to an axial, unbridged or to a bridged isomer, even in refluxing THF in the presence of piperidine. Therefore, the unbridged isomers that we actually isolate are *not* intermediates in the formation of the bridged products.

It might seem reasonable to postulate that the orientation of the initial attack of P–H at the olefinic carbon in these reactions might be determined by the isomeric constitution of the starting complex. If we ignore the very minor symmetric isomer, the two forms present in solution at room temperature are **2a** and **2b**. Upon their reaction with an unsaturated substrate, we should expect isomer **2a** to lead only to the bridged complex and isomer **2b** to lead to one or both of the two possible unbridged forms. The experimental evidence suggests, however, that the starting complex does not maintain its isomeric integrity during the course of the reaction. For example, reaction of **2** with mesityl oxide gives a 62% yield of a single unbridged isomer (presumably with the new organic fragment in the equatorial position), a result that should not be possible if only isomer **2b** can give rise to this product. A similar but even more dramatic scrambling of isomers was observed in the $Et_3N$-promoted reaction of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ with iodomethane, which gave a 99% yield of $(\mu\text{-}PhPMe)_2Fe_2(CO)_6)$, as a 0.93/1 mixture of the e,e-$CH_3$ and a,e-$CH_3$ isomers.[2a] Therefore, we feel that the distribution of products in these reactions is primarily determined by the steric demands of the organic electrophile, with terminally unsubstituted and monosubstituted olefins allowing formation of intermediates with an axially bound organic residue, and thus of bridged product, and with terminally disubstituted olefins such as mesityl oxide giving only the less crowded, equatorially substituted, unbridged compound.

## Experimental Section

**General Comments.** The general comments of our previous papers on the chemistry of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ and $(\mu\text{-}PhPLi)_2Fe_2(CO)_6$[2] are applicable. All reactions were carried out under an atmosphere of prepurified nitrogen.

**Reaction between Bis($\mu$-phenylphosphido)bis(tricarbonyliron) and Methyl Acrylate. (a) 1:1 Molar Ratio.** In a drybox, a 200-mL Schlenk flask equipped with a stirbar and a serum cap ("standard apparatus") was charged with 0.6094 g (1.22 mmol) of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$.[5] THF (50 mL) was added and the resulting solution cooled to −78 °C. Next, 0.11 mL (1.22 mol) of $CH_2{=}CHCO_2CH_3$ (Eastman) and 0.20 mL (2.092 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 silicic acid column. Elution with 40% $CH_2Cl_2$/hexane separated a bright yellow band, which, after removal of solvent, yielded 0.5278 g (0.90 mmol, 74%) of orange crystals of $(\mu\text{-}PhPH)(\mu\text{-}CH_3O_2CCH_2CH_2PPh)Fe_2(CO)_6$, **4**. (This was the "standard workup" used in all of the succeeding experiments.) After recrystallization from dichloromethane/pentane, material with mp 133–137 °C was obtained.

Anal. Calcd for $C_{22}H_{18}O_8Fe_2P_2$: C, 45.25; H, 3.61. Found: C, 45.30; H, 3.19. IR ($CHCl_3$): $\nu$(C=O) 1738 (vs); terminal carbonyl region, 2056 (s), 2020 (vs), 1991 (s), 1978 (s) cm$^{-1}$. 250-MHz $^1H$ NMR ($CDCl_3$): $\delta$ 2.30–2.39 and 2.57–2.66 (both m, $(CH_2)_2$, 4 H), 3.51 (dd, $J(P_1\text{–}H)$ = 388.9 Hz, $J(P_2\text{–}H)$ = 23.4 Hz, P–*H*, 1 H), 3.57 (s, $CH_3$–, 3 H) and 7.32–7.64 (complex m, *Ph*P, 10 H). $^{31}P$ NMR ($CHCl_3$): $\delta_P$ 83.1, 132.4 (AX quartet, $J$(P–P) = 146.5 Hz, one diastereomer) and 73.8, 135.5 (AX quartet, $J$(P–P) = 166.0 Hz, other diastereomer).

**(b) 1:2 Molar Ratio.** The standard apparatus was charged with 0.6001 g (1.20 mmol) of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$. THF (50 mL) was added and the resulting solution cooled to −78 °C. Next, 0.216 mL (2.40 mmol) of $CH_2{=}CHCO_2Me$ 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 80% $CH_2Cl_2$/hexane separated two yellow bands:

(1) Orange crystals (0.3658 g, 0.54 mmol, 45%) of (e,e-$\mu$-$CH_3O_2CCH_2CH_2PPh)_2Fe_2(CO)_6$, **4a**, were recrystallized from dichloromethane/pentane, mp 138–139.5 °C. Anal. Calcd for $C_{26}H_{24}O_{10}Fe_2P_2$: C, 46.60; H, 3.61. Found: C, 46.76; H, 3.69. IR ($CHCl_3$): $\nu$(C=O) 1723 (vs); terminal carbonyl region, 2067 (s), 2032 (vs), 1997 (vs), 1977 (s), cm$^{-1}$. 250-MHz $^1H$ NMR ($CDCl_3$): $\delta$ 2.12–2.22 and 2.44–2.53 (both m, $-(CH_2)_2-$, 8 H), 3.51 (s, $-CO_2CH_3$, 6 H) and 6.75–7.03 (complex m, *Ph*P, 10 H). $^{31}P$ NMR ($CHCl_3$): $\delta_P$ 135.1 (s).

(2) Orange crystals (0.407 g, 0.61 mmol, 51%) of (a,e-$\mu$-$CH_3O_2CCH_2CH_2PPh)_2Fe_2(CO)_6$, **4b**, were recrystallized from pentane, mp 107–108 °C. Anal. Calcd for $C_{26}H_{24}O_{10}Fe_2P_2$: C, 46.60; H, 3.61. Found: C, 46.68; H, 3.64. IR ($CHCl_3$): $\nu$(C=O) 1730 (vs); terminal carbonyl region, 2073 (s), 2035 (vs), 1993 (s), 1978 (s) cm$^{-1}$. 250-MHz $^1H$ NMR ($CDCl_3$): $\delta$ 1.13–1.24, 1.88–1.98, 2.37–2.45 and 2.51–2.60 (all m, $-(CH_2)_2-$, 8 H), 3.33 and 3.56 (both s, $-CO_2CH_3$, 6 H), and 7.32–7.66 (complex m, *Ph*P, 10 H). $^{31}P$ NMR ($CDCl_3$): $\delta_P$ 140.5 (s).

**Reaction between Bis($\mu$-phenylphosphido)bis(tricarbonyliron) and Methyl Vinyl Ketone.** The standard apparatus was charged with 0.6579 g (1.32 mmol) of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ and 50 mL of THF and the resulting solution cooled to −78 °C. Next, 0.107 mL (1.32 mmol) of $CH_2{=}CH\text{-}C(O)CH_3$ (Eastman) 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. Standard workup left an orange-red residue that was chromatographed on a 2.5 × 30 cm Florisil column. Elution with 30% $CH_2Cl_2$/hexane separated one yellow band and 60% $CH_2Cl_2$/hexane another:

(1) Orange crystals (0.3110 g, 0.55 mmol, 41%) of $(\mu\text{-}H_2CCH_2C(OH)(CH_3)(PPh)(PPh))Fe_2(CO)_6$, **6**, were recrystallized from pentane, mp 166–168 °C. Anal. Calcd for $C_{22}H_{18}Fe_2P_2O_7$: C, 46.52; H, 3.19. Found: C, 46.61; H, 3.28. IR ($CHCl_3$): $\nu$(OH) 3584 (m), 3400 (broad); terminal carbonyl region, 2073 (vs), 2032 (vs), 2000 (s), 1974 (s) cm$^{-1}$. 250-MHz $^1H$ NMR ($CDCl_3$): $\delta$ 1.27 (d, $J$(P–H) = 12.3 Hz, $CH_3$–, 3 H), 1.65 (d, $J$(P–H) = 1.5 Hz, *-OH*, 1 H), 2.04–2.26 (complex m, $-(CH_2)_2-$, 4 H) and 7.43–7.72 (complex m, *Ph*P, 10 H). $^{31}P$ NMR ($CHCl_3$): $\delta_P$ 129.2, 154.3 (AX quartet, $J$(P–P) = 185.5 Hz).

(2) $(\mu\text{-}PhPH)$ $(\mu\text{-}CH_3C(O)CH_2CH_2PPh)Fe_2(CO)_6$, **7**, (0.3162 g, 0.56 mmol, 42%) as a yellow orange oil, was recrystallized from pentane, mp 131–133 °C. Anal. Calcd for $C_{22}H_{18}Fe_2P_2O_7$: C,

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[7] Seyferth, O.; Wood, T. G., submitted for publication in *Organometallics*.

46.52; H, 3.19. Found: C, 46.54; H, 3.22. IR ($CHCl_3$): $\nu$(C═O) 1708; terminal carbonyl region, 2051 (s), 2013 (vs), 1990 (m), 1965 (m) cm$^{-1}$. 250-MHz $^1$H NMR ($CDCl_3$): $\delta$ 2.02 (s, C*H*$_3$, 3 H), 2.38–2.56 (m, –(C*H*$_2$)$_2$–, 4 H), 3.44 (dd, *J*(P$_1$–H) = 387.1 Hz, *J*(P$_2$–H) = 23.2 Hz, P-*H*, 1 H), and 7.28–7.78 (complex m, *Ph*P, 10 H). $^{31}$P NMR ($CHCl_3$): $\delta_P$ 83.9, 133.4 (AX quartet, *J*(P–P) = 146.5 Hz).

**Reaction between Bis($\mu$-phenylphosphido))bis(tricarbonyliron) and *trans*-3-Penten-2-one.** The standard apparatus was charged with 0.6831 g (1.37) mmol) of ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$ and 50 mL of THF and the resulting solution was cooled to −78 °C. Next, 0.134 mL (1.37 mmol) of *trans*-CH$_3$CH═CHC(O)CH$_3$ (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. The orange-red residue obtained on standard workup was chromatographed on a 2.5 × 30 cm Florisil column. Elution with 50% CH$_2$Cl$_2$/hexane separated two yellow bands and 20% Et$_2$O/CH$_2$Cl$_2$ a third:

(1) Orange crystals (0.3540 g, 0.61 mmol, 44%) of ($\mu$-CH$_3$-(H)$\overline{\text{CCH}_2\text{C(OH)(CH}_3\text{)(PPh)(P}}$Ph))Fe$_2$(CO)$_6$, **8**, were recrystallized from pentane, mp 149–150 °C. Anal. Calcd for $C_{23}H_{20}O_7P_2Fe_2$: C, 47.46; H, 3.46. Found: C, 47.49; H, 3.52. IR ($CHCl_3$): $\nu$(OH) 3380 (broad); terminal carbonyl region, 2054 (s), 2014 (vs), 1988 (s), 1964 (s) cm$^{-1}$. 250-MHz $^1$H NMR ($CDCl_3$): shows a 75:25 mixture of two diastereomers. $\delta$ 0.72–0.87 (6-line pattern-overlapping dd of –C(H)C*H*$_3$, major and minor diastereomers, *J*(H–H) = 7.4 Hz, *J*(P–H) = 16.2 Hz, 3 H), 1.08, 1.39 (both dd, *J*(P–H) = 12.8, 11.7 Hz, respectively, –C(OH)C*H*$_3$ of major and minor diastereomers, 3 H), 1.82 (d, *J*(P–H) = 2.9 Hz, –O*H* of both diastereomers, 1 H), 1.80–2.20 (complex m, –C*H*$_2$–C(*H*)CH$_3$ of both diastereomers, 3 H), and 7.44–7.71 (complex m, *Ph*P, 10 H). $^{31}$P NMR ($CHCl_3$): $\delta_P$ 145.2, 159.1 (AX quartet, *J*(P–P) = 175.7 Hz, one diastereomer) and 144.6, 158.2 (AX quartet, *J*(P–P) = 185.6 Hz, other diastereomer). The $^{31}$P spectrum was recorded by using an unrecrystallized sample and shows a 50:50 mixture of diastereomers.

(2) Orange crystals (0.264 g, 0.46 mmol, 33%) of ($\mu$-PhPH)($\mu$-CH$_3$C(O)CH$_2$CH(CH$_3$)PPh)Fe$_2$(CO)$_6$, **9**, were recrystallized from pentane, mp 91.5–93 °C. Anal. Calcd for $C_{23}H_{20}O_7P_2Fe_2$: C, 47.46; H, 3.46. Found: C, 47.62; H, 3.54. IR($CHCl_3$): $\nu$(C═O) 1718 (vs); terminal carbonyl region, 2050 (s), 2016 (vs), 1980 (s), 1969 (s) cm$^{-1}$. 250-MHz $^1$H NMR ($CDCl_3$): $\delta$ 1.19 (dd, *J*(P–H) = 17.0 Hz, *J*(H–H) = 6.8 Hz, P–C(C*H*$_3$)–, 3 H), 2.11 (s, –C(O)C*H*$_3$–, 3 H), 2.15–2.23 (m, P–C(*H*)–, 1 H), 2.60–2.65, 2.80–2.91 (both m, –C*H*$_2$–, 2 H), 3.23 (dd, *J*(P$_1$–H) = 390.1 Hz, *J*(P$_2$–H) = 24.0 Hz, P-*H*, 1 H), and 7.26–7.61 (complex m, *Ph*P, 10 H). $^{31}$P NMR ($CHCl_3$): $\delta_P$ 84.1, 155.3 (AX quartet, *J*(P–P) = 141.6 Hz).

(3) A yellow-orange oil (0.034 g, 0.05 mmol, 4%) was tentatively identified as (a,e-$\mu$-CH$_3$C(O)CH$_2$CH(CH$_3$)PPh)$_2$Fe$_2$(CO)$_6$ on the basis of its $^{31}$P NMR spectrum. Due to the low yield and noncrystallinity of this material, further characterization was not pursued. $^{31}$P NMR ($CHCl_3$): $\delta_P$ 159.4, 164.1 (AX quartet, *J*(P–P) = 129.5 Hz).

**Reaction between Bis($\mu$-phenylphosphido)bis(tricarbonyliron) and Mesityl Oxide.** The standard apparatus was charged with 0.6699 g (1.34 mmol) of ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$ and 50 mL of THF and the resulting solution cooled to −78 °C. Next, 0.154 mL (1.34 mmol) of Me$_2$C═CHC(O)Me 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. Standard workup gave an orange-red residue that was chromatographed on a 2.5 × 30 cm Florisil column. Elution with 50% CH$_2$Cl$_2$/hexane eluted one yellow band and 60% CH$_2$Cl$_2$/hexane another:

(1) ($\mu$-PhPH)$_2$Fe$_2$(CO)$_6$ (0.234 g 0.47 mmol, 35% recovery) was identified by comparison of its $^{31}$P NMR spectrum and melting point with those of an authentic sample.

(2) Yellow-orange crystals (0.500 g, 0.84 mmol, 62%) of ($\mu$-PhPH)($\mu$-CH$_3$(O)CCH$_2$C(CH$_3$)$_2$PPh)Fe$_2$(CO)$_6$, **10**, were recrystallized from pentane, mp 134.5–136 °C. Anal. Calcd for $C_{24}H_{22}O_7Fe_2P_2$: C, 48.36; H, 3.72. Found: C, 48.52; H, 3.79. IR ($CHCl_3$): $\nu$(C═O) 1709 (s); terminal carbonyl region, 2070 (s), 2033 (vs), 1990 (s), 1974 (s) cm$^{-1}$. 250-MHz $^1$H NMR ($CDCl_3$): $\delta$ 1.42 (d, *J*(P–H) = 17.6 Hz, –C(C*H*$_3$)$_2$–, 6 H), 2.01 (s, –C(O)C*H*$_3$, 3 H), 2.40 (d, *J*(P–H) = 10.9 Hz, –C(O)C*H*$_2$–, 2 H), 2.82 (dd, *J*(P$_1$–H) = 393.0 Hz, *J*(P$_2$–H) = 17.9 Hz, P–H, 1 H), and 7.26–7.64 (complex m, *Ph*P, 10 H). $^{31}$P NMR ($CHCl_3$): $\delta_P$ 86.6, 182.5 (AX quartet, *J*(P–P) = 117.0 Hz).

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**Registry No.** **2**, 39049-79-1; **4a**, 110569-69-2; **4b**, 110658-03-2; **6**, 110569-70-5; **7**, 110569-71-6; **8** (isomer), 110569-72-7; **8** (isomer 2), 110658-04-3; **9**, 110569-73-8; **10**, 110569-74-9; (a,e-$\mu$-CH$_3$C(O)CH$_2$CH(CH$_3$)PPh)$_2$Fe$_2$(CO)$_6$, 110569-75-0; *trans*-CH$_3$CH═CHC(O)CH$_3$, 3102-33-8; CH$_2$═CHCO$_2$CH$_3$, 96-33-3; CH$_2$═CHC(O)CH$_3$, 78-94-4; Me$_2$C═CHC(O)Me, 141-79-7; piperidine, 110-89-4.