Organometallics **2000,** *19,* 4557−4562 4557

Reactions of Alkynes with $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$: Formation of Diphenylvinylphosphine-Functionalized Vinyl Carbenes via Carbon−Carbon and Carbon−Phosphorus Bond Formation and Hydrogen Migration[⊥]

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Reaction of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) with $PhC{\equiv}CPh$ results in allenyl−alkyne−phosphido coupling to give $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P){:}\eta^3(C){:}\eta^1(C)\text{-}C(Ph)C(Ph)C(H)C({=}CH_2)PPh_2\}]$ (**2**), bridged by a diphenylvinylphosphine-substituted vinyl carbene. Under similar conditions **1** reacts with $PhC{\equiv}CMe$ to give an equal mixture of the two possible regioisomers, $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P){:}\eta^3(C){:}\eta^1(C)\text{-}C(Ph)C(Me)C(H)C({=}CH_2)PPh_2\}]$ (**3a**) and $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P){:}\eta^3(C){:}\eta^1(C)\text{-}C(Me)C(Ph)C(H)C({=}CH_2)PPh_2\}]$ (**3b**). In contrast, **1** reacts with 2 equiv of $PhC{\equiv}CH$ to give the vinyl carbene bridged $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{-}(P){:}\eta^3(C){:}\eta^1(C)\text{-}(Ph)C\overline{CC(H)MeCH{=}CPhC}(PPh_2)\}]$ (**4**), which results from a complex sequence of carbon−carbon and carbon−phosphorus bond formation and hydrogen migration steps.

Introduction

The reactivity of homobinuclear σ−η-coordinated allenyl/propargyl complexes is dominated by the electrophilic character of the C_3 ligand, and examples of addition of protic and nonprotic nucleophiles to C_α, C_β, and C_γ are well documented.[1] However, several recent articles have reported nucleophilic reactivity for binuclear allenyl complexes,[2,3] which include addition of *p*-toluenesulfonyl isocyanate to C_γ to give modified σ,η-allenyl derivatives,[2a] formation of a [3+2] cycloaddition adduct,[2a] and protonation at C_β to afford a binuclear μ-vinylcarbene.[3] In contrast, the reactivity of alkynes with bi- and multinuclear allenyl complexes is less well developed, somewhat surprising considering that the product of alkyne−allenyl coupling would be highly unsaturated and potentially reactive toward further functionalization. A survey of the literature reveals only two examples of alkyne−allenyl coupling. The first, a comparative study by Carty, examined the reactivity of σ−η-allenyl and σ−η-acetylide complexes of group 8 with internal alkynes, and in both cases unusual η^5-cyclopentadienyl complexes formed via alkyne−allenyl and alkyne−acetylide coupling, respectively.[4] In the second, reaction of the trinuclear allenyl cluster $[Ru_3(CO)_8(\mu\text{-}PPh_2)\{\mu_3\text{-}\eta^2\text{-}C(Pr^i)C{=}CH_2\}]$ with alkynes results in allenyl−alkyne coupling to give a “wrap-around” five-carbon penta-1,4-dien-2,3,5,-triyl hydrocarbon.[5]

We have recently undertaken a detailed study of the reactivity of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ and reported a number of diverse and interesting transformations including the synthesis of diiron-coordinated α,β-unsaturated carbonyl compounds via nucleophile−carbonyl−allenyl coupling with alkyllithium reagents,[6] amines,[7] and alcohols;[8] dealkylation of trialkyl phosphites to give a α,β-unsaturated phosphonates;[9] the first examples of nucleophilic addition to the α-carbon atoms of a σ−η-coordinated allenyl;[10] and a host of unusual transformations involving phos-

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[⊥] This paper is dedicated to Professor Arthur J. Carty on the occasion of his 60th birthday.

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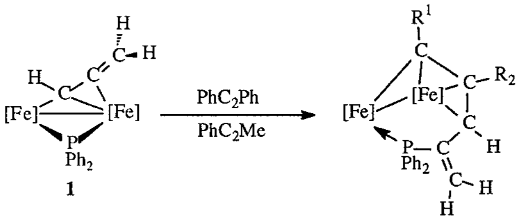
phorus- and nitrogen-based nucleophiles.[11] In a continuation of these studies we have now extended the range of nucleophiles to include alkynes and herein report that **1** reacts with alkynes to give vinyl−carbene-bridged products via carbon−carbon and carbon−phosphorus coupling.

Results and Discussion

Thermolysis of a solution $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) with an excess of diphenylacetylene in toluene at 90 °C for 6 h results in the formation of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P):\eta^3(C):\eta^1(C)\text{-}C(Ph)C(Ph)C(H)C({=}CH_2)PPh_2\}]$ (**2**) as the major product (eq 1). The reaction of **1** with unsymmetrical alkynes offers the possibility of regioselective insertion in the carbon−carbon coupling step as there are two possible regioisomers. Under conditions similar to those used to prepare **2**, PhC≡CMe reacts with **1** to generate a mixture of two compounds, identified by ^1H and ^{31}P NMR spectroscopy as the two possible regioisomers $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P):\eta^3(C):\eta^1(C)\text{-}C(Ph)C(Me)C(H)C({=}CH_2)PPh_2\}]$ (**3a**) and $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P):\eta^3(C):\eta^1(C)\text{-}C(Me)C(Ph)C(H)C({=}CH_2)PPh_2\}]$ (**3b**) in a 1:1 ratio. Attempts to separate **3a** and **3b** by column chromatography proved unsuccessful, although fractional crystallization from a hexamethyldisiloxane solution yielded orange crystals of a single regioisomer, **3a**.



(1)

[Fe] = Fe(CO)$_3$

$R^1 = R^2 = Ph$, **2**
$R^1 = Ph$, $R^2 = Me$, **3a**; $R^1 = Me$, $R^2 = Ph$, **3b**

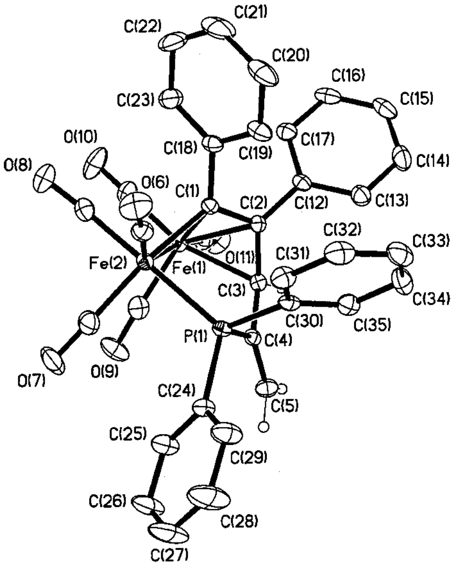


Figure 1. Molecular structure of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P):\eta^3(C):\eta^1(C)\text{-}C(Ph)C(Ph)C(H)C({=}CH_2)PPh_2\}]$ (**2**). Phenyl hydrogen atoms have been omitted. Carbonyl carbons have the same numbers as oxygen atoms. Ellipsoids are at the 50% probability level.

The $^{31}P\{^1H\}$ NMR spectrum of **2** contains a singlet at δ 45.8, shifted to high-field compared to that of **1** and consistent with a transformation involving coupling of the phosphido bridge with a hydrocarbyl fragment. The ^1H NMR spectrum contains doublets at δ 5.97 ($^3J_{PH}$ = 28.8 Hz) and 4.96 ($^3J_{PH}$ = 13.4 Hz), which correspond to the vinylic protons, and another at δ 4.39 ($^3J_{PH}$ = 25.3 Hz), associated with the proton attached to the terminal carbon atom of the bridging vinyl carbene. In the $^{13}C\{^1H\}$ NMR spectrum a low-field signal at δ 154.3 corresponds to the bridging alkylidene carbon and appears in the same region as that previously reported for related vinyl carbene complexes including $[Fe_2(CO)_4(\mu\text{-dppm})\{\mu\text{-}\eta^1:\eta^3\text{-}HCC(Me){=}C(Me)PPh_2\}]$,[12] $[Fe_2(CO)(\mu\text{-}CO)Cp_2\{\mu\text{-}\eta^1:\eta^3\text{-}(E)\text{-}CHC(Me){=}CHMe\}]$,[13] $[Fe_2(CO)(\mu\text{-}CO)Cp_2\{\mu\text{-}\eta^1:\eta^3\text{-}(E)\text{-}C(CO_2Me)C(CO_2Me){=}CHMe\}]$,[14] and $[Ru_2(CO)(\mu\text{-}CO)Cp_2\{\mu\text{-}\eta^1:\eta^3\text{-}CHC(R){=}CH_2\}]$ (R = H, Me).[15] The central carbon atom of the C_3-bridge appears as a doublet at δ 110.8 ($^3J_{PC}$ = 15.6 Hz) and the terminal vinylic carbon as a doublet at δ 65.3 ($^2J_{PC}$ = 21.7 Hz). The remaining two carbons of the C_5-hydrocarbon, namely, those of the diphenylvinylphosphine unit, appear as a doublet and singlet at δ 174.5 ($^1J_{PC}$ = 25.8 Hz) and 118.3, respectively. This value of $^1J_{PC}$ is similar to that reported by Knox and co-workers for closely related complexes of σ-vinyl phosphines generated during the thermal and photochemical cleavage of the 1,1-bis(diphenylphosphino)ethene ligand in $[Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}(Ph_2P)_2C{=}CH_2\}]$.[16] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **3a** and **3b** are strikingly similar to those of **2** and strongly support our formulation. The $^{31}P\{^1H\}$ NMR spectrum of **3a**,**b** showed an approximately equal mixture of isomers and confirms the complete lack of selectivity in the alkyne insertion step.

To establish precise details of the connectivity and, in the case of **3a**,**b** to assign the spectroscopic data to their respective regioisomers, single-crystal X-ray analyses of **2** and **3a** were undertaken, the results of which are illustrated in Figures 1 and 2, respectively. A selection of bond lengths and angles for both compounds is listed in Table 1. The most striking feature of **2** is the newly formed hydrocarbyl bridge, which can most aptly be considered as a σ-η^2-diphenylvinylphosphine-substituted vinyl carbene. The two iron atoms are separated by 2.6772(4) Å and bridged by a three-carbon hydrocarbon, σ-bonded to Fe(2) [Fe(2)−C(1) = 2.033(2) Å], and η^3-bonded to Fe(1) [Fe(1)−C(1) = 2.072(2) Å, Fe(1)−C(2) = 2.088(2) Å, Fe(1)−C(3) = 2.113(2) Å]. Similar three-carbon bridging fragments have been

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 2, 3a, and 4

2		3a[a]		4	
Fe(1)−Fe(2)	2.6772(4)	Fe(1)−Fe(2)	2.6668(3)	Fe(1)−Fe(2)	2.6182(6)
Fe(1)−C(2)	2.088(2)	Fe(1)−C(3)	2.1128(18)	Fe(1)−C(7)	2.166(3)
Fe(1)−C(1)	2.072(2)	Fe(1)−C(4)	2.0917(17)	Fe(1)−C(11)	2.082(3)
Fe(1)−C(3)	2.113(2)	Fe(1)−C(6)	2.0804(16)	Fe(1)−C(12)	2.070(3)
Fe(2)−C(1)	2.033(2)	Fe(2)−C(6)	2.0308(16)	Fe(2)−C(12)	2.041(3)
Fe(2)−P(1)	2.2640(6)	Fe(2)−P(1)	2.2578(5)	Fe(2)−P(1)	2.2433(8)
C(1)−C(2)	1.419(3)	C(1)−C(2)	1.336(2)	C(7)−C(11)	1.432(4)
C(2)−C(3)	1.441(3)	C(2)−C(3)	1.462(2)	C(11)−C(12)	1.407(4)
C(3)−C(4)	1.469(3)	C(3)−C(4)	1.442(2)	C(7)−C(8)	1.494(4)
C(4)−C(5)	1.334(3)	C(4)−C(5)	1.515(2)	C(8)−C(9)	1.342(4)
C(4)−P(1)	1.806(2)	C(4)−C(6)	1.415(2)	C(9)−C(10)	1.495(4)
		C(2)−P(1)	1.8095(17)	C(10)−C(11)	1.516(4)
Fe(1)−Fe(2)−P(1)	92.386(18)	Fe(1)−Fe(2)−P(1)	91.278(14)	Fe(1)−Fe(2)−P(1)	75.71(2)
Fe(1)−C(1)−Fe(2)	81.41(8)	Fe(1)−C(6)−Fe(2)	80.87(6)	Fe(1)−C(12)−Fe(2)	79.12(10)
Fe(1)−Fe(2)−C(1)	49.94(6)	Fe(1)−Fe(2)−C(6)	50.37(5)	Fe(1)−Fe(2)−C(12)	50.93(7)
Fe(2)−Fe(1)−C(1)	48.65(6)	Fe(2)−Fe(1)−C(6)	48.75(4)	Fe(2)−Fe(1)−C(12)	49.95(8)
Fe(2)−C(1)−C(2)	125.86(15)	Fe(2)−C(6)−C(4)	126.61(12)	Fe(2)−C(12)−C(11)	115.9(2)
Fe(1)−C(1)−C(2)	70.67(12)	Fe(1)−C(6)−C(4)	70.60(9)	Fe(1)−C(12)−C(11)	70.67(15)
C(1)−C(2)−C(3)	118.74(19)	C(6)−C(4)−C(3)	119.36(14)	C(12)−C(11)−C(7)	118.1(2)
C(3)−C(4)−C(5)	122.4(2)	C(6)−C(4)−C(5)	122.47(15)	C(12)−C(11)−C(10)	132.4(3)
P(1)−C(4)−C(5)	124.34(17)	C(4)−C(3)−C(2)	125.83(15)	C(11)−C(7)−C(8)	106.9(2)
		C(3)−C(2)−C(1)	122.77(16)	C(7)−C(8)−C(9)	108.3(3)
		C(3)−C(2)−P(1)	114.31(12)	C(8)−C(9)−C(10)	113.5(3)
		C(1)−C(2)−P(1)	122.91(14)	C(9)−C(10)−C(11)	101.7(2)
		C(2)−P(1)−Fe(2)	107.74(6)		

[a] Data for one of two similar molecules in the asymmetric unit.

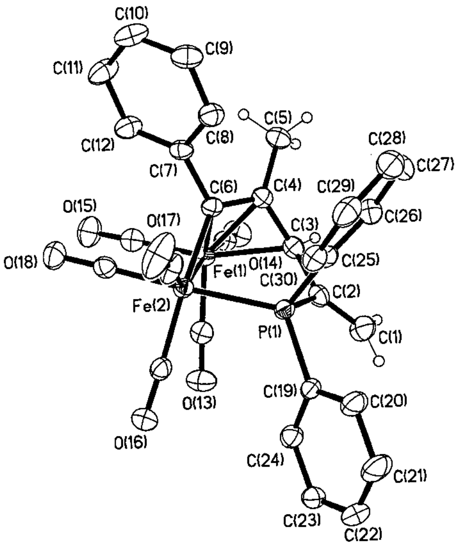
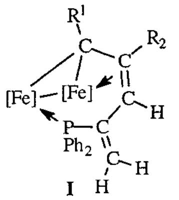
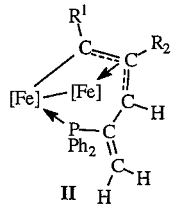


Figure 2. Molecular structure of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{-}(P)\text{:}\eta^3(C)\text{:}\eta^1(C)\text{-}C(Ph)C(Me)C(H)C(=CH_2)PPh_2\}]$ (**3a**). Phenyl hydrogen atoms have been omitted. Carbonyl carbons have the same numbers as oxygen atoms. Ellipsoids are at the 50% probability level.

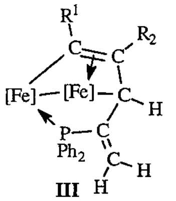
generated from the insertion of an alkyne into an M−C bond of a bridging alkylidene, and in each case structural features have suggested contributions from three possible resonance forms: a μ-η^2-vinyl carbene **I**, a σ-η^3-coordinated 1-metallallyl **II**, and a dimetallacyclopentene **III** in which the ethylenic bond is η^2-bound to Fe(2).



I



II



III

The similarity in the carbon−carbon bond lengths C(1)−C(2) [1.419(3) Å] and C(2)−C(3) [1.441(3) Å] and the difference in Fe−C bond lengths to C(1) (ΔFe−C = 0.039 Å) favor the σ-η^3-allylic structure. The terminal carbon atom of the bridging C_3-fragmant is substituted with a diphenylvinylphosphine group which coordinates to Fe(2) via the phosphorus atom [Fe(2)−P(1) = 2.2640(6) Å]. The C(4)−C(5) bond length of the pendent vinylic substituent [1.334(3) Å] is similar to those previously reported for $[Os_3(CO)_{11}(Ph_2PCH{=}CH_2)]$ and $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH_2)]$[17] and close to that expected for an uncoordinated C−C double bond. Knox and co-workers have reported that ethyne inserts into the M−C bond of the alkylidene carbon in $[M_2(CO)_2(\mu\text{-}CO)Cp_2(\mu\text{-}CHMe)]$ (M = Fe, Ru) to give the vinyl carbene derivative $[M_2(CO)(\mu\text{-}CO)Cp_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(H)C(H){=}CHMe\}]$.[14] For M = Fe, the bridging carbon is equidistant from both metal centers and the vinyl fragment is asymmetrically bonded to one metal atom. In the case of M = Ru, a second insertion gave $[Ru_2(CO)(\mu\text{-}CO)Cp_2\{\mu\text{-}C(H)C(H){=}C(H)C(H){=}CHMe\}]$, which is bridged by a vinyl carbene containing a pendent vinylic unit similar to that in **2**.[18] The solid-state structure of **3a**, shown in Figure 2, is qualitatively similar to that of **2** in that it contains a diphenylvinylphosphine-substituted vinylcarbene, σ-bonded to Fe(2) [Fe(2)−C(6) = 2.0308(16) Å], and η^3-bonded to Fe(1) [Fe(1)−C(6) = 2.0804(16) Å, Fe(1)−C(4) = 2.0917(17) Å, Fe(1)−C(3) = 2.1128(18) Å]. The remaining structural features associated with the metal atom framework and supporting ligands are similar to those of **2** and will not be discussed further.

The overall transformation of **1** into **2** most likely involves initial phosphorus−carbon bond formation via an intramolecular 1,3-migration of the phosphido bridge

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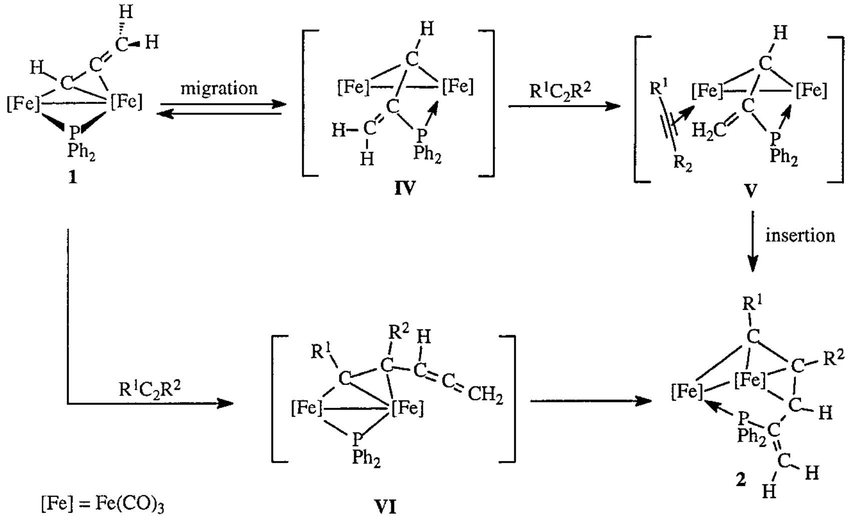
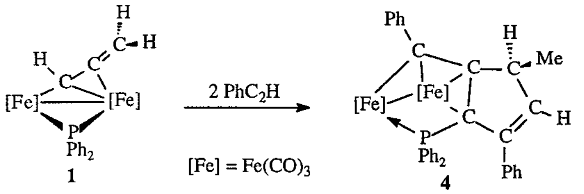
Scheme 1



to C_β of the $\sigma-\eta$-coordinated allenyl fragment, to give a coordinatively unsaturated alkylidene-bridged intermediate such as **IV**, followed by 1,2-insertion of the coordinated alkyne into the Fe$-C_\alpha$ bond of the bridging alkylidene, **V**, to generate **2** (Scheme 1). However, we cannot exclude an alternative pathway involving initial 1,2-migratory insertion of the alkyne into the Fe$-C_\alpha$ bond of the bridging allenyl, to give **VI**, prior to the phosphorus$-$carbon coupling step. However, we favor the former mechanism since there are a number of reports of 1,3-migration of bridging phosphido groups to coordinated hydrocarbyl ligands. Such insertions are relatively common place and may well occur via a transient terminal phosphido group that results from M$-$P bond cleavage.[19] For instance, addition of PPh_2Cl to $[Mo_2(CO)_4(\mu\text{-}R^1C{\equiv}CR^2)Cp_2]$ results in P$-$Cl bond cleavage to give $[Mo_2(CO)_2(\mu\text{-}Cl)\{\mu\text{-}C(R^1)C(R^2)PPh_2\}Cp_2]$, which presumably involves coupling of the resulting phosphido group with the alkyne.[20] Moreover, the vacant site for alkyne coordination is generated as a natural consequence of 1,3-phosphido migration in the former pathway, whereas it is not clear how alkyne coordination and migratory insertion would be facilitated in the latter pathway.

The use of terminal alkynes offers alternative reaction pathways including carbon$-$hydrogen activation and hydrogen migration with the possibility of generating more elaborate products. With this in mind, the reaction of **1** toward phenyl ethyne was investigated to establish whether the coupling sequence described above could be extended to include terminal alkynes. Thermolysis of a toluene solution of **1** and excess PhC≡CH at 90 °C resulted in a darkening of the solution and disappearance of **1** to give low yields of **4** as the only isolable product (eq 2). It is clear from the pattern of CO absorptions in the IR spectrum that **4** is not the PhC≡CH analogue of **2**. A singlet at δ 58.0 in the $^{31}P\{^1H\}$ NMR spectrum again suggests phosphido$-$hydrocarbyl coupling, while the ^1H NMR spectrum contains a doublet at 6.04 (1H, $^3J_{HH} = 2.5$ Hz), a quartet of doublets at 3.91 (1H, $^3J_{HH} = 2.5$ Hz), and a doublet at δ 0.72 (3H, $^3J_{HH} = 7.1$ Hz). It is clear from this pattern of resonances that formation of **4** involves (i) incorporation of two PhC≡CH fragments, (ii) migration of both acetylenic protons to the allenyl fragment, and (iii) phosphorus$-$carbon bond formation. The uncertainty in the exact nature of this transformation prompted a single-crystal X-ray analysis using synchrotron radiation, due to the small size of the crystals. A perspective view of the molecular structure is shown in Figure 3, and selected bond lengths and angles are listed in Table 1. The molecular structure identifies **4** as $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P){:}\eta^3(C){:}\eta^1(C)\text{-}(Ph)\overline{C\text{-}CC(H)MeCH{=}CPhC}(PPh_2)\}]$. The bridging hydrocarbyl fragment in **4** bears a close similarity to those in **2** and **3a** in that it can be considered as an asymmetrically bridging substituted alkylidene [Fe(2)$-$C(12) = 2.041(3) Å, Fe(1)$-$C(12) = 2.070(3) Å]. The vinylic substituent C(7)$-$C(11) [1.432(4) Å] attached to C(12) coordinates to Fe(1) [Fe(1)$-$C(11) = 2.082(3) Å, Fe(1)$-$C(7) = 2.166(3) Å] and forms part of a 2-diphenylphosphino-5-methylcyclopentadiene ring and shows the expected elongation upon coordination to a metal center. The remaining carbon$-$carbon bond lengths in the cyclopentadiene ring show that the uncoordinated double bond C(8)$-$C(9) [1.342(4) Å] is localized[21] and that C(7)$-$C(8), C(9)$-$C(10), and C(10)$-$C(11) are all single bonds [1.494(4), 1.495(4), 1.516(4) Å, respectively] and similar to those found in other η^2-cyclopentadiene complexes,[22] as is the planarity of the cyclopentadiene ring (maxi-



(2)

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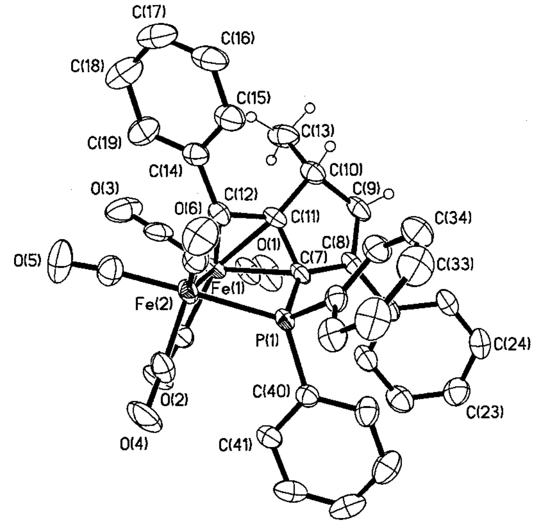

Figure 3. Molecular structure of bridged $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P){:}\eta^3(C){:}\eta^1(C)\text{-}(Ph)C\overline{CC(H)MeCH{=}CPhC}\text{-}(PPh_2)\}]$ (**4**). Phenyl hydrogen atoms have been omitted. Carbonyl carbons have the same numbers as oxygen atoms. Ellipsoids are at the 50% probability level.

mum deviation from the best least-squares plane of 0.010 Å). The bridging hydrocarbon in **4** could alternatively be described as a η^2-coordinated cyclopentadiene, tethered to the binuclear metal center through diphenylphosphine and alkylidene substituents. The 2-diphenylphosphine substituent coordinates to a single metal center [Fe(2)−P(1) = 2.2433(8) Å] to form a four-membered dimetallaphosphacycle containing Fe(1), Fe(2), P(1), and C(7). In contrast, coordination of the diphenylphosphine group in **2** and **3** forms a five-membered metalacycle. The allenyl fragment of **1** provides two of the cyclopentadiene ring carbons and the 5-methyl substituent, while the two molecules of phenyl ethyne provide the remaining three carbons of the ring and the bridging alkylidene carbon atom via tail-to-tail coupling. A related alkylidene-bridged complex, $[Fe_2(CO)_4(\mu\text{-dppm})\{\mu\text{-}\eta^1{:}\eta^3\text{-}HCC(Me){=}C(Me)PPh_2\}]$, is the major product of the reaction between $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}(H_2C{=}CMe)C{=}CH_2\}]$ and dppm.[12]

In summary, the reaction of alkynes with $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}(H)C{=}C{=}CH_2\}]$ (**1**) results in carbon−carbon and carbon−phosphorus bond formation to give a range of vinyl carbene bridged complexes. Diphenyl acetylene and 1-phenyl propyne react in a similar manner, although insertion of the latter lacks regioselectivity and gives an equal mixture of the two possible regioisomers. In contrast, phenyl acetylene reacts via multiple insertions coupled with hydrogen transfer to give an unusual diphenylphosphine−alkylidene-substituted cyclopentadiene. These studies suggest that it should be possible to prepare a more elaborate range of hydrocarbons simply by extending these coupling reactions to include diynes, enynes, ynenitriles, yneones, and variously functionalized alkynes.

Experimental Section

General Procedures. Unless otherwise stated all manipulations were carried out in an inert atmosphere glovebox or by using standard Schlenk line techniques. Diethyl ether and hexane were distilled from Na/K alloy, tetrahydrofuran was distilled from potassium, and dichloromethane was distilled from CaH_2. $CDCl_3$ was predried with CaH_2, vacuum transferred, and stored over 4 Å molecular sieves. Reactions were monitored by thin-layer chromatography (Baker flex silica gel, 1B-F). Column chromatography was carried out with alumina purchased from Aldrich Chemical Co. and deactivated with 6% w/w water prior to loading. Alkynes were purchased from Aldrich Chemical Co. and used without further purification. The diiron complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}(H)C{=}C{=}CH_2\}]$ (**1**) was prepared as previously described.[6]

Preparation of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P){:}\eta^3(C){:}\eta^1(C)\text{-}C(Ph)C(Ph)C(H)C({=}CH_2)PPh_2\}]$ (2). $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2_{\alpha,\beta}\text{-}(H)C{=}C{=}CH_2\}]$ (**1**) (0.20 g, 0.4 mmol) and diphenyl ethyne (0.71 g, 4.0 mmol) were dissolved in toluene (20 mL), and the solution was heated to 90 °C for 6 h, after which time the toluene was removed in vacuo. The resulting oily residue was extracted into dichloromethane (2−3 mL) and the solution absorbed onto deactivated alumina, desolvated, placed on a 300 × 30 mm column, and eluted with *n*-hexane/dichloromethane (90:10 v/v) to give orange-red **2** in 40% yield (0.11 g). Crystallization from *n*-hexane gave X-ray quality crystals. IR (ν(CO), cm^{-1}, C_6H_{14}): 2054 m, 2011 s, 1992 m, 1977 w, 1959 w. $^{31}P\{^1H\}$ (202.35 MHz, $CDCl_3$, δ): 45.8 (s, PPh_2). ^1H NMR (500.1 MHz, $CDCl_3$, δ): 7.75−6.66 (m, 10H, C_6H_5), 5.97 (d, $^3J_{PH}$ = 28.8 Hz, 1H, *trans*-$Ph_2PC{=}CH\{H\}$), 4.96 (d, $^3J_{PH}$ = 13.4 Hz, 1H, *cis*-$Ph_2PC{=}CH\{H\}$), 4.39 (d, $^3J_{PH}$ = 25.3 Hz, 1H, $CHC{=}CH\{H\}$). $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, δ): 213.1 (br, CO), 174.5 (d, $^1J_{PC}$ = 25.8 Hz, $PhCC\{Ph\}HCPh_2PC{=}CH_2$), 154.3 (s, $PhCC\{Ph\}HCPPh_2C{=}CH_2$), 144.8 (d, $^1J_{PC}$ = 25.8 Hz, C_6H_5), 133.1−124.3 (m, C_6H_5), 118.3 (s, $PhCC\{Ph\}HCPPh_2C{=}CH_2$), 110.8 (d, $^2J_{PC}$ = 15.6 Hz, $PhCC\{Ph\}HCPPh_2C{=}CH_2$), 65.3 (d, $^2J_{PC}$ = 21.7 Hz, $PhCC\{Ph\}HCPPh_2C{=}CH_2$). Anal. Calcd for $C_{35}H_{23}Fe_2O_6P$: C, 61.62; H, 3.40. Found: C; 61.59; H, 3.24.

$[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P){:}\eta^3(C){:}\eta^1(C)\text{-}C(Ph)C(Me)C(H)C({=}CH_2)PPh_2\}]$ (3a) and $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P){:}\eta^3(C){:}\eta^1(C)\text{-}C(Me)C(Ph)C(H)C({=}CH_2)PPh_2\}]$ (3b). A toluene solution of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}(H)C{=}C{=}CH_2\}]$ (**1**) (0.20 g, 0.4 mmol) and 3-phenylpropyne (0.5 mL, 4.0 mmol) was heated to 90 °C. After 8 h all the starting material had been consumed and the toluene was removed in vacuo to leave a dark oily residue. This residue was dissolved in a minimum amount of dichloromethane, absorbed onto deactivated alumina, desolvated, and placed on a 300 × 30 mm column. Elution with *n*-hexane/dichloromethane (90:10 v/v) gave **3a,b** as an orange-red solid in 20% yield (0.05 g), which was crystallized from neat hexamethyldisiloxane to give orange-red crystals of **3a**, leaving the mother liquor enriched in **3b**. Complex **3a:** IR (ν(CO), cm^{-1}, C_6H_{14}): 2054 m, 2009 s, 1994 m, 1969 w, 1957 w. $^{31}P\{^1H\}$ (202.35 MHz, $CDCl_3$, δ): 52.1 (s, PPh_2). ^1H NMR (500.1 MHz, $CDCl_3$, δ): 7.69−6.97 (m, C_6H_5), 5.54 (d, $^3J_{PH}$ = 28.6 Hz, 1H, *trans*-$PPh_2C{=}CH\{H\}$), 5.17 (d, $^3J_{PH}$ = 12.5 Hz, 1H, *cis*-$Ph_2PC{=}CH\{H\}$), 3.87 (d, $^3J_{PH}$ = 25.6 Hz, 1H, $HCPPh_2C{=}CH\{H\}$), 2.85 (d, $^5J_{PH}$ = 1.8 Hz, 3H, $PhCC\{CH_3\}HCPh_2PC{=}CH_2$). $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, δ): 211.0−212.1 (br, CO), 174.4 (d, $^1J_{PC}$ = 28.0 Hz, $\{Ph\}CC\{Me\}HCPh_2PC{=}CH_2$), 145.9 (d, $^1J_{PC}$ = 33.5 Hz, C_6H_5), 145.1 (d, $^1J_{PC}$ = 44.5 Hz, C_6H_5), 141.0 (s, $\{Ph\}CC\{Me\}HCPh_2PC{=}CH_2$), 134.4−124.7 (m, C_6H_5), 114.2 (s, $\{Ph\}CC\{Me\}HCPh_2PCCH_2$), 111.9 (d, $^2J_{PC}$ = 16.6 Hz, $\{Ph\}CC\{Me\}HCPh_2PC{=}CH_2$), 65.9 (d, $^2J_{PC}$ = 22.8 Hz, $\{Ph\}CC\{Me\}HCPh_2PCCH_2$), 37.6 (s, *Me*). Anal. Calcd for $C_{35}H_{23}Fe_2O_6P$: C, 58.11; H, 3.41. Found: C; 58.43; H, 3.21. Complex **3b**: IR (ν(CO), cm^{-1}, C_6H_{14}): 2054 m, 2009 s, 1994 m, 1969 w, 1957 w. $^{31}P\{^1H\}$ (202.35 MHz, $CDCl_3$, δ): 48.3 (s, PPh_2). ^1H NMR (500.1 MHz, $CDCl_3$, δ): 7.69−6.97 (m, 10H, C_6H_5), 5.72 (d, $^3J_{PH}$ = 29.0 Hz, 1H, $HCPh_2PC{=}CH\{H\}$), 4.71 (d, $^3J_{PH}$ = 13.7 Hz, 1H, $HCPh_2PC{=}CH\{H\}$), 4.15 (d, $^3J_{PH}$ = 24.7 Hz, 1H, $HCPh_2PC{=}CH\{H\}$), 1.49 (d, $^4J_{PH}$ = 0.9 Hz, 3H, $\{CH_3\}CC\{Ph\}HCPh_2PC{=}CH_2$). $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, δ): 211.0−212.0 (br, CO),

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Table 2. Summary of Crystal Data and Structure Determination for 2, 3a, and 4

	2	3a	4
mol form	$C_{35}H_{23}Fe_2O_6P$	$C_{30}H_{21}Fe_2O_6P$	$C_{37}H_{25}Fe_2O_6P$
fw	682.20	620.14	708.24
cryst size, mm	0.40 × 0.22 × 0.16	0.78 × 0.58 × 0.29	0.10 × 0.04 × 0.04
temperature, K	160(2)	160(2)	160(2)
cryst syst	orthorhombic	triclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/c$
a, Å	20.8592(12)	12.5509(6)	15.3078(19)
b, Å	10.3433(6)	15.3144(8)	9.5600(12)
c, Å	28.1509(15)	15.9483(8)	21.656(3)
α, deg		109.143(2)	
β, deg		99.880(2)	91.133(3)
γ, deg		104.577(2)	
V, Å^3	6073.6(6)	2692.3(2)	3168.5(7)
Z	8	4	4
D_{calcd}, g cm^{-3}	1.492	1.530	1.485
μ, mm^{-1}	1.054	1.180	1.013
F(000)	2784	1264	1448
θ range, deg	1.75−28.89	1.41−29.03	2.21−29.49
max. indices: h, k, l	27, 13, 37	17, 20, 21	21, 13, 30
no. reflns measd	36 167	22 404	22 243
no. reflns unique reflns	7452	12 746	8859
no. reflns with $F^2 > 2\sigma(F^2)$	5514	9987	5372
transmn coeff range	0.753−0.928	0.460−0.726	0.578−0.962
R_{int} (on F^2)	0.0535	0.0159	0.0664
weighting params[a] a, b	0.0295, 4.3513	0.0440, 0.00	0.0635, 0.00
R[b]	0.0415	0.0302	0.0526
R_w[c]	0.0833	0.0736	0.1220
no. of params	407	711	416
GOF[d] on F^2	1.046	0.984	0.890
max, min diff map e Å^{-3}	0.476, −0.352	0.545, −0.347	1.385, −0.534

[a] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. [b] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$. For "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. [d] GOF $= [\sum w(F_o^2 - F_c^2)^2/(\text{no. unique reflns} - \text{no. of params})]^{1/2}$.

175.2 (d, $^1J_{PC}$ = 25.9 Hz, {Me}CC{Ph}HCPh$_2$P*C*=CH$_2$), 154.4 (s, {Me}C*C*{Ph}HCPh$_2$PC=CH$_2$), 145.9 (d, $^1J_{PC}$ = 33.5 Hz, *C*$_6$H$_5$), 145.9 (d, $^1J_{PC}$ = 43.5 Hz, *C*$_6$H$_5$), 134.4−124.7 (m, *C*$_6$H$_5$), 117.5 (s, {Me}CC{Ph}HCPh$_2$PC=*C*H$_2${PPh$_2$}), 105.4 (d, $^2J_{PC}$ = 14.5 Hz, {Me}*C*C{Ph}HCPh$_2$PC=CH$_2$), 64.1 (d, $^2J_{PC}$ = 20.7 Hz, {Me}CC{Ph}H*C*Ph$_2$PC=CH$_2$), 25.9 (s, *Me*).

Preparation of [Fe$_2$(CO)$_6$(μ-PPh$_2$){μ-$\eta^1(P)$:$\eta^3(C)$:$\eta^1(C)$-(Ph)C$\overline{\mathrm{CC(H)MeCH{=}CPhC}}$(PPh$_2$)}] (4). A toluene solution of [Fe$_2$(CO)$_6$(μ-PPh$_2$){μ-η^1:η^2-(H)C=C=CH$_2$}] (**1**) (0.20 g, 0.4 mmol) and phenyl ethyne (0.44 mL, 4.0 mmol) was heated to 90 °C for 8 h, after which time the solvent was removed to leave a dark oily residue. This was dissolved in 2−3 mL of dichloromethane, absorbed onto deactivated alumina, desolvated, placed on a column, and eluted with *n*-hexane/dichloromethane (90:10 v/v) to give **4** as an orange-red solid in 10% yield (0.03 g). Small X-ray quality crystals of **4** were grown from *n*-hexane at room temperature. IR (ν(CO), cm^{-1}, C$_6$H$_{14}$): 2058 m, 2015 s, 1994 w, 1977 s, 1967 w. ^{31}P{^{1}H} (202.35 MHz, CDCl$_3$, δ): 58.0 (s, PPh$_2$). ^{1}H NMR (500.1 MHz, CDCl$_3$, δ): 7.48−6.81 (m, 10H, C$_6$H$_5$), 6.04 (d, $^3J_{HH}$ = 2.5 Hz, 1H, PhC=C*H*C{H}CH$_3$), 3.91 (qd, $^3J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, PhC=CHC{*H*}CH$_3$), 0.72 (d, $^3J_{HH}$ = 7.1 Hz, 3H, PhC=CHC{H}C*H*$_3$). Anal. Calcd for C$_{35}$H$_{23}$Fe$_2$O$_6$P: C, 62.71; H, 3.56. Found: C, 62.97; H, 3.40.

Crystal Structure Determination of 2, 3a, and 4. All measurements were made on a Bruker AXS SMART CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and narrow frame exposures (0.3° in ω) for **2** and **3a** and using silicon 111 monochromated synchrotron radiation at Daresbury SRS station 9.8 (λ = 0.6890 Å; 0.2° frames) for **4**, as reported previously.[23] Intensities were corrected semiempirically for absorption and for 65% X-ray beam decay in the case of **4**. The structures were solved by direct methods (Patterson synthesis for **3a**) and refined on F^2 values for all unique data by full-matrix least squares. Table 2 gives further details. All non-hydrogen atoms were refined anisotropically. H atoms, located in difference maps, were constrained with a riding model except for those attached to C(3) and C(5) in **2** and C(3) and C(33) in **3a**, which had their coordinates freely refined because of nonstandard geometry; U(H) was set to 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs used were Bruker AXS SMART and SAINT for diffractometer control and frame integration,[24] Bruker SHELXTL for structure solution, refinement, and molecular graphics,[25] and local programs.

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Supporting Information Available: For **2**, **3a**, and **4** details of structure determination, non-hydrogen atomic positional parameters, full listings of bond distances and angles, anisotropic displacement parameters, and hydrogen atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor tables are available from the authors upon request.

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