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Nucleophilic and Electrophilic Behavior of the Phosphinidene-Bridged Complex $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PCy)(\mu\text{-}CO)(CO)_2]$

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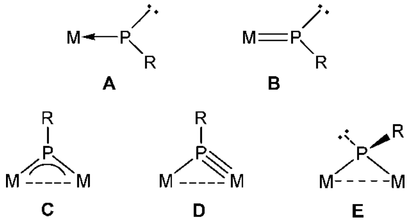
*Summary: The phosphinidene-bridged complex $[Fe_2Cp_2(\mu\text{-}PCy)(\mu\text{-}CO)(CO)_2]$ (**1**) reacts with $HC{\equiv}CR$ (R = p-tol, CO_2Me) to give products incorporating one or two alkyne molecules and involving further coupling with Cp or CO ligands, as shown by the formation of the complexes $[Fe_2Cp\{\mu\text{-}\eta^5:\kappa^1\text{-}C_5H_4PCyCHCH(p\text{-}tol)\}(CO)_3]$, $[Fe_2Cp_2\{\mu\text{-}\kappa^1:\kappa^1,\eta^1\text{-}CyPCHC(p\text{-}tol)C(O)\}(\mu\text{-}CO)(CO)]$, and $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PCy(CHCHCO_2Me)(C_2CO_2Me)\}]$. In contrast, the reactions of **1** with benzyl azide or (trimethylsilyl)diazomethane initially give the simple 1:1 adducts $[Fe_2Cp_2(\mu\text{-}CyPN_3CH_2Ph)(\mu\text{-}CO)(CO)_2]$ and $[Fe_2Cp_2\{\mu\text{-}CyPN_2CH(SiMe_3)\}(\mu\text{-}CO)(CO)_2]$, respectively, although the latter rearranges to yield $[Fe_2Cp_2\{\mu\text{-}\kappa^1:\kappa^1,\eta^1\text{-}CyPN(SiMe_3)NCH\}(\mu\text{-}CO)(CO)]$ under photolytic conditions.*

The chemistry of phosphinidene complexes is an active area of study within the current organometallic research.[1] This is especially so in the case of the bent-terminal complexes, which can be compared to carbene complexes and are analogously classified as either electrophilic or nucleophilic, depending on the nature of the metal fragments to which these ligands are bound.[1a,b] In a simplified way, the metal−phosphorus bonding in these complexes can be described as essentially single or double, respectively (**A** and **B** in Chart 1), and there is in any case a nonbonding electron pair at the phosphorus atom, all of which makes these complexes highly (but differently) reactive toward a great variety of unsaturated organic molecules, thus making them useful in the synthesis of numerous organophosphorus compounds.[1] In contrast, the chemistry of binuclear complexes having phosphinidene bridges has remained comparatively little explored until recently, even though the presence of multiple M−P bonds or lone pairs at phosphorus in their different coordination modes (**C**−**E** in Chart 1) should make these complexes quite reactive toward unsaturated organic molecules or other metal complexes.[2,3] Recent work from our laboratory[2,4] and the group of Carty[3a,b,d] has shown that this is indeed the case for several complexes exhibiting trigonal-phosphinidene bridges of types **C** and **D**, but apparently the reactivity of binuclear complexes having bent-phosphinidene bridges (**E** in Chart 1) toward organic molecules has not been explored to date, with the exception of the transient species $[Fe_2\{\mu\text{-}P(N^iPr_2)\}_2(CO)_6]$.[5] Recently we developed a high-yield route to the stable diiron compounds $[Fe_2Cp_2(\mu\text{-}PR)(\mu\text{-}CO)(CO)_2]$ (R = Cy, Ph) and found that the cyclohexylphosphinidene complex was quite reactive toward electrophiles such as IMe and methyl acrylate.[6] This prompted us to carry out a wider and more systematic study on the reactivity of these phosphinidene complexes toward different unsaturated organic molecules, which turned out to be quite complex. In this paper we report our preliminary results on the reactions of the cyclohexylphosphinidene complex $[Fe_2Cp_2(\mu\text{-}PCy)(\mu\text{-}CO)(CO)_2]$ (**1**) toward 1-alkynes and some unsaturated N-containing molecules such as diazoalkanes and organic azides (Scheme 1). As it will be seen, novel transformations occur that have not been observed in comparable reactions using complexes with bent-terminal (**A**, **B**) or trigonal-bridging (**C**, **D**) phosphinidene ligands.

Chart 1



The reactions of compound **1** with alkynes are strongly dependent on the nature of the alkyne and the reaction conditions, and they may involve quite different elemental processes. For example, the reaction of **1** with (*p*-tolyl)acetylene at room temperature gives almost quantitatively the phosphine

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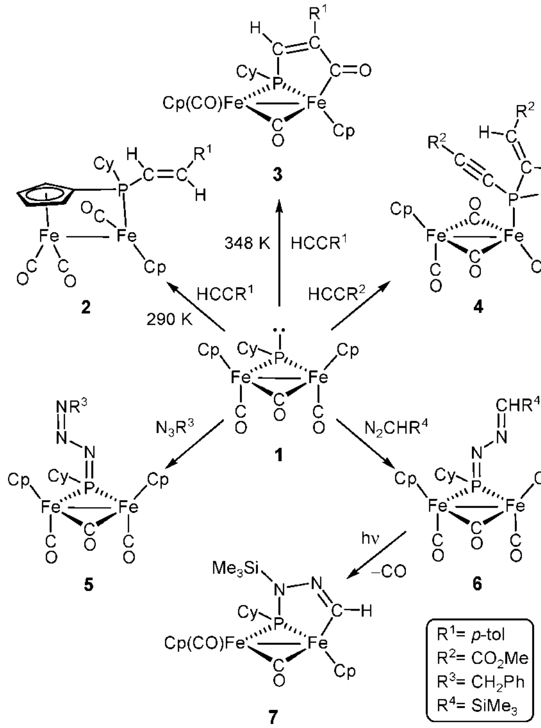
10.1021/om701238f CCC: $40.75

Scheme 1



derivative [Fe$_2$Cp{μ-η^5:κ^1-C$_5$H$_4$PCyCHCH(p-tol)}(CO)$_3$] (**2**),[7] which results from the coupling of the phosphinidene ligand to both the entering alkyne and one of the cyclopentadienyl groups to yield a bridging seven-electron-donor (cyclopentadienylidene)(alkenyl)phosphine ligand (Figure 1).[8] Reactions of phosphinidene ligands with coordinated cyclopentadienyl rings are rare processes generally observed only on some transient mononuclear complexes,[2] but the simultaneous coupling to the alkyne here observed is unprecedented. Interestingly, similar reactions between an alkyne, a phosphinidene ligand, and the C−H bond of a ^{t}Bu group in the latter have been recently reported for nucleophilic Ru phosphinidene complexes of the type **B**.[9] In the crystal state, compound **2** displays three terminal CO ligands, which was also unexpected, since diiron phosphine complexes isoelectronic with **2** display exclusively CO-bridged structures of the type [Fe$_2$Cp$_2$(μ-CO)$_2$(CO)(PR$_3$)], even for the closely related complex [Fe$_2$Cp{μ-η^5:κ^1-C$_5$H$_4$CH$_2$PPh$_2$}(μ-CO)$_2$(CO)].[10] In solution, however, the presence of a small amount of the expected CO-bridged isomer can be deduced from the appearance of a low-frequency C−O stretching band in the IR spectrum (1734 cm^{-1} in CH$_2$Cl$_2$ solution).[7]

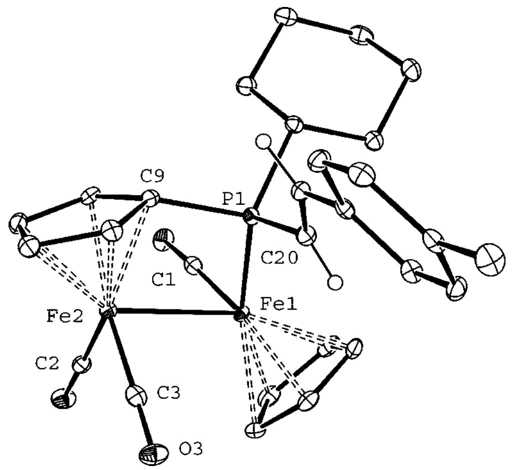
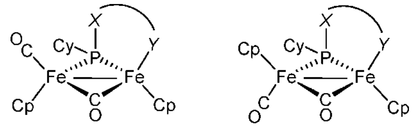


Figure 1. ORTEP drawing (30% probability) of **2**, with H atoms (except the olefinic ones) omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.6930(7), Fe(1)−P(1) = 2.164(1), Fe(1)−C(1) = 1.746(3), Fe(2)−C(2) = 1.756(3), Fe(2)−C(3) = 1.756(3), P(1)−C(9) = 1.815(3), P(1)−C(20) = 1.820(3), C(20)−C(21) = 1.317(4); Fe(2)−Fe(1)−C(1) = 86.7(1), Fe(1)−Fe(2)−C(2) = 80.7(1), Fe(1)−Fe(2)−C(3) = 89.8(1).

Chart 2



***cis*-3,7** ***trans*-3,7**

When the reaction of **1** with (p-tolyl)acetylene is carried out at 348 K, a mixture of compound **2** and two isomers of the phosphide−acyl complex [Fe$_2$Cp$_2${μ-κ^1:κ^1,η^1-CyPCHC(p-tol)-C(O)}(μ-CO)(CO)] (*trans*-**3** and *cis*-**3**, X−Y = CHC(p-tol)C(O); Chart 2) is rapidly obtained in a ca. 6:2:1 ratio.[11] The complexes **3** result from the coupling of the phosphinidene ligand to the entering alkyne, as observed for **2**, but now further coupling to a carbonyl ligand occurs (rather than insertion into a H−C(Cp) bond). Presumably, this process yields the trans isomer first, since an independent experiment shows that the latter isomer does transform into *cis*-**3** slowly at room temperature. Note also that, as found for **2** and presumably for steric reasons, compound **3** follows from the stereospecific coupling of phosphorus with the terminal C atom of the alkyne, as confirmed by an X-ray analysis, which also reveals a strong asymmetry in the coordination of the bridging P and C atoms to balance the different donor abilities of the terminal (carbonyl vs acyl) ligands (Figure 2).[12] The formation of **3** is somehow reminiscent of the [2 + 2] addition reactions of nucleophilic

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(7) Preparation of **2**: neat (p-tolyl)acetylene (144 μL, 1.136 mmol) was added to a freshly prepared toluene solution (5 mL) of complex **1** (ca. 0.025 g, 0.057 mmol), and the mixture was stirred at room temperature for 16 h to give a dark green solution yielding compound **2** (0.028 g, 88%) after chromatographic purification. Selected data: ν(CO) (CH$_2$Cl$_2$) 1960 (s), 1942 (sh, m), 1908 (vs), 1881 (sh, w), 1734 (m) cm^{-1}; ^{31}P{^{1}H} NMR (121.52 MHz, 290 K, CDCl$_3$) δ 68.6 (s); ^{1}H NMR (300.13 MHz, 290 K, CDCl$_3$) δ 7.35 (t, $J_{HH} = J_{HP} = 18$ Hz, 1H, P−CH), 6.48 (dd, $J_{HH} = 18$, $J_{HP} = 12$ Hz, 1H, CH), 5.24, 5.19 (2 × m, br, 2 × 1H, C$_5$H$_4$), 4.54 (s, 5H, Cp), 4.43, 4.36 (2 × m, br, 2 × 1H, C$_5$H$_4$); ^{13}C{^{1}H} NMR (75.48 MHz, tol-d_8, 233 K) δ 238.7, 236.5, 220.1 (3 × s, 3 × FeCO).

(8) X-ray data for **2**: green crystals, triclinic ($P\bar{1}$), $a = 8.761(2)$ Å, $b = 12.321(3)$ Å, $c = 12.427(3)$ Å, $\alpha = 105.131(4)°$, $\beta = 100.907(4)°$, $\gamma = 106.022(4)°$, $V = 1194.3(5)$ Å^3, $T = 120$ K, $Z = 2$, $R = 0.0369$ (observed data with $I > 2\sigma(I)$), GOF = 1.055.

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(11) Preparation of compounds **3**: neat (p-tolyl)acetylene (300 μL, 2.366 mmol) was added to a freshly prepared toluene solution (10 mL) of complex **1** (ca. 0.104 g, 0.236 mmol), and the mixture was stirred at 348 K for 15 min to give a dark green solution yielding, after chromatographic separation, compounds **2** (0.079 g, 60%), *trans*-**3** (0.014 g, 11%), and *cis*-**3** (0.027 g, 21%). Selected data for *cis*-**3**: ν(CO) (CH$_2$Cl$_2$) 1958 (vs), 1790 (m), 1594 (m, C=O) cm^{-1}; ^{31}P{^{1}H} NMR (121.52 MHz, 290 K, CDCl$_3$) δ 268.3 (s); ^{1}H NMR (300.13 MHz, 290 K, CDCl$_3$) δ 7.59 (d, $J_{HP} = 13$ Hz, 1H, CH), 4.68 (s, 5H, Cp), 4.66 (s, 5H, Cp); ^{13}C{^{1}H} NMR (75.48 MHz, 290 K, CDCl$_3$) δ 260.9, 257.2 (2 × d, $J_{CP} = 5$ Hz, μ-CO and FeC(O)), 215.0 (d, $J_{CP} = 20$ Hz, FeCO), 157.8 (d, $J_{CP} = 22$ Hz, C(p-tol)), 150.5 (d, $J_{CP} = 24$ Hz, CH).

(12) X-ray data for *cis*-**3**: green crystals, monoclinic ($P2_1/c$), $a = 13.158(2)$ Å, $b = 13.171(2)$ Å, $c = 14.280(3)$ Å, $\beta = 91.119(4)°$, $V = 2474.3(7)$ Å^3, $T = 120$ K, $Z = 4$, $R = 0.0352$ (observed data with $I > 2\sigma(I)$), GOF = 1.058.

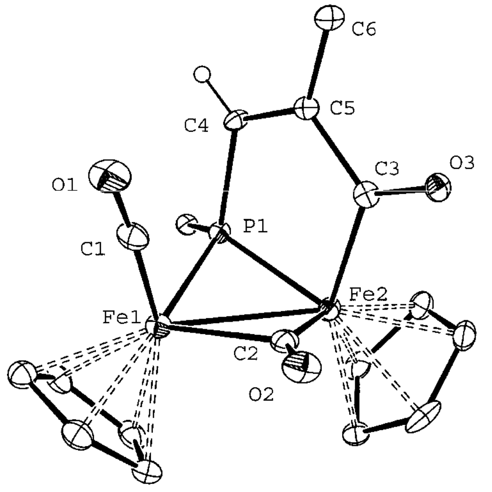

Figure 2. ORTEP drawing (30% probability) of *cis*-**3**, with H atoms (except the olefinic one) and cyclohexyl and *p*-tolyl groups (except the C^1 atoms) omitted for clarity. Selected bond lengths (Å): Fe(1)–Fe(2) = 2.6069(8), Fe(1)–P(1) = 2.185(1), Fe(2)–P(1) = 2.139(1), Fe(1)–C(1) = 1.743(4), Fe(1)–C(2) = 2.059(4), Fe(2)–C(2) = 1.834(4), Fe(2)–C(3) = 1.967(3), C(3)–C(5) = 1.541(5), C(5)–C(4) = 1.328(4), C(4)–P(1) = 1.792(4), C(5)–C(6) = 1.486(5).

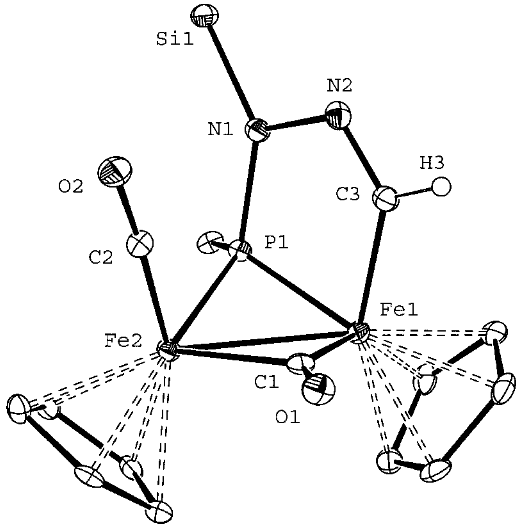

Figure 3. ORTEP drawing (30% probability) of *cis*-**7**, with H atoms (except that on C(3)), cyclohexyl rings (except the C^1 atoms), and Me groups omitted for clarity. Selected bond lengths (Å): Fe(1)–Fe(2) = 2.5890(8), Fe(1)–P(1) = 2.149(1), Fe(2)–P(1) = 2.203(1), Fe(1)–C(1) = 1.856(4), Fe(2)–C(1) = 2.016(4), Fe(2)–C(2) = 1.743(5), Fe(1)–C(3) = 1.936(4), C(3)–N(2) = 1.284(5), N(2)–N(1) = 1.437(5), N(1)–P(1) = 1.711(4), N(1)–Si(1) = 1.760(4).

Zr[1g] and Ti[13] phosphinidene complexes with alkynes to give the corresponding metallaphosphabutenes. Similar reactions have been observed also on some binuclear complexes with trigonal-phosphinidene bridges of types **C**[4a,14] and **D**.[4c] In the case of **3**, however, further coupling to a carbonyl ligand has taken place, perhaps to yield a less strained five-membered phosphametallacycle.

The reactions of **1** with a more activated alkyne such as methyl propiolate turned out to be even more complex, since some five new complexes can be formed in significant amounts depending on the reaction conditions, yet under study. The most significant observation here is the incorporation of two alkyne molecules in most of the new products, a result previously featured only by some transient electrophilic complexes of type **A**.[1f] Thus, the slow addition of a solution of **1** into a solution of HC_2CO_2Me at 273 K gives the complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PCy(CHCHCO_2Me)(C_2CO_2Me)\}]$ (**4**) in high yield, which contains an (alkenyl)(alkynyl)phosphine ligand formally resulting from the coupling of two alkyne molecules to the P atom (through their terminal C atoms) and an H shift between the alkyne moieties. Compound **4** adopts the usual CO-bridged structure found for phosphine tricarbonyl complexes of the type $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PR_3)]$.

The reactions of **1** with benzyl azide or (trimethylsilyl)diazomethane follow a pathway different from those with alkynes. At room temperature, these reactions give selectively the corresponding 1:1 adducts $[Fe_2Cp_2(\mu\text{-}CyPN_3CH_2Ph)(\mu\text{-}CO)(CO)_2]$ (**5**) and $[Fe_2Cp_2\{\mu\text{-}CyPN_2CH(SiMe_3)\}(\mu\text{-}CO)(CO)_2]$ (**6**), respectively,[16,17] but further transformations occur upon thermal or photochemical activation. The formation of compounds **5** and **6** is completely analogous to the recently reported reactions of the stable electrophilic phosphinidene complexes $[ML(PN^iPr_2)(CO)_x]^+$ (M = Fe, Ru, Cr, Mo, W; L = Cp, C_5Me_5; x = 2, 3) toward diazoalkanes to give κ^1-phosphazine derivatives.[18] Structurally, the new complexes are comparable to the oxophosphinidene complex $[Fe_2Cp_2\{\mu\text{-}CyP(O)\}(\mu\text{-}CO)(CO)_2]$,[6] but the substantial differences in their ^{31}P chemical shifts (δ_P 343.8 ppm, in comparison to 319.1 (**5**) and 304.8 ppm (**6**)) point to significant differences in the electron distributions within these ligands.

Attempts to induce denitrogenation on **6** photochemically (so as to give a phosphaalkene ligand) caused decarbonylation instead and led to a mixture of the cis and trans isomers of the dicarbonyl complex $[Fe_2Cp_2\{\mu\text{-}\kappa^1{:}\kappa^1,\eta^1\text{-}CyPN(SiMe_3)NCH\}(\mu\text{-}CO)(CO)]$ (**7**) almost quantitatively (Chart 2; X–Y =

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(15) Preparation of **4**: a freshly prepared dichloromethane solution (10 mL) of complex **1** (ca. 0.027 g, 0.061 mmol) was added dropwise for 10 min into a solution of methyl propiolate (12 μL, 0.125 mmol) in dichloromethane (2 mL) at 273 K to give a green solution yielding compound **4** (0.033 g, 90%) after chromatographic purification. Selected data: ν(CO) (CH_2Cl_2) 1938 (s), 1778 (w) 1739 (vs), 1717 (sh, s, C=O) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, 290 K, CD_2Cl_2) δ 59.7 (s); ^1H NMR (300.13 MHz, 290 K, CD_2Cl_2) δ 6.54 (dd, ABX, J_{HH} = 17 Hz, J_{HP} = 29 Hz, 1H, P–CH), 6.37 (dd, ABX, J_{HH} = 17 Hz, J_{HP} = 15 Hz, 1H, CH), 4.74 (s, 5H, Cp), 4.50 (d, J_{HP} = 2 Hz, 5H, Cp), 3.83, 3.75 (2 × s, 2 × 3H, OMe); $^{13}C\{^1H\}$ NMR (75.48 MHz, 290 K, CD_2Cl_2) δ 279.7 (s, br, 2 × μ-CO), 216.6 (s, br, FeCO), 138.3 (d, J_{CP} = 35 Hz, P–CH), 131.5 (d, J_{CP} = 3 Hz, CH), 98.8 (s, CCO_2Me), 79.2 (d, J_{CP} = 50 Hz, P$C\equiv C$).

(16) Preparation of **5**: neat benzyl azide (12 μL, 0.096 mmol) was added to a freshly prepared solution of complex **1** (ca. 0.040 g, 0.091 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 1 min to give a dark green solution yielding compound **5** (0.051 g, 98%) after workup. Selected data: ν(CO) (CH_2Cl_2) 1989 (vs), 1957. (w), 1793 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, 290 K, CD_2Cl_2) δ 319.1 (s); ^1H NMR (300.13 MHz, 290 K, CD_2Cl_2) δ 4.99 (s, 10H, Cp), 4.82 (s, 2H, CH_2).

(17) Preparation of **6**: a solution of $N_2CH(SiMe_3)$ (70 μL of a 2 M solution in petroleum ether, 0.140 mmol) was added to a freshly prepared solution of complex **1** (ca. 0.040 g, 0.091 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 16 h to give a dark green solution yielding compound **6** (0.045 g, 90%) after workup. Selected data: ν(CO) (CH_2Cl_2) 1980 (vs), 1947. (w), 1782 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, 290 K, CD_2Cl_2) δ 304.8 (s); ^1H NMR (400.13 MHz, 290 K, CD_2Cl_2) δ 7.75 (s, 1H, CH), 5.13 (s, 10H, Cp), 0.15 (s, 9H, Me).

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N($SiMe_3$)NCH).[19] These isomers display a bridging aminophosphide−iminoacyl ligand resulting from an unexpected 1,3-shift of the $SiMe_3$ group, as confirmed by an X-ray study on the cis isomer (Figure 3).[20] The interatomic distances in the PNNC skeleton suggest the presence of single P−N and N−N bonds, as well as a double N−C bond, so that the almost planar environment around N(1) is possibly a steric effect. Apart from this, the structure of *cis*-**7** is very similar to that of *cis*-**3**. We should stress that the bidentate phosphide−acyl ligands present in compounds **3** and **7** are quite unusual. In the case of **3**, we are only aware of two comparable complexes previously reported,[6,21] while no complex having a similarly coordinated PNNC ligand appears to have been reported.

In summary, we have shown that the cyclohexylphosphinidene complex **1** is quite reactive toward unsaturated molecules such as alkynes, diazo compounds, and organic azides, thus leading to the formation of novel and unexpected organophosphorus ligands coordinated to a diiron center. These reactions also reveal that the bent-phosphinidene ligand in **1** has a chemical behavior in part comparable to those of terminal nucleophilic phosphinidene complexes, in part comparable to those of the electrophilic complexes. Further work on the reactivity of compound **1** toward other unsaturated organic molecules is currently in progress.

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Supporting Information Available: Text giving experimental procedures and spectroscopic data for new compounds and a CIF file giving crystallographic data for the compounds **2**, **3**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Preparation of compounds **7**: a toluene solution (6 mL) of complex **6** (0.065 g, 0.117 mmol) was irradiated with visible−UV light at 288 K in a quartz Schlenk tube for 1 h, while a gentle N_2 purge was kept, to give a dark green solution yielding compound **7** (0.060 g, 97%) after workup. This product was shown (by NMR) to be a mixture of cis and trans isomers in a ratio of ca. 3:1. Selected data for *cis*-**7**: ν(CO) (CH_2Cl_2) 1964 (vs), 1782 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, 290 K, CD_2Cl_2) δ 352.7 (s); ^1H NMR (300.13 MHz, 290 K, CD_2Cl_2) δ 7.66 (d, $J_{HP} = 6$ Hz, 1H, CH), 4.73 (s, 5H, Cp), 4.56 (s, 5H, Cp), 0.25 (s, 9H, Me); $^{13}C\{^1H\}$ NMR (100.63 MHz, 290 K, CD_2Cl_2) δ 266.5 (d, $J_{CP} = 5$ Hz, μ-CO), 214.1 (d, $J_{CP} = 21$ Hz, FeCO), 182.5 (d, $J_{CP} = 11$ Hz, CH).

(20) X-ray data for *cis*-**7**: black crystals, monoclinic ($P2_1/c$), $a = 18.5613(4)$ Å, $b = 10.1935(2)$ Å, $c = 12.5422(2)$ Å, $\beta = 102.496(1)°$, $V = 2316.83(8)$ Å^3, $T = 100$ K, $Z = 4$, $R = 0.0472$ (observed data with $I > 2\sigma(I)$), GOF = 1.222.

(21) Clucas, J. A.; Harding, M. M.; Nicholls, B. S.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 1835.