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Deprotonation of Iron Vinylidene Complexes Containing a dppe Ligand

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Two iron complexes each containing a 1-ferra-2,5-diphospha-[2.1.1] ring are prepared by deprotonation reaction of cationic vinylidene complexes $[Fe]{=}C{=}C(Ph)CH_2R^+$ ($[Fe] = (\eta^5\text{-}C_5H_5)(dppe)Fe$, $R = CH{=}CH_2$ and Ph). The deprotonation takes place at the methylene proton of the dppe ligand, which is followed by an intramolecular addition giving the product. For similar vinylidene complexes with R = CN, $p\text{-}C_6H_4\text{-}CN$, and $p\text{-}C_6H_4CF_3$, the deprotonation reaction gave the cyclopropenyl complexes. The deprotonation of the vinylidene complex with $R = C_6F_5$ gave both the cyclopropenyl complex and the product containing a 1-ferra-2,5-diphospha-[2.1.1] ring system. The electron-withdrawing ability of the substituent near the C_γ-methylene group of the vinylidene ligand determines the selectivity of deprotonation. Characterizations of vinylidene, cyclopropenyl complexes, and a complex containing a 1-ferra-2,5-diphospha-[2.1.1] ring are carried out using single-crystal X-ray diffraction analysis.

Introduction

Vinylidene complexes of various metals[1] commonly function as strategic intermediates for catalytic conversion of alkynes such as cycloaromatization of conjugated enediynes,[2] dimerization of terminal alkynes,[3] and addition of oxygen, nitrogen, and carbon nucleophiles to alkynes.[4] Recently, the importance of vinylidene intermediates in catalysis has been pointed out.[5] Therefore the synthesis and stoichiometric reactivity of these unsaturated ligands are under active investigation.[6] The formation of metal vinylidene intermediates has been used to promote new carbon−carbon bond forming reactions by the addition of carbon centers to the electrophilic vinylidene carbon atom. The reactivity of ruthenium vinylidene complexes finds their applications broadly in synthetic chemistry; however, studies on iron complexes with highly unsaturated carbon-rich ligands such as acetylide, vinylidene, and allenylidene are relatively scarce.[7] We previously reported[8] synthesis of a number of ruthenium cyclopropenyl complexes by deprotonation reaction of readily accessible ruthenium vinylidene complexes containing a $-CH_2R$ group bound to C_β. With the presence of a terminal vinyl group suitably placed at a proper site, the ruthenium vinylidene complex displays novel intramolecular metathesis reactivity between the two C═C double bonds.[8] Encouraged by the rich chemistry of ruthenium vinylidene complexes, we set out to explore the chemical reactivity of iron complexes. Since relatively few vinylidene complexes of iron with a dppe ligand[9] have been obtained, we therefore studied the iron complexes with such a ligand. Interestingly, deprotonation could take place either at the methylene group on C_γ of the vinylidene ligand or at the methylene group of the dppe ligand.

Results and Discussion

Iron Acetylide and Vinylidene Complexes. The reported preparation of iron acetylide complexes in the literature[10] via

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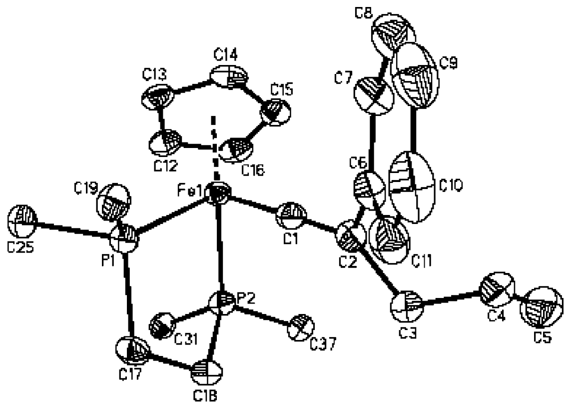
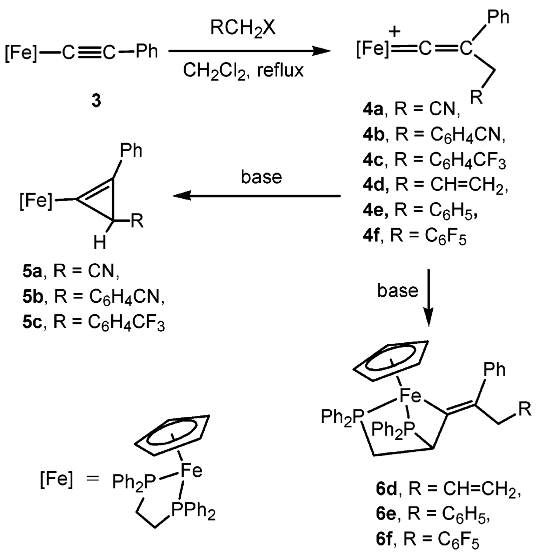


Figure 1. Molecular structure of complex **4d** (hydrogen atoms and phenyl groups on dppe except the ipso carbon are removed for clarity). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: Fe(1)−P(1), 2.207(1); Fe(1)−P(2), 2.199(1); Fe(1)−C(1), 1.766(4); C(1)−C(2), 1.320(5); C(2)−C(3), 1.532(5); C(4)−C(5), 1.268(7); P(1)−Fe(1)−P(2), 84.81(4); Fe(1)−C(1)−C(2), 178.7(3); C(1)−C(2)−C(3), 120.7(3); C(2)−C(3)−C(4), 114.2(3).

deprotonation of the vinylidene intermediate was modified to give [Fe]C≡CPh (**3**, [Fe] = (η^5-C_5H_5)(dppe)Fe) and [Fe*]C≡CPh, (**3***, [Fe*] = (η^5-C_5Me_5)(dppe)Fe) both with moderate yields without isolation of the vinylidene precursor. Reaction of the iron acetylide complex **3** with ICH_2CN at room temperature afforded the cationic vinylidene complex {[Fe]=C=C(Ph)CH_2CN}I (**4a**). Similarly, preparation of various vinylidene complexes [Fe]=C=C(Ph)CH_2R^+ (**4b**, R = *p*-C_6H_4-CN; **4c**, R = *p*-$C_6H_4CF_3$; **4d**, R = CH=CH_2; **4e**, R = Ph; **4f**, R = C_6F_5) have been successfully accomplished by reacting **3** with corresponding primary alkyl halides in CH_2Cl_2 at room temperature all with high yields. All iron vinylidene complexes **4a**−**f** display a characteristic deep red color in $CDCl_3$. Pentamethyl-cyclopentadienyl vinylidene complexes [Fe*]=C=C(Ph)CH_2R^+ (**4a***, R = CN; **4b***, R = *p*-C_6H_4CN) can also be prepared from electrophilic addition of primary alkyl halides to the acetylide ligand of complex **3***.

Distinctive spectroscopic data of **4a** consist of a strongly deshielded C_α resonance as a triplet at δ 353.4 with J_{P-C} = 32.7 Hz in the ^{13}C NMR spectrum.[11] In the ^{13}C NMR spectrum of **4a*** a strongly deshielded C_α resonance as a triplet at δ 346.6 with J_{P-C} = 32.4 Hz is also observed. Single crystals of **4d** suitable for X-ray diffraction analysis were obtained by recrystallization from acetone/diethyl ether. An ORTEP drawing is shown in Figure 1. The coordination around the Fe atom can be described as a three-legged piano stool. The Fe−C(1) bond length of 1.766(4) Å is in the range of a regular iron−carbon double bond in other crystallographically characterized iron vinylidene complexes.[12] The C(1)−C(2) bond length of 1.320(5) Å is a typical double bond. The bond angles Fe−C(1)−C(2) and C(1)−C(2)−C(3) are 178.7(3)° and 120.7(3)°, respectively. Cationic vinylidene complexes are known to react with alcohols or water to give alkoxycarbene or acyl complexes, respectively.[13,14] The reaction is thought to proceed by nucleophilic attack at the vinylidene α carbon, followed by a proton shift from the oxonium ion to the β-carbon. However, vinylidene complexes **4** and **4*** are inert to alcohols and water, giving no alkoxy carbene complexes.

Scheme 1



Synthesis of Cyclopropenyl Complexes. Deprotonation of the vinylidene complex **4a** by $^nBu_4NOH$ in acetone induces a cyclization reaction affording the neutral cyclopropenyl complex **5a** in high yield; see Scheme 1. The same reaction is also observed in THF and CH_2Cl_2. Complex **5a** is stable in benzene, toluene, and hexane but unstable in $CHCl_3$ and MeOH, in which **5a** is protonated to give back **4a** quantitatively. Formation of the cyclopropenyl ring from the vinylidene ligand should generate a stereogenic carbon center giving two doublet ^{31}P resonances at δ 109.7 and 107.9 with $^2J_{P-P}$ = 33.0 Hz assignable to the dppe ligand in the ^{31}P NMR spectrum of **5a**.[8] Single crystals of **5a** were obtained by slow evaporation of a diethyl ether solution of **5a** at low temperature. The solid-state structure of **5a** is determined by an X-ray diffraction analysis. An ORTEP drawing of **5a** is shown in Figure 2. The cyclopropenyl ring is clearly seen with the cyano group bound to the unique sp^3 carbon of the cyclopropenyl ligand. The Fe−C(1) bond length is 1.903(4) Å and the C(1)−C(4) bond length of 1.328(5) Å is a double bond, indicating coordination of the sp^2 carbon of the cyclopropenyl ligand. The bond angles Fe−C(1)−C(4) and C(1)−C(4)−C(5) of 163.3(3)° and 155.0(3)°, respectively, are both far greater than that of an idealized C(sp^2) hybridization. The C(1)−C(2) and C(2)−C(4) bond lengths of 1.580(5) and 1.489(6) Å, respectively, are significantly different, consistent with the favorable cleavage of the C(1)−C(2) bond of **5a** in acid.

The same deprotonation-induced cyclization process in acetone takes place for a number of vinylidiene complexes. We prepared similar cyclopropenyl complexes (**5b**, R = *p*-C_6H_4-CN; **5c**, R = *p*-$C_6H_4CF_3$; **5a***, R = CN; **5b***, R = *p*-C_6H_4CN);

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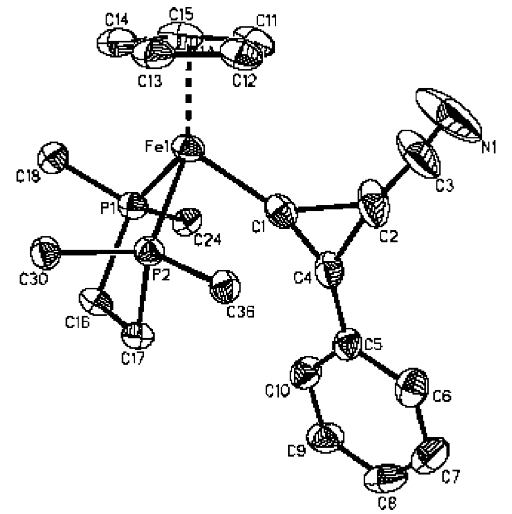

Figure 2. Molecular structure of complex **5a** (hydrogen atoms and phenyl groups on dppe except the ipso carbon are removed for clarity). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: Fe(1)−P(1), 2.164(1); Fe(1)−P(2), 2.156(1); Fe(1)−C(1), 1.903(4); C(1)−C(2). 1.580(5); C(1)−C(4), 1.328(5); C(2)−C(4), 1.489(6); P(1)−Fe(1)−P(2), 87.06(3); Fe(1)−C(1)−C(2), 135.2(3); Fe(1)−C(1)−C(4), 163.3(3); C(2)−C(1)−C(4), 60.9(3); C(1)−C(2)−C(4), 51.2(2); C(1)−C(4)−C(2), 67.9(3).

see Scheme 1. Spectroscopic data of complexes **5b**, **5c**, **5a*,** and **5b*** are all consistent with their formula.

Previously, iron cyclopropenyl derivatives in which the iron bonds to C(sp^3) of the cyclopropenyl ring have been prepared by the reaction of cyclopropenylium salts with sodium dicarbonyl(cyclopentadienyl)ferrate.[15] However, a derivative in which the metal is bound to the C(sp^2) of the three-membered ring is rare.[16] A few structurally different transition metal cyclopropenylidene complexes, mostly prepared from dichlorocyclopropene,[16] and a number of π-cyclopropene complexes[17] are also known. Our synthetic strategy provides a convenient route to a metal-coordinated cyclopropenyl moiety with a M−C(sp^2) bonding.

Alternative Intramolecular Addition of Iron Vinylidiene Complexes. In the deprotonation reaction of **4d**, with R = CH=CH$_2$ no cyclopropenyl complex is observed. Instead, the deprotonation of **4d** at one methylene proton of the dppe ligand by ^{n}Bu$_4$NOH is followed by an intramolecular nucleophilic addition of the deprotonated carbon to C$_\alpha$ of the vinylidene ligand, affording complex **6d** (see Scheme 1). The orange solid product **6d** is air stable at room temperature. A neutral ruthenium cyclopropenyl triphenylphosphine complex[8] with a vinyl substituent at the three-membered ring could be prepared from deprotonation of their vinylidene precursor. The relatively more acidic proton of the dppe ligand in the cationic iron complex **4d** could direct the reaction to proceed via a different route.

The ^{31}P NMR spectrum of **6d** in C$_6$D$_6$ shows two doublet resonances at δ 90.0 and 44.9 with $^2J_{P-P}$ = 45.5 Hz assignable to two different phosphorus atoms, with the latter shifted upfield significantly. The ^{1}H NMR spectrum of **6d** shows resonances at δ 5.86 and 4.96 assignable to the vinyl group. The ^{13}C NMR spectrum shows a doublet of doublets signal at δ 140.5 with J_{P-C} = 9.5, 6.4 Hz assignable to C$_\alpha$, confirming the nucleophilic addition at the α-carbon of the vinylidene ligand. The doublet of doublets resonance at δ 57.9 with J_{P-C} = 36.1 and 18.1 Hz assignable to CH resulted from deprotonation of the dppe ligand shifted significantly toward the downfield region from that of a regular CH$_2$ of dppe. In the 2D ^{1}H−^{13}C HSQC NMR spectrum correlation between ^{1}H resonances at δ 4.60 with one proton and ^{13}C resonance at δ 57.9 as well as the correlation between 2.54, 1.98 (^{1}H two protons) and 32.5 (^{13}C) assignable to the bridging group of the dppe ligand clearly reveal the site of deprotonation. Formation of complex **6d** resulted from initial deprotonation of the dppe ligand to afford a zwitterionic intermediate followed by an intramolecular addition of the ethanide carbon atom to C$_\alpha$ of the vinylidene ligand. Formation of a few related complexes of Fe and Ru as a result of similar intramolecular coupling between a deprotonated dppe ligand and a vinylidene moiety has been reported.[18] Recently, Gimeno and his co-workers have studied intramolecular carbon−carbon coupling of a dppm ligand with a vinyilidene and allenyidene moiety in an indenyl−ruthenium system.[19]

Single crystals of **6d** suitable for X-ray diffraction analysis are obtained by slow evaporation from a hexane solution. An ORTEP drawing is shown in Figure 3, with representative bond lengths and bond angles. Complex **6d** contains a 1-ferra-2,5-diphospha-[2.1.1] ring system. The central coordination sphere of the iron atom contains a Cp ring, a vinylic carbon, and two phosphorus atoms. The vinylic α-carbon C(1) bonds both to the iron atom and to one (C(17)) of the carbons in the ethylene bridge of the dppe ligand. The four-membered ring has bond angles of 68.84(9)°, 86.94(10)°, 88.6(2)°, and 98.7(2)° at Fe, P(1), C(17), and C(1), respectively. The C(1)−C(17) bond length of 1.551(4) Å is relatively long. The Fe−C(1) bond length is 2.045(3) Å, slightly longer than a normal Fe−C(sp^2) bond.[20−22] The five-membered ring shows less sign of strain, although the P(2)−C(18)−C(17) angle of 102.2(2)° is rather acute. The C(1)−C(2) bond length of 1.339(4) Å is typical for a carbon−carbon double bond, and substituents on these two carbon atoms are nearly coplanar.

Deprotonation of the vinylidene complex **4e** with R = Ph gave similar metallacyclic complex **6e** exclusively. Both metallacyclic derivatives **6d** and **6e** are air-stable orange solids. Noticeably, the ^{31}P NMR spectrum of **6e** shows that there are *Z*-form and *E*-form isomers in a 6:1 ratio. In refluxing THF the *E* isomer is converted to the *Z* isomer. Previously, it has been

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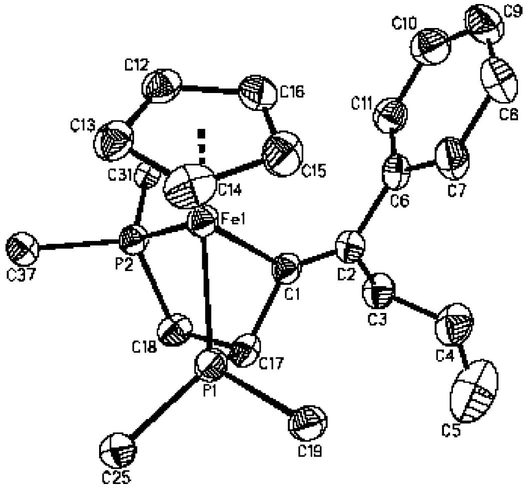

Figure 3. Molecular structure of complex **6d** (hydrogen atoms and phenyl groups on dppe except the ipso carbon are removed for clarity). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: Fe(1)−P(1), 2.147(1); Fe(1)−P(2), 2.156(1); Fe(1)−C(1), 2.045(3); C(1)−C(2), 1.339(4); C(1)−C(17), 1.551(4); C(2)−C(3), 1.535(5); C(4)−C(5), 1.248(6); P(1)−Fe(1)−P(2), 87.73(4); C(1)−Fe(1)−P(1), 68.84(9); Fe(1)−P(1)−C(17), 86.94(10); Fe(1)−C(1)−C(2), 139.7(2); Fe(1)−C(1)−C(17), 98.7(2); C(1)−C(2)−C(3), 124.4(3); C(1)−C(17)−P(1), 88.6(2).

reported that in the ruthenium indenyl complex the steric requirements of the indenyl ligand and the bulky ^{t}Bu group on the alkenyl group would favor the *E* configuration.[19b,23] When a less sterically demanding phenyl group replaces the ^{t}Bu group, a mixture of *Z*-form and *E*-form isomers was obtained. In our system the steric hindrance between the Cp ring and the substituents on C_β probably is insignificant, therefore giving the *Z*-form as the more stable isomer.

Interestingly, deprotonation of the vinylidene complex **4f** with a C_6F_5 group was observed to give a mixture of the cyclopropenyl complex **5f** and the metallacyclic complex **6f** in a 2:8 ratio. The presence of the electron-withdrawing C_6F_5 group enhances the acidity of the neighboring methylene proton, making protons at the dppe and vinylidene ligand comparable in acidity. Therefore the deprotonation could take place at each site. For **6f** two isomers (*Z*/*E*) are observed in a 13:1 ratio. Spectroscopic data for complex **6f** (*Z*-form) are in accordance with the proposed structure. No attempt was made to isolate the cyclopropenyl compound **5f** from the mixture.

Concluding Remarks

In the deprotonation reaction of iron vinylidene complexes containing a dppe ligand, various electron-withdrawing groups at C_γ of the vinylidene ligand control the site of deprotonation reaction, leading to different products. Neutral iron cyclopropenyl complexes **5a**−**c** containing a bidentate dppe ligand are obtained from the deprotonation of an iron complex with an electron-withdrawing group such as CN or *p*-C_6H_4CN at C_γ of the vinylidene ligand. Namely, the deprotonation takes place at the C_γ-methylene group of the vinylidene ligand. For complexes without an electron-withdrawing group, deprotonation takes place at the dppe ligand, affording the 1-ferra-2,5-diphosphabicyclo[2.1.1]hexane complex **6**. For the iron complex containing a pentafluorophenyl group at C_γ of the vinylidene ligand, the deprotonation reaction could take place at both sites and a mixture was obtained.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification. Compounds [Fe]−C≡C−Ph (**3**, [Fe] = (η^5-C_5H_5)(dppe)Fe) and [Fe*]−C≡C−Ph, (**3***, [Fe*] = (η^5-C_5Me_5)(dppe)Fe) were prepared by following the methods reported in the literature.[10] Infrared spectra were recorded on a Nicolet-MAGNA-550 spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra (FAB) were recorded using a JEOL SX-102A spectrometer; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker AC-300 instrument or a DMX 500 FT-NMR spectrometer at room temperature using $SiMe_4$ or 85% H_3PO_4 as standard.

Synthesis of {[Fe]=C=C(Ph)CH$_2$CN}I, 4a. To a Schlenk flask charged with **3** (0.10 g, 0.161 mmol) in CH_2Cl_2 (15 mL) was added ICH_2CN (0.11 mL, 1.64 mmol) under nitrogen. The resulting solution was stirred at room temperature for 5 h, then the solvent was reduced to about 5 mL. The mixture was slowly added to vigorously stirred diethyl ether (50 mL). The gray precipitate thus formed was filtered off and washed with diethyl ether and dried under vacuum to give **4a** (99 mg, yield 78%, mp = 197 °C, dec). Spectroscopic data for **4a**: ^{1}H NMR ($CDCl_3$) δ 7.45−6.79 (m, 25H, Ph), 5.31 (s, 5H, Cp), 3.48−3.12 (m, 4H, CH_2CH_2 of dppe), 2.64 (s, 2H, CH_2CN); ^{13}C NMR ($CDCl_3$) δ 353.4 (t, J_{P-C} = 32.7 Hz, C_α), 135.0−124.8 (C_β, Ph), 118.0 (CN), 89.2 (Cp), 27.9 (t, J_{P-C} = 22.6 Hz, dppe), 14.7 (CH_2CN); ^{31}P NMR ($CDCl_3$) δ 93.4 (s, dppe); MS *m*/*z* 660.2 ($M^+ - I$), 519.1 ($M^+ - I$, C_2PhCH_2CN). Anal. Calcd for $C_{41}H_{36}NFeIP_2$ (787.43): C, 62.54; H, 4.61; N, 1.78. Found: C, 62.81; H, 4.52; N, 1.91.

Synthesis of {[Fe]=C=C(Ph)CH$_2$R}X (4b, R = p-C$_6$H$_4$CN, X = Br; 4c, R = *p*-C$_6$H$_4$CF$_3$, X = Br; 4d, R = CH=CH$_2$, X = I; 4e, R = Ph, X = Br; 4f, R = C$_6$F$_5$, X = Br). Synthesis of **4b**−**f** followed the same procedure as that used for the preparation of **4a**. Spectroscopic data of **4b** (yield 87%, mp = 190 °C, dec): ^{1}H NMR ($CDCl_3$) δ 7.42−6.52 (m, 29H, Ph), 5.21 (s, 5H, Cp), 3.17−3.06 (m, 4H, CH_2CH_2 of dppe), 3.02 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 357.3 (t, J_{P-C} = 32.7 Hz, C_α), 144.3−127.5 (Ph), 118.8 (CN), 109.8 (C_β), 88.8 (Cp), 31.7 (CH_2), 28.7 (t, J_{P-C} = 22.7 Hz, CH_2); ^{31}P NMR ($CDCl_3$) δ 94.1 (s, dppe); MS *m*/*z* 736.2 ($M^+ -$ Br), 519.1 ($M^+ -$ Br, C_2PhCH_2(*p*-C_6H_4CN)). Anal. Calcd for $C_{47}H_{40}NBrFeP_2$ (816.49): C, 69.13; H, 4.94; N, 1.72. Found: C, 69.19; H, 4.90; N, 1.65. Spectroscopic data of **4c** (yield 83%): ^{1}H NMR ($CDCl_3$) δ 7.34−6.49 (m, 29H, Ph), 5.16 (s, 5H, Cp), 3.08−3.05 (m, 4H, CH_2CH_2 of dppe), 2.97 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 357.8 (t, J_{P-C} = 33.2 Hz, C_α), 138.0−125.0 (Ph), 88.7 (Cp), 31.4 (CH_2), 28.6 (t, J_{P-C} = 23.1 Hz, CH_2); ^{31}P NMR ($CDCl_3$) δ 94.9 (s, dppe); MS *m*/*z* 779.3 ($M^+ -$ Br), 519.2 ($M^+ -$ Br, C_2PhCH_2(*p*-$C_6H_4CF_3$)). Anal. Calcd for $C_{47}H_{40}F_3FeBrP_2$ (859.48): C, 65.68; H, 4.69. Found: C, 65.74; H, 4.78. Spectroscopic data of **4d** (yield 92%): ^{1}H NMR ($CDCl_3$) δ 7.41−6.63 (m, 25H, Ph), 5.28 (m, 1H, CH=), 5.17 (s, 5H, C_5H_5), 4.82 (dd, 1H, *J* = 10.3 Hz, *J* = 1.35 Hz, CH_2), 4.61 (dd, 1H, *J* = 16.9 Hz, *J* = 1.35 Hz, CH_2), 3.30−3.07 (m, 4H, CH_2CH_2 of dppe), 2.35 (d, 2H, *J* = 6.13 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 359.3 (t, J_{p-c} = 32.8 Hz, C_α), 137.8−126.8 (Ph, C_β, CH=), 116.6 (=CH_2), 88.4 (Cp), 51.5 (CH_2), 30.1 (CH_2), 28.2 (t, J_{p-c} = 22.9 Hz, CH_2CH_2 of dppe); ^{31}P NMR ($CDCl_3$) δ 94.4 (s, dppe); MS *m*/*z* 660.3 ($M^+ - I$). Anal. Calcd for $C_{42}H_{39}FeIP_2$ (788.43): C, 63.98; H, 4.99. Found: C, 63.80; H, 4.97.

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(23) Reger, D. L. *Acc. Chem. Res.* **1988**, *21*, 229.

Spectroscopic data of **4e** (yield 91%): ^{1}H NMR (CDCl$_3$) δ 7.41−6.54 (m, 30H, Ph), 5.18 (s, 5H, Cp), 3.44 (m, 2H, CH$_2$ of dppe), 3.19 (m 2H, CH$_2$ of dppe), 2.95 (s, 2H, CH$_2$); ^{13}C NMR (CDCl$_3$) δ 358.9 (t, $J_{\mathrm{P-C}} = 32.7$ Hz, C$_\alpha$), 138.6−126.2 (Ph, C$_\beta$), 88.5 (Cp), 31.7 (*C*H$_2$Ph), 28.6 (t, $J_{\mathrm{P-C}} = 23.0$ Hz, CH$_2$); ^{31}P NMR (CDCl$_3$) δ 94.4 (s, dppe). Anal. Calcd for $C_{46}H_{41}FeBrP_2$ (791.48): C, 69.80; H, 5.22. Found: C, 69.75; H, 5.57. Spectroscopic data of **4f** (yield 86%): ^{1}H NMR (CDCl$_3$) δ 7.40−6.53 (m, 25H, Ph), 5.23 (s, 5H, Cp), 3.16 (m, 4H, CH$_2$CH$_2$ of dppe), 2.87 (s, 2H, CH$_2$); ^{13}C NMR (CDCl$_3$) δ 352.7 (t, $J_{\mathrm{P-C}} = 32.4$ Hz, C$_\alpha$), 137.0−127.7 (Ph, C$_\beta$), 88.9 (Cp), 28.1 (t, $J_{\mathrm{P-C}} = 23.0$ Hz, CH$_2$), 19.1 (CH$_2$); ^{31}P NMR (CDCl$_3$) δ 93.7 (s, dppe); MS *m/z* 801.1 (M$^+$ − Br), 724.1 (M$^+$ − Br, Ph), 519.1 (M$^+$ − Br, Ph, C$_2$CH$_2$C$_6$F$_5$). Anal. Calcd for $C_{46}H_{36}F_5FeBrP_2$ (881.43): C, 62.68; H, 4.12. Found: C, 62.47; H, 4.29.

Synthesis of $\{[\mathrm{Fe}^*]{=}\mathrm{C}{=}\mathrm{C(Ph)CH_2R}\}\mathrm{X}$ (4a*, R = CN, X = I; 4b*, R = *p*-C$_6$H$_4$CN, X = Br). Syntheses of **4a*** and **4b*** followed the same procedure as that used for the preparation of **4a**. Spectroscopic data for **4a*** (yield 90%): ^{1}H NMR (CDCl$_3$) δ 7.57−6.91 (m, 25H, Ph), 3.22 (m, 2H, dppe), 2.78 (m, 2H, CH$_2$-CH$_2$ of dppe), 2.41 (s, 2H, CH$_2$), 1.60 (s, 15H, C$_5$Me$_5$); ^{13}C NMR (CDCl$_3$) δ 346.6 (t, $J = 32.4$ Hz, C$_\alpha$), 133.3−127.8 (Ph), 118.0 (CN), 116.2 (C$_\beta$), 101.0 (*C*$_5$Me$_5$), 30.1 (t, $J_{\mathrm{P-C}} = 22.6$ Hz, CH$_2$), 16.3 (*C*H$_2$CN), 10.5 (C$_5$*Me*$_5$); ^{31}P NMR (CDCl$_3$) δ 88.6 (s, dppe); MS *m/z* 730.2 (M$^+$ − I), 690.1 (M$^+$ − I, CH$_2$CN), 589.2 (M$^+$ − I, CH$_2$CN, C$_2$Ph). Anal. Calcd for $C_{46}H_{46}NFeIP_2$ (857.53): C, 64.42; H, 5.41; N, 1.63. Found: C, 64.37; H, 5.58; N, 1.59. Spectroscopic data for **4b*** (yield 90%): ^{1}H NMR (CDCl$_3$) δ 7.47−6.58 (m, 29H, Ph), 3.36 (s, 2H, CH$_2$), 3.36 (m, 2H, dppe), 3.01 (m, 2H, dppe), 1.63 (s, C$_5$Me$_5$); ^{13}C NMR (CDCl$_3$): δ 352.1 (t, $J = 32.7$ Hz, C$_\alpha$), 143.7−126.9 (Ph), 118.8 (CN), 109.7 (C$_\beta$), 100.4 (*C*$_5$Me$_5$), 32.8 (CH$_2$), 31.9 (t, $J_{\mathrm{P-C}} = 21.3$ Hz, CH$_2$, dppe), 11.9 (C$_5$*Me*$_5$); ^{31}P NMR (CDCl$_3$) δ 89.9 (s, dppe); MS *m/z* 806.4 (M$^+$ − Br), 690.4 (M$^+$ − Br, CH$_2$-*p*-C$_6$H$_4$CN). Anal. Calcd for $C_{52}H_{50}NFeBrP_2$ (886.62): C, 70.44; H, 5.68; N, 1.58. Found: C, 70.72; H, 5.82; N, 1.49.

Synthesis of 5a. To a 15 mL acetone solution of **4a** (0.40 g, 0.51 mmol) was added a solution of ^{n}Bu$_4$NOH (1.3 mL, 1 M in MeOH). The mixture was stirred at room temperature for 2 h to give an orange microcrystalline precipitate, which was filtered off and washed with 2 × 5 mL of acetone and 10 mL of diethyl ether, then dried under vacuum. The product was analytically pure and was identified as **5a** (0.30 g, 90% yield, mp = 174 °C, dec). Spectroscopic data of **5a**: ^{1}H NMR (C$_6$D$_6$) δ 7.85−6.55 (m, 25H, Ph), 4.59 (s, Cp), 2.60−2.50 (m, 1H, dppe), 2.08−1.89 (m, 3H, dppe), 0.13 (s, CH); ^{13}C NMR (C$_6$D$_6$) δ 143.7−125.0 (C$_\alpha$, Ph), 139.9 (t, C$_\alpha$, $J_{\mathrm{P-C}} = 7.8$ Hz), 118.8 (CN), 81.0 (Cp), 29.1 (dd, $J_{\mathrm{P-C}} = 34.0$ Hz, $J_{\mathrm{P'-C}} = 15.1$ Hz, CH$_2$ of dppe), 27.4 (dd, $J_{\mathrm{P-C}} = 34.0$ Hz, $J_{\mathrm{P'-C}} = 15.1$ Hz, CH$_2$ of dppe), 5.35 (d, CH, $^3J_{\mathrm{P-C}} = 2.9$ Hz); ^{31}P NMR (C$_6$D$_6$) δ 109.7, 107.9 (2d, $J_{\mathrm{P-P}} = 33.0$ Hz, dppe); MS *m/z* 660.2 (M$^+$ + 1), 519.1 (M$^+$ + 1 − C(Ph)CHCN). Anal. Calcd for $C_{41}H_{35}NFeP_2$ (659.49): C, 74.67; H, 5.35; N, 2.12. Found: C, 74.65; H, 5.45; N, 2.09. Synthesis of **5b**,**c** followed the same procedure as that used for the preparation of **5a**. Spectroscopic data of **5b** (yield 82%): ^{1}H NMR (C$_6$D$_6$) δ 7.90−6.42 (m, 25H, Ph), 4.19 (s, Cp), 2.68−2.50 (m, 1H, dppe), 2.17−1.87 (m, 3H, dppe), 0.89 (s, CH); ^{13}C NMR (CD$_2$Cl$_2$) δ 162.5 (Ph), 148.7−120.5 (C$_\alpha$, Ph), 104.4 (CN), 79.5 (Cp), 31.0 (CH), 28.4 (dd, $J_{\mathrm{P-C}} = 33.7$ Hz, $J_{\mathrm{P'-C}} = 15.2$ Hz, CH$_2$ of dppe), 26.6 (dd, $J_{\mathrm{P-C}} = 26.7$ Hz, $J_{\mathrm{P'-C}} = 15.1$ Hz, CH$_2$ of dppe); ^{31}P NMR (C$_6$D$_6$) δ 109.8, 107.7 (2d, $J_{\mathrm{P-P}} = 33.0$ Hz, dppe); MS *m/z* 736.2 (M$^+$ + 1), 519.1 (M$^+$ + 1 − C(Ph)CH(*p*-C$_6$H$_4$CN)). Anal. Calcd for $C_{47}H_{39}NFeP_2$ (735.58): C, 76.74; H, 5.34; N, 1.90. Found: C, 76.81; H, 5.23; N, 1.87. Spectroscopic data of **5c** (yield 72%): ^{1}H NMR (C$_6$D$_6$) δ 7.91−6.54 (m, 29H, Ph), 4.21 (s, 5H, Cp), 2.69−2.54 (m, 1H, dppe), 2.17−1.90 (m, 3H, dppe), 1.00 (s, 1H, CH); ^{31}P NMR (C$_6$D$_6$) δ 109.9, 108.0 (2d, $J_{\mathrm{P-P}} = 34.0$ Hz, dppe); MS *m/z* 779.2 (M$^+$), 620.1 (M$^+$ − CH(*p*-C$_6$H$_4$CF$_3$)), 519.1 (M$^+$ − CH(*p*-C$_6$H$_4$CF$_3$), C$_2$-Ph). Anal. Calcd for $C_{47}H_{39}F_3FeP_2$ (778.57): C, 72.50; H, 5.05. Found: C, 72.61; H, 4.95. Spectroscopic data of **5a*** (yield 85%): ^{1}H NMR (C$_6$D$_6$) δ 7.82−6.52 (m, 25H, Ph), 2.68 (m, 1H, dppe), 2.04−1.84 (m, 3H, dppe), 1.59 (s, 15H, C$_5$Me$_5$), 0.34 (s, CH); ^{31}P NMR (C$_6$D$_6$) δ 105.8, 101.1 (2d, $J_{\mathrm{P-P}} = 13.1$ Hz, dppe); MS *m/z* 730.2 (M$^+$ + 1), 690.2 (M$^+$ − CHCN). Anal. Calcd for $C_{46}H_{45}NFeP_2$ (729.62): C, 75.72; H, 6.22; N, 1.92. Found: C, 75.65; H, 6.34; N, 1.90. Spectroscopic data of **5b*** (yield 83%): ^{1}H NMR (C$_6$D$_6$) δ 7.98−6.32 (m, 29H, Ph), 2.46 (m, 1H, dppe), 2.18−2.00 (m, 3H, dppe), 1.52 (s, 15H, C$_5$Me$_5$), 0.70 (s, 1H, CH); ^{31}P NMR (C$_6$D$_6$) δ 107.1, 103.2 (2d, $J_{\mathrm{P-P}} = 13.4$ Hz). Anal. Calcd for $C_{52}H_{49}NFeP_2$ (805.71): C, 77.51; H, 6.13; N, 1.74. Found: C, 77.42; H, 6.40; N, 1.70.

Synthesis of 6d and 6e. To a 15 mL acetone solution of **4d** (0.26 g, 0.33 mmol) was added a solution of ^{n}Bu$_4$NOH (1.5 mL, 1 M in MeOH). The mixture was stirred at room temperature for 2 h, and the solvent was removed under vacuum. The residue was washed with 10 mL of MeOH to give an orange precipitate, which was filtered off and washed with 2 × 5 mL of MeOH and 10 mL of diethyl ether, then dried under vacuum. The product was analytically pure and was identified as **6d** (0.23 g 92% yield). Spectroscopic data of **6d**: ^{1}H NMR (C$_6$D$_6$) δ 7.98−6.89 (m, 25H, Ph), 5.86 (m, 1H, CH=), 4.96 (m, 2H, =CH$_2$), 4.60 (m, 1H, CH on dppe), 3.98 (s, 5H, Cp), 3.35 (m, 2H, CH$_2$), 2.54 (m, 1H, CH$_2$ of dppe), 1.98 (m, 1H, CH$_2$ of dppe); ^{13}C NMR (C$_6$D$_6$) δ 149.8−125.4 (Ph, CH=), 140.5 (dd, $J_{\mathrm{P-C}} = 9.5$, 6.4 Hz, C$_\alpha$), 113.4 (=CH$_2$), 75.4 (Cp), 57.9 (dd, $J_{\mathrm{P-C}} = 36.1$ Hz, $J_{\mathrm{P'-C}} = 18.1$ Hz, CH), 41.8 (CH$_2$), 32.5 (d, $J_{\mathrm{P-C}} = 33.7$ Hz, CH$_2$); ^{31}P NMR (C$_6$D$_6$) δ 90.0, 44.9 (2d, $J_{\mathrm{P-P}} = 45.5$ Hz, dppe); MS *m/z* 660.1 (M$^+$). Anal. Calcd for $C_{42}H_{38}FeP_2$ (660.52): C, 76.37; H, 5.80. Found: C, 76.41; H, 5.92. Complex **6e** (0.17 g, 73% yield, mp = 209 °C) was prepared similarly from **4e** (0.26 g, 0.33 mmol). Spectroscopic data of **6e**: ^{1}H NMR (CDCl$_3$) δ 8.00−6.95 (m, 30H, Ph), 4.81−4.66 (m, 1H, CHPPh$_2$), 3.99 (s, 5H, Cp), 3.82 (m, 2H, CH$_2$Ph), 2.57−2.43 (m, 1H, CH$_2$PPh$_2$), 2.01 (m, 1H, CH$_2$PPh$_2$); ^{31}P NMR (C$_6$D$_6$) δ 89.8, 45.4 (2d, $J_{\mathrm{P-P}} = 45.3$ Hz); MS *m/z* 710.2 (M$^+$). Anal. Calcd for $C_{46}H_{40}FeP_2$ (710.58): C, 77.75; H, 5.67. Found: C, 77.91; H, 5.72.

Deprotonation of 4f. To a 15 mL acetone solution of **4f** (0.21 g, 0.24 mmol) was added a solution of ^{n}Bu$_4$NOH (1.3 mL, 1 M in MeOH). The mixture was stirred at room temperature for 2 h to give an orange microcrystalline precipitate, which was filtered off and washed with 2 × 5 mL of acetone and 10 mL of diethyl ether, then dried under vacuum. The mixture was further extracted with MeOH twice to give the product identified as **6f** (0.12 g, 63% yield). Spectroscopic data of **6f**: ^{1}H NMR (C$_6$D$_6$) δ 7.94−6.90 (m, 25H, Ph), 4.69 (1H, $J_{\mathrm{P-Ha}} = 45.21$ Hz, $J_{\mathrm{P'-Ha}} = 7.36$ Hz, $J_{\mathrm{Ha-Hb,c}} = 3.50$ Hz, CH), 3.90 (s, 5H, Cp), 3.84 (d, 1H, $J = 14.6$ Hz, CH$_2$), 3.63 (d, 1H, $J = 13.5$ Hz, CH$_2$C$_6$F$_5$), 2.67 (m, 1H, $J_{\mathrm{P-Hb}} = 43.23$ Hz, $J_{\mathrm{P'-Hb}} = 10.35$ Hz, $^3J_{\mathrm{Hb-Ha}} = 3.91$ Hz, $^2J_{\mathrm{Hb-Hc}} = 13.98$ Hz, dppe), 2.11 (m, 1H, $J_{\mathrm{P-Hc}} = 13.12$ Hz, $J_{\mathrm{P'-Hc}} = 5.17$ Hz, $^2J_{\mathrm{Hc-Hb}} = 13.11$ Hz, dppe); ^{31}P NMR (C$_6$D$_6$) δ 89.7, 45.4 (2d, $J_{\mathrm{P-P}} = 45.5$ Hz, dppe). Anal. Calcd for $C_{46}H_{35}F_5FeP_2$ (800.53): C, 69.01; H, 4.41. Found: C, 68.85; H, 4.72. Monitoring the same reaction in a smaller scale by ^{31}P NMR indicated formation of the cyclopropenyl complex **5f** as revealed by a set of two doublet resonances at δ 109.6 and 108.5 with $J = 32.1$ Hz. The ratio of **5f**:**6f** was 1:4. No attempt was made to isolate complex **5f**. While complex **5f** is only slightly soluble in MeOH, purification of the desired product **6f** was carried out by methanol extraction.

Structure Determination of Complexes 4d, 5a, and 6d. Single-crystal X-ray diffraction data were measured on a Bruker SMART Apex CCD diffractometer using μ(Mo Kα) radiation ($\lambda = 0.71073$ Å). The data collection was executed using the SMART program;

cell refinement and data reduction were performed with the SAINT program. The structure was determined using the SHELXTL/PC program and refined using full-matrix least-squares.[24] Crystallographic refinement parameters[25] of complexes **4d**, **5a**, and **6d** and selected bond distances and angles are listed in the Supporting Information.

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Supporting Information Available: Complete crystallographic data for **4d**, **5a**, and **6d** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] (a) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33. (b) *SHELXTL*: Structure Analysis Program, version 5.04; Siemens Industrial Automation Inc.: Madison, WI, 1995.

[25] GOF = $[\sum[w(F^2_o - F^2_c)^2]/(n - p)]^{1/2}$, where n and p denote the number of data and parameters. R1 = $(\sum||F_o| - |F_c||)/\sum|F_o|$, wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F^2_o) + (aP)^2 + bP]$ and $P = [(\max; 0, F^2_o) + 2F_c^2]/3$.