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Redox Chemistry of Bis(phosphaethenyl)pyridine Iron Complexes

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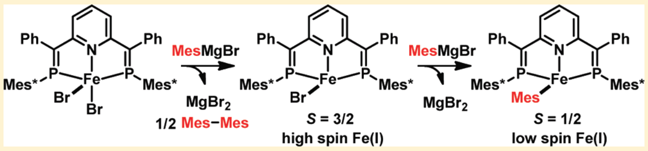
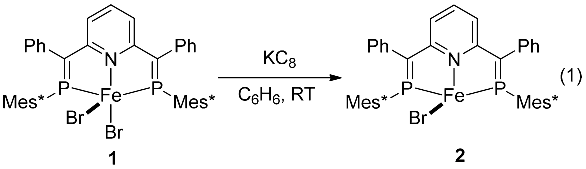
Ⓢ *Supporting Information*



ABSTRACT: Redox reactions of iron complexes bearing a PNP-pincer-type phosphaalkene ligand, 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine (BPEP), are reported. The Fe(II) dibromide [FeBr$_2$(BPEP)] (**1**) is readily reduced by [Cp$_2$Co] to afford the four-coordinate Fe(I) monobromide [FeBr(BPEP)] (**2**), while **2** reacts with PhCH$_2$Br to reproduce **1**. Treatment of **1** with MesMgBr or Mes$_2$Mg(THF)$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) results in one-electron reduction of **1**, followed by transmetalation of the resulting **2** with mesitylmagnesium compounds to give the Fe(I) mesityl complex [FeMes(BPEP)] (**3**). The single-crystal diffraction study of **3** has revealed a distorted trigonal monopyramidal arrangement around the iron center. SQUID magnetometry has established a low-spin ground state (S = 1/2) of **3**. Complex **2** reacts with Me$_2$Mg(THF)$_2$ to afford Fe(0) and Fe(II) complexes (**4** and **5**, respectively) coordinated with novel multidentate ligand systems containing a phosphonium ylide structure. The formation processes of **4** and **5** via an [FeMe(BPEP)] intermediate are discussed on the basis of their X-ray structures.

INTRODUCTION

Phosphaalkenes with a P=C bond constitute an interesting class of supporting ligands in coordination chemistry. They possess an extremely low-lying π^* orbital and undergo effective π-back-bonding with transition metals.[1,2] We have documented that 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine (BPEP) as a PNP-pincer-type phosphaalkene ligand effectively stabilizes coordinatively unsaturated complexes in low-oxidation states.[3] Representative examples include [FeBr(BPEP)] (**2**) with a four-coordinate Fe(I) center, which is formed by one-electron reduction of [FeBr$_2$(BPEP)] (**1**) with KC$_8$ (eq 1).[3b] While Fe(I) complexes having low-coordination numbers have been limited,[4] the four-coordinate structure of **2** has been established by experimental and theoretical studies. The complex adopts a distorted trigonal monopyramidal configuration around iron. This unique geometry enables effective orbital interactions between Fe (dπ) and BPEP (π^*) to form highly delocalized orbitals, responsible for the stability of **2**.



1 **2** (1)

Mes* = 2,4,6,-tri-*tert*-butylphenyl

This paper reports redox reactions of **1** and **2**. Redox chemistry of iron complexes has drawn increasing attention in connection with the activation of small molecules in enzymatic systems.[5] Such information is also important to develop iron-catalyzed organic transformations such as cross-coupling reactions.[6] However, studies using well-defined complexes have been limited.[7] Recently, Chirik et al. investigated reduction behavior of 2,6-bis(imino)pyridine Fe(II) complexes [FeX$_2$(^{i}PrPDI)] (X = Cl, Br; ^{i}PrPDI = 2,6-(^{i}Pr$_2$C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N) in detail.[8] The Fe(II) dihalides undergo stepwise two-electron reduction by sodium amalgam under a nitrogen atmosphere to afford [Fe(N$_2$)$_2$(^{i}PrPDI)] via monohalide intermediates [FeX(^{i}PrPDI)]. Interestingly, while the dinitrogen and monohalide complexes adopt the formal oxidation states of 0 and +1, respectively, the iron centers of both complexes have been proven to remain in an Fe(II) state in reality. The reduction occurs on the ^{i}PrPDI ligand, and the reducing electrons are accommodated in ligand-centered π^* orbitals.

On the other hand, since the π^* orbital of the BPEP ligand effectively interacts with the dπ orbital of iron to form highly delocalized orbitals, it is expected that complexes **1** and **2** exhibit unique redox properties, significantly different from those of the ^{i}PrPDI complexes. Thus, we examined their reactivities toward reducing agents. It has been found that treatment of **1** with MesMgBr or Mes$_2$Mg(THF)$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) in benzene results in one-electron reduction of **1** to afford **2**, followed by transmetalation of the resulting **2**, giving [FeMes(BPEP)] (**3**) as a four-coordinate Fe(I) complex. On the other hand, the reaction of complex **2** with Me$_2$Mg(THF)$_2$ forms unexpected phosphonium ylide complexes.

RESULTS AND DISCUSSION

Redox Properties of 1 and 2. First, redox properties of **1** were examined by an electrochemical method. As shown in Figure 1, the cyclic voltammogram recorded in CH$_2$Cl$_2$ in the presence of [Bu$_4$N][BF$_4$] at room temperature exhibited three sets of redox waves: (i), (ii), and (iii). The potentials are

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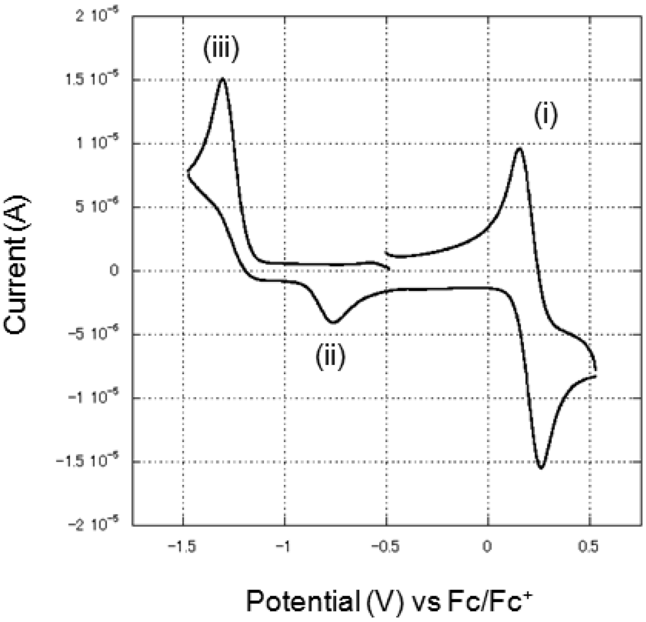
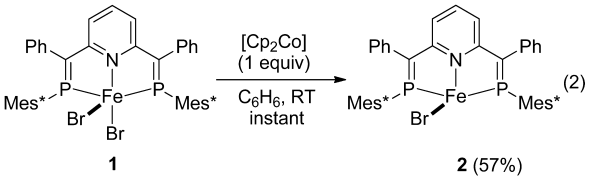
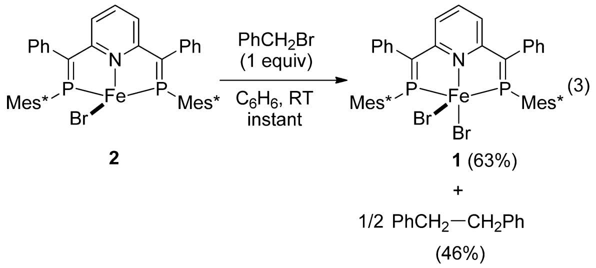


Figure 1. Cyclic voltammogram of [FeBr$_2$(BPEP)] (**1**) in CH$_2$Cl$_2$ (0.1 mM) at 22 °C (0.1 M [Bu$_4$N][BF$_4$], scan rate 100 mV/s, versus Fc/Fc$^+$).

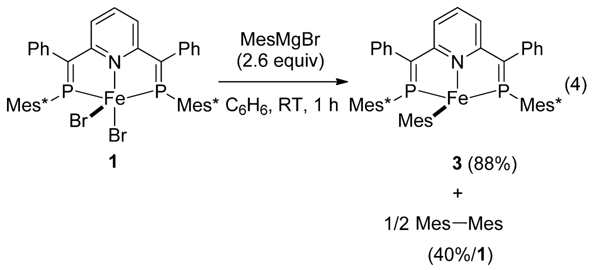
reported in V vs Fc/Fc$^+$. The reversible wave (i) at +0.20 V ($E_{1/2}$) corresponds to the [FeBr$_2$(BPEP)]/[FeBr$_2$(BPEP)]$^+$ cycle, while the small oxidation wave (ii) at −0.75 V (E_p) may be formed from a decomposition product because its intensity gradually increases with time. On the other hand, the irreversible wave (iii) at −1.31 V (E_p) is attributed to the conversion of **1** to **2**, and its reduction potential is much less negative than that of [FeCl$_2$(^{i}PrPDI)] (E_p = −1.87 V). Indeed, complex **1** was instantly reduced by [Cp$_2$Co] as a mild reducing agent (E^0 = −1.33 V)[9] at room temperature, giving **2** in 57% isolated yield (eq 2).



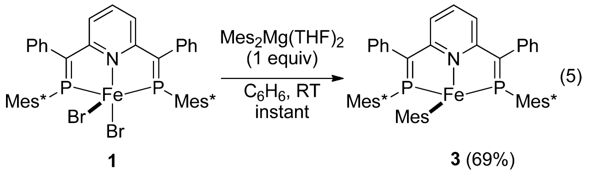
On the contrary, complex **2** reacted with PhCH$_2$Br (1 equiv) at room temperature to afford **1** (63% after isolation), together with PhCH$_2$CH$_2$Ph (46%/**2**) (eq 3). Thus, the interconversion between **1** and **2** was accomplished by chemical reactions. In the reaction with PhCH$_2$Br, no trace of toluene was detected even in the presence of 1,4-cyclohexadiene as a good hydrogen atom donor, indicating the occurrence of a rapid one-electron oxidation process involving a short-lived benzyl radical. On the other hand, complex **2** was stable toward 3-hexenyl bromide, cyclohexyl bromide, and *tert*-butyl bromide under the same reaction conditions.



Reactions with Mesitylmagnesiums. Complex **1** was readily reduced by Grignard reagents as well. The reaction with 2.6 equiv of MesMgBr (Mes = 2,4,6-Me$_3$C$_6$H$_2$) in benzene at room temperature afforded [FeMes(BPEP)] (**3**) in 88% isolated yield as a brownish-green solid. The reaction proceeded along with the formation of bimesityl (40%/**1**) (eq 4). In this system, slow addition of MesMgBr over 1 h was essential to obtain **3** in high yield. Otherwise, a mixture of **1**, **2**, and **3** was formed, and further addition of MesMgBr (4 equiv) caused decomposition of **3**, providing a complex mixture of unidentified compounds. Complex **3** is probably formed by one-electron reduction of **1** with MesMgBr, followed by transmetalation of the resulting **2** with another molecule of MesMgBr. Actually, complex **2**, which was independently prepared from **1** and KC$_8$, reacted with 1 equiv of MesMgBr to afford **3** in 55% yield. A related reductive alkylation process has been reported for the reactions of [FeCl$_2$(^{i}PrPDI)] with MeLi and Me$_3$SiCH$_2$Li.[10] Unlike the present system, however, the occurrence of Fe(II) alkyl intermediates [Fe(R)Cl(^{i}PrPDI)] (R = Me, CH$_2$SiMe$_3$) has been proposed.



The conversion of **1** to **3** was accomplished more cleanly by using Mes$_2$Mg(THF)$_2$ instead of MesMgBr (eq 5). The reaction was completed with 1 equiv of Mes$_2$Mg(THF)$_2$, and complex **3** was isolated in 69% yield. Unlike the reaction with MesMgBr, complex **3** was formed as the sole product even if the magnesium reagent was added in one portion to the system. The reaction is likely to proceed via a two-step process consisting of one-electron reduction and transmetalation. Indeed, a mixture of **2** and **3** was obtained under controlled reaction conditions using less than 0.5 equiv of Mes$_2$Mg(THF)$_2$. Treatment of **2** with Mes$_2$Mg(THF)$_2$ (0.6 equiv) resulted in selective formation of **3**, which was isolated in 70% yield.



While complex **3** did not give a satisfactory elemental analysis, probably due to instability toward air and moisture, its structure could be confirmed by X-ray diffraction analysis of a single crystal grown from a toluene solution at −35 °C. Figure 2 shows the ORTEP diagram, together with selected bond distances and angles. Similarly to **2**, complex **3** adopts a distorted trigonal monopyramidal configuration with the basal plane consisting of P1, P2, C8, and Fe atoms. The sum of the three bond angles in the basal plane is 357.4°. The N−Fe−C8 angle (135.98(12)°) is much larger than the corresponding bond angle of **2** (i.e., N−Fe−Br = 119.19(13)°), reflecting the bulkiness of the Mes group. The bond lengths around iron are

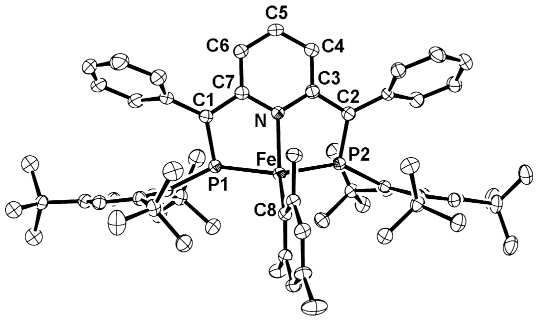


Figure 2. Molecular structure of **3** with 50% probability ellipsoids. Hydrogen atoms and a disordered ^{t}Bu group are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe—P1, 2.2603(10); Fe—P2, 2.2552(10); Fe—N, 2.042(3); Fe—C8, 1.980(3); P1—C1, 1.735(3); P2—C2, 1.735(3); C2—C3, 1.448(4); C3—C4, 1.397(5); C4—C5, 1.384(5); C5—C6, 1.378(5); C6—C7, 1.396(5); C7—C1, 1.440(4); P1—Fe—P2, 137.25(4); P1—Fe—C8, 111.00(10); P2—Fe—C8, 109.10(10); N—Fe—C8, 135.98(12); N—Fe—P1, 80.93(8); N—Fe—P2, 80.60(8).

in a typical range of Fe(I) complexes.[4b−g] The P—C bond lengths (both 1.735(3) Å) are comparable to those of iron(I) monobromide **2** (1.713(6) and 1.719(6) Å), but longer than the values of the corresponding iron(II) dibromide **1** (1.682(11) and 1.712(11) Å). These structural deviations are consistent with the occurrence of an effective π-back-donation from the Fe(I) center to BPEP. Geometrical distortion in the pyridine ring, which is often observed for redox-active 2,2′-bipyridine complexes after reduction,[11] was not detected. Thus, little contribution of an anionic pyridyl form to the structure of **3** was evidenced.

The ^{1}H NMR signals of **3** were significantly broadened, showing its paramagnetic nature. SQUID measurements established the μ_{eff} values ranging from 1.68 to 1.94 μ_{B} at 50—300 K, which correspond to the $S = 1/2$ ground state (Figure 3). Thus, unlike **2** in the $S = 3/2$ state,[3b] complex **3** adopts a low-spin state with one unpaired electron. It is likely that the Mes group as a higher-field ligand than the Br ligand in **2** provides the low-spin state. It is also possible that the relatively more planar configuration of **3** than **2** contributes to the change in the spin state (i.e., N—Fe—C8 = 135.98(12)° in **3** versus N—Fe—Br = 119.19(13)° in **2**).

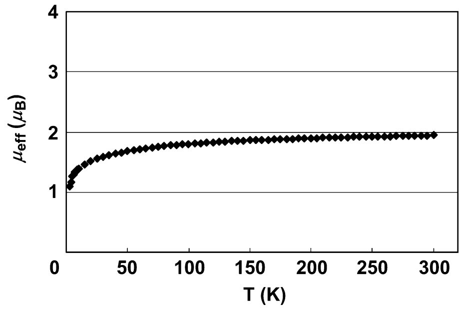
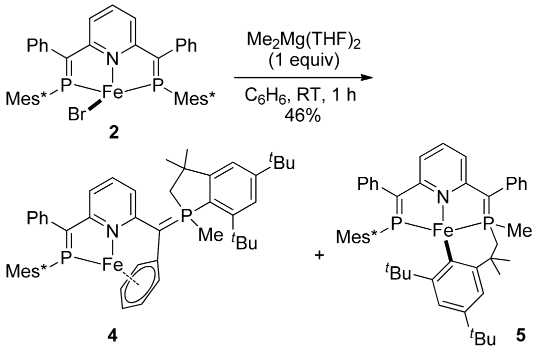


Figure 3. Variable-temperature SQUID magnetic data for **3**.

Reactions with Methylmagnesiums. The reduction of **1** also took place with PhMgBr and MeMgBr. However, while complex **2** was generated in low yields (up to 22%), phenyl and methyl complexes were not detected in the systems. This is probably due to the instability of Fe(I) complexes of the type [FeR(BPEP)] (R = Ph, Me) toward Grignard reagents. This assumption is consistent with the fact that [FeMes(BPEP)] (**3**) decomposes in the presence of an excess amount of MesMgBr. On the other hand, the ^{1}H NMR spectrum of the reaction solution of **1** with $Me_2Mg(THF)_2$ (1 equiv) in benzene-d_6 indicated the formation of two products, **4** and **5**, which exhibited characteristic signals at δ −3.16 and −5.16, respectively. Although this reaction had a reproducibility problem, **4** and **5** were successfully prepared by the reaction of **2** with $Me_2Mg(THF)_2$ (1.0 equiv) in toluene at room temperature (eq 6). The solvent was evaporated, and the residue was extracted with Et_2O and cooled to −30 °C, giving a mixture of red and purple crystals of **4** and **5** in 46% total yield. As we discuss below, both complexes are likely to be formed from [FeMe(BPEP)] as a common intermediate.



(6)

Complexes **4** and **5** could not be isolated independently by recrystallization, but their structures were successfully determined by X-ray diffraction studies. The single crystal of **4** contains two crystallographically independent molecules with essentially the same structures in the asymmetric unit. Figure 4 shows the ORTEP diagram of one of the molecules. It is seen that the BPEP ligand transforms into an η^{6}-benzene ligand with a PN-chelate arm, which combines with an Fe(0) center to form the two-legged piano stool structure of **4**. The Fe—N and Fe—P1 bond lengths (1.9237(17) and 2.1012(8) Å, respectively) are typical of Fe(0) complexes.[8b,12] The P1—C1 bond in

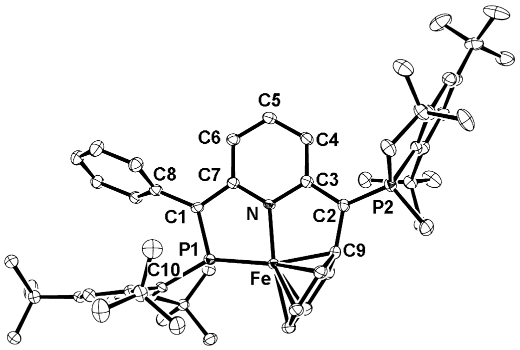


Figure 4. Molecular structure of **4** (molecule 1) with 50% probability ellipsoids. One of the two independent molecules (molecule 2), hydrogen atoms, and a solvent molecules (Et_2O) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe—P1, 2.1012(8); Fe—N, 1.9237(17); P1—C1, 1.725(3); P2—C2, 1.6751(19); P1—C10, 1.827(3); C2—C3, 1.432(3); C3—C4, 1.400(4); C4—C5, 1.391(4); C5—C6, 1.374(3); C6—C7, 1.4127; C1—C7, 1.416(3); N—C3, 1.415(3); N—C7, 1.382(3); N—Fe—P1, 81.16(6); P2—C2—C9, 122.36(15); C3—C2—C9, 112.19(19); P1—C1—C7, 110.16(18); P1—C1—C8, 127.1(2); C7—C1—C8, 122.7(2).

the PN-chelate preserves the phosphaalkene structure. On the other hand, the other phosphaalkene part (P2−C2) is converted to a phosphonium ylide consisting of four-coordinate phosphorus (P2) and three-coordinate carbon (C2) atoms, where a benzophospholane framework is constructed by intramolecular cyclization of the P2−Mes* moiety via P−C bond formation. The P2−C2 bond length (1.6751(19) Å) is among the longest values of phosphonium ylides.[13] The sum of the three angles around C2 is 358.3°. It is known that phosphonium ylides stabilized by a π-conjugating substituent on the carbon have a significant contribution of the ylene form. As a result, the carbon atom exhibits planarity and the P−C bond length becomes longer. The structural parameters around P2−C2 faithfully reproduce this feature.

Figure 5 shows the X-ray structure of **5** having a tetradentate PNPC-chelate ligand, which may be formed by oxidative addition of the P2−C(Ar) bond of the phosphonium ylide in **4**, along with dissociation of the η^6-benzene ligand. The P1−C1 bond remains a neutral phosphaalkene ligand. On the other hand, the P2−C2 bond is incorporated into the five-membered PN-chelate with λ^5-phosphaethenyl-*P* and pyridine units, which serve as anionic and neutral ligands, respectively. It is known that this type of ligand system possesses a structural contribution of the PN-chelate consisting of a neutral λ^3-phosphane and an anionic 2-methylenepyridyl ligand.[14,15] Thus, the structure of **5** is described by canonical structures **A** and **B** in eq 7. In both structures, the iron center has a formal oxidation state of +2. The P2−C2 bond (1.766(11) Å) is longer than the P1−C1 double bond (1.693(10) Å), but significantly shorter than the P1−C10(Mes*) single bond (1.872(9) Å). The C2−C3(pyridine) distance is 1.449(13) Å. This value is clearly longer than that of a C═C bond (ca. 1.34 Å) and comparable to that of C1−C7(pyridine) (1.460(13) Å). Therefore, it is reasonable that the contribution of **A** is predominant over that of **B** in **5**. The structure **A** may be regarded as a metallophosphonium ylide in the ylene form.

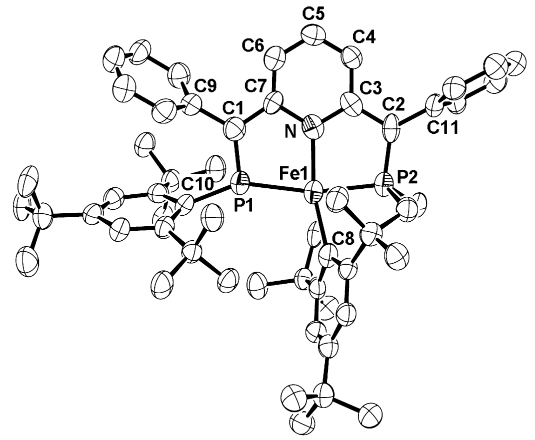
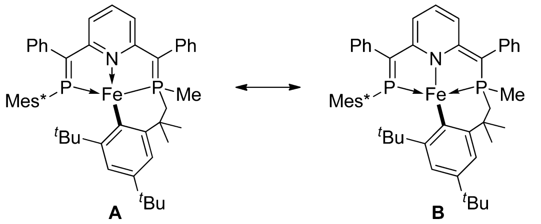


Figure 5. Molecular structure of **5** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe−P1, 2.312(3); Fe−P2, 2.205(3); Fe−N, 2.032(8); Fe−C8, 2.051(10); P1−C1, 1.693(10); P1−C10, 1.872(9); P2−C2, 1.766(11); C2−C3, 1.449(13); C3−C4 1.455(13); C4−C5, 1.386(13); C5−C6, 1.408(13); C6−C7, 1.378(13); C7−C1, 1.460(13); N−C3, 1.396(11); N−C7, 1.449(11); P1−Fe−P2, 165.58(12); P1−Fe−C8, 109.2(3); P2−Fe−C8, 83.1(3); N−Fe−C8, 163.0(3); N−Fe−P1, 82.0(2); N−Fe−P2, 84.3(2); C7−C1−C9, 116.2(8); C7−C1−P1, 118.0(7); C9−C1−P1, 125.8(7); C3−C2−C11, 121.1(9); C3−C2−P2, 113.8(7); C11−C2−P2, 125.1(7).



(7)

Scheme 1 illustrates a plausible reaction process for the formation of **4** and **5**. The Fe(I) complex **2** formed by one-electron reduction of **1** reacts with Me$_2$Mg(THF)$_2$ to give [FeMe(BPEP)] (**C**) and MeMgBr. Migration of the methyl ligand to one of the low-coordinate phosphorus atoms forms **D**, bearing a highly coordinatively unsaturated Fe(I) center, which subsequently undergoes oxidative addition of the terminal C−H bond of the ^{t}Bu group to give Fe(III) hydride **E**. Homolysis of the Fe−H bond in **E** followed by P−C reductive elimination in **F** forms **4**, accompanied by π-coordination of the phenyl group. Finally, P−C oxidative addition in **4** affords **5**. In this stage, MeMgBr generated in the system possibly induces the Fe−H bond cleavage. Finally, P−C oxidative addition in **4** affords **5**.

■ CONCLUSION

It has been found that the Fe(II) complex [FeBr$_2$(BPEP)] (**1**) supported by BPEP as a tridentate phosphaalkene ligand readily

Scheme 1. Plausible Reaction Process for the Formation of 4 and 5 from 2 and Me$_2$Mg(THF)$_2$

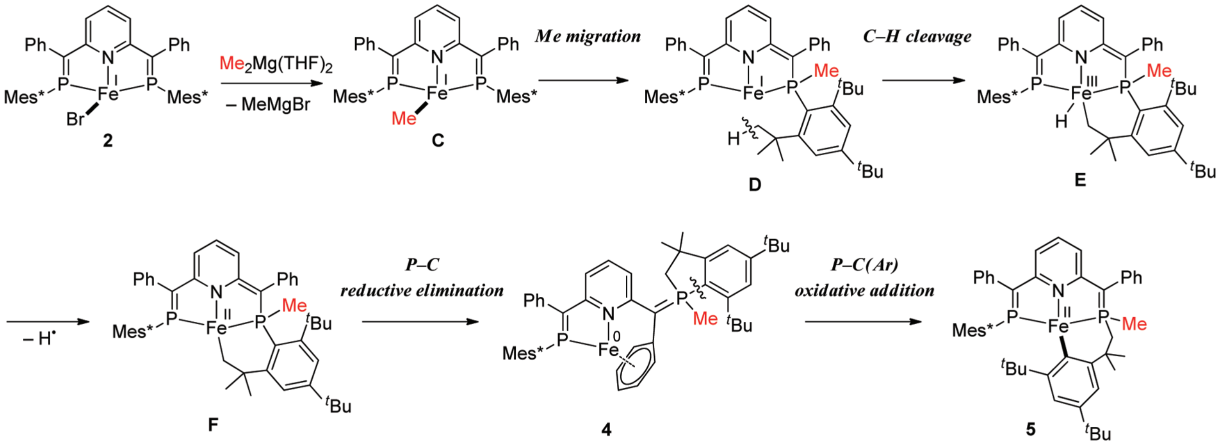


Table 1. Crystal Data and Details of the Crystal Structure Determination for 3, 4, and 5

	3	4	5
empirical formula	$C_{64}H_{82}FeNP_2$	$C_{56}H_{73}FeNP_2 \cdot C_4H_{10}O$	$C_{56}H_{73}FeNP_2$
fw	983.10	970.59	877.94
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$
a (Å)	18.960(4)	16.2808(2)	41.171(11)
b (Å)	10.792(2)	17.5874(2)	9.514(3)
c (Å)	27.945(6)	22.8589(4)	27.100(15)
α (deg)		96.1553(6)	
β (deg)	99.235(4)	106.0147(7)	107.470(15)
γ (deg)		114.7727(10)	
V (Å^3)	5644(2)	5523.06(13)	10126(7)
Z	4	4	8
d_{calc} (g cm^{-3})	1.157	1.145	1.152
T (K)	103	173	103
μ(Mo Kα) (mm^{-1})	0.363	0.370	0.397
F(000)	2116	2056	3776
cryst size	0.16 × 0.15 × 0.09	0.03 × 0.02 × 0.01	0.15 × 0.05 × 0.03
θ range (deg)	3.06-31.38	1.32−32.40	2.13−25.00
no. of reflns collected	52 106	63 205	32 464
no. of unique reflns (R_{int})	16797 (0.0871)	33934 (0.0398)	8782 (0.1890)
no. of reflns with $I > 2\sigma(I)$	9539	15 466	4208
no. of params (restraints)	611 (0)	1143 (12)	541 (0)
GOF on F^2	1.077	0.652	1.073
R_1, wR_2 ($I > 2\sigma(I)$)	0.0781, 0.1824	0.0578, 0.1552	0.1195, 0.2530
R_1, wR_2 (all data)	0.1488, 0.2337	0.0980, 0.1689	0.2254, 0.3277
largest peak and hole (e Å^{-3})	1.051, −0.589	2.491, −0.646	1.402, −0.565

undergoes one-electron reduction by electrochemical and chemical means to afford [FeBr(BPEP)] (**2**), having a distorted trigonal monopyramidal Fe(I) center. While complex **2** is isolated by using [Cp_2Co] as a mild reducing agent, the use of $Mes_2Mg(THF)_2$ leads to further conversion of **2** into [FeMes(BPEP)] (**3**) via transmetalation. The unique ligand properties of BPEP, which undergoes effective dπ−pπ interactions with an Fe(I) center, will be responsible for the easy reduction of the Fe(II) complex **1** to the Fe(I) complexes **2** and **3**. The single-crystal diffraction study has revealed the distorted trigonal monopyramidal structure of **3**, which is in sharp contrast to the planar structure of related [FeMe(^{i}PrPDI)].[10] We have demonstrated for **2** using DFT calculations[3b] that the structural distortion to trigonal monopyramidal geometry enables effective dπ−pπ interactions between Fe and BPEP. The sequence of one-electron reduction and transmetalation is operative for $Me_2Mg(THF)_2$ as well. In this case, however, the resulting [FeMe(BPEP)] undergoes intramolecular migration of the methyl ligand to a low-coordinate phosphorus atom, leading to the formation of **4** and **5**, bearing novel ligand systems containing a phosphonium ylide structure.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glovebox. Solvents (toluene, benzene, benzene-d_6, Et_2O) were dried over sodium benzophenone ketyl and distilled. MesMgBr was purchased from a commercial source (Sigma-Aldrich) and used without purification. $Mes_2Mg(THF)_2$,[16] $Me_2Mg(THF)_2$,[16] and KC_8[17] were prepared according to the literature procedure.

^{1}H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400.13 MHz). Chemical shifts are reported in δ (ppm), referenced to the residual solvent signal as an internal standard. Elemental analysis was performed by ICR Analytical Laboratory, Kyoto University. ESI-mass spectra were recorded on a Bruker micrOTOF I spectrometer for **3** and on a Bruker solariX Hybrid Qq-FTMS system for **4** and **5**. Solid-state magnetic moments were recorded using a Quantum Design SQUID magnetometer. Magnetization versus temperature data were recorded in a magnetic field of 10 000 G, using crystalline samples sealed in quartz tubes. An impurity correction was made by fitting experimental data to the formula $\chi_{impurity} = C/T$. Cyclic voltammetry was performed with a BAS ALS600B. The data were collected in CH_2Cl_2 (1 mM of **1**) in the presence of [Bu_4N][BF_4] electrolyte (0.1 M), using a glassy carbon working electrode, platinum wire as the counter electrode, and silver electrode as the reference electrode in a drybox equipped with electrochemical outlets, at a scan rate of 100 mV/s at 295 K. GLC analysis was performed on a Shimadzu GC-14B instrument (FID; CBP-1, 25 m × 0.25 mm).

Reaction of 1 with [Cp_2Co]. Complex **1** (48.3 mg, 0.0471 mmol) was dissolved in C_6H_6 (0.4 mL), and to this was added a C_6H_6 solution (0.1 mL) of [Cp_2Co] (8.90 mg, 0.0471 mmol) at room temperature. Immediately, the solution was filtered through a Celite pad, and the solvent was removed under vacuum. The residue was washed with hexane and dried under vacuum to give **2** as a green solid (26.5 mg, 0.0269 mmol, 57%). Formation of **2** was confirmed by ^{1}H NMR spectroscopy.

Reaction of 2 with $PhCH_2Br$. To a C_6H_6 solution (0.4 mL) of **2** (15.5 mg, 0.0164 mmol) was added $PhCH_2Br$ (2.0 μL, 0.0168 mmol) at room temperature. Immediately, the green color of the solution slightly darkened. GLC analysis revealed the formation of biphenyl (0.00748 mmol, 46%/**2**). After the solvent was removed under vacuum, the residue was washed with hexane repeatedly and dried under vacuum to afford **1** (10.6 mg, 0.0104 mmol, 63%). The ^{1}H NMR spectrum in C_6D_6 revealed selective formation of **1**.

Reaction of 2 with $PhCH_2Br$ in the Presence of 1,4-Cyclohexadiene. Similarly, the reaction of **2** (7.48 mg, 0.00792 mmol) with $PhCH_2Br$ (1 μL, 0.0084 mmol) in C_6D_6 (0.4 mL) was examined in the presence of 1,4-cyclohexadiene (1 μL, 0.011 mmol). GLC analysis revealed the formation of biphenyl (0.0033 mmol, 83%). No trace amount of toluene was detected. Complex **1** was isolated in 73% yield (5.93 mg, 0.00579 mmol).

Reaction of 1 with MesMgBr. Complex **1** (15.6 mg, 0.0152 mmol) was dissolved in C_6H_6 (2 mL), and a THF solution of MesMgBr (0.2 M, 200 μL, 0.040 mmol) was slowly added over 1 h at room temperature. The solvent was removed under vacuum, and the residue was washed with hexane (0.5 mL × 3), extracted with C_6H_6, and filtered through a Celite pad. The filtrate was concentrated to dryness under vacuum to afford **3** as a dark brown solid (13.1 mg, 0.0130 mmol, 88%). The hexane washings were concentrated under vacuum, dissolved in C_6D_6 (0.4 mL), and analyzed by ^{1}H NMR spectroscopy using CH_2Cl_2 (2 μL, 0.031 mmol) as an internal standard, showing the formation of bimesityl (0.0061 mmol, 80%). Single crystals of **3** for X-ray diffraction analysis were grown by slow evaporation of a toluene solution at room temperature. ^{1}H NMR (C_6D_6, 20 °C): δ −4.89 (brs), −2.38 (brs), −1.29 (brs), 0.52 (s), 4.75 (s), 5.86 (brs), 8.37 (brs), 21.13 (brs). ESI-MS (m/z): 982.5 (M^+). This complex did not give a satisfactory elemental analysis.

Reaction of 2 with MesMgBr. To a C_6H_6 solution (2 mL) of **2** (12.2 mg, 0.0129 mmol) was added a THF solution of MesMgBr (0.06 M, 200 μL, 0.012 mmol) over 1 h at room temperature. The solution was stirred for 1 h and filtered through a Celite pad. The solvent was evaporated, and the residue was washed with hexane (0.5 mL) and dried under vacuum to give **3** (7.06 mg, 0.0718 mmol, 55%).

Reaction of 1 with $Mes_2Mg(THF)_2$. To a C_6H_6 solution (1 mL) of **1** (30.6 mg, 0.0299 mmol) was added a C_6H_6 solution (0.5 mL) of $Mes_2Mg(THF)_2$ (12.0 mg, 0.0295 mmol). The mixture was stirred at room temperature for 1 h and filtered through a Celite pad. Removal of the solvent under vacuum afforded **3** as a dark brown solid (20.3 mg, 0.0206 mmol, 69%).

Reaction of 2 with $Mes_2Mg(THF)_2$. Complex **2** (26.8 mg, 0.0284 mmol) was dissolved in C_6H_6 (1 mL), and a C_6H_6 solution of $Mes_2Mg(THF)$ (6.92 mg, 0.0170 mmol) was added. The mixture was stirred at room temperature for 30 min and filtered through a Celite pad. The solvent was evaporated, and the residue was washed with hexane (0.5 mL) and dried under vacuum to give **3** (19.4 mg, 0.0198 mmol, 70%).

Reaction of 1 with PhMgBr. To a toluene solution (3 mL) of **1** (45.7 mg, 0.0446 mmol) was added a THF solution of PhMgBr (90 μL, 1.0 M THF solution, 0.090 mmol) at −78 °C. The mixture was stirred at room temperature for 2 h. The solution was concentrated under vacuum, and the resulting slurry was extracted with hexane (0.5 mL). The extract was allowed to stand at −30 °C to afford green crystals of **2** (9.30 mg, 0.00990 mmol, 22%). The supernatant was concentrated to dryness to afford a mixture containing a small amount of **2**, free BPEP, and some unidentified compounds.

Reaction of 2 with $Me_2Mg(THF)_2$. To a C_6H_6 solution (1 mL) of **2** (10.5 mg, 0.0112 mmol) was added a C_6H_6 solution (0.5 mL) of $Me_2Mg(THF)_2$ (1.17 mg, 0.00589 mmol). The mixture was allowed to stand at room temperature for 1 h, and volatiles were removed under vacuum. The residue was extracted with Et_2O and filtered through a Celite pad. The filtrate was concentrated to dryness, and the residue was again dissolved in Et_2O (0.5 mL) and allowed to stand at −30 °C for a few days to afford a mixture of red and purple crystals of **4** and **5** (4.53 mg, 0.00516 mmol, 46%). Attempts to separate these complexes by repeated recrystallization were unsuccessful. ESI-MS measurements were not successful due to decomposition.

X-ray Crystal Structure Determination. The intensity data for **3** and **5** were collected on Rigaku Mercury CCD and Rigaku VariMax diffractometers with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å), respectively. For **4**, a synchrotron radiation experiment (λ = 0.71069 Å) was carried out at the BL38B1 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2010B1488). The data sets were corrected for Lorentz and polarization effects and absorption. The structures were solved by direct methods (SHELXS-97)[18] and refined by least-squares calculations on F^2 for all reflections (SHELXL-97)[19] using Yadokari-XG 2009 (Software for Crystal Structure Analyses).[20] In the structure of **3**, one ^{t}Bu group was disordered with an occupancy ratio of 79:21. In the case of **4**, two solvent molecules (Et_2O) were incorporated in the unit cell; one Et_2O molecule was disordered with an occupancy ratio of 87:13. Anisotropic refinement was applied to all non-hydrogen atoms except for disordered groups. Hydrogen atoms were placed at calculated positions. The crystallographic data and the summary of solution and refinement are listed in Table 1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cyclic voltammogram of [$FeCl_2$(^{i}PrPDI)], ESI-mass spectrum of **3**, and crystallographic data (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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