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Change in Coordination of NCN Pincer Iron Complexes Containing Bis(oxazolinyl)phenyl Ligands

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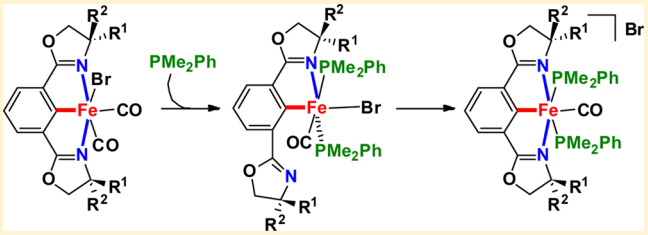
Supporting Information

ABSTRACT: The coordination of bis(oxazolinyl)phenyl (phebox) ligands to an Fe center was investigated in the reaction of (phebox-R)Fe(CO)$_2$Br (**1a**: R = Me$_2$; **1b**: R = *i*-Pr) with phosphine and isocyanide compounds. Reaction of **1** with an excess amount of PMe$_3$ in toluene proceeded at 50 °C to give the corresponding cationic complexes [(phebox-R)Fe(CO)(PMe$_3$)$_2$]Br [**2a**: R = Me$_2$ (79%); **2b**: R = *i*-Pr (83%)]. The molecular structures of **2a** and **2b** were confirmed by X-ray diffraction analysis that revealed the pseudo-octahedral geometry with NCN meridional coordination of the phebox ligand. In contrast, reaction of **1** with PMe$_2$Ph gave the neutral phosphine complexes (η^2-phebox-R)Fe(CO)(PMe$_2$Ph)$_2$Br [**3a**: R = Me$_2$ (87%); **3b**: R = *i*-Pr (79%)], in which the phebox ligand was coordinated to Fe as an NC bidentate ligand with the oxazoline and phenyl groups. Subsequent reaction of the neutral phosphine complex **3a** resulted in the formation of the corresponding cationic complexes [(phebox-Me$_2$)Fe(CO)(PMe$_2$Ph)$_2$]Br (**4**) *via* change in coordination to the tridentate mode. The reaction of **1** with *tert*-butylisocyanide CN(*t*-Bu) gave a mixture of neutral isocyanide complexes (phebox-Me$_2$)Fe(CO)[CN(*t*-Bu)]Br (**5**, **6**) in 57 and 10% yields, respectively, *via* exchange of one of the CO ligands. Subsequent reaction of **5** with CN(*t*-Bu) resulted in formation of the cationic complex {(phebox-Me$_2$)Fe[CN(*t*-Bu)]$_3$}Br (**7a**). Similarly, treatment of **1** with an excess amount of CN(t-Bu) afforded {(phebox-R)Fe[CN(*t*-Bu)]$_3$}Br [**7a**: R = Me$_2$ (83%); **7b**: R = *i*-Pr (69%)].



INTRODUCTION

Phosphine-based pincer ligands tightly bound to a transition metal produce a robust structure induced by a metal−carbon σ-bond and two metallacycles.[1] In contrast, introduction of a hemilabile amino functionality with flexible methylene linkers allows a change in coordination number by dissociation of the amino group. Such a change in the coordination mode is considered to be significant to generate a vacant site on a metal center. Previously, van Koten described the fluxional behavior of the amino-based NCN pincer ligand, C$_6$H$_3$(CH$_2$NMe$_2$)$_2$. For example, the NCN−Ru complex (NCN)RuCl(PPh$_3$) underwent the rearrangement from tridentate NCN bonding to bidentate NC bonding in the reaction with Na(C$_5$H$_5$), giving the NC−Ru complex (NC)Ru(PPh$_3$)(C$_5$H$_5$).[2] Similarly, an NCN−Ta complex was found to afford the corresponding NC−Ta complex by the reaction with alkoxide or ZnCl(CH$_2$*t*-Bu).[3] Such an NC bonding coordination of the bis(amino)-phenyl ligand was also observed in Ti and W complexes.[4] In the case of group 9 metals, coordination geometry depended on the valence number of the metals. The Rh(III) complex has a pseudo-octahedral geometry with an NCN coordination,[5] while the Rh(I) and Ir(I) complexes had a square-planar geometry with a bidentate NC coordination.[6] Bergman and Tilley reported that a bisoxazoline NCN ligand, namely, a benbox ligand, exhibited different coordination modes depending on the property of the metal centers. In this system, the Rh(III) center adopted NCN meridional coordination, whereas the Rh(II) center contained NN bidentate coordination without an M−C bond.[7] Recently, Milstein reported that a PCN pincer complex with a hemilabile NMe$_2$ group underwent a coordination change between PCN and PC chelates.[8] In particular, detachment and attachment of the amine group in a PNN framework was proposed as a mechanism for formation of the reaction site on a metal center in a catalytic cycle.[9,10]

The bis(oxazolinyl)phenyl (phebox) ligand serves as an NCN meridional ligand with a rigid structure induced by two oxazolines and the benzene backbone.[11] Usually, phebox complexes containing late transition metals adopt square-planar and pseudo-octahedral geometries.[12] For Au and Sn complexes, η^1-C-coordination of the phebox ligand without the M−N bonds was observed.[12i,j] However, intermediate structures containing NC bidentate chelation have not been directly observed.

A recent study described the chiral and achiral phebox−Fe complexes (phebox-R)Fe(CO)$_2$Br (**1a**: R = Me$_2$; **1b**: R = *i*-Pr), in which the phebox ligand was meridionally coordinated to the Fe center with the Fe−C σ-bond.[13] Such cyclometalated Fe complexes are of interest for cyclometalation and transmetalation reactions[14,15] as well as application to catalytic reactions.[16] The present report describes investigation of the ligand-exchange reactions of the CO and Br ligands in phebox−

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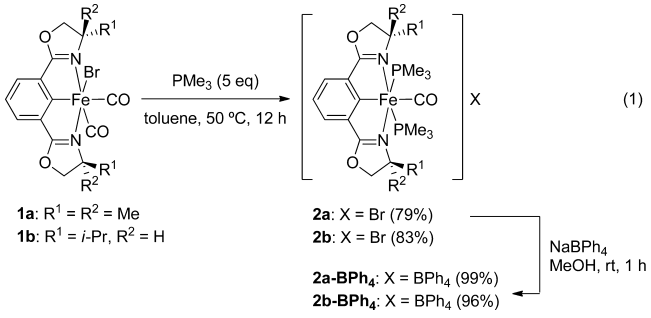
Fe complexes with two-electron donor ligands, namely, phosphine and isocyanide ligands. In this system, the fluxional behavior of the phebox ligand between the NCN meridional coordination and the NC bidentate coordination proceeded during the reaction with phosphine.

RESULTS AND DISCUSSION

Reaction of 1 with PMe_3. Reaction of (phebox-Me_2)Fe-$(CO)_2Br$ (**1a**) with PMe_3 in toluene proceeded at room temperature to give a cationic phosphine complex [(phebox-Me_2)Fe$(CO)(PMe_3)_2$]Br (**2a**) (eq 1). After purification by



column chromatography on silica gel, the complex **2a** was isolated as red crystals in 79% yield. Similarly, the chiral complex [(phebox-*i*-Pr)Fe$(CO)(PMe_3)_2$]Br (**2b**) was obtained in 83% yield by reaction of **1b** with PMe_3. When the reaction of **1a** with PMe_3 was also carried out in MeOH at 50 °C for 12 h, the cationic phosphine complex **2a** was also obtained in 94% yield. The anion-exchange reaction of **2a** and **2b** with $NaBPh_4$ in methanol gave the corresponding BPh_4 salts **2a-BPh$_4$** and **2b-BPh$_4$**, respectively.

In the ^{1}H NMR spectrum of **2a-BPh$_4$**, the singlet signal for the methyl groups on the oxazoline rings was observed at δ 1.17 ppm (12H), and a doublet of doublets signal for the PMe_3 ligand appeared at δ 0.81 ppm (9H). The integral ratio of the BPh_4 anion indicated formation of the cationic complex. In the ^{31}P NMR spectrum, a signal for PMe_3 was observed at δ 19.5 ppm. These spectral features indicated the C_2-symmeric structure with *trans* arrangement of two PMe_3 ligands in solution. The IR spectrum revealed an absorption for the carbonyl group at ν = 1922 (**2a**) and 1953 (**2a-BPh$_4$**) cm^{-1}, which shifted to lower energy compared to that of **1a** (ν_{CO} = 2026, 1965 cm^{-1}), probably due to the increase in the π-back-donation by coordination of the electron-rich PMe_3 ligands.

The molecular structures of **2a-BPh$_4$** and **2b-BPh$_4$** were confirmed by X-ray diffraction analysis (Figures 1 and 2). The ORTEP diagrams showed that **2a-BPh$_4$** and **2b-BPh$_4$** had pseudo-octahedral geometry with N−Fe−N bond angles of 158.83(8)° and 157.50(12)°, respectively. Two PMe_3 ligands occupied the position perpendicular to the phebox plane. In contrast, the two PMe_3 ligands of the (PCP)Fe(H)$(PMe_3)_2$ complex took the *cis* arrangement.[14r] The Fe−P bond lengths (**2a-BPh$_4$**: 2.2786(6) and 2.2727(7) Å; **2b-BPh$_4$**: 2.2814(13) and 2.2765(13) Å) were slightly longer than those of (CNC)Fe$(PMe_3)_3$ (Fe−P = 2.2247(4)−2.2393(4) Å),[14n] (PC)FeMe$(PMe_3)_3$ (Fe−P = 2.229(4)−2.261(10) Å),[14o] and (NC)FeH$(PMe_3)_3$ (Fe−P = 2.1739(5)−2.1874(5) Å).[14q] The CO ligand was located in the *trans* position of the phenyl group of the phebox ligand. The Fe−CO bond length of 1.796(4) Å was slightly shorter than that of **1a** (Fe−CO = 1.839(2) Å).[13] As expected, the phebox ligand was bound to the Fe center with the NCN tridentate coordination. The Fe−C(sp^2) bond lengths (**2a-BPh$_4$**: 1.904(2); **2b-BPh$_4$**: 1.917(4) Å) were comparable to those of **1a** (1.930(2) Å)[13] and (PCP)$FeCl_2$ (1.937(2) Å)[15d] and were longer than those of the (phebox)Ni complexes (1.8491(19)−1.859(4) Å).[12a,b]

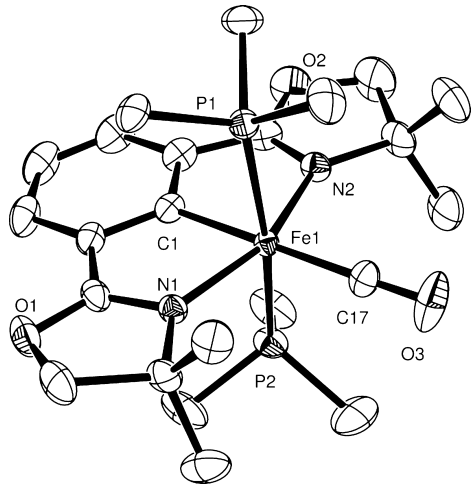


Figure 1. ORTEP diagram of **2a-BPh$_4$**. Selected bond lengths (Å) and angles (deg): Fe(1)−C(1) 1.904(2), Fe(1)−C(17) 1.782(2), Fe(1)−N(1) 2.0113(17), Fe(1)−N(2) 2.0075(18), Fe(1)−P(1) 2.2786(6), Fe(1)−P(2) 2.2727(7), C(17)−O(3) 1.142(3); N(2)−Fe(1)−N(1) 158.83(8).

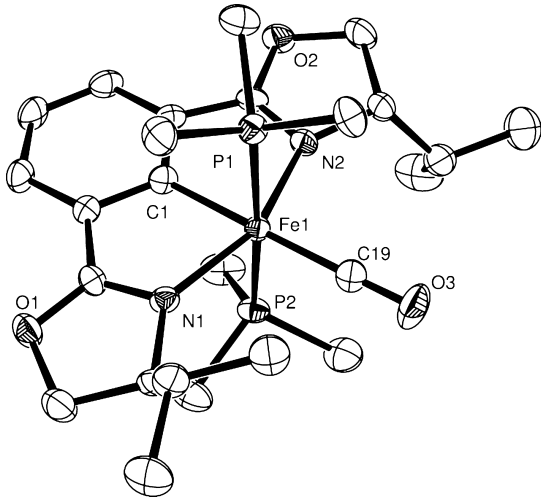


Figure 2. ORTEP diagram of **2b-BPh$_4$**. Selected bond lengths (Å) and angles (deg): C(1)−Fe(1) 1.917(4), Fe(1)−C(19) 1.796(4), Fe(1)−N(1) 2.075(3), Fe(1)−N(2) 2.021(3), Fe(1)−P(1) 2.2814(13), Fe(1)−P(2) 2.2765(13), C(19)−O(3) 1.147(5); N(2)−Fe(1)−N(1) 157.50(12).

Substitution reactions of carbonyl ligands with phosphines have been studied in the $CpFe(CO)_2$ (Fp) and $Cp^*Fe(CO)_2$ (Fp*) systems.[17] For example, the reaction of $CpFe(CO)_2X$ (X = Cl, I) with PPh_3 afforded the cationic substituted products, $[CpFe(CO)_2(PPh_3)]^+$, *via* substitution with a halogen, whereas $CpFe(CO)_2Br$ gave a neutral complex $CpFe(CO)(PPh_3)Br$ *via* substitution with a carbonyl ligand. The $Cp^*Fe(CO)_2Br$ also reacted with PPh_3 under UV irradiation to give the neutral complex $Cp^*Fe(CO)(PPh_3)Br$.[18] In the reaction of $CpFe(CO)_2X$ with PMe_3, distribution of the products, $CpFe(CO)_{2-n}(PMe_3)_nX$ and $[CpFe(CO)_{3-n}(PMe_3)_n]^+$, strongly depended on the reaction conditions and the halogen.[19]

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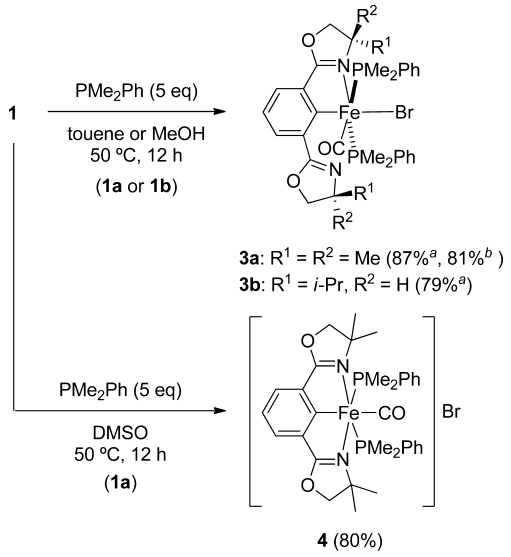
Reactivity of the phebox–Fe complex toward PMe_3 resembles that of the Fp system.

Reaction of 1 with PMe_2Ph. The reaction of **1a** with PMe_2Ph in toluene at 50 °C resulted in formation of neutral phosphine complex **3a** instead of a cationic complex, as observed in the reaction with PMe_3 (Scheme 1). Purification by column chromatography on silica gel afforded **3a** in 87% yield. Similarly, the chiral complex **1b** reacted with PMe_2Ph to give the neutral phosphine complex **3b** in 79% yield. Complexes **3a** and **3b** were identified on the basis of NMR and IR spectra. The ^1H NMR spectrum of **3a** exhibited signals for the methyl groups on the oxazoline at δ 1.58 and 1.89 ppm and two singlet signals for methylene protons at the 5-position of the oxazoline ring at δ 3.46 and 3.90 ppm. In addition, the ^{13}C NMR spectrum exhibited two sets of signals for the oxazoline groups. These spectral features indicated that the two oxazoline groups were in different environments. The two methyl groups of PMe_2Ph produced signals at δ_H 1.10 and 1.35 ppm and δ_C 16.1 and 17.4 ppm in the ^1H and ^{13}C NMR spectra, respectively. In the ^{31}P NMR spectrum of **3a**, the signal for PMe_2Ph appeared at δ 14.7 ppm. The IR spectrum of **3a** showed an absorption signal for CO at 1916 cm^{-1}.

Scheme 1. Reaction of 1 with PMe_2Ph in Toluene, MeOH, or DMSO[a,b]



[a]In toluene. [b]In MeOH.

The molecular structure of **3a** was determined by X-ray diffraction analysis (Figure 3). Of particular significance was the bidentate coordination of the phebox ligand, in which one of the oxazoline groups did not attach to the Fe center. This structural feature is quite different from that of other phebox metal complexes, which usually have NCN coordination geometry. The Fe–C(1) bond length of 1.977(3) Å was slightly longer than those of the PMe_3 complexes **2**, probably due to the less-hindered bidentate structure of **3a**. The two phosphine ligands occupied the *trans* position to reduce steric repulsion. The Fe–P bond lengths were 2.3076(8) and 2.2808(8) Å, which are comparable to those of **2a-BPh_4** (2.2786(6), 2.2727(7) Å). The Br and CO ligands were bound to the *trans* position to the phenyl and oxazoline groups, respectively.

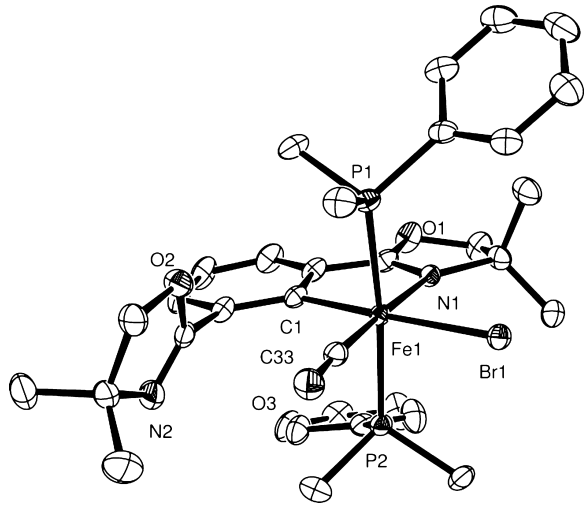
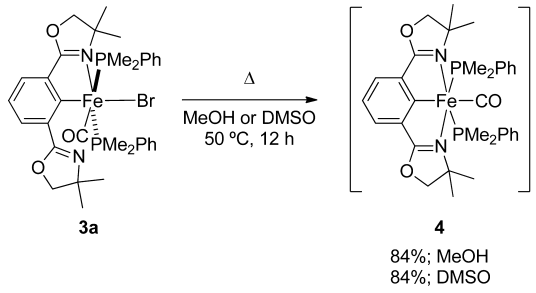


Figure 3. ORTEP diagram of **3a**. Selected bond lengths (Å) and angles (deg): Fe(1)–C(1) 1.977(3), Fe(1)–C(33) 1.728(3), Fe(1)–Br(1) 2.5105(5), Fe(1)–N(1) 2.073(2), Fe(1)–P(2) 2.2808(8), Fe(1)–P(1) 2.3076(8); C(1)–Fe(1)–N(1) 82.36(10), P(1)–Fe(1)–P(2) 174.19(3), C(33)–Fe(1)–N(1) 177.40(12), C(1)–Fe(1)–Br(1) 176.67(9).

To obtain the insight into the solvent effect, we carried out the reaction of **1a** with PMe_2Ph in polar solvents, MeOH or DMSO, at 50 °C for 12 h (Scheme 1). The heating reaction of **1a** in MeOH resulted in the formation of the neutral phosphine complex **3a** in 81% yield. On the other hand, the reaction in DMSO afforded a cationic phosphine complex $[(phebox\text{-}Me_2)Fe(CO)(PMe_3)_2]Br$ (**4**). After purification by column chromatography, complex **4** was isolated in 80% yield.

Complex **3a** is considered to be a precursor for the formation of the cationic phosphine complex **4**. Reaction of the phosphine complex **3a** in methanol at 50 °C for 12 h resulted in the formation of the corresponding cationic complex **4** in 84% yield (eq 2). When complex **3a** was heated in DMSO at 50 °C for 12 h, the yield of **4** was 84%. This reaction was found to be promoted by a nonprotic polar solvent.



(2)

The ^1H NMR spectrum of **4** exhibited the signal for the four methyl groups of the oxazoline rings at δ 1.00 ppm. The signal for the methyl groups of the phosphine ligands appeared at δ 1.19 ppm. In the ^{31}P NMR spectrum, the signal for the two phosphine ligands was shifted to the lower field and observed at δ 61.5 ppm. In the HRMS of **4**, the peak at m/z = 631.1958 also supported the structure of **4**. These spectral data indicated the formation of the cationic phosphine complex **4**.

In this reaction, dissociation of the Br ligand and association of the oxazoline group proceeded to form the NCN coordination. Thus, the phebox–Fe complexes underwent a change in coordination number between bidentate and

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tridentate in both directions. In addition, complex **3a** acted as an intermediate for formation of **4** by reaction of **1** with phosphines. We assumed that the fluxional behavior of the phebox ligand might promote the initial substitution reaction with a phosphine ligand on the Fe center.

Reaction of 1 with CN(*t*-Bu). In the reaction of **1** with phosphine, the formation of bisphosphine complexes **2** and **3** proceeded prior to the formation of a monophosphine complex, even in the presence of an equivalent amount of phosphine. In this case, the strong σ-donating ability of the alkylphosphine ligand might promote dissociation of the Br ligand or the oxazoline of the phebox ligand to accept a second phosphine ligand. Thus, the ligand-exchange reaction with isocyanide as a strong π-accepting ligand was also examined.

Reaction of **1** with 1.2 equiv of CN(*t*-Bu) at 50 °C gave a mixture of neutral isocyanide complexes (phebox-Me_2)FeBr(CO)[CN(*t*-Bu)] (**5** and **6**). Purification by column chromatography on silica gel afforded complexes **5** and **6** in 57 and 10% yields, respectively.

The major product **5** was identified as the monosubstituted isocyanide complex on the basis of NMR and IR spectra. In the ^{1}H NMR spectrum of **5**, two singlet signals for the methyl groups of the oxazolines were observed at δ 0.99 (6H) and 1.32 (6H), and the singlet signal for the *t*-Bu group of the isocyanide ligands was observed at δ 1.23 (9H). The IR spectrum of **5** showed absorptions for the CO and CN(*t*-Bu) ligand at 1937 and 2143, respectively.

The molecular structure of **5** was determined by X-ray diffraction analysis. The ORTEP diagram indicated that the phebox ligand was meridionally coordinated to the Fe center (Figure 4). The CN(*t*-Bu) ligand was *trans* to the phenyl group of the phebox ligand. The Br and CO ligands were attached perpendicular to the phebox plane. This coordination geometry of the phebox–Fe complex is similar to that of the related phebox–Ru isocyanide complex.[20] The Fe(1)–C(18) bond length of 1.910(7) Å is comparable to that of $FeCl_2[CNC_6H_3(t\text{-}Bu)_2]_4$ (Fe–C: 1.895(6) Å),[21] and shorter than that of the phebox–Ru isocyanide complex (Ru–C = 2.058(3) Å).[20] The structural features of **5** suggest that ligand exchange of **1** occurred readily at the equatorial site.

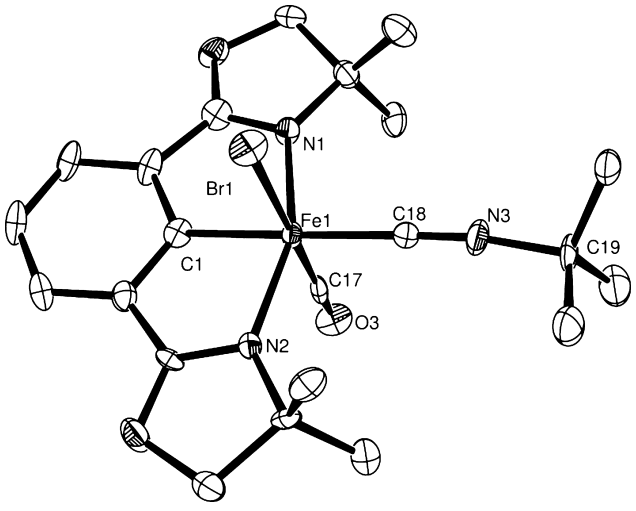
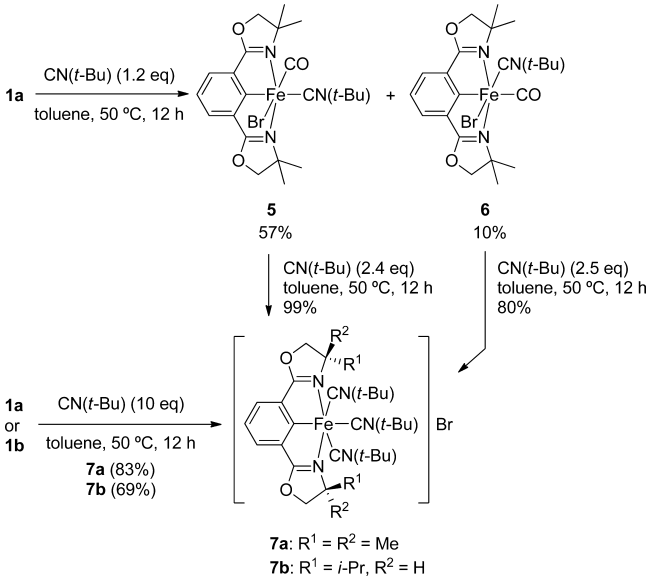


Figure 4. ORTEP diagram of **5**. Selected bond lengths (Å) and angles (deg): Fe(1)–C(1) 1.923(7), Fe(1)–C(17) 1.804(9), Fe(1)–C(18) 1.910(7), Fe(1)–Br(1) 2.5210(13), Fe(1)–N(1) 2.001(5), Fe(1)–N(2) 2.026(6), C(17)–O(3) 1.067(9), C(18)–N(3) 1.161(8); N(1)–Fe(1)–N(2) 158.1(2), C(17)–Fe(1)–Br(1) 179.2(2), C(1)–Fe(1)–C(18) 174.2(3), N(3)–C(18)–Fe(1) 178.3(7), C(18)–N(3)–C(19) 172.1(8).

Complex **6** was identified as a geometrical isomer of **5** on the basis of the ^{1}H and ^{13}C NMR and IR spectra. In the ^{1}H NMR spectrum of **6**, the signal of the *t*-Bu group of the isocyanide ligand was observed at δ 0.49 (9H). Singlet signals for the methyl groups of the oxazolines appeared at δ 0.91 (6H) and 1.46 (6H). The IR spectrum showed absorption of the CO and CN(*t*-Bu) ligands at 1963 and 2149 cm^{-1}, respectively. These spectral features are consistent with the structure described in Scheme 2.

Scheme 2. Reaction of 1 with CN(*t*-Bu)



To evaluate the kinetic or thermodynamic products in the reaction of **1** with CN(*t*-Bu), reaction of **5** in benzene-d_6 at 50 °C was monitored by ^{1}H NMR spectroscopy. Although the decomposition of **5** was observed, the formation of **6** was not detected after heating for 12 h. Similarly, the heating reaction of **6** in benzene-d_6 at 50 °C exhibited decomposition of **6** and no formation of **5**. The lack of conversion between **5** and **6** implied that **5** and **6** were the kinetic products. In this case, dissociation of the CO ligand *trans* to the phenyl fragment of the phebox ligand occurred easily due to the high *trans* effect of the phenyl fragment.

Further reaction of **5** with an excess amount of CN(*t*-Bu) gave the cationic complex (phebox-Me_2)Fe[CN(*t*-Bu)$_3$]Br (**7a**) quantitatively *via* ligand exchange of CO and Br. Similarly, complex **7a** was obtained in 80% yield by the reaction of **6** with CN(*t*-Bu). Reaction of **1a** with CN(*t*-Bu) also gave the cationic complex **7a** in 83% yield (Scheme 2). Similarly, a chiral complex **7b** was obtained in 69% yield by the reaction of **1b** with CN(*t*-Bu). Complexes **7a** and **7b** were purified by column chromatography on silica gel to yield an air- and moisture-stable yellow solid. The IR spectrum of **7a** showed CN stretching absorptions at 2170 and 2118 cm^{-1}. The ^{1}H NMR spectrum of **7a** showed the singlet signals of the *t*-Bu groups in the isocyanide ligands at δ 1.17 and 1.19 in the ratio of 9H:18H, indicating coordination of three isocyanide ligands at equatorial and axial positions. The molecular structure of **7a**, confirmed by X-ray diffraction analysis, showed pseudo-

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octahedral geometry with N−Fe−N bond angles of 157.1(3)° (Figure 5). The phebox ligand was meridionally coordinated to the Fe center. The Fe−C and Fe−N bond lengths were similar to those of the PMe_3 complexes **2a-BPh$_4$** and **2b-BPh$_4$**.

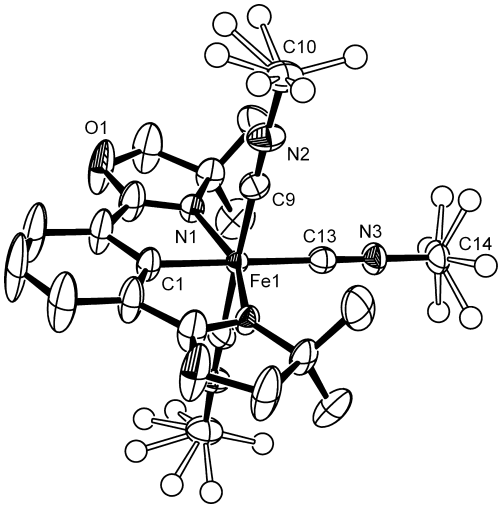

Figure 5. ORTEP diagram of **7a**. Selected bond lengths (Å) and angles (deg): Fe(1)−C(1) 1.909(9), Fe(1)−C(9) 1.881(7), Fe(1)−C(13) 1.886(10), Fe(1)−N(1) 2.010(5), C(9)−N(2) 1.160(10), C(13)−N(3) 1.168(12); N(1)−Fe(1)−N(1) 157.1(3).

This reactivity of the phebox−Fe complex **1** toward isocyanide was similar to that of $CpFe(CO)_2X$, in which stepwise substitution of the CO ligand with isocyanide gave neutral complexes $CpFe(CO)(CNR)X$ and $CpFe(CNR)_2X$ and a cationic complex $[CpFe(CNR)_3]X$.[22]

CONCLUSIONS

The fundamental reactivity of NCN pincer Fe complexes toward two-electron donor ligands phosphine and isocyanide was elucidated. Reaction of the carbonyl complex (phebox-R)Fe(CO)$_2$Br (**1**) with PMe_3 underwent ligand exchange with both CO and Br ligands to give the cationic phosphine complex [(phebox-R)Fe(PMe$_2$)$_2$(CO)]Br (**2**). In contrast, reaction with PMe_2Ph resulted in a change in coordination number of the phebox ligand to give the NC chelated neutral phosphine complex **3**. Subsequent reaction of **3** in a polar solvent led to the formation of the NCN pincer complex **4** *via* a coordination number change of the phebox ligand. This fluxional behavior of the Fe complex contrasts with the second-row transition-metal complexes, which contain a rigid NCN coordination of the phebox ligand. In the reaction of **1** with a π-accepting ligand CN(*t*-Bu), the ligand-exchange reaction with one of the CO ligands proceeded to give neutral isocyanide complexes (phebox-Me$_2$)Fe(CO)[CN(*t*-Bu)]Br (**5**, **6**). The resulting isocyanide complexes **5** and **6** reacted with excess CN(*t*-Bu) to afford the cationic complex {(phebox-Me$_2$)Fe[CN(*t*-Bu)]$_3$}Br (**7a**). These phebox Fe complex coordination processes can provide fundamental insights into NCN pincer Fe complexes as a catalyst.

EXPERIMENTAL SECTION

General Information. All air- and moisture-sensitive compounds were manipulated using standard Schlenk and vacuum line techniques under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were obtained at 25 °C on a Varian Mercury 300 spectrometer and a Varian Inova 500 spectrometer. ^{1}H NMR chemical shifts were reported in δ units, in parts per million relative to the singlet at 7.26 ppm for $CDCl_3$ and 7.16 ppm for C_6D_6. ^{13}C NMR spectra were reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.1 ppm for $CDCl_3$ and 128.0 ppm for C_6D_6. ^{31}P NMR spectra were reported in terms of chemical shift (δ, ppm) relative to the signal at δ = 0 ppm for H_3PO_4. Infrared spectra were recorded on a JASCO FT/IR-230 spectrometer. Complexes **1a** and **1b** were prepared by the reported method.[10]

Reaction of 1 with PMe$_3$. To a toluene solution (20 mL) of **1a** (463 mg, 1.0 mmol) was added a 1 M toluene solution of PMe_3 (5.0 mL, 5.0 mmol) under an argon atmosphere. The resulting mixture was stirred at 50 °C for 12 h. After removal of the solvent under reduced pressure, the residue was crystallized by slow concentration of a mixed solution of methanol, diethylether, and toluene at room temperature to give red crystals of **2a** (464 mg, 0.79 mmol, 79%). The similar procedure using **1b** (491 mg, 1.0 mmol) gave red crystals of **2b** (510 mg, 0.83 mmol, 83%).

A methanol solution of **2a** (176 mg, 0.30 mmol) and $NaBPh_4$ (123 mg, 0.36 mmol) was stirred for 1 h at room temperature. Recrystallization of the crude product afforded red crystals of **2a-BPh$_4$** (246.1 mg, 0.30 mmol, 99%). The similar procedure using **1b** (306 mg, 0.50 mmol) gave **2b-BPh$_4$** (412 mg, 0.48 mmol, 96%).

2a: ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.81(dd, J_{PH} = 3.9, 3.9 Hz, 18 H, PCH_3), 1.27 (s, 12H, C(CH_3)$_2$), 4.53 (s, 4H, CH_2), 7.55 (t, J = 7.6 Hz, 1H), 7.87 (d, J = 7.6, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 14.1 (dd, J = 13.4, 13.4 Hz), 28.2, 65.6, 82.5, 124.6, 126.1 (t, J = 2.2 Hz), 134.2, 170.3, 215.6 (t, J = 15.7 Hz), 216.0 (t, J = 23.9 Hz). ^{31}P NMR (121 MHz, C_6D_6, rt): δ 13.7. IR (KBr, cm^{-1}): 2979, 1922, 1601, 1541, 1470, 1397, 1340, 1288, 1204, 949. Anal. Calcd for $C_{23}H_{37}BrFeN_2O_3P_2$: C, 47.04; H, 6.35; N, 4.77. Found: C, 46.57; H, 6.44; N, 3.83. HRMS (FAB, m/z) calcd 507.1629 [M$^+$], found 507.1616.

2b: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.76 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 0.87 (dd, J_{PH} = 3.3 Hz, 18H, PCH_3), 1.15 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.94 (br, 2H), 3.23 (br, 2H), 4.50 (m, 2H), 4.81 (m, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.86 (t, J = 7.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 14.5 (dd, J = 13.1, 13.1 Hz), 17.6, 22.3, 29.8, 71.1, 72.6, 124.2, 126.7, 132.8, 172.4, 214.4 (t, J_{PC} = 35.9 Hz), 218.2 (t, J_{PC} = 43.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$, rt): δ 14.3. IR (KBr, cm^{-1}): 2962, 2903, 1937, 1603, 1576, 1543, 1487, 1389, 1284, 1201, 1145, 948. Anal. Calcd for $C_{25}H_{41}BrFeN_2O_3P_2$: C, 47.80; H, 6.72; N, 4.55. Found: C, 48.28; H, 6.77; N, 4.09. HRMS (FAB, m/z) calcd 535.1942 [M$^+$], found 535.1948.

2a-BPh$_4$: ^{1}H NMR (300 MHz, DMSO-d_6, rt): δ 0.74 (dd, J_{PH} = 4.2, 4.2 Hz, 18 H, PCH_3), 1.17 (s, 12H, C(CH_3)$_2$), 4.57 (s, 4H, CH_2), 6.78 (t, J = 7.1 Hz, 4H), 6.91 (t, J = 7.2 Hz, 8H), 7.17 (br, 8H), 7.59 (t, J = 7.6 Hz, 1H), 7.92 (d, J = 7.5, 2H). ^{13}C NMR (75 MHz, DMSO-d_6, rt): δ 13.1 (dd, J = 13.1, 13.7 Hz), 27.5, 65.3, 81.8, 121.2, 124.5, 125.0 (t, J = 2.6 Hz), 125.3, 133.9, 135.2, 162.9 (q, J = 18.8 Hz), 169.4, 215.7, 216.4. ^{31}P NMR (121 MHz, DMSO-d_6, rt): δ 19.5. IR (KBr, cm^{-1}): 3054, 2994, 2908, 1953, 1599, 1578, 1542, 1481, 1380, 1335, 1286, 1202, 1147, 945. Anal. Calcd for $C_{47}H_{57}BFeN_2O_3P_2$: C, 68.29; H, 6.95; N, 3.39. Found: C, 68.31; H, 7.06; N, 3.02.

2b-BPh$_4$: ^{1}H NMR (300 MHz, DMSO-d_6, rt): δ 0.69 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 0.76 (dd, J_{PH} = 3.6 Hz, 18H, PCH_3), 1.05 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.85 (br, 2H), 3.28 (br, 2H), 4.59 (m, 2H), 4.71 (m, 2H), 6.78 (t, J = 6.9 Hz, 4H, BPh_4), 6.91 (t, J = 7.2 Hz, 8H, BPh_4), 7.17 (br, 8H), 7.56 (t, J = 7.5 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, rt): δ 13.2 (dd, J = 13.1, 13.1 Hz), 17.0, 21.4, 29.3, 70.0, 72.2, 121.2 (BPh_4), 124.0, 125.0 (d, J = 2.9 Hz, BPh_4), 125.9, 132.4, 135.2 (BPh_4), 162.9 (q, J_{BC} = 48.9 Hz, BPh_4), 171.2, 214.7 (t, J_{PC} = 18.2 Hz), 218.2 (t, J_{PC} = 22.2 Hz). ^{31}P NMR (121 MHz, DMSO-d_6, rt): δ 20.0. IR (KBr, cm^{-1}): 3054, 2982, 2914, 1943, 1605, 1577, 1541, 1485, 1389, 1337, 1146, 944. Anal. Calcd for $C_{49}H_{61}BFeN_2O_3P_2$: C, 68.86; H, 7.19; N, 3.28. Found: C, 68.89; H, 7.34; N, 3.26.

Reaction of 1 with PPhMe$_2$. To a toluene solution (20 mL) of **1a** (463 mg, 1.0 mmol) was added a 1 M toluene solution of PMe_2Ph (5.0 mL, 5 mmol) under an argon atmosphere. The reaction mixture was heated at 50 °C for 12 h. After removal of the solvent under reduced

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pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:3) to give **3a** (619 mg, 0.87 mmol, 87%). The similar procedure using **1b** (491 mg, 1.0 mmol) gave red crystals of **3b** (584 mg, 0.79 mmol, 79%).

3a: ^{1}H NMR (300 MHz, C_6D_6, rt): δ 1.10 (m, 6H, PCH_3), 1.35 (m, 6H, PCH_3), 1.58 (s, 6H), 1.89 (t, J = 3.8 Hz, 6H), 3.46 (s, 2H), 3.90 (s, 2H), 6.70−7.10 (m, 11), 7.23 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 6.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 16.1 (t, J_{PC} = 12.5 Hz, PCH_3), 17.4 (t, J_{PC} = 13.7 Hz, PCH_3), 28.6, 67.3, 69.3, 78.3, 82.2, 120.6, 127.1, 127.2 (t, J_{PC} = 4.0 Hz), 128.3, 130.6 (t, J_{PC} = 3.7 Hz), 133.1, 136.3, 137.5 (t, J_{PC} = 14.8 Hz), 144.3, 166.7, 168.8, 187.1 (t, J_{PC} = 25.4 Hz), 221.4(t, J_{PC} = 32.5 Hz). ^{31}P NMR (121 MHz, C_6D_6, rt): 14.7. IR (KBr, cm^{-1}): 3047, 2979, 2960, 2914, 1916, 1660, 1621, 1415, 1296, 1134, 910. Anal. Calcd for $C_{33}H_{41}BrFeN_2O_3P_2$: C, 55.72; H, 5.81; N, 3.94. Found: C, 55.40; H, 5.76; N, 3.39.

3b: ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.53 (d, J = 6.9 Hz, 3H), 0.62 (d, J = 7.2 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H), 1.09 (d, J = 8.4 Hz, 3H), 1.11 (d, J = 8.1 Hz, 3H), 1.64 (dd, J = 0.9, 9 Hz, 3H), 1.70 (m, 2H), 2.01 (d, J = 9.0 Hz, 3H), 2.44−2.68 (m, 1H), 2.86 (dd, J = 8.4, 9.6 Hz, 1H), 3.58−3.70 (m, 2H), 3.89−4.02 (m, 2H), 6.83 (t, J = 7.4 Hz, 1H), 6.88−6.94 (m, 2H), 7.07−7.19 (m, 4H, obscured by C_6D_6), 7.33 (dt, J = 1.8, 8.1 Hz, 2H), 7.41 (dd, J = 1.7, 7.4 Hz, 1H), 7.53 (dd, J = 1.4, 7.4 Hz, 1H), 7.86 (dt, J = 0.9, 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 12.5 (d, J = 23.4 Hz), 15.6, 15.9 (d, J = 30.2 Hz), 16.3 (d, J = 30.2 Hz), 17.8, 18.2 (d, J = 20.9 Hz), 19.3, 20.3, 28.8, 32.2, 68.2, 68.8, 70.4, 71.4, 120.8, 126.5, 127.4 (d, J = 8.5 Hz), 127.6 (d, J = 8.0 Hz), 128.3, 128.8, 130.6 (d, J = 7.4 Hz), 130.7 (d, J = 6.9 Hz), 131.7, 134.6, 137.5 (d, J = 22.2 Hz), 139.5, 140.0, 144.1, 167.4, 170.8, 188.8, 220.3 (dd, J = 31.4, 35.3). ^{31}P NMR (121 MHz, C_6D_6, rt): δ 13.3 (d, J = 155.4 Hz), 21.6 (d, J = 155.4 Hz). IR (KBr, cm^{-1}): 2960, 2912, 2871, 1921, 1630, 1415, 1245, 1143, 903, 734. Anal. Calcd for $C_{35}H_{45}BrFeN_2O_3P_2$: C, 56.85; H, 6.13; N, 3.79. Found: C, 56.78; H, 6.22; N, 3.27.

Heating Reaction of 3a. A methanol solution (2 mL) of **3a** (71 mg, 0.10 mmol) was heated at 50 °C for 24 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate/methanol (10:3) to give **4** (60 mg, 0.084 mmol, 84%). Similarly, heating reaction of **3a** (71 mg, 0.10 mmol) in DMSO gave **4** (60 mg, 0.084 mmol, 84%).

4: ^{1}H NMR (300 MHz, C_6D_6, rt): δ 1.00 (s, 12H), 1.19 (t, J_{PH} = 3.8 Hz, 12H, PCH_3), 3.76 (s, 4H), 6.54 (br, 4H), 7.20 (t, J = 7.4 Hz, 4H), 7.32 (t, J = 7.4 Hz, 2H), 7.85 (t, J = 7.4 Hz, 1H), 7.99 (d, J = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 14.6 (t, J_{CP} = 12.5 Hz), 28.1, 65.4, 82.4, 125.4, 126.6, 128.0, 130.0, 130.6, 133.1 (t, J_{CP} = 18.5 H), 136.3, 170.8, 215.2 (t, J_{CP} = 23.4 Hz), 215.7 (t, J_{CP} = 16.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$, rt): δ 61.5. IR (KBr, cm^{-1}): 2979, 2905, 1930, 1573, 1537, 1481, 1395, 1334, 1202, 1146, 971, 903. Anal. Calcd for $C_{33}H_{41}BrFeN_2O_3P_2$: C, 55.72; H, 5.81; N, 3.94. Found: C, 55.30; H, 6.15; N, 2.71. HRMS (FAB, m/z) calcd 631.1942 [M$^+$], found 631.1958.

Reaction of 1 with CN(*t*-Bu). To a toluene solution (20 mL) of **1a** (232 mg, 0.5 mmol) was added a 1 M toluene solution of CN(t-Bu) (600 μL, 0.6 mmol) under an argon atmosphere. The reaction mixture was stirred at 50 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1) to give **5** (148 mg, 0.29 mmol, 57%) and **6** (26 mg, 0.050 mmol, 10%).

5: ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.99 (s, 6H), 1.23 (s, 9H), 1.32 (s, 6H), 3.70 (d, J = 8.1 Hz, 2H), 3.80 (d, J = 8.1 Hz, 2H), 7.09 (t, J = 7.1 Hz, 1H), 7.75 (d, J = 7.1 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 28.0, 28.2, 30.9, 65.4, 82.6, 122.7, 125.7, 134.8, 165.0, 171.4, 217.3, 218.3. IR (KBr, cm^{-1}): 2978, 2930, 2143, 1937, 1613, 1484, 1379, 1204, 978, 742. Anal. Calcd for $C_{22}H_{28}BrFeN_3O_3$: C, 50.99; H, 5.45; N, 8.11. Found: C, 51.05; H, 5.56; N, 7.68.

6: ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.49 (s, 9H), 0.91 (s, 6H), 1.46 (s, 6H), 3.73 (d, J = 8.7 Hz, 2H), 3.77 (d, J = 8.7 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6, rt): δ 27.8, 28.3, 30.6, 65.7, 82.4, 123.0, 125.3, 134.4, 165.3, 170.4, 215.6, 225.4. IR (KBr, cm^{-1}): 2981, 2928, 2149, 1963, 1611, 1483, 1379, 1204, 976, 742. Anal. Calcd for $C_{22}H_{28}BrFeN_3O_3(H_2O)_{0.5}$: C, 50.12; H, 5.54; N, 7.97. Found: C, 50.20; H, 5.49; N, 7.68.

To a toluene solution (20 mL) of **1a** (463 mg, 1.0 mmol) was added a 1 M toluene solution of CN(t-Bu) (10 mL, 10 mmol). The mixture was stirred at 50 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with ethyl acetate/methanol (5:1) to give **7a** (545 mg, 0.83 mmol, 83%). The similar procedure using **1b** (491 mg, 1.0 mmol) gave **7b** (472 mg, 0.69 mmol, 69%).

7a: ^{1}H NMR (300 MHz, C_6D_6, rt): δ 1.17 (s, 9H), 1.19 (s, 18H), 4.41 (s, 4H), 7.32 (t, J = 7.2 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 27.5, 30.6, 31.2, 57.0, 57.6, 64.7, 82.4, 122.0, 124.8, 133.0, 159.8 (CN), 165.0 (CN), 169.1, 217.1. IR (KBr, cm^{-1}): 2977, 2930, 2870, 2170, 2118, 1609, 1484, 1398, 1203, 974, 747. Anal. Calcd for $C_{31}H_{46}BrFeN_5O_2{\cdot}H_2O_2$: C, 55.20; H, 7.17; N, 10.38. Found: C, 55.20; H, 7.20; N, 10.15. HRMS (FAB, m/z) 576.2988, calcd 576.3001 [M$^+$].

7b: ^{1}H NMR (300 MHz, C_6D_6, rt): δ 0.63 (d, J = 6.6 Hz, 6H), 0.94 (d, J = 7.2 Hz, 6H), 1.18 (s, 18H), 1.77 (s, 9H), 1.92−2.00 (m, 2H), 3.24−3.36 (m, 2H), 4.51−4.58 (m, 4H), 7.33 (t, J = 7.5 Hz, 1H), 7.68 (d, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 14.2, 18.8, 21.2, 29.0, 30.4, 31.0, 57.0, 57.2, 68.0, 71.4, 121.1, 124.8, 132.2, 159.7, 163.8, 170.7, 217.4. IR (KBr, cm^{-1}): 2979, 2171, 2132, 1608, 1487, 1388, 1202, 958, 736. Anal. Calcd for $C_{33}H_{50}BrFeN_5O_2{\cdot}2H_2O$: C, 55.01; H, 7.55; N, 9.72. Found: C, 55.07; H, 7.45; N, 9.32. HRMS (FAB, m/z) 604.3315, calcd 604.3314 [M$^+$].

Reaction of 5 or 6 with CN(*t*-Bu). To a toluene solution (1 mL) of **5** (27 mg, 0.052 mmol) was added a 1 M toluene solution of CN(t-Bu) (125 μL, 0.125 mmol). The mixture was stirred at 50 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with ethyl acetate/methanol (5:1) to give **7a** (33 mg, 0.050 mmol, 99%). The similar procedure using **6** (13 mg, 0.025 mmol) gave **7a** (13 mg, 0.020 mmol, 80%).

X-ray Diffraction. The diffraction data for **2a-BPh$_4$**, **2b-BPh$_4$**, **3a**, **5**, and **7a** were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied by using SADABS. The structure was solved by direct method and refined by full-matrix least-squares on F^2 using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located on calculated positions and refined as rigid groups.

2a-BPh$_4$: empirical formula, $C_{47}H_{57}BFeN_2O_3P_2$; formula weight, 826.55; T = 153(2) K; crystal system, monoclinic; space group, $P2_1/n$; a = 15.0715(17) Å, b = 18.818(2) Å, c = 15.2704(17) Å, β = 99.854(2)°; V = 4267.0(8) Å^3; Z = 4; d_{calcd} = 1.287 mg/m^3; μ = 0.471 mm^{-1}; F(000) = 1752; θ_{max} = 28.33°; index ranges, $-20 \le h \le 20$, $-12 \le k \le 25$, $-20 \le l \le 20$; rflns collected, 31408; indep rflns, 10570 [R(int) = 0.0425]; max and min transmission, 1.000000 and 0.799873; restraints/parameters = 0/515; GOF = 1.119; final R indices [$I > 2\sigma(I)$], R1 = 0.0569, wR2 = 0.1262; R indices (all data), R1 = 0.0688, wR2 = 0.1317; largest diff. peak and hole, 0.719 and −0.318 e·Å^{-3}. **2b-BPh$_4$**: empirical formula, $C_{49}H_{61}BFeN_2O_3P_2$; formula weight, 854.60; T = 153(2) K; crystal system, triclinic; space group, $P1$; a = 9.374(4) Å, b = 10.985(5) Å, c = 12.126(5) Å, α = 89.317(11)°, β = 73.436(10)°, γ = 82.832(10)°; V = 1187.1(9) Å^3; Z = 1; d_{calcd} = 1.195 mg/m^3; μ = 0.426 mm^{-1}; F(000) = 454; θ_{max} = 28.40°; index ranges, $-12 \le h \le 11$, $-14 \le k \le 14$, $-16 \le l \le 7$; rflns collected, 8992; indep rflns, 7163 [R(int) = 0.0311]; max and min transmission, 1.000000 and 0.583871; restraints/parameters = 3/533; GOF = 0.951; final R indices [$I > 2\sigma(I)$], R1 = 0.0475, wR2 = 0.0996; R indices (all data), R1 = 0.0616, wR2 = 0.1041; largest diff. peak and hole, 0.654 and −0.343 e·Å^{-3}. **3a**: empirical formula, $C_{33}H_{41}BrFeN_2O_3P_2$; formula weight, 711.38; T = 153(2) K; crystal system, monoclinic; space group, $P2_1/c$; a = 11.1090(16) Å, b = 9.2697(14) Å, c = 32.130(5) Å, β = 95.778(3)°; V = 3291.8(8) Å^3; Z = 4; d_{calcd} = 1.435 mg/m^3; μ = 1.805 mm^{-1}; F(000) = 1472; θ_{max} = 28.33°; index ranges, $-14 \le h \le 14$, $-12 \le k \le 10$, $-33 \le l \le 42$; rflns collected, 23974; indep rflns, 8182 [R(int) = 0.0419]; max. and min transmission, 0.749408 and

1.000000; restraints/parameters = 0/387; GOF = 1.147; final R indices [$I > 2\sigma(I)$], R1 = 0.0495, wR2 = 0.1005; R indices (all data), R1 = 0.0623, wR2 = 0.1072; largest diff. peak and hole, 0.777 and −0.546 e.Å^{-3}. **5**: empirical formula, $C_{22}H_{28}BrFeN_3O_3$; formula weight, 518.23; T = 153(2) K; crystal system, monoclinic; space group, $P2_1/c$; a = 16.697(3) Å, b = 16.925(3) Å, c = 16.737(3) Å, β = 94.476(6) °; V = 4715.2(15) Å^3; Z = 8; d_{calcd} = 1.460 mg/m^3; μ = 2.361 mm^{-1}; $F(000)$ = 2128; θ_{max} = 28.33°; index ranges, $-18 \le h \le 2$, $-22 \le k \le 20$, $-22 \le l \le 17$; rflns collected, 34527; indep rflns, 11679 [R(int) = 0.1229]; max. and min transmission, 1.00000 and 0.542524; data/restraints/parameters = 11679/0/550; GOF = 1.034; final R indices [$I > 2\sigma(I)$], R1 = 0.0864, wR2 = 0.1707; R indices (all data), R1 = 0.1612, wR2 = 0.2181; largest diff. peak and hole, 1.327 and −0.894 e·Å^{-3}. **7a**: empirical formula, $C_{35}H_{54}BrFeN_5O_3$; formula weight, 728.59; T = 153(2) K; crystal system, orthorhombic; space group, *cmcm*; a = 17.304(4) Å, b = 17.373(4) Å, c = 14.898(4) Å; V = 4478.7(17) Å^3; Z = 4; d_{calcd} = 1.081 mg/m^3; μ = 1.261 mm^{-1}; $F(000)$ = 1536; θ_{max} = 28.43°; index ranges, $-23 \le h \le 23$, $-14 \le k \le 23$, $-18 \le l \le 19$; rflns collected, 16776; indep rflns, 3018 [R(int) = 0.0707]; max. and min transmission, 1.000000 and 0.734197; restraints/parameters = 4/139; GOF = 1.106; final R indices [$I > 2\sigma(I)$], R1 = 0.0781, wR2 = 0.2311; R indices (all data), R1 = 0.1088, wR2 = 0.2513; largest diff. peak and hole, 1.676 and −0.628 e·Å^{-3}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving experimental and crystallographic data for **2a-BPh$_4$**, **2b-BPh$_4$**, **3a**, **5**, and **7a**. 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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