Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 9032

Reduction of an Fe(I) mesityl complex induced by π-acid ligands†

Ya-Fan Lin, Yumiko Nakajima*‡ and Fumiyuki Ozawa*

Received 17th January 2014,
Accepted 11th February 2014

DOI: 10.1039/c4dt00170b

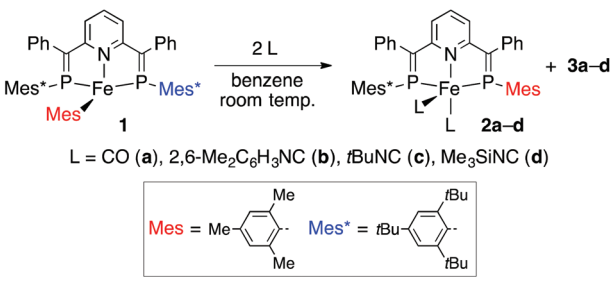
www.rsc.org/dalton

Treatment of the Fe(I) mesityl complex [Fe(Mes)(BPEP-Ph)] (BPEP-Ph = 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine) with π-acid ligands (L = CO, RNC) leads to one-electron reduction *via* Mes group migration from Fe to P, followed by homolytic elimination of the 2,4,6-$tBu_3C_6H_2$ group, to afford Fe(0) complexes of the formula [Fe(L)$_2$(BPEP-Ph*)] (BPEP-Ph* = 2-[1-phenyl-2-mesityl-2-phosphaethenyl]-6-[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine). This reduction process is supported by radical trapping experiments and theoretical studies. The 2,4,6-$tBu_3C_6H_2^{\bullet}$ radical is captured by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in high yield. DFT calculations reveal the mechanism of Mes group migration with a reasonable energy profile.

Introduction

Low-coordinate Fe(I) complexes have been recognized to play an important role in catalytic organic transformations and enzymatic reaction systems.[1,2] However, their chemical properties including redox behaviour and substrate reactivity have been poorly explored owing to the lack of well-defined Fe(I) complexes.[3,4] Recently, we have reported that four-coordinate Fe(I) complexes of the formula [Fe(X)(BPEP-Ph)] (X = Br, Mes) are successfully prepared by using a PNP-pincer type phosphaalkene ligand, 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine (BPEP-Ph).[5] Unlike PNP-pincer ligands with phosphine arms,[6] BPEP-Ph having P=C bonds at the 2,6-positions of pyridine possesses an extremely low-lying π* orbital, thus serving as a strong π-acceptor towards transition metals.[7] We have demonstrated that this particular ligand property effectively stabilizes coordinatively unsaturated Fe(I) complexes with a 15e configuration.

This paper reports a novel reduction process of the Fe(I) mesityl complex [Fe(Mes)(BPEP-Ph)] (**1**). We found that complex **1** readily undergoes one-electron reduction in the presence of isocyanides and CO (Scheme 1). Interestingly, the reaction involves Mes group migration from iron to phosphorus, followed by homolytic elimination of the Mes* group.



Scheme 1 Me_3SiNC was employed as the isomeric form Me_3SiCN.

DFT calculations indicate that the highly flexible nature of the π orbital system of BPEP-Ph, which is characteristic of phosphaalkene compounds, facilitates the Mes group migration.

Results and discussion

Reactions of [Fe(Mes)(BPEP-Ph)] (1) with π-acid ligands

Complex **1** was stable in neat benzene, but was rapidly converted to Fe(0) complexes of the formula [Fe(L)$_2$(BPEP-Ph*)] (**2a–d**) in the presence of π-acid ligands (L = CO, RNC). For example, treatment of **1** with *t*BuNC (2 equiv.) in C_6D_6 at room temperature led to an instant colour change of the reaction solution from brown to green. The $^{31}P\{^1H\}$ NMR spectrum exhibited two sets of AX signals at δ 263.0 and 239.3 ($^2J_{PP}$ = 131 Hz) and δ 165.7 and 58.3 ($^2J_{PP}$ = 93 Hz), which were assignable to **2c** and unidentified complex **3c**, respectively. Complex **2c** was formed in 50% yield based on **1**, and remained unchanged for several days in the reaction solution. Complex **3c** was also detected in considerable quantity (45%/**1**), but readily changed into a paramagnetic species. Reactions of **1** with other π-acid

International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.
E-mail: ozawa@scl.kyoto-u.ac.jp

†Electronic supplementary information (ESI) available: Details of crystal structure determination and DFT calculations. CCDC 973730 and 973731. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00170b

‡Present address: National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan. E-mail: yumiko-nakajima@aist.go.jp

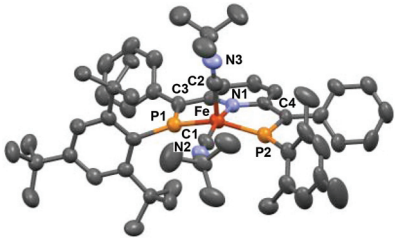


Fig. 1 Crystal structure of **2c**·0.5Et_2O with 50% probability ellipsoids. Hydrogen atoms and a crystal solvent (Et_2O) are omitted for clarity. Selected bond distances (Å) and angles (°): Fe–C1 1.820(6), Fe–C2 1.869(7), Fe–P1 2.151(2), Fe–P2 2.126(2), Fe–N1 2.011(5), P1–C3 1.747(6), P2–C4 1.717(6), C1–N2 1.179(8), C2–N3 1.184(8), C1–Fe–N1 169.2(2), P1–Fe–P2 146.14(8), C1–Fe–C2 88.8(3), C2–Fe–P1 106.1(2), C2–Fe–P2 105.6(2), C2–Fe–N1 101.3(2).

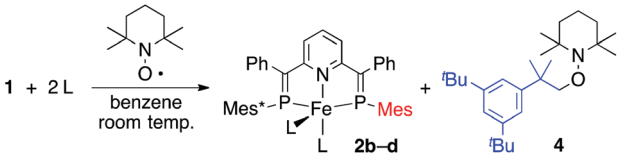
ligands similarly proceeded (see the Experimental section). In contrast, treatment of **1** with phosphine ligands such as PMe_3 and PPh_3 resulted in dissociation of BPEP-Ph from iron.

Complexes **2a–d** were isolated in 35–52% yields/**1** by column chromatography, and characterized by IR and NMR spectroscopy. The crystal structures of **2c** and **2d** were determined by X-ray diffraction analysis. Fig. 1 shows the structure of **2c**, which adopts a square pyramidal geometry around iron (τ = 0.38).[8] The *t*BuNC ligands are accommodated at the apical and equatorial positions, respectively. Complex **2d** has a similar structure (τ = 0.39, see Fig. S1†). The most striking feature of **2c** is the replacement of one of the Mes* groups on phosphorus by the Mes group which was originally bonded to iron. Thus, BPEP-Ph was converted to the unsymmetrical ligand BPEP-Ph* with Mes and Mes* groups on phosphorus atoms, respectively. The P–C bond lengths (1.747(6), 1.717(6) Å) are comparable to those of **1** (1.735(3) Å).[5b] The conversion of BPEP-Ph into BPEP-Ph* was also confirmed for **2a**, **2b** and **2d** by NMR spectroscopy and/or by X-ray structural analysis (**2d**).

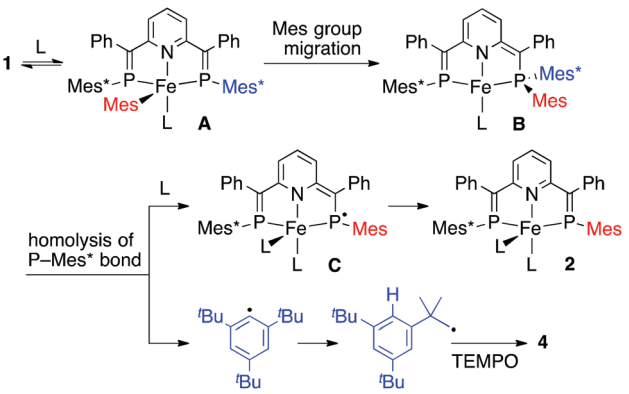
Radical trapping experiments with TEMPO

The conversion of **1** into **2a–d** involved replacement of one of the P-Mes* groups with the Fe-Mes group. The reaction also involved one-electron reduction from Fe(I) to Fe(0), where one of the Mes* groups was missing from the reaction products, probably due to the occurrence of homolytic elimination of the Mes* group. Because we could not observe the expected organic products such as 1,3,5-tri-*tert*-butylbenzene and 1,4-bis-(3,5-di-*tert*-butylphenyl)-1,1,4,4-tetramethylbutane in the reaction solution, we supposed that the ˙Mes* radical was combined with an Fe(I) species to form **3a–d**, although they were too unstable to be identified. Therefore, we next tried to capture the ˙Mes* radical by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Scheme 2).[9]

Complex **1** was stable towards TEMPO itself (1 equiv.) at room temperature, but instantly converted to **2c** (100%) and **4** (98%) in the presence of *t*BuNC. Similarly, treatment of **1** with 2,6-$Me_2C_6H_3NC$ and TMSCN in the presence of TEMPO formed **2b** (92%) and **2d** (71%), respectively, along with **4**



Scheme 2 Formation of **2** in the presence of TEMPO.



Scheme 3 Proposed mechanism for the formation of **2** and **4**.

(89 and 84%). Scheme 3 presents a plausible reaction process affording **2** and **4**. The first step should be coordination of a π-acid ligand (L) to **1**, because the addition of L is essential for the reaction to be initiated. Then, five-coordinate intermediate **A** undergoes migration of the Mes ligand to one of the phosphorus atoms to form **B**.[10] Finally, homolytic cleavage of the P–Mes* bond in **B**, along with the coordination of L, provides **2**. At the same time, the ˙Mes* radical generated in the system combines with TEMPO to yield **4** *via* the known intramolecular radical rearrangement.[11] Although P–C bond cleavage in a homolytic manner under non-photochemical conditions has been scarcely documented, it seems reasonable to assume that the highly sterically demanding phosphine moiety in **B** with Mes and Mes* groups undergoes homolytic elimination of the Mes* group to relieve the steric congestion,[12] where the stability of the resulting phosphaalkene radical **C** with an extended π-conjugated system[13] should also facilitate the reaction.

DFT calculations on Mes group migration

Next, we examined the formation process of **B** by DFT calculations using [Fe(Mes)(BPEP′)] (**1′**; BPEP′ = 2,6-bis(2-mesityl-2-phosphaethenyl)pyridine) and MeNC as computational models of **1** and L, respectively. Because we already confirmed that the real complex **1** is in a low-spin state (S = 1/2),[5b] and isocyanides commonly act as a strong field ligand, all calculations were conducted postulating the spin multiplicity of 2.

Fig. 2(a) presents the energy diagram thus evaluated. In accord with the crystal structure of **1**,[5b] complex **1′** adopts a distorted trigonal monopyramidal configuration with the basal plane consisting of P1, P2, C(Mes) and Fe atoms; the sum of three bond angles in the basal plane is 360.0°. The pyridine ring is located at the apical position, and its opposite side is

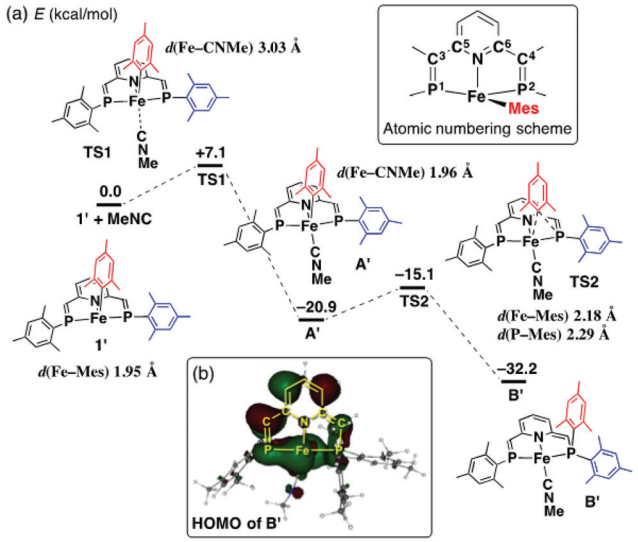


Fig. 2 (a) Schematic geometrical changes and energy changes in the reaction of **1′** with MeNC evaluated by DFT calculations. (b) HOMO of B′.

widely opened. Accordingly, MeNC approaches iron from this side to form **A′**. This step is a highly exothermic process (ΔE = −20.9 kcal mol^{-1}) with small activation energy (E_a = 7.1 kcal mol^{-1}). The subsequent migration of the Mes group from iron to phosphorus (**A′** → **B′**) also proceeds with a small activation barrier (5.8 kcal mol^{-1}).

As depicted in Scheme 3, the Mes group migration (**A** → **B**) is considered to involve a large structural variation in the BPEP-Ph ligand.[14] This situation was clearly reflected in the bond orders of **A′**, **TS2** and **B′** as listed in Table 1. In accord with the presumed structures of **A** and **B** in Scheme 3, the bond order of P2–C4 decreases whereas that of C4–C6 increases when the Mes group shifts from Fe to P2. To our surprise, the bond order of P1–C3 is also reduced to a considerable extent upon the migration, showing the occurrence of strong π-back-donation from Fe to P1. It is reasonable that the phosphine moiety (P2) with two Mes groups in **B′** possesses a strong σ-donating ability, thereby increasing the electron density of iron. As a result, the P1–C3 bond undergoes an effective π-back-donation from iron, and reduces its bond order.

Fig. 2(b) shows the HOMO of **B′**, which clearly demonstrates the occurrence of π-bonding interaction between Fe and P1. Accordingly, we may conclude that the Mes group migration is promoted by strong π-accepting properties of the phosphaalkene unit (P1–C3). In other words, the highly flexible nature of the π orbital system of BPEP-Ph causes the facile migration of the Mes group from iron to phosphorus.

Table 1 Changes in Mayer bond orders upon Mes group migration[a]

Description	A′	TS2	B′
P1–C3	1.40	1.19	1.06
C3–C5	1.24	1.31	1.35
P2–C4	1.40	1.35	1.11
C4–C6	1.24	1.24	1.44

[a] The atomic numbering scheme is given in Fig. 2.

Conclusions

We have found a novel reduction process of the Fe(I) mesityl complex [Fe(Mes)(BPEP-Ph)] (**1**) induced by π-acid ligands (L = CO, RNC). Coordination of L to **1** causes Mes group migration from iron to phosphorus, and homolytic elimination of Mes* from a highly congested phosphorus atom results in one-electron reduction to form [Fe(L)$_2$(BPEP-Ph*)] (**2a–d**). DFT calculations have indicated that the strong π-accepting ability of phosphaalkene effectively promotes the Mes group migration.

Experimental

All manipulations were performed under an inert atmosphere using Schlenk techniques and a glove box. Toluene (Kanto, dehydrated), hexane, and Et$_2$O (Wako, dehydrated) were purified by a solvent purification system (MBRAUN SPS-800) prior to use. *t*BuNC and TMSCN were dried over CaH_2 and distilled. CO gas was passed through a P_2O_5 column (Merck, SICAPENT). C_6D_6 was dried over sodium benzophenone ketyl and distilled. Al_2O_3 was dried overnight at 180 °C under vacuum prior to use. The complex [Fe(Mes)(BPEP-Ph)] (**1**) was prepared as previously reported.[5b]

NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H NMR, 400.13 MHz; ^{13}C NMR, 100.62 MHz; ^{31}P NMR, 161.98 MHz) or a Bruker Avance III 800US Plus spectrometer (^{1}H NMR, 800.15 MHz; ^{13}C NMR, 201.20 MHz). Chemical shifts are reported in δ (ppm), referenced to ^{1}H (residual) and ^{13}C signals of deuterated solvents as internal standards or to ^{31}P signal of 85% H_3PO_4 as an external standard. Assignments of ^{1}H and ^{13}C NMR resonances are based on HH COSY and CH HSQC and HMBC experiments. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. HRMS was carried out on a Bruker micrOTOF II spectrometer using an ESI technique. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University.

Reactions of 1 with π-acid ligands

Reaction with CO (1 atm). An NMR sample tube equipped with a Teflon cock was charged with a solution of **1** (15.0 mg, 0.015 mmol) in C_6D_6 (0.5 mL). After the solution was degassed by freeze–pump–thaw cycles, CO (1 atm) was introduced to the solution using a balloon at −78 °C. The colour of the solution instantly turned dark green. The reaction solution was filtered through a Celite pad and concentrated to dryness under vacuum. The resulting green solid was dissolved in toluene, and subjected to a column chromatography (Al_2O_3, hexane–toluene = 5/1), to give a dark green solid of **2a** (5.5 mg, 0.0069 mmol, 46%).

2a: ^{1}H NMR (C_6D_6): δ 1.32 (s, 9H, *p*-*t*Bu), 1.67 (s, 18H, *o*-*t*Bu), 1.97 (s, 3H, *p*-Me), 2.68 (6H, *o*-Me), 6.69 (s, 2H, *m*-Mes), 6.99 (m, 4H, *o*-Ph), 7.07 (m, 4H, *m*-Ph), 7.29 (m, 3H, *p*-Ph, 4-Py), 7.46 (s, 2H, *m*-Mes*), 7.90 (1H, 3-Py), 8.03 (1H, 3-Py). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.6 (s, *p*-Me), 24.1 (d, *o*-Me, J_{CP} = 8 Hz), 32.0 (s, *p*-*t*Bu), 34.4 (s, *o*-*t*Bu), 35.1 (s, *p*-*t*Bu), 39.6 (s, *o*-*t*Bu), 116.2 (d, J_{CP} = 12 Hz, Ar), 118.0 (d, J_{CP} = 16 Hz, Ar), 122.6 (d, J_{CP} = 8 Hz, Ar), 126.1 (s, Ar), 126.3 (d, J_{CP} = 11 Hz, Ar), 126.6 (d, J_{CP} = 7 Hz, Ar), 126.9 (s, Ar), 127.8 (s, Ar), 129.5 (d, J_{CP} = 7 Hz, Ar), 130.3 (d, J_{CP} = 15 Hz, Ar), 131.3 (d, J_{CP} = 7 Hz, Ar), 131.5 (d, J_{CP} = 16 Hz, Ar), 131.8 (d, J_{CP} = 5 Hz, Ar), 135.1 (d, J_{CP} = 11 Hz, Ar), 137.5 (d, J_{CP} = 11 Hz, Ar), 141.7 (s, Ar), 143.0 (d, J_{CP} = 9 Hz, Ar), 153.1 (s, Ar), 158.5 (s, Ar), 203.8 (s, CO). The chemical shift of one of the Ar carbons was obscured due to the overlap with the signal of C_6D_6. The signals of two C═P groups and two of the *ipso*-Ar carbons were not observed due to low signal intensities. ^{31}P{^{1}H} NMR (C_6D_6): δ 278.7 (d, J_{PP} = 86 Hz), 250.8 (d, J_{PP} = 86 Hz). IR (ATR): 1978, 1931 cm^{-1} (ν_{CO}). Complex **2a** is a highly air sensitive solid, and did not give a satisfactory elemental analysis.

Reaction with 2,6-$Me_2C_6H_3NC$ (DMPI). A solution of **1** (20.5 mg, 0.021 mmol) in C_6D_6 (0.6 mL) was charged to an NMR sample tube. DMPI (5.7 mg, 0.044 mmol, 2.1 equiv.) was added at room temperature, and the mixture was examined by ^{31}P{^{1}H} NMR spectroscopy using a C_6D_6 solution of PPh_3 (0.13 M) sealed in a capillary tube as an internal standard. A set of doublets assignable to **2b** and a set of doublets at δ 183.7 and 50.2 (J_{PP} = 78 Hz) arising from an unidentified compound **3b** instantly appeared in an intensity ratio of 1 : 1. After 4 h, the signals of **3b** disappeared, whereas the signals of **2b** remained unchanged. The solution was filtered through a Celite pad, and concentrated to dryness under vacuum. The residue was subjected to a column chromatography (Al_2O_3, Et_2O–toluene = 1/1), to give a dark green solid of **2b** (8.7 mg, 0.0087 mmol, 41%).

2b: ^{1}H NMR (C_6D_6): δ 1.35 (s, 9H, *p*-*t*Bu), 1.71 (18H, *o*-*t*Bu), 1.88 (s, 3H, *p*-Me), 1.93 (12H, 2,6-$Me_2C_6H_3NC$), 2.67 (6H, *o*-Me), 6.56 (s, 2H, *m*-Mes), 6.64 (br, 6H, m, *p*-2,6-$Me_2C_6H_3NC$), 7.00 (m, 4H, *o*-Ph), 7.07 (m, 4H, *m*-Ph), 7.28 (m, 2H, *p*-Ph,), 7.44 (dd, J_{HH} = 7.6 and 7.6 Hz, 1H, 4-Py), 7.48 (s, 2H, *m*-Mes*), 8.10 (1H, 3-Py), 8.15 (1H, 3-Py). ^{13}C{^{1}H} NMR (C_6D_6): δ 19.1 (2,6-$Me_2C_6H_3NC$), 21.5 (s, *p*-Me), 24.2 (s, *o*-Me), 24.3 (s, *o*-Me), 32.0 (s, *p*-*t*Bu), 34.6 (s, *o*-*t*Bu), 35.6 (s, *p*-*t*Bu), 39.6 (s, *o*-*t*Bu), 115.6 (d, J_{CP} = 12 Hz, Ar), 116.3 (d, J_{CP} = 11 Hz, Ar), 122.3 (d, J_{CP} = 6 Hz, Ar), 125.1 (br, Ar), 125.7 (m, Ar), 127.3 (d, J_{CP} = 8 Hz, Ar), 127.6 (s, Ar), 127.9 (br, Ar), 131.6 (d, J_{CP} = 4 Hz, Ar), 131.9 (s, Ar), 132.1 (br, Ar), 133.7 (d, J_{CP} = 11 Hz, Ar), 133.9 (s, Ar), 136.1 (d, J_{CP} = 18 Hz, Ar), 138.2 (d, J_{CP} = 15 Hz, Ar), 140.3 (s, Ar), 141.9 (d, J_{CP} = 8 Hz, Ar), 143.1 (d, J_{CP} = 9 Hz, Ar), 152.0 (s, *p*-Mes*), 157.7 (s, *o*-Mes*), 160.7 (br, 2,6-$Me_2C_6H_3NC$), 167.2 (d, J_{CP} = 42 Hz, C═P). The chemical shifts of two Ar carbons were obscured due to the overlap with the signal of C_6D_6. ^{31}P{^{1}H} NMR (C_6D_6): δ 267.0 (d, J_{PP} = 117 Hz), 241.5 (d, J = 117 Hz). IR (ATR): 2051, 1992 cm^{-1} (ν_{CN}). Complex **2b** is a highly air sensitive solid, did not give a satisfactory elemental analysis.

Reaction with *t*BuNC. A solution of **1** (15.0 mg, 0.015 mmol) in C_6D_6 (0.5 mL) was charged to an NMR sample tube. *t*BuNC (3.5 μL, 0.031 mmol, 2.1 equiv.) was added at room temperature, and the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy using a C_6D_6 solution of PPh_3 (0.13 M) sealed in a capillary tube as an internal standard. A set of doublets assignable to **2c** and a set of doublets at δ 165.7 and 58.3 (J_{PP} = 93 Hz) of an unidentified compound **3c** instantly appeared in an intensity ratio of 10 : 9. After 2 h, the signals of **3c** disappeared, whereas the signal intensity of **2c** remained unchanged. The solution was filtered through a Celite pad, and concentrated to dryness under vacuum. The residue was subjected to a column chromatography (Al_2O_3, Et_2O), to give **2c** as a dark green solid (7.0 mg, 0.0077 mmol, 51%). Single crystals suitable for X-ray diffraction analysis were grown from a mixed solvent of Et_2O and isooctane (3 : 2) at −35 °C.

2c: ^{1}H NMR (C_6D_6): δ 0.78 (s, 18H, *t*BuNC), 1.38 (s, 9H, *p*-*t*Bu), 1.81 (br, 18H, *o*-*t*Bu), 2.10 (s, 3H, *p*-Me), 2.77 (6H, *o*-Me), 6.84 (2H, *m*-Mes), 7.02 (m, 2H, *p*-Ph), 7.12 (m, 2H, *m*-Ph), 7.19 (m, 2H, *m*-Ph), 7.28 (br, 2H, *o*-Ph,), 7.37 (dd, 1H, 4-Py), 7.55 (s, 2H, *m*-Mes*), 7.56 (d, J_{HH} = 10.0 Hz, 2H, *o*-Ph), 8.08 (1H, 3-Py), 8.20 (1H, 3-Py). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.7 (s, *p*-Me), 24.4 (s, *o*-Me), 24.5 (s, *o*-Me), 31.3 (s, *t*BuNC), 32.0 (s, *p*-*t*Bu), 34.5 (s, *o*-*t*Bu), 35.5 (s, *p*-*t*Bu), 39.6 (s, *o*-*t*Bu), 56.3 (s, *t*BuNC), 114.4 (d, J_{CP} = 22 Hz, Ar), 115.5 (d, J_{CP} = 24 Hz, Ar), 121.8 (d, J_{CP} = 4 Hz, Ar), 124.5 (br, Ar), 124.8 (br, Ar), 125.2 (br, Ar), 127.5 (br, Ar), 129.1 (br, Ar), 131.9 (br, Ar), 132.5 (d, J_{CP} = 13 Hz, Ar), 134.7 (d, J_{CP} = 12 Hz, Ar), 134.8 (d, J_{CP} = 12 Hz, Ar), 135.6 (d, J_{CP} = 10 Hz, Ar), 136.2 (d, J_{CP} = 10 Hz, Ar), 137.9 (d, J_{CP} = 9 Hz, Ar), 139.6 (s, Ar), 142.8 (br, *t*BuNC), 151.6 (s, Ar), 157.5 (s, Ar), 157.9 (s, Ar), 160.8 (d, J_{CP} = 46 Hz, C═P), 161.0 (d, J_{CP} = 47 Hz, C═P). The chemical shifts of two Ar carbons were obscured due to the overlap with the signal of C_6D_6. ^{31}P{^{1}H} NMR (C_6D_6): δ 263.0 (d, J_{PP} = 131 Hz), 239.3 (d, J_{PP} = 131 Hz). IR (ATR): 2086, 2017 cm^{-1} (ν_{CN}). Anal. calcd for $C_{56}H_{71}N_3P_2Fe$: C, 74.40; H, 7.92; N, 4.65. Found: C, 74.56; H, 8.12; N, 4.38.

Reaction with Me_3SiCN. A solution of **1** (18.3 mg, 0.019 mmol) in C_6D_6 (0.5 mL) was charged to an NMR sample tube, and Me_3SiCN (5.5 μL, 0.044 mmol, 2.4 equiv.) was added at room temperature. The reaction was monitored by ^{1}H NMR spectroscopy to reveal disappearance of **1** after 2 h. The reaction solution was filtered through a Celite pad, and evaporated under vacuum. The resulting green solid was extracted with hexane (*ca.* 1.5 mL × 3), and evaporated under vacuum to give a dark green solid of **2d** (7.3 mg, 0.0077 mmol, 41%). Single crystals suitable for X-ray diffraction analysis were obtained from a 2 : 1 mixture of Et_2O and hexane at −35 °C.

2d: ^{1}H NMR (C_6D_6): δ −0.20 (s, 18H, TMSNC) 1.35 (s, 9H, *p*-*t*Bu), 1.82 (s, 18H, *o*-*t*Bu), 2.10 (s, 3H, *p*-Me), 2.76 (6H, *o*-Me), 6.82 (2H, *m*-Mes), 7.01 (m, 2H, *p*-Ph), 7.10 (m, 2H, *m*-Ph), 7.18 (m, 2H, *m*-Ph), 7.27 (m, 2H, *o*-Ph,) , 7.37 (br, 1H, 4-Py), 7.54 (s, 2H, *m*-Mes*), 7.55 (d, J_{HH} = 8.8 Hz, 2H, *o*-Ph), 8.06 (1H, 3-Py), 8.20 (1H, 3-Py). ^{13}C{^{1}H} NMR (C_6D_6): δ 0.59 (s, TMSNC), 21.6 (s, *p*-Me), 24.2 (s, *o*-Me), 24.3 (s, *o*-Me), 32.1 (s, *p*-*t*Bu), 34.4 (s, *o*-*t*Bu), 35.6 (s, *p*-*t*Bu), 39.5 (s, *o*-*t*Bu), 115.1 (d, J_{CP} = 12 Hz, Ar), 116.4 (d, J_{CP} = 12 Hz, Ar), 121.8 (d, J_{CP} = 6 Hz, Ar), 124.8 (s, Ar),

125.0 (s, Ar), 125.5 (s, Ar), 127.5 (s, Ar), 131.4 (d, J_{CP} = 5 Hz, Ar), 132.0 (d, J_{CP} = 4 Hz, Ar), 133.8 (d, J_{CP} = 12 Hz, Ar), 135.0 (d, J_{CP} = 15 Hz, Ar), 136.1 (d, J_{CP} = 10 Hz, Ar), 136.8 (d, J_{CP} = 10 Hz, Ar), 140.0 (s, Ar), 143.3 (br, TMSNC), 151.9 (s, Ar), 157.7 (s, Ar). The chemical shift of an Ar carbon was obscured due to the overlap with the signal of C_6D_6. The carbon signals of two C═P groups were not observed due to low signal intensities. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 266.5 (d, J_{PP} = 117 Hz), 241.2 (d, J_{PP} = 117 Hz). IR (ATR): 1998, 1921 cm^{-1} (ν_{CN}). Anal. calcd for $C_{54}H_{71}N_3P_2Si_2Fe{\cdot}C_4H_{10}O$: C, 69.02; H, 7.99; N, 4.16. Found: C, 68.54; H, 8.21; N, 3.97.

Radical trapping experiments with TEMPO

Reaction with *t*BuNC. An NMR sample tube equipped with a Teflon cock (J-Young) was charged with a 1 : 1 mixture of **1** (12.0 mg, 0.012 mmol) and TEMPO (1.9 mg, 0.012 mmol) in C_6D_6. *t*BuNC (2.8 μL, 0.025 mmol) was added, and the mixture was examined by ^1H NMR spectroscopy using mesitylene (0.012 mmol) as an internal standard. The reaction was completed instantly at room temperature to form **2c** and **4** in 100 and 98% yields, respectively.

Compound **4** was identified by NMR and HRMS: ^1H NMR (C_6D_6): δ 1.07 (s, 6H, Me), 1.12 (s, 6H, Me), 1.26 (br, 2H, CH_2) 1.37 (s, 18H, *t*Bu), 1.42 (br, 4H, CH_2) 1.49 (s, 6H, Me), 3.96 (s, 2H, OCH_2), 7.43 (s, H, Ar), 7.45 (s, 2H, Ar). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 17.8, 20.6, 26.6, 32.2, 33.7, 35.4, 40.1, 40.4, 60.5, 86.5, 120.2, 121.1, 147.5, 150.5. HRMS (*m*/*z*): calcd for $C_{27}H_{47}NO$ 402.3730 $[M + H]^+$; obsd 402.3737.

Reaction with DMPI. Similarly, **1** was treated with DMPI (2 equiv.) in C_6D_6 in the presence of TEMPO (1 equiv.). The reaction was completed instantly at room temperature to afford **2b** and **4** in 92 and 89% yields, respectively.

Reaction with TMSCN. The reaction with TMSCN (2.5 equiv.) under otherwise the same conditions formed **2d** and **4** in 26 and 36% yields, respectively, along with the formation of *Z*,*Z*-BPEP-Ph in 16% yield. The yields of **2d** and **4** increased to 71 and 84%, respectively, when excess TMSCN (13 equiv.) was employed.

Reaction with CO. Treatment of **1** with CO (1 atm) in the presence of TEMPO (1 equiv.) resulted in decomposition of the complex; neither **2a** nor **4** could be observed by ^1H NMR spectroscopy.

X-Ray crystal structure determination

The intensity data were collected on Rigaku Mercury CCD diffractometers with monochromated Mo Kα radiation (λ = 0.71070 Å). The data sets were corrected for Lorentz and polarization effects and for absorption (numerical). The structures were solved by direct methods (SHELXS-97),[15] and refined by least-square calculations on F^2 for all reflections (SHELXL-97)[15] using Yadokari-XG 2009 (Software for Crystal Structure Analyses).[16] Both **2c** and **2d** contained Et_2O as a crystal solvent. 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 S1.†

DFT calculations

Intermediates and transition structures on potential energy surfaces were searched by DFT calculations using the Gaussian 09 program[17] and the UB3LYP density functional. The Fe atom was described with the SDD basis set including a triple-ζ basis set and effective core potentials (ECPs up to 2p).[18] The 6-31G(d) basis set was employed for the atoms bonded to Fe in the Mes, pyridyl, phosphaalkene, and isocyanide ligands.[19] The 6-31G basis set was applied to other atoms.[19] All structures were optimized in the gas phase. Systematic vibrational analyses were carried out for all reaction species to characterize stationary-point structures. Complexes **1′** and **TS1** exhibit small imaginary frequencies due to methyl group rotations even after applying a tight convergence. An appropriate connection between a reactant and a product for each reaction step was confirmed by IRC calculations.[20,21] The orbital plot in Fig. 2 was generated with Molekel.[22]

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from Mext Japan (no. 24109010) and a JST PRESTO program. Y.L. is grateful to the MEXT Project "Integrated Research on Chemical Synthesis" for the provision of a post-doctoral fellowship.

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