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Disproportionation of Bis(phosphaethenyl)pyridine Iron(I) Bromide Induced by *t*BuNC

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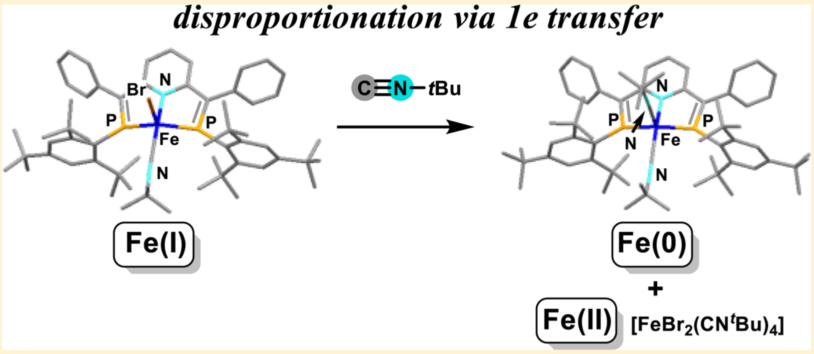
Supporting Information



ABSTRACT: Redox behavior of Fe(I) complexes bearing a PNP-pincer-type phosphaalkene ligand, 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine (BPEP-Ph), is reported. The four-coordinate Fe(I) complex [FeBr(BPEP-Ph)] (**1**) readily reacts with 1 equiv of *t*BuNC in toluene at −35 °C to give [FeBr(*t*BuNC)(BPEP-Ph)] (**2**) with a 17e configuration. Complex **2** is fairly stable in neat benzene at room temperature, but smoothly undergoes disproportionation in the presence of added *t*BuNC to afford the Fe(0) complex [Fe(*t*BuNC)$_2$(BPEP-Ph)] (**3**) and the Fe(II) complex [FeBr$_2$(*t*BuNC)$_4$] (**4**) along with free BPEP-Ph. The single-crystal X-ray diffraction studies of **3** and **4** reveal distorted trigonal bipyramidal and square pyramidal arrangements around Fe, respectively. The yield of **3** increases up to 50%/**2** when 2 equiv of *t*BuNC is added to the system. A disproportionation process involving a 19e intermediate is proposed.

INTRODUCTION

Transition metal complexes with an odd number of valence electrons have attracted attention because of their crucial roles in catalytic organic transformations and enzymatic reactions.[1] However, structures and chemical properties of such complexes have not been fully explored due to the instability arising from their radical character. Indeed, in many cases, they are in situ generated as transient species by either electrochemical or photochemical methods.[2] In this connection, rational design of supporting ligands that enable the isolation of odd-electron transition metal species has received continuous research interest.[3] Fe(I) complexes with 15e and 17e configurations constitute the central subjects in such chemistry.[4]

Recently, we have reported that the four-coordinate Fe(I) complexes [FeX(BPEP-Ph)] (X = Br, Mes (2,4,6-Me$_3$C$_6$H$_2$)) are successfully stabilized by a PNP-pincer-type phosphaalkene ligand, 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine (BPEP-Ph).[5] The BPEP-Ph ligand, having P═C double bonds at the 2,6-positions of pyridine, possesses an extremely low-lying π^* orbital around the phosphorus atoms, thereby serving as a strong π-acceptor toward transition metals.[6−9] This particular ligand property enables the isolation of Fe(I) complexes with a 15e configuration.[5]

This paper describes redox behavior of [FeBr(BPEP-Ph)] (**1**) in solution. Recently, we carried out a related study on [Fe(Mes)(BPEP-Ph)] and demonstrated a novel one-electron reduction process induced by π-acid ligands (L = RNC and CO). In this study, we found that *t*BuNC also induces a redox reaction leading to disproportionation of the Fe(I) bromide (**1**). A detailed analysis of the reaction stoichiometry indicates that [FeBr(L)$_2$(BPEP-Ph)], with a 19e configuration, serves as a key intermediate for one-electron transfer.

RESULTS AND DISCUSSION

Reaction of [FeBr(BPEP-Ph)] (1) with *t*BuNC. Complex **1** reacted with 1 equiv of *t*BuNC in toluene at −35 °C to give [FeBr(*t*BuNC)(BPEP-Ph)] (**2**) with a 17e configuration,[10] which was isolated as a dark green crystalline solid in 79% yield (Scheme 1).

Complex **2** was fairly stable in neat C$_6$D$_6$ at room temperature, but in the presence of *t*BuNC (2.3 equiv) the same complex was smoothly converted to the Fe(0) complex [Fe(*t*BuNC)$_2$(BPEP-Ph)] (**3**) and the Fe(II) complex [FeBr$_2$(*t*BuNC)$_4$] (**4**)[11] along with free BPEP-Ph. Complexes

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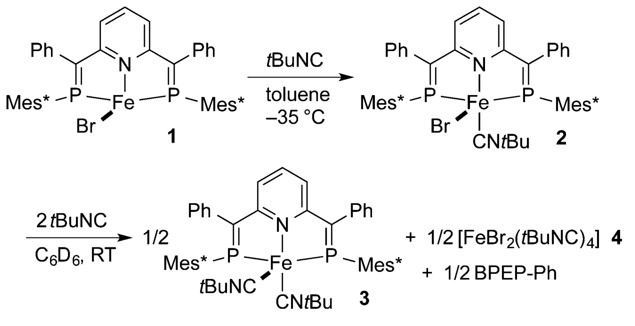
Scheme 1



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

3 and **4** were isolated as a dark green and reddish-brown solid in 52% and 46% yields, respectively. Therefore, we concluded that half of **2** was converted to **3**, whereas the other half was converted to **4** and BPEP-Ph. It is likely that **4** and BPEP-Ph are afforded from an Fe(II) dibromide species, generated by disproportionation of **2** in the presence of *t*BuNC. As an indirect evidence, we confirmed that $[FeBr_2(BPEP\text{-}Ph)]$ (**5**)[5a] instantly reacted with *t*BuNC (4.1 equiv) in benzene at room temperature to afford **4** and BPEP-Ph in 77% and 63% isolated yields, respectively.

Unlike the reaction with *t*BuNC, treatment of **1** with PhCN as a much weaker π-acid ligand resulted in simple coordination to form [FeBr(PhCN)(BPEP-Ph)][5a] even when an excess amount of PhCN was employed. On the other hand, treatment of **1** with CO (1 atm) in C_6D_6 at room temperature caused disproportionation. In this case, $[FeBr_2(BPEP\text{-}Ph)]$ (**5**), $[Fe(CO)_2(BPEP\text{-}Ph)]$ (**6**), and BPEP-Ph were isolated from the reaction solution in 14%, 39%, and 15% yields, respectively. Free BPEP-Ph is the product generated from Fe(II) dibromide and CO along with $[FeBr_2(CO)_4]$,[11] as confirmed by an independent experiment using isolated $[FeBr_2(BPEP\text{-}Ph)]$ (**5**).

Identification of [FeBr(*t*BuNC)(BPEP-Ph)] (2). Complexes **2** and **3** in Scheme 1 are new compounds and identified by elemental analysis, IR and/or NMR spectroscopy, and X-ray diffraction analysis.

Figure 1 shows the crystal structure of **2**. The BPEP-Ph ligand is coordinated with the Fe(I) center via P1, N2, and P2 atoms in a meridional arrangement. The Br and *t*BuNC ligands are located at the apical and equatorial positions, respectively. The P1−Fe−P2 bond (134.84(4)°) is significantly bent, whereas the N2−Fe−C5 bond (175.19(12)°) retains the linearity. Thus, the geometry around the Fe atom is described as a distorted trigonal bipyramid ($\tau = 0.67$).[12] The P−C lengths (1.703(3) and 1.715(3) Å) are comparable to those of **1** (1.713(6) and 1.719(6) Å).[5a] On the other hand, Fe−P1, Fe−P2, and Fe−N2 bonds of **2** (2.1987(9), 2.1952(10), and 1.974(3) Å) are slightly shorter than those of **1** (2.2716(17), 2.2883(17), and 2.035(5) Å), respectively. The IR spectrum exhibited a strong ν_{CN} band at 2107 cm^{-1} (ATR).

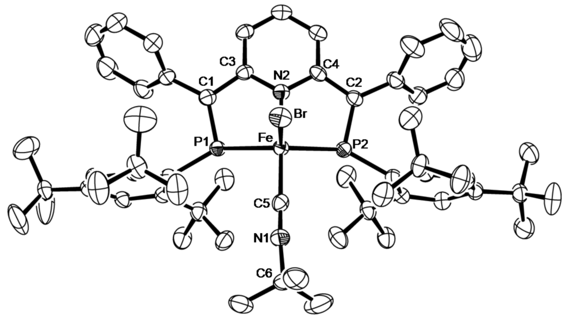


Figure 1. X-ray crystal structure of $[FeBr(tBuNC)(BPEP\text{-}Ph)]\cdot C_6H_6$ (**2**) with 50% probability ellipsoids. Hydrogen atoms and a crystal solvent (benzene) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe−P1 2.1987(9), Fe−P2 2.1952(10), Fe−N2 1.974(3), Fe−C5 1.854(3), P1−C1 1.703(3), P2−C2 1.715(3), C5−N1 1.154(4), N1−C6 1.466(4), C1−C3 1.449(4), C2−C4 1.431(4), P1−Fe−P2 134.84(4), N2−Fe−C5 175.19(12), Fe−C5−N1 179.5(3), C5−N1−C6 173.8(3).

Identification of [Fe(*t*BuNC)$_2$(BPEP-Ph)] (3). Complex **3** is a diamagnetic species, showing a singlet signal at δ 257.8 in the $^{31}P\{^1H\}$ NMR spectrum; the chemical shift is in a typical region of phosphaalkene compounds. The ^1H NMR signals of two *t*BuNC ligands appeared at δ 0.82 and 0.95, independently. The *t*Bu substituents at the ortho-positions of Mes* (2,4,6-$(tBu)_3C_6H_2$) groups on phosphorus displayed two singlets at δ 1.59 and 1.98, whereas those at the para-position showed one singlet at δ 1.39. These signal patterns are consistent with C_s symmetry of the complex. The IR spectrum exhibited two strong ν_{CN} bands at 2094 and 2041 cm^{-1} (ATR).

Figure 2 shows the X-ray structure of **3**, having a mirror plane including Fe, C3, N1, C5, C4, N2, C8, and N3 atoms. The bond angles of C3−Fe−N3 and P1−Fe−P1′ are 170.99(16)° and 146.08(5)°, respectively. Thus, the complex adopts a distorted square pyramidal configuration around Fe ($\tau = 0.42$).[12] The bond lengths of Fe−P1 (2.1381(8) Å), Fe−N3 (1.999(3) Å), Fe−C3 (1.813(4) Å), and Fe−C4 (1.838(5) Å) are comparable to those of **2**. The P1−C1 bond length (1.713(3) Å) is also very close to that of **2**.

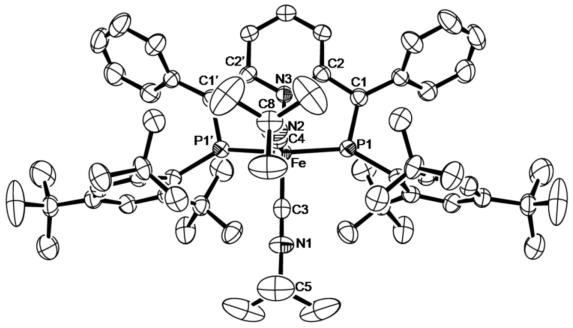


Figure 2. X-ray crystal structure of $[Fe(tBuNC)_2(BPEP\text{-}Ph)]$ (**3**) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe−P1 2.1381(8), Fe−N3 1.999(3), Fe−C3 1.813(4), Fe−C4 1.838(5), P1−C1 1.713(3), C1−C2 1.427(4), C3−Fe−N3 170.99(16), P1−Fe−P1′ 146.08(5), Fe−C3−N1 179.6(4), Fe−C4−N2 179.1(4), C3−N1−C5 169.8(5), C4−N2−C8 176.1(4).

Examination of the Disproportionation Process. We have confirmed that the Fe(I) bromide [FeBr(BPEP-Ph)] (**1**), having a 15e configuration, readily combines with 1 equiv of *t*BuNC to form the five-coordinate complex [FeBr(*t*BuNC)(BPEP-Ph)] (**2**), having a 17e configuration. This complex is fairly stable in neat solvent at room temperature. On the other hand, in the presence of excess *t*BuNC, the same complex undergoes disproportionation to afford $[Fe(tBuNC)_2(BPEP\text{-}Ph)]$ (**3**), $[FeBr_2(tBuNC)_4]$ (**4**), and free BPEP-Ph. To ensure the reaction stoichiometry, we next examined the disproportionation reaction of **2** with changing the amounts of added *t*BuNC.

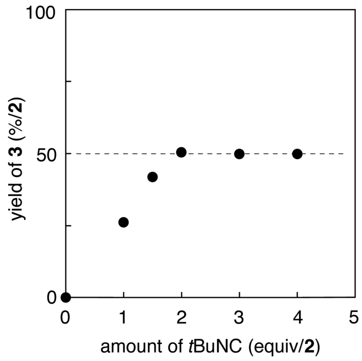
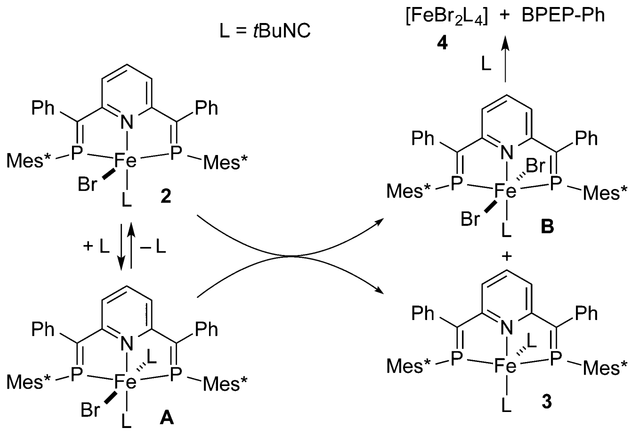


Figure 3. Plot of the yield of **3** against the amount of *t*BuNC added to the solution of **2** (8.5 mM) in C_6D_6 at room temperature.

Figure 3 shows the relationship between the yield of **3** and the amount of *t*BuNC added to the system. The formation of **3** as a diamagnetic species was followed by ^1H NMR spectroscopy using an internal standard. It is seen that the amount of **3** increases with increasing amount of *t*BuNC and becomes constant at 50% yield/**2** when over 2 equiv/**2** of *t*BuNC is added. Hence the reaction stoichiometry given in Scheme 1 was established.

Scheme 2



Scheme 2 illustrates a plausible process for disproportionation. The first step should be the coordination of **2** with *t*BuNC (L) to form [FeBr(tBuNC)$_2$(BPEP-Ph)] (**A**), with a 19e configuration, because the addition of *t*BuNC is the essential requirement to start the reaction. Then, **A** undergoes one-electron transfer with **2** to afford [FeBr$_2$(tBuNC)(BPEP-Ph) (**B**) and [Fe(tBuNC)$_2$(BPEP-Ph)] (**3**). Finally, complex **B** reacts with *t*BuNC to generate [FeBr$_2$(tBuNC)$_4$] (**4**) and free BPEP-Ph.

■ CONCLUSIONS

We have shown that [FeBr(BPEP-Ph)] (**1**) undergoes disproportionation via one-electron transfer in the presence of *t*BuNC. Complex **1** readily combines with 1 equiv of *t*BuNC, but the resulting complex [FeBr(tBuNC)(BPEP-Ph)] (**2**), with a 17e configuration, is sufficiently stable to be isolated as a crystalline solid. On the other hand, when an additional *t*BuNC is present, disproportionation giving [Fe(tBuNC)$_2$(BPEP-Ph)] (**3**), [FeBr$_2$(tBuNC)$_4$] (**4**), and free BPEP-Ph takes place. This reaction very probably involves the 19e intermediate [FeBr(tBuNC)$_2$(BPEP-Ph)] (**A**), which undergoes one-electron transfer with **2**. Although such a disproportionation process involving a 19e Fe(I) species has been documented for several instances including [Fe(C_5H_5)(benzene)] and [Fe(CO)$_3$(PPh$_3$)$_2$]$^+$,[13] most of them are caused by σ-donor ligands such as nitriles, pyridines, and phosphines, where the ligand coordination enhances the reducing ability of 19e species, enabling the subsequent electron transfer. In contrast, disproportionation promoted by π-acid ligands has been scarcely documented.[14] In our present system, it seems reasonable that BPEP-Ph as a strong π-acceptor ligand reduces the reduction potential of the electron-acceptor unit (**2**), thereby facilitating the one-electron transfer. We already confirmed a remarkably positive shift of reduction potential caused by BPEP-Ph for [FeBr$_2$(BPEP-Ph)] (**5**).[5b]

■ EXPERIMENTAL SECTION

Reaction of 1 with *t*BuNC (1 equiv). A solution of **1** (14.0 mg, 0.015 mmol) in toluene (0.4 mL) was cooled to −35 °C in a glovebox freezer, and *t*BuNC (2.0 μL, 0.018 mmol) was slowly added by means of a syringe. The solution was filtrated through a Celite pad and concentrated to dryness under vacuum. The residue was washed with hexane (1.5 mL × 4) and dried under vacuum to give analytically pure **2** (12.1 mg, 0.012 mmol, 79%). **2**: IR (ATR): 2107 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{60}H_{80}N_2P_2BrFe$: C, 70.17; H, 7.85; N, 2.73. Found: C, 70.36; H, 7.81; N, 2.49.

Reaction of 2 with with *t*BuNC. A solution of **2** (4.2 mg, 0.0041 mmol) in C_6D_6 (0.4 mL) was charged into an NMR sample tube, and a C_6D_6 solution of *t*BuNC (0.48 M, 19.5 μL, 0.0094 mmol) was added. The mixture was allowed to stand at room temperature and examined at intervals by ^1H NMR spectroscopy using mesitylene (0.20 M in C_6D_6, 7.0 μL, 0.0014 mmol) as an internal standard. The reaction attained a steady state after ca. 6 h. The mixture was concentrated to dryness and extracted with hexane. The hexane extract was subjected to column chromatography (Al_2O_3) to give BPEP-Ph (1.3 mg, 0.0016 mmol, 39%; eluent: hexane/toluene, 4:1) and [Fe(tBuNC)$_2$(BPEP-Ph)] (**3**) (2.2 mg, 0.0021 mmol, 52%; eluent: Et_2O), respectively. On the other hand, the residue remaining after hexane extraction was dissolved in Et_2O. Slow evaporation of the Et_2O solution at room temperature afforded [FeBr$_2$(tBuNC)$_4$][10] (**4**) (1.0 mg, 0.0019 mmol, 46%). **3**: ^1H NMR (C_6D_6, 298 K): δ 0.82 (s, 9H, *t*BuNC), 0.95 (s, 9H, *t*BuNC), 1.39 (s, 18H, *p*-*t*Bu), 1.59 (s, 18H, *o*-*t*Bu), 1.98 (s, 18H, *o*-*t*Bu), 7.02–7.12 (m, 10H, Ph), 7.21 (br, 1H, 4-Py), 7.44 (s, 2H, Mes*), 7.65 (s, 2H, Mes*), (d, $^3J_{HH}$ = 8.0 Hz, 2H, 3-Py). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 31.4, 31.7, 32.0, 34.7, 35.1, 35.6, 39.5, 39.8, 56.3, 114.6, 121.8, 122.0, 122.2, 124.4, 125.1, 127.4, 128.5, 131.8, 134.8, 136.4, 145.7, 151.6, 155.4, 159.0, 161.2. $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 257.8 (s). IR (ATR): 2094, 2041 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{65}H_{89}N_3P_2Fe$: C, 75.78; H, 8.71; N, 4.08. Found: C, 74.98; H, 8.82; N, 3.94. **4**: ^1H NMR (C_6D_6, 298 K): δ 1.07 (br, 18H, *t*BuNC), 1.26 (br, 18H, *t*BuNC). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 31.1, 31.2, 57.7, 58.1, 162.9, 169.1. IR (ATR): 2165 cm^{-1} (ν_{CN}).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section (supplementary); X-ray data (CIF) for **2** and **3**. 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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