

Synthesis and Characterization of Monomeric (Aryloxo)iron Complexes: $[\text{Fe}^{\text{II}}\text{L}(\text{OAr})]$ and $[\text{Fe}^{\text{III}}\text{L}(\text{OAr})_2]$ $\{\text{L}=\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}^-$

Masami Ito,^{*,#} Hironobu Amagai, Hidenori Fukui, Nobumasa Kitajima, and Yoshihiko Moro-oka^{*}

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

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A series of (aryloxo)iron(II) complexes $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OAr})]$ ($\text{Ar}=\text{C}_6\text{H}_5$ (**4**); $\text{C}_6\text{H}_4\text{-}p\text{-Cl}$ (**5**); $\text{C}_6\text{H}_4\text{-}p\text{-F}$ (**6**); $\text{C}_6\text{H}_4\text{-}p\text{-Me}$ (**7**); $\text{C}_6\text{H}_3\text{-}2,6\text{-Cl}_2$ (**8**); C_6F_5 (**9**)) were synthesized by the anion ligand replacement of $[\text{Fe}(\text{Cl})\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}]$ (**1**) with NaOAr. Crystallography was performed for **1** and **9**. All these tetrahedral (aryloxo)iron(II) complexes react with dioxygen readily, to afford the bis(aryloxo)iron(III) complexes $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OAr})_2]$ ($\text{Ar}=\text{C}_6\text{H}_5$ (**10**); $\text{C}_6\text{H}_4\text{-}p\text{-Cl}$ (**11**); $\text{C}_6\text{H}_4\text{-}p\text{-F}$ (**12**); $\text{C}_6\text{H}_4\text{-}p\text{-Me}$ (**13**); $\text{C}_6\text{H}_3\text{-}2,6\text{-Cl}_2$ (**14**); C_6F_5 (**16**)) as sole isolable products (the maximum yield based on the iron(II) complex was ca. 50%). The MeCN adduct of **13** was structurally characterized by X-ray crystallography.

From a bioinorganic point of view, the coordination environment provided by tris(pyrazolyl)borate ligand is fascinating, since the geometry and the ligand donor set reasonably mimic the coordination of three histidyl nitrogen atoms in a pyramidal array often found at the metal sites in proteins. Such coordination structures have been established by X-ray crystallography for a number of metalloproteins which include hemocyanin,¹⁾ hemerythrin,²⁾ ascorbate oxidase,³⁾ Cu, Zn-SOD,⁴⁾ Fe-/Mn-SOD,^{5,6)} carbonic anhydrase,⁷⁾ and the non-heme iron at the photosynthetic reaction center.⁸⁾ Moreover, numerous other proteins are known to contain a metal ion ligated by one or two histidyl nitrogen atoms.⁹⁾ Previously, with $\text{BH}(\text{pz})_3^-$ or $\text{BH}(3,5\text{-Me}_2\text{pz})_3^-$ as a ligand,¹⁰⁾ model complexes for blue copper proteins,¹¹⁾ hemerythrin,¹²⁾ and hemocyanin¹³⁾ have been successfully synthesized. However, their marked peculiarity in forming bis-chelated complexes ML_2 causes the utility of these ligands to be very limited.

We have recently demonstrated a much higher synthetic utility of a more hindered tris(pyrazolyl)borate ligand $[\text{BH}(3,5\text{-Pr}_2\text{pz})_3]^-$ (hydrotris(3,5-diisopropyl-1-pyrazolyl)borate) over $\text{BH}(\text{pz})_3^-$ and $\text{BH}(3,5\text{-Me}_2\text{pz})_3^-$.^{15,16)} The advantageous characteristics of this ligand are as follows: 1) preventing formation of bis-chelated complexes completely, 2) high solubility in non-coordinating solvents such as toluene and pentane, 3) highly shielding effect of isopropyl groups to stabilize unusual coordination structures, 4) moderate steric hindrance to allow formation of dimeric complexes, 5) strong electron donating property. Owing to these properties, we have succeeded in preparing a series of Cu, Fe, Mn, and Zn complexes with $[\text{BH}(3,5\text{-Pr}_2\text{pz})_3]^-$, some of which serve as models for the active sites of the metalloproteins.^{15–18)}

Here, we describe the preparation of monomeric iron(II) complexes which are coordinatively unsaturated by using $[\text{BH}(3,5\text{-Pr}_2\text{pz})_3]^-$. Many non-heme iron proteins are suggested to be involved in a variety of physiologically important reactions, especially dioxygen metabolism, although the details of the active site structure and the mechanism of the dioxygen activation remain unresolved. The amino acid residues functioning as metal ligands are limited. Thus, the histidyl nitrogen atom is predominant, as described above. The oxygen atoms which come from the amino acid side chains such as threonine, tyrosine, aspartic acid and sulfur atoms of thiolate and thioether from cysteine and methionine can be ligated to the metal. Therefore, our synthetic strategy lies in the synthesis of four or five coordinate monomeric iron(II) complexes $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{X})]$ where X denotes a monoanionic ligand of biological relevance such as RO^- , ArO^- , RCOO^- , and RS^- . The reaction chemistry of the complexes with dioxygen may provide mechanistic insight into the functions of the non-heme iron proteins whose role is dioxygen transport or monooxygenase catalytic reaction. We have already reported the reactivity of the (carboxylato)iron(II) complex, $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OOCCH}_3)]$ toward the dioxygen. In that system, the formation of dinuclear (μ -peroxo)diiron(III) complex could be observed. In the present paper, we describe the synthesis and characterization of the novel tetrahedral (aryloxo)iron(II) complexes and their reaction products resulting upon dioxygen treatment, the bis(aryloxo)iron(III) complexes.

Experimental

Instrumentation. ¹H NMR spectra were recorded on a JEOL-FX-100 (100 MHz) spectrometer. Chemical shifts (δ /ppm) are reported as values downshifted from internal standard SiMe₄. IR works were carried out on a Hitachi 260-50 by the KBr method. Magnetic susceptibilities were determined by the Faraday method on a magnetometer (Shimadzu MB 100) at Ochanomizu University

#Author to whom correspondence should be addressed. Research and Development Center, Oita University, 700 Dannoharu, Oita 870-11.

at 25 °C. Electronic spectra were measured on a Shimadzu UV-260. Field desorption mass spectra (FD-MS) were recorded on a Hitachi M-80. X-Ray data collection and analyses were performed on a four-circle diffractometer (Rigaku AFC-5) interfaced to a FACOM A-70 computer system. (The AFC and CRYSTAN program package used were provided by Rigaku.)

Materials and Methods. All preparations of the iron(II) complexes were performed under an argon atmosphere by using standard Schlenk techniques. Toluene was prepurified by distillation and, prior to use, freshly distilled from sodium benzophenone ketyl under argon. Methylene chloride was dried over calcium hydride and distilled under argon. All deuterium NMR solvents were dried over molecular sieves and distilled prior to use. $\text{K}[\text{BH}(3,5\text{-Pr}_2\text{pz})_3]$ was prepared by the method described before.^{15,16a} $\text{K}[\text{BD}(3,5\text{-Pr}_2\text{pz})_3]$ was prepared in the same method by using KBD_4 (from Aldrich). $\text{K}[\text{BH}(4\text{-Br-}3,5\text{-Pr}_2\text{pz})_3]$ was obtained by KBH_4 and 3,5-diisopropyl-4-bromopyrazole which was synthesized by bromine bromination of 3,5-diisopropyl-pyrazole. Anhydrous iron(II) chloride was purchased from Kanto Chemical Co., Inc. and used without further purification.

[Fe(Cl){BH(3,5-Pr₂pz)₃}] (1). A mixture of 1.87 g (14.7 mmol) of FeCl_2 and 6.18 g (12.3 mmol) of $\text{K}[\text{BH}(3,5\text{-Pr}_2\text{pz})_3]$ was stirred under argon in 30 ml of CH_2Cl_2 overnight. After removal of the salt by filtration, the liquid phase was dried under vacuum. The resultant solid was washed three times with a 10 ml portion of MeCN, resulting analytically pure **1** as a white solid. Yield, 62%; ¹H NMR (CDCl_3 , 25 °C) δ = -27.6 (s, br, 3H, CHMe_2), -9.8 (s, 18H, CHMe_2), 9.4 (s, 18H, CHMe_2), 30.5 (s, 3H, CHMe_2), 32.0 (s, br, 1H, BH), 66.1 (s, 3H, pz); IR 2550 cm^{-1} (BH). μ_{eff} 5.42 μ_{B} /mol. Found: C, 58.13; H, 8.24; N, 14.95; Cl, 6.35%. Calcd for $\text{C}_{27}\text{H}_{46}\text{N}_6\text{BClFe}$: C, 58.24; H, 8.33; N, 15.09; Cl, 6.37%.

[Fe(Cl){BD(3,5-Pr₂pz)₃}] (2). The complex was synthesized in the same manner as that applied for the preparation of **1** using $\text{K}[\text{BD}(3,5\text{-Pr}_2\text{pz})_3]$ instead of $\text{K}[\text{BH}(3,5\text{-Pr}_2\text{pz})_3]$. Yield, 64%; ¹H NMR (CDCl_3 , 25 °C) δ = -34.3 (s, br, 3H, CHMe_2), -13.1 (s, 18H, CHMe_2), 10.4 (s, 18H, CHMe_2), 33.4 (s, 3H, CHMe_2), 64.4 (s, 3H, pz); IR 1900 cm^{-1} (BD).

[Fe(Cl){BH(4-Br-3,5-Pr₂pz)₃}] (3). The complex was prepared by the same method as that used for **1** with $\text{K}[\text{BH}(4\text{-Br-}3,5\text{-Pr}_2\text{pz})_3]$. Yield, 58%; ¹H NMR (CDCl_3 , 25 °C) δ = -38.0 (s, br, 3H, CHMe_2), -12.2 (s, 18H, CHMe_2), 10.4 (s, 18H, CHMe_2), 30.7 (s, 3H, CHMe_2), 44.9 (s, br, 1H, BH). Found: C, 39.59; H, 5.31; N, 9.95; Br+Cl, 34.47%. Calcd for $\text{C}_{27}\text{H}_{43}\text{N}_6\text{Br}_3\text{BClFe}$: C, 40.87; H, 5.46; N, 10.59; Br+Cl, 34.86%.

Synthesis of (Aryloxo)iron(II) Complexes. In a typical experiment, 303 mg (0.54 mmol) of **1** and 86 mg (0.57 mmol) of $\text{Na}(\text{OC}_6\text{H}_4\text{-}p\text{-Cl})$ were stirred in 20 ml of toluene overnight under argon atmosphere. After filtration, the liquid phase was dried under vacuum. Recrystallization of the resultant solid from pentane at -20 °C afforded $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_4\text{-}p\text{-Cl})]$ (**5**) as colorless microcrystalline solids. Yield, 35%. The other (aryloxo)-iron(II) complexes were synthesized in the same manner.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆H₅)] (4). Yield, 42%; ¹H NMR (C_6D_6 , 25 °C) δ = -53.8 (s, br, 3H, CHMe_2), -27.6 (s, br, 1H, $p\text{-Ph}$), -20.6 (s, 18H, CHMe_2), -11.1 (s, br, 2H, $o\text{-Ph}$), 13.1 (s, 18H, CHMe_2), 39.8 (s, 3H, CHMe_2), 56.0 (s, 2H, $m\text{-Ph}$), 59.8 (s, 3H, pz), 63.7 (s, br, 1H, BH); IR 2538 (BH), 1589 cm^{-1} (C=C). Found: C, 64.36; H, 8.38; N, 13.51%. Calcd for $\text{C}_{33}\text{H}_{51}\text{N}_6\text{BOFe}$: C, 64.51; H, 8.37; N, 13.68%.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆H₄- $p\text{-Cl}$)] (5). Yield, 42%; ¹H NMR (C_6D_6 , 25 °C) δ = -43.9 (s, br, 3H, CHMe_2), -17.4 (s, 18H, CHMe_2), -13.1 (s, br, 2H, $o\text{-Ph}$), 11.6 (s, 18H, CHMe_2),

35.1 (s, 3H, CHMe_2), 47.4 (s, 2H, $m\text{-Ph}$), 53.9 (s, 3H, pz), 59.2 (s, br, 1H, BH); IR 2541 (BH), 1585 cm^{-1} (C=C). Found: C, 64.36; H, 8.38; N, 13.51%. Calcd for $\text{C}_{33}\text{H}_{50}\text{N}_6\text{BOClFe}$: C, 64.51; H, 8.37; N, 13.68%.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆H₄- $p\text{-F}$)] (6). Yield, 45%; ¹H NMR (C_6D_6 , 25 °C) δ = -52.7 (s, br, 3H, CHMe_2), -20.2 (s, 18H, CHMe_2), -11.1 (s, br, 2H, $o\text{-Ph}$), 12.9 (s, 18H, CHMe_2), 39.5 (s, 3H, CHMe_2), 48.8 (s, 2H, $m\text{-Ph}$), 60.4 (s, 3H, pz); IR 2552 (BH), 1597 cm^{-1} (C=C). Found: C, 62.65; H, 8.11; N, 12.77%. Calcd for $\text{C}_{33}\text{H}_{50}\text{N}_6\text{BOFeF}$: C, 62.67; H, 7.97; N, 13.29%.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆H₄- $p\text{-Me}$)] (7). Yield, 30%; ¹H NMR (C_6D_6 , 25 °C) δ = -54.6 (s, br, 3H, CHMe_2), -20.1 (s, 18H, CHMe_2), -12.4 (s, br, 2H, $o\text{-Ph}$), 1.3 (s, 3H, Me), 13.1 (s, 18H, CHMe_2), 39.8 (s, 3H, CHMe_2), 57.8 (s, 2H, $m\text{-Ph}$), 59.0 (s, 3H, pz), 64.3 (s, br, 1H, BH); IR 2531 (BH), 1604 cm^{-1} (C=C). Found: C, 65.15; H, 8.79; N, 12.86%. Calcd for $\text{C}_{34}\text{H}_{53}\text{N}_6\text{BOFe}$: C, 64.98; H, 8.50; N, 13.37%.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆H₃-2,6-Cl₂)] (8). Yield, 45%; ¹H NMR (C_6D_6 , 25 °C) δ = -39.0 (s, br, 3H, CHMe_2), -25.6 (s, br, 1H, $p\text{-Ph}$), -16.0 (s, 18H, CHMe_2), 10.7 (s, 18H, CHMe_2), 31.7 (s, 3H, CHMe_2), 45.8 (s, 1H, BH), 54.1 (s, 2H, $m\text{-Ph}$), 61.1 (s, 3H, pz); IR 2540 (BH), 1578 cm^{-1} (C=C). Found: C, 57.81; H, 7.32; N, 12.15; Cl, 10.49%. Calcd for $\text{C}_{33}\text{H}_{49}\text{N}_6\text{BOFeCl}_2$: C, 58.00; H, 7.23; N, 12.30; Cl, 10.38%.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆F₅)] (9). Yield, 39%; ¹H NMR (C_6D_6 , 25 °C) δ = -48.7 (s, br, 3H, CHMe_2), -15.2 (s, 18H, CHMe_2), 11.2 (s, 18H, CHMe_2), 34.1 (s, 3H, CHMe_2), 47.6 (s, br, 1H, BH), 63.8 (s, 3H, pz); IR 2540 (BH), 1589 cm^{-1} (C=C). Found: C, 56.62; H, 6.47; N, 11.86%. Calcd for $\text{C}_{33}\text{H}_{46}\text{N}_6\text{BOF}_5\text{Fe}$: C, 56.31; H, 6.54; N, 11.95%.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆H₅)₂] (10). A toluene solution of **4** (280 mg; 0.46 mmol, in 10 ml) was exposed to pure dioxygen at -78 °C, resulting in an immediate color change of the solution to dark purple. The solution was warmed to room temperature and stirred for 30 min. After removal of toluene under vacuum, the resulting solid was dissolved in 5 ml of pentane, and the residue was removed by filtration. The clear filtrate was cooled at -20 °C overnight, to afford **10** as deep red purple crystals (82 mg, yield 26%). IR 2540 (BH), 1580 cm^{-1} (C=C); UV-vis (pentane, nm, $\epsilon/\text{M}^{-1}\text{cm}^{-1}$) (1 M = 1 mol dm⁻³) 313 (8100), 582 (4150). Found: C, 66.00; H, 8.46; N, 11.57%. Calcd for $\text{C}_{39}\text{H}_{56}\text{N}_6\text{BO}_2\text{Fe}$: C, 66.24; H, 7.98; N, 11.87%.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆H₄- $p\text{-Cl}$)] (11). In a schlenk tube, 323 mg (0.50 mmol) of **5** was dissolved in 10 ml MeCN under argon. At -78 °C, the atmosphere was replaced with pure dioxygen three times with a freeze-thaw method. The solution was warmed to room temperature and stirred for 30 min. Cooling of the resulting deep blue purple solution gave **11** as blue purple prisms. 161 mg, yield 40%; IR 2539 (BH), 1582 cm^{-1} (C=C); UV-vis (pentane, nm, $\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 320 (9900), 572 (3750). Found: C, 60.36; H, 7.51; N, 11.92; Cl, 8.45%. Calcd for $\text{C}_{39}\text{H}_{54}\text{N}_6\text{BCl}_2\text{O}_2\text{Fe}$: C, 60.35; H, 6.95; N, 10.83; Cl, 9.15%.

[Fe{BH(3,5-Pr₂pz)₃}(OC₆H₄- $p\text{-F}$)₂] (12). Complex **6** (201 mg; 0.32 mmol) was dissolved in 20 ml MeCN under argon. The atmosphere was replaced with dioxygen at -78 °C with the freeze-thaw method. After being warmed to room temperature and stirred for 30 min, the solution was concentrated to ca. a half by evaporation. The resultant residue was eliminated by filtration, and the filtrate was cooled at -20 °C overnight to give **12** as red purple crystals (99 mg, yield 42%). IR 2542 (BH), 1580 cm^{-1} (C=C); UV-vis (pentane, nm, $\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 340 (4980), 575 (3300). Found: C, 62.50; H, 7.47; N, 11.31%. Calcd for $\text{C}_{39}\text{H}_{54}\text{N}_6\text{BF}_2\text{O}_2\text{Fe}$: C,

62.94; H, 7.32; N, 11.30%.

[Fe{BH(3,5-Prⁱp₂z)₃}(OC₆H₄-*p*-Me)₂] (13). A toluene solution of **7** (220 mg; 0.35 mmol, in 10 ml) was exposed to dioxygen at -20°C for 30 min. After the atmosphere was replaced with Ar, the solution was warmed to room temperature. The deep blue filtrate was cooled overnight at -20°C , affording **13** as deep blue crystals (70 mg, yield 27%). IR 2538 (BH), 1600 cm^{-1} (C=C); UV-vis (pentane, nm, $\epsilon/\text{M}^{-1}\text{ cm}^{-1}$) 322 (6600), 611 (3400). Found: C, 66.50; H, 7.65; N, 11.76%. Calcd for C₄₁H₆₀N₆BO₂Fe: C, 66.98; H, 8.16; N, 11.43%.

[Fe{BH(3,5-Prⁱp₂z)₃}(OC₆H₃-2,6-Cl)₂] (14). A toluene solution of **8** (251 mg; 0.37 mmol, in 10 ml) was treated with dioxygen at room temperature for 5 h, yielding a dark blue green solution. The toluene was dried under vacuum, and the resulting solid was dissolved in pentane. Cooling of the filtrate resulted in a red residue, which was removed by filtration. The resulting filtrate was cooled at -20°C , affording **14** as dark blue microcrystals (31 mg, 10% yield). IR 2545 (BH), 1572 cm^{-1} (C=C); UV-vis (pentane, nm, $\epsilon/\text{M}^{-1}\text{ cm}^{-1}$) 370 (sh, ca. 5700), 585 (4500). Found: C, 56.06; H, 6.59; N, 9.68%. Calcd for C₃₉H₅₂N₆BCl₄O₂Fe: C, 55.44; H, 6.45; N, 9.93%.

[Fe{BH(3,5-Prⁱp₂z)₃}(OC₆F₅)₂] (15). A pentane solution of **9** (230 mg; 0.33 mmol, in 10 ml) was treated with dioxygen at -78°C . An immediate color change of the solution to dark brownish purple was noted. After being stirred for 20 min at -78°C , the solution was replaced by MeCN, and this was cooled at -20°C overnight. A dark brownish purple powder was obtained by washing with MeCN (10 ml); an analytically pure sample **15** was obtained (88 mg, yield 30%). IR 2542 (BH), 1586 cm^{-1} (C=C); UV-vis (pentane, nm, $\epsilon/\text{M}^{-1}\text{ cm}^{-1}$) 323 (6400), 520 (2300). Found: C, 52.23; H, 5.59; N, 10.08%. Calcd for C₃₉H₄₆N₆BF₁₀O₂Fe: C, 52.78; H, 5.22; N, 9.47%.

[Fe{BH(3,5-Prⁱp₂z)₃}(OC₆H₄-*p*-NO₂)₂] (16). The complex (**16**) was synthesized by use of anhydrous iron(III) chloride. K[(HB(3,5-Prⁱp₂z)₃)] 1.09 g (2.09 mmol) and FeCl₃ 406 mg (2.51 mmol) were dissolved in CH₂Cl₂ (10 ml) and stirred for 5 h. On treatment of the reaction mixture with Na(OC₆H₄-*p*-NO₂) 447 mg (2.51 mmol), a color change from brown to red purple was noted. The solvent was removed under reduced pressure after 10 min. of stirring. The resultant solid was dissolved by Et₂O 10 ml. After removal of the salt by filtration, an analytically pure sample **16** was obtained by recrystallization by adding pentane (88 mg, yield 30%). IR 2555 (BH), 1584 (C=C), 1285 cm^{-1} (NO₂); UV-vis (pentane:Et₂O = 3:1, nm, $\epsilon/\text{M}^{-1}\text{ cm}^{-1}$) 320 (7150), 528 (2360). Found: C, 58.87; H, 7.20; N, 14.21%. Calcd for C₃₉H₃₄N₈BO₈Fe: C, 58.73; H, 6.82; N, 14.05%.

X-Ray Data Collections and Structural Determinations. The single crystals of **1** were prepared by the recrystallization from MeCN, and the crystal was sealed in a thin-wall glass capillary. The diffraction data were collected at room temperature. Single crystals of **9** were prepared by recrystallization from pentane at room temperature. Recrystallization of **13** from MeCN yielded single crystals of MeCN adduct, [Fe{BH(3,5-Prⁱp₂z)₃}(MeCN)(OC₆H₄-*p*-Me)₂](MeCN) (**13**(MeCN))·(MeCN). The crystal was reasonably stable when it was sealed in a thin-wall glass capillary, and the diffraction data were recorded at room temperature. A Mo X-ray source equipped with a graphite-monochromator (Mo K α , $\lambda = 0.710680\text{ \AA}$) was used. Automatic centering and least-squares routines (the AFC program provided by Rigaku) were carried out for all the component at 2θ , ca. 30° , to determine the cell dimensions. Data collection was performed by ω - 2θ scan. The data were corrected for Lorentz and polarization effects. No serious de-

cay of the standard three checked reflections monitored every 100 reflections was observed for any sample. A summary of the cell parameters, data collection details, and refinement results for **1**, **9**, and **13** are given in Table 1.

The positional parameters of iron atoms of all compounds were determined by the Patterson method. Subsequent difference Fourier synthesis located all non-hydrogen atoms, which were refined anisotropically. The hydrogen atoms except on methyl groups and the solvent of crystallization were calculated and fixed for the final refinement cycles isotropically ($d(\text{C-H})$, 1.0 \AA). The calculations were performed by CRYSTAN provided by Rigaku. The weighting scheme is as follows:

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$$

$$\text{with } w = 1/[\sigma(F_o)^2 + (pF_o)^2]$$

$$(p = 0.02 (\textbf{1}), 0.017 (\textbf{9}), \text{ and } 0.017 ((\textbf{13})(\text{MeCN})) \cdot (\text{MeCN}).)$$

The final R (R_w) values and refinement data are presented in Table 1. The disorder of the isopropyl substituents effect the R factor, while the X-ray data shows the good refinement around the metal. In this paper, every structure shows that type of trend.

Full bond lengths, bond angles, anisotropic thermal parameters for non-hydrogen atoms, hydrogen coordinates, and F_o/F_c tables for **1**, **9**, and **13** are available as supplementary material.

Results and Discussion

Synthesis and X-Ray Structure of [Fe(Cl){BH(3,5-Prⁱp₂z)₃}] (1). The reaction of FeCl₂ and K[BH(3,5-Prⁱp₂z)₃] in CH₂Cl₂ yields a monomeric high spin complex **1** of which the crystal structure is presented in Fig. 1. The selected bond distances and bond angles are given in Table 2. Complex **1** is a tetrahedral complex which possesses a crystallographic ally imposed Miller plane. Significant disorders are seen for the position of the methyl groups. The bond length of Fe-Cl (2.20 \AA) is slightly shorter than those found in other known (chloro)iron(II) complexes; 2.25 \AA for [Fe₂Cl₂(OC₆H₄-*p*-Me)₂]²⁻ and 2.29 \AA for [FeCl₄]²⁻.^{19,20} As an analogous complex, Parkin et al. recently reported

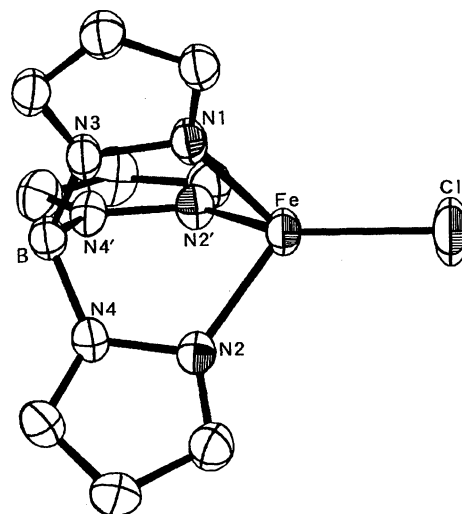


Fig. 1. ORTEP view of [Fe{BH(3,5-Prⁱp₂z)₃}(Cl)] (**1**). Iso-propyl groups were omitted for clarity.

Table 1. Crystal Data Collection Detail for [Fe(BH(3,5-*i*Pr₂pz)₃)(Cl)] (**1**), [Fe(BH(3,5-*i*Pr₂pz)₃)(OC₆F₅)] (**9**), [Fe(BH(3,5-*i*Pr₂pz)₃)(MeCN)(OC₆H₄-*p*-Me)₂·MeCN] ((**13**·MeCN)·MeCN)

| Complex | (1) | (9) | ((13 ·MeCN)·MeCN) |
|--|---|--|--|
| Formula | C ₂₇ H ₄₆ N ₆ BClFe | C ₃₃ H ₄₅ N ₆ OBF ₅ Fe | C ₄₅ H ₆₆ N ₈ O ₂ BF |
| F. W. | 556.81 | 703.61 | 817.73 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>m</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> /Å | 10.031(1) | 25.085(1) | 19.160(3) |
| <i>b</i> /Å | 16.587(3) | 9.660(5) | 18.029(7) |
| <i>c</i> /Å | 9.881(5) | 15.674(5) | 14.172(3) |
| β /° | 102.52(2) | 104.14(3) | 103.44(2) |
| <i>V</i> /Å ³ | 1605.0(5) | 3713(3) | 4762(2) |
| <i>Z</i> | 2 | 4 | 4 |
| <i>D_c</i> /g cm ⁻³ | 1.152 | 1.260 | 1.141 |
| Crystal size/mm | 0.2 × 0.2 × 0.1 | 0.3 × 0.3 × 0.2 | 1.0 × 0.4 × 0.3 |
| Radiation | Graphite-monochromatized Mo <i>K</i> α (λ = 0.710680Å) | | |
| Scan mode | ω -2 θ | | |
| Scan speed/min | 6.0 | | |
| Scan range | 1.30+0.14 tan θ | | |
| 2 θ range/° | 2—50 | | |
| Octant measure | $\pm h, +k, +l$ | $\pm h, +k, +l$ | $\pm h, +k, +l$ |
| No. of measured reflections | 5251 | 7256 | 9328 |
| No. of observed data | 2253 ($F_o \geq 3\sigma(F_o)$) | 3287 ($F_o \geq 6\sigma(F_o)$) | 5528 ($F_o \geq 3\sigma(F_o)$) |
| <i>R</i> /% | 8.0 | 7.7 | 8.0 |
| <i>R_w</i> /% | 7.5 | 9.8 | 8.0 |

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Fe{BH(3,5-*i*Pr₂pz)₃}(Cl)] (**1**)

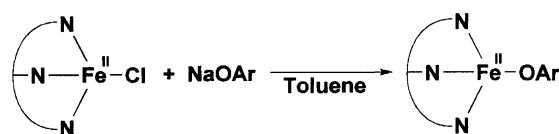
| Distances (Å) | | | |
|---------------|----------|----------|-----------|
| Fe–N1 | 2.054(5) | Fe–N2 | 2.053(4) |
| Fe–C1 | 2.204(2) | N1–N3 | 1.390(8) |
| N2–N4 | 1.392(5) | N3–B | 1.546(11) |
| N4–B | 1.537(6) | | |
| Angles (deg) | | | |
| N2–Fe–N1 | 90.4(2) | N2–Fe–C1 | 124.0(1) |
| N1–Fe–C1 | 126.1(2) | Fe–N1–N3 | 115.2(4) |
| Fe–N2–N4 | 114.9(5) | N1–N3–B | 118.9(5) |
| N2–N4–B | 114.9(3) | N3–B–N4 | 109.4(4) |

the synthesis and the crystal structure of [Fe{BH(3-*i*Bu₂pz)₃}(Cl)].²¹ The structure of the complex is essentially identical to **1**, including the Fe–Cl bond length of 2.23 Å. Other structural features of **1** are not exceptional.

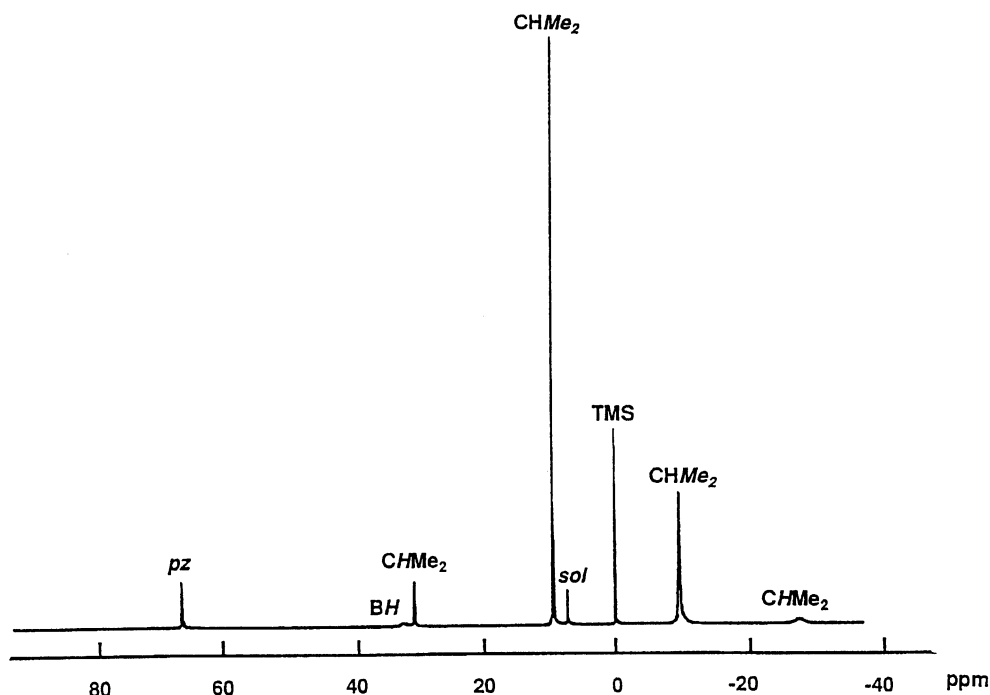
¹H NMR spectroscopy is an effective mean to characterize the present series of high-spin (aryloxo)iron(II) complexes. Figure 2 indicates the ¹H NMR spectrum of **1** recorded in CDCl₃ at room temperature. Paramagnetically shifted resonances are observed in the range of –30—+70 ppm with reasonable resolutions, although some of the signals are considerably broadened. Table 3 represents the ¹H NMR chemical shift of iron(II) complexes which are described here. Comparison of ¹H NMR spectra of complex **2** led to a clear assignment in which the signal observed at 32 ppm is ascribed to the hydrogen on the boron. When the 4-position of pyrazole ring was brominated, the signal at 66 ppm disappeared, indicating that the signal can be assigned to the hydrogen on 4-position of the pyrazole ring. Based on these labeling experiments together with the signal integrations, ¹H NMR

spectrum of **1** can be assigned reasonably as described in Table 3.

Synthesis of (Aryloxo)iron(II) Complexes. Monomeric (aryloxo)iron(II) complexes **4**—**10** were prepared by the simple ligand replacement reaction of **1** with Na(OAr) (Scheme 1). The aryloxo complexes are extremely oxygen sensitive, while the complexes with an electron-withdrawing aryloxo group are relatively stable. All complexes were characterized by ¹H NMR spectroscopy in conjunction with analytical data and IR spectroscopy. Most of the ¹H NMR features of these aryloxo complexes are analogous to those of **1**, while the aryloxo complexes give extra resonances assignable to the phenyl ring protons. For instance, the signals attributable to the proton at the 4-position of the pyrazole ring are observed in the range of 59—61 ppm, which are close to the value of 66 ppm for **1**. This implies that the magnetic property of the series of these aryloxo complexes is essentially identical to that of **1**, leading us to suggest that all these aryloxo complexes are monomeric in solution like **1** is. If the complex has a dinuclear structure, the magnetism should be affected significantly due to the magnetic interaction occurring between the two iron(II) ions through a bis(aryloxo) bridge. Assignments of *o*-Ph proton, *p*-Ph proton, and *m*-Ph proton were performed by the substitution of ligated phenoxide. Thus, –11—13 ppm can be assigned as *o*-Ph proton,



Scheme 1.

Fig. 2. ^1H NMR (100 MHz, at 25 °C) of $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{Cl})]$ (1) in toluene- d_8 .Table 3. Comparison of ^1H NMR Chemical Shift of $[\text{Fe}(\text{BD}(3,5\text{-Pr}_2\text{pz})_3)(\text{X})]$

| Assignment | 1 | 2 | 3 | 4 | |
|-------------------|-------------|-------------|-------------|-------------|-------------|
| CHMe ₂ | −27.6 (3H) | −34.3 (3H) | −38.0 (3H) | −53.8 (3H) | |
| | 30.5 (3H) | 33.4 (3H) | 30.7 (3H) | 39.8 (3H) | |
| CHMe ₂ | −9.8 (18H) | −13.1 (18H) | −12.2 (18H) | −20.6 (18H) | |
| | 9.4 (18H) | 10.4 (18H) | 10.4 (18H) | 13.1 (18H) | |
| BH | 32.0 (1H) | | 44.9 (1H) | 63.7 (1H) | |
| pz | 66.1 (3H) | 64.4 (3H) | | 59.8 (1H) | |
| <i>o</i> -Ph | | | | −11.1 (2H) | |
| <i>p</i> -Ph | | | | −27.6 (1H) | |
| <i>m</i> -Ph | | | | 56.0 (2H) | |
| Assignment | 5 | 6 | 7 | 8 | 9 |
| CHMe ₂ | −43.9 (3H) | −52.7 (3H) | −54.6 (3H) | −39.0 (3H) | −48.7 (3H) |
| | 35.1 (3H) | 39.5 (3H) | 39.8 (3H) | 31.7 (3H) | 34.1 (3H) |
| CHMe ₂ | −17.4 (18H) | −20.2 (18H) | −20.1 (18H) | −16.0 (18H) | −15.2 (18H) |
| | 11.6 (18H) | 12.9 (18H) | 13.1 (18H) | 10.7 (18H) | 11.2 (18H) |
| BH | 59.2 (1H) | 64.3 (1H) | 54.1 (1H) | 47.6 (1H) | |
| pz | 53.9 (3H) | 60.4 (3H) | 59.0 (3H) | 61.1 (3H) | 61.1 (3H) |
| <i>o</i> -Ph | −13.1 (2H) | −11.1 (2H) | −12.4 (2H) | | |
| <i>p</i> -Ph | | | | −25.6 (1H) | |
| <i>m</i> -Ph | 47.4 (2H) | 48.8 (2H) | 57.8 (2H) | 54.1 (2H) | |
| <i>p</i> -Me | | | 1.3 (3H) | | |

1 = $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{Cl})]$, 2 = $[\text{Fe}\{\text{BD}(3,5\text{-Pr}_2\text{pz})_3\}(\text{Cl})]$, 3 = $[\text{Fe}\{\text{BH}(4\text{-Br-}3,5\text{-Pr}_2\text{-pz})_3\}(\text{Cl})]$, 4 = $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_5)]$, 5 = $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_4\text{-}p\text{-Cl})]$, 6 = $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_4\text{-}p\text{-F})]$, 7 = $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_4\text{-}p\text{-Me})]$, 8 = $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Cl}_2)]$, 9 = $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{F}_5)]$.

-25—-28 ppm as *p*-Ph proton, 47—56 ppm as *m*-proton. In the case of the (aryloxo)iron(III) complex, NMR studies on paramagnetic Schiff base complexes have shown that unpaired spin density of iron(III) center is delocalized via a π mechanism, resulting in an alternation in the sign of the contact shift exhibited by the ortho, meta, and para protons of the phenolate moiety.^{22–24)} Thus the lower the energy of the

charge transfer band from phenolato to iron(III), the greater the extent of mixing between the iron d orbital and phenolate orbitals, and the larger the shift observed. However we could not find such a correlation of the NMR contact shift and the substituent of the ligated aryloxo. Namely, the NMR contact shifts of the series of (aryloxo)iron(II) complexes described in this paper do not exhibit any systematic changes

dependent on the substituents of the ligated phenoxide. The plausible reason is that (aryloxo)iron(II) complexes have no CT band at the visible region, that means the phenoxide does not affect the iron(II) $S=4/2$ center very strongly. The same trends are also observed at the monomeric (thiolato)iron(II) and (carboxylato)iron(II) complexes by using $\text{BH}(3,5\text{-Pr}_2\text{pz})_3$ ligand system.

X-Ray Structure of $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{F}_5)]$ (9). In order to ascertain the monomeric structure, we have completed the X-ray structural analysis of **9**. Figure 3 indicates the ORTEP view of **9**. The iron(II) ion adopts a slightly distorted tetrahedral geometry.¹⁸⁾ The particular feature of the structure is the short Fe–O distance (1.875 Å), whereas the Fe–N bond distances are all typical for such bonds (Table 4). Only three X-ray structures of iron(II) complexes containing aryloxo groups are available to date, to our knowledge; a dinuclear bis(aryloxo) complex having a tetrahedral coordination geometry and two examples of five-coordinate iron(II) complex with a Schiff base.^{25,26)} While the number of the examples may not be sufficient to conclude a general trend, the Fe–O bond lengths of these complexes are located in the range of 1.96–2.04 Å. Therefore, the Fe–O distance of **9** is much shorter than those reported for other (aryloxo)iron(II) complexes. Although we do not have any

theoretical interpretation at the present stage, it is noteworthy that the M–X distances of the series of the tetrahedral complexes $[\text{M}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{X})]$ are significantly short; e.g. $[\text{Cu}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{Cl})]$ (Cu–Cl = 2.13 Å),^{16c)} $[\text{Cu}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_4\text{-}p\text{-F})]$ (Cu–O = 1.76 Å),²⁸⁾ $[\text{Zn}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_4\text{-}p\text{-NO}_2)]$ (Zn–O = 1.88 Å),²⁸⁾ $[\text{Cu}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OO}^t\text{Bu})]$ (Cu–O = 1.83 Å),²⁷⁾ $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{SC}_6\text{H}_4\text{-}p\text{-NO}_2)]$ (Fe–S = 2.26 Å).²⁸⁾ This trend is seen even for **1** as already described. The other structural features of **9** are not exceptional.

Reaction of the (Aryloxo)iron(II) Complexes with Dioxygen. The reactions of **4–8** with dioxygen were explored. At the outset of the present work, we expect the formation of a monomeric (superoxo)iron(III) complex or (μ -peroxo)diiron(III) complex at a low temperature. However, such a product was not obtained. Instead, fast ligand transfer reactions of the (aryloxo)iron(II) complexes to bis(aryloxo)iron(III) complexes did take place even at -78°C (Scheme 2). Although we carefully examined the time dependent low temperature electronic spectra during the reactions, no absorption band which could be ascribed to the reaction intermediate was detectable. Such results are very striking for us, because in this ligand system we could observe the (μ -peroxo)diiron(III) complexes by the reaction of (carboxylato)iron(II),¹⁷⁾ (acetylacetonato)iron(II),³⁰⁾ and even (thiolato)iron(II)²⁸⁾ complexes with dioxygen at a low temperature. As a typical example, the time dependent change of the electronic spectrum of the aerobic oxidation of **6** is shown in Fig. 4. Since the rate of the reaction between **6** and dioxygen was not very high, the experiments were carried out at room temperature. With the reaction proceeding, a new band at 575 nm ascribed to the bis(aryloxo) complex **12** developed and reached the maximum within 2 h. From the maximum intensity of the 575 nm band, the yield of **12** from **6** was calcu-

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{F}_5)]$ (**9**)

| Distances (Å) | | | |
|---------------|----------|----------|----------|
| Fe–O | 1.875(5) | Fe–N1 | 2.047(5) |
| Fe–N2 | 2.053(5) | Fe–N3 | 2.077(5) |
| N1–N5 | 1.375(6) | N3–N4 | 1.395(6) |
| N2–N6 | 1.392(6) | N4–B | 1.570(9) |
| N5–B | 1.541(9) | N6–B | 1.51(1) |
| Angles (deg) | | | |
| O–Fe–N1 | 132.2(2) | O–Fe–N2 | 126.6(2) |
| O–Fe–N3 | 113.7(2) | N1–Fe–N2 | 91.9(2) |
| N1–Fe–N3 | 90.0(2) | N2–Fe–N3 | 90.5(2) |
| Fe–N1–N5 | 116.5(4) | Fe–N2–N6 | 114.5(4) |
| Fe–N3–N4 | 113.9(4) | N1–N5–B | 117.4(5) |
| N3–N4–B | 118.6(4) | N2–N6–B | 119.4(5) |

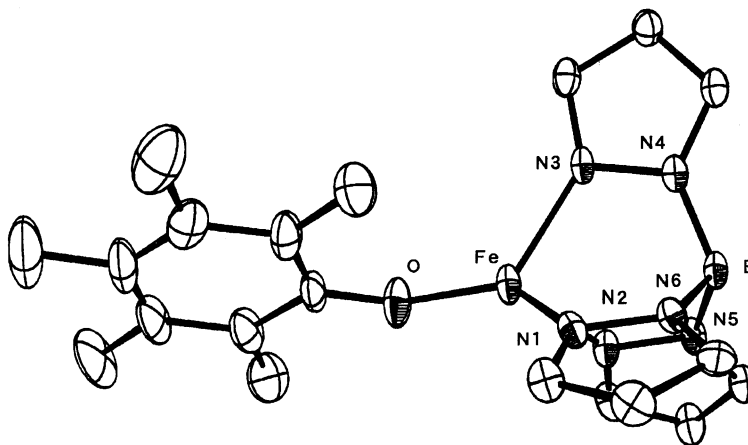
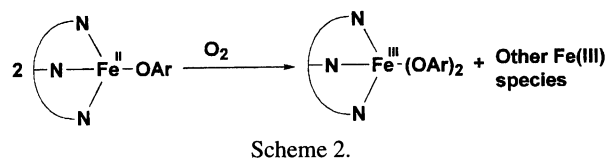


Fig. 3. ORTEP view of $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OC}_6\text{F}_5)]$ (**9**). Isopropyl groups were omitted for clarity.

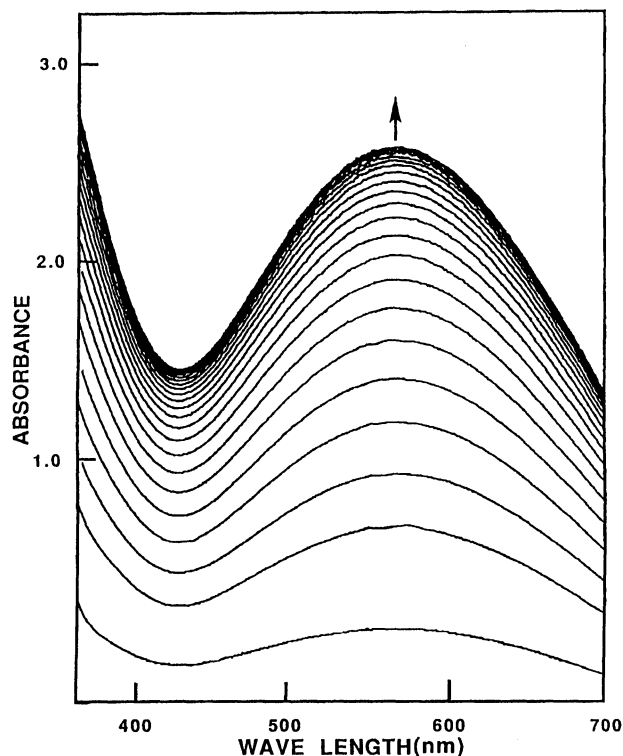


Fig. 4. The aerobic oxidation of **6** at 25 °C in pentane monitored by absorption spectroscopy; the concentration of **6** 0.75 mM; scan interval, 5 min; cell length, 1 cm.

lated to be ca. 50%, which accounts for the stoichiometry of the aryloxo groups. This means that some other iron complex, which does not possess aryloxo as a ligand, should be formed with 50% yield, but we could not identify the species. As possible candidates for the product, we assumed several iron(III) complexes such as a monomeric iron(III) complex $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OH})_2]$. However, other independent experimental results suggested that the formation of this type of monomeric iron(III) complex is unlikely for the present system. Thus, we recently succeeded in preparing a (μ -hydroxo)diiron(II) complex $[[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}_2(\mu\text{-OH})_2]$.³⁰ The treatment of this iron(II) complex with dioxygen resulted in, in part, hydroxylation of the ligand isopropyl groups³¹ as we reported for the aerobic oxidation of an analogous di(μ -hydroxo)dimanganese(II) complex $[[\text{Mn}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}_2(\mu\text{-OH})_2]$.³² However, the hydroxylated complex, initially formed, is very unstable and undergoes a subsequent decomposition to unidentified iron(III) compounds (possibly iron(III) hydroxide and oxide) with formation of free pyrazole 3,5- Pr_2pzH via the decomposition of $[\text{HB}(3,5\text{-Pr}_2\text{pz})_3]^-$. That is confirmed by the isolation of 3,5- Pr_2pzH and no BH signal in the IR spectra of the reaction mixture. In light of these observations, we infer a similarly messy decomposition reaction takes place in the aerobic oxidation of the (aryloxo)iron(II) complex, besides the stoichiometric disproportionation to form the bis(aryloxo) complex.

X-Ray Structure of $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{MeCN})\text{-(OC}_6\text{H}_4\text{-}i\text{-Me)}_2\text{-(MeCN)}]$ ((13**)(MeCN))·(MeCN).** Recrystallization of **13** from MeCN gave single crystals of

the MeCN adduct $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{MeCN})(\text{OC}_6\text{H}_4\text{-}i\text{-Me})_2]$ solvated with MeCN. The IR spectrum of the crystalline sample of ((**13**)(MeCN))·(MeCN) exhibits a sharp band at 2280 cm^{-1} , which is attributable to $\nu(\text{CN})$ of the coordinated MeCN. However, the IR band at 2280 cm^{-1} is easily decreased by drying the complex under vacuum. That indicates the ligated acetonitrile is released from the complex and the coordination number of this complex changed from six to five. The ORTEP view of ((**13**)(MeCN))·(MeCN) is given in Fig. 5. Complex ((**13**)(MeCN))·(MeCN) is a monomeric octahedral iron(III) complex which contains two aryloxo groups with cis-configuration. The selected bond lengths and angles are summarized in Table 5. A number of bis(aryloxo)iron(III) complexes, mostly with a Schiff base ligand, have been studied extensively, particularly in detail by Que and co-workers as models for dioxygenases containing a non-heme iron.³³ The Fe–O bond distances reported for bis(aryloxo)iron(III) complexes are in the range of 1.88–1.93 Å.³⁴ Other structural features are not unusual either.

Absorption Spectra of the Bis(aryloxo) Complexes. (Aryloxo)iron(III) complexes are known to exhibit an intense $\text{ArO-Fe}^{\text{III}}$ LMCT band in a 400–600 nm region.^{22,23} All the bis(aryloxo)iron(III) complexes obtained in the present work exhibit the LMCT band at 570–640 nm. The relatively high wave lengths of the band reflect the strongly electron donating property of $\text{BH}(3,5\text{-Pr}_2\text{pz})_3^-$. Figure 6 shows the pK_a value of substituted phenol vs. the absorbance maxima of the complexes. As pointed out by Que et al., the wave number

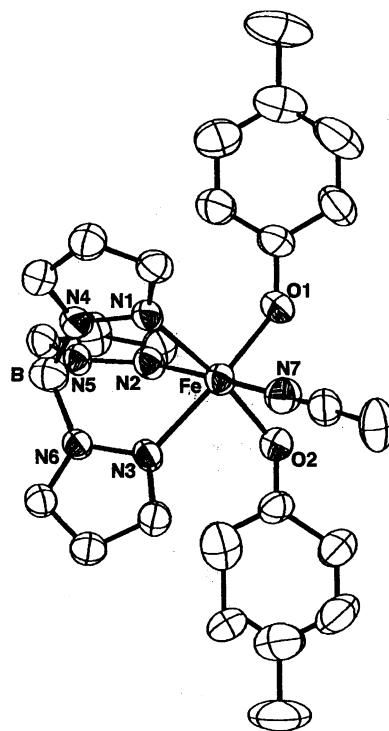


Fig. 5. ORTEP view of $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{MeCN})\text{-(OC}_6\text{H}_4\text{-}i\text{-Me)}_2\text{-(MeCN)}]$ ((**13**)(MeCN))·MeCN. Isopropyl groups and MeCN molecule in the crystal were omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{MeCN})(\text{OC}_6\text{H}_4\text{-}p\text{-Me})_2](\text{MeCN})$ (**13**)(MeCN)·(MeCN)

| Distances (Å) | | | |
|---------------|-----------|----------|----------|
| Fe–O1 | 1.887(1) | Fe–O2 | 1.897(2) |
| Fe–N7 | 2.202(3) | Fe–N1 | 2.193(3) |
| Fe–N2 | 2.144(3) | Fe–N3 | 2.207(3) |
| N1–N4 | 1.383(4) | N2–N5 | 1.379(4) |
| N3–N6 | 1.383(4) | N4–B | 1.537(5) |
| N5–B | 1.547(5) | N6–B | 1.541(5) |
| Angles (deg) | | | |
| O1–Fe–O2 | 94.3(1) | O1–Fe–N7 | 87.7(1) |
| O2–Fe–N7 | 88.9(1) | O1–Fe–N1 | 92.9(1) |
| O1–Fe–N2 | 95.8(1) | O1–Fe–N3 | 92.9(1) |
| O2–Fe–N1 | 172.47(1) | O2–Fe–N2 | 95.1(1) |
| O2–Fe–N3 | 92.8(1) | N7–Fe–N1 | 89.1(1) |
| N7–Fe–N2 | 174.45(1) | N7–Fe–N3 | 88.1(1) |
| N1–Fe–N2 | 86.4(1) | N1–Fe–N3 | 79.9(1) |
| N2–Fe–N3 | 88.0(1) | Fe–N1–N4 | 118.2(2) |
| Fe–N2–N5 | 119.8(2) | Fe–N3–N6 | 115.6(3) |
| N1–N4–B | 120.3(3) | N2–N5–B | 119.5(3) |
| N3–N6–B | 121.5(3) | N4–B–N6 | 108.3(3) |
| N4–B–N5 | 108.6(3) | N5–B–N6 | 109.0(3) |

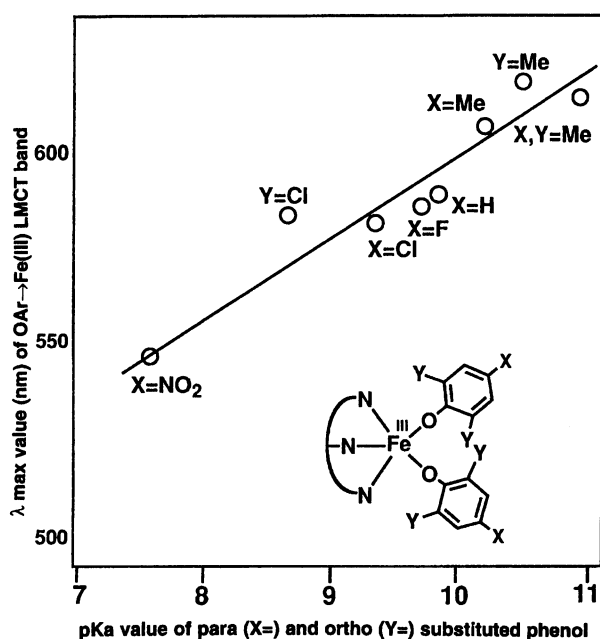


Fig. 6. Plot of the absorbance maximum of $[\text{Fe}\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{OAr})_2]$ in pentane vs. the pK_a value of the ligated aryloxo.

of the LMCT band is strongly correlated with the acidity of the aryloxo group.²² Thus, when the aryloxo group is more electron-donating, the wave length of the LMCT band is blue-shifted. Accordingly, the order of the wave length of the LMCT band is mostly correlated with the pK_a of the corresponding phenol.

Conclusion

Novel iron(II) tetrahedral complexes could be obtained by the reaction of $[\text{Fe}(\text{II})\{\text{BH}(3,5\text{-Pr}_2\text{pz})_3\}(\text{Cl})]$ (**1**) with NaOAr.

The NMR chemical shifts of the each of those iron(II) complexes can be explained by a π mechanism, while paramagnetic shifts are not affected by the substituents of the ligated aryloxo systematically. The reaction of (aryloxo)iron(II) complex with dioxygen afforded bis(aryloxo)iron(III) complex as a sole isolable product. We could not observe any reactive intermediate in the system, while (μ -peroxo)diiron(III) complexes were detected by the reaction of (carboxylato)iron(II), (acetylacetonate)iron(II) and (thiolato)iron(II) complex by using $\text{BH}(3,5\text{-Pr}_2\text{pz})_3$ system with dioxygen. We don't have a clear reason for that difference at the present stage.

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Supplementary Material Available

Atomic coordinates, anisotropic thermal parameters of non-hydrogen atoms, full bond distances and bond angles for **1**, **9**, and $(\text{13})(\text{MeCN})\cdot(\text{MeCN})$ (29 pages), the $F_o - F_c$ data for **1**, **9**, and $(\text{13})(\text{MeCN})\cdot(\text{MeCN})$ (48 pages) are deposited as Document No. 69034 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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