Electronic Structure of Four-Coordinate Iron(I) Complex Supported by a Bis(phosphaethenyl)pyridine Ligand

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Abstract: A 15-electron iron complex with a formal Fe(I) center, [FeBr(BPEP)] (BPEP = 2,6-bis(1-phenyl-2-phosphaethenyl)pyridine), was prepared by one-electron reduction of the dibromide precursor [FeBr₂(BPEP)]. The single-crystal diffraction analysis revealed a distorted trigonal monopyramidal arrangement around the iron center, and SQUID magnetometry established the $S = 3/2$ ground state. The Mössbauer isomer shift value ($\delta = 0.59$ mm/s) was consistent with a high-spin Fe(I) center of [FeBr(BPEP)]. DFT calculations for a model complex revealed two highly delocalized molecular orbitals formed by bonding and antibonding interactions between the d_{z^2} (Fe) and π^* (BPEP) orbitals. Orbital occupancy analysis demonstrated the electronic structure with a high-spin Fe(I) center. The effective $d\pi - p\pi$ interaction between iron and BPEP was concluded to be responsible for the highly distorted structure of [FeBr(BPEP)], with its rather uncommon trigonal monopyramidal configuration.

Coordinatively unsaturated complexes with low-valent iron centers have been recognized as key intermediates in catalytic transformations and metalloenzymatic activation systems.[1,2] Low-coordinate Fe(I) complexes have attracted particular interest recently because of their capabilities in small-molecule activation.[3] However, there are a limited number of well-defined Fe(I) complexes, and their highly changeable spin states, which are thought to be responsible for the complexity of iron-catalyzed reactions, are not well understood.[3i,4] For example, a recent report by Chirik et al. demonstrated the profundity of iron chemistry.[5] They found that [FeCl(ⁱPrPDI)] (**3**; ⁱPrPDI = 2,6-(ⁱPr₂C₆H₃N=CMe)₂C₅H₃N), a formal Fe(I) complex with a ground state of $S = 3/2$, is in reality an Fe(II) complex, with the Fe(II) center ($S = 2$) coupled with a ligand-centered radical ($S = 1/2$) to form the $S = 3/2$ state.

Herein we report a four-coordinate complex, [FeBr(BPEP)] (**2**), supported by a novel 2,6-bis(1-phenyl-2-phosphaethenyl)pyridine ligand (BPEP, Scheme 1). BPEP is a phosphaalkene analogue of 2,6-bis(imino)pyridines such as ⁱPrPDI (in **3** above). Unlike imines, however, phosphaalkenes, containing a P=C bond, have an extremely low-lying π^* orbital as well as high-lying lone pair electrons and effectively stabilize low-valent transition-metal complexes.[6] We found that this unique ligand property allowed successful stabilization of **2**, which contains a coordinatively unsaturated 15-electron system with a high-spin Fe(I) center.

Scheme 1

Mes* = 2,4,6,-tri-*tert*-butylphenyl
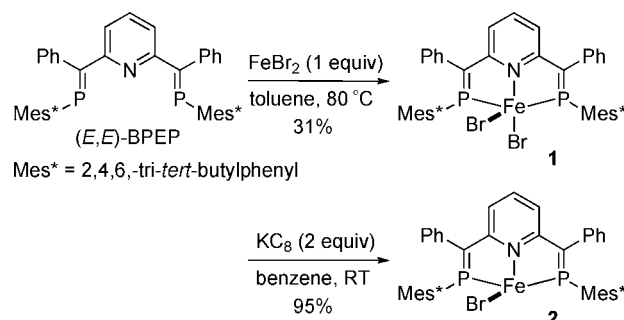
The BPEP-coordinated iron dibromide [FeBr₂(BPEP)] (**1**) was synthesized in 31% yield by the reaction of FeBr₂ with (*E,E*)-BPEP in toluene at 80 °C. SQUID magnetization data established a ground state of $S = 2$, which is consistent with a high-spin Fe(II) center. The Mössbauer spectroscopic parameters ($\delta = 0.78$ mm/s, $\Delta E_Q = 2.96$ mm/s) were also in the range of high-spin Fe(II) complexes.[7] The geometric structure was determined by single-crystal X-ray analysis, showing a pseudo square pyramidal configuration around the iron atom.

Complex **1** underwent one-electron reduction with KC₈ at ambient temperature to give [FeBr(BPEP)] (**2**) in 95% yield. The magnetic moment of **2** ranged from 3.5 to 4.2 μ_B at 5−300 K, demonstrating an $S = 3/2$ ground state. The Mössbauer isomer shift of $\delta = 0.59$ mm/s ($\Delta E_Q = 2.68$ mm/s) was clearly smaller than that of **1** and relatively closer to the values hitherto reported for four-coordinate Fe(I) complexes with high-spin states (0.41−0.46 mm/s).[3i,8] Actually, the observed isomer shift was consistent with the calculated value for a model compound of **2** with a high-spin Fe(I) center (0.64 mm/s, vide infra).

Figure 1 shows the X-ray structure of **2**. The iron atom adopts neither a tetrahedral nor square planar configuration but rather a distorted trigonal monopyramidal configuration, which is uncommon for four-coordinate iron complexes.[9] The basal plane is composed of the two phosphorus and the bromine and iron atoms, while the nitrogen atom occupies the apex.[10,11] The sum of the angles in the basal plane is nearly 360°. The P=C bond lengths (1.719(6), 1.713(6) Å) are comparable to those of **1** (1.712(11), 1.681(11) Å); however, the Fe−P (2.2716(17), 2.2883(17) Å) and Fe−N (2.035(5) Å) bond lengths are significantly shorter than those of **1** (2.501(4), 2.507(4), and 2.216(9) Å, respectively) and in the range of formal Fe(I) complexes with high-spin states.[3d,5]

A remarkable feature of **2** is the highly distorted structure, which appears to have been formed by elimination of one of the equatorial Br atoms from **1**. Another point that we noted
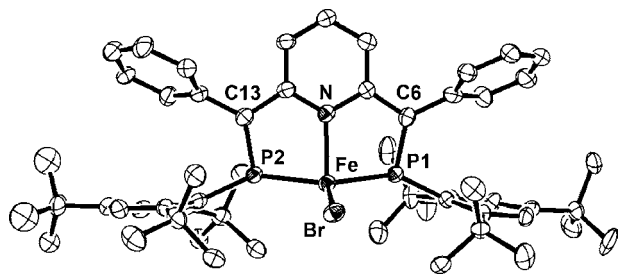
Figure 1. ORTEP drawing of [FeBr(BPEP)] (**2**) with 50% probability ellipsoids. Hydrogen atoms, a disordered ^tBu group, and an E_2O molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe−P1, 2.2716(17); Fe−P2, 2.2883(17); Fe−N, 2.035(5); Fe−Br, 2.3304(10); P1−C6, 1.719(6); P2−C13, 1.713(6); P1−Fe−P2, 132.27(7); P1−Fe−Br, 112.27(5); P2−Fe−Br, 115.32(5); N−Fe−Br, 119.19(13); N−Fe−P1, 80.04(14); N−Fe−P2, 80.35(14).

was the Mössbauer isomer shift consistent with a high-spin Fe(I) center. To study these points in detail, we carried out DFT calculations for the model compound [FeBr(bpep)] (**2a**), in which the 2,4,6-tri-*tert*-butylphenyl (Mes*) groups on the BPEP ligand are replaced by 3,5-dimethylphenyl (Xyl) groups (Figure 2).

The distorted trigonal monopyramidal geometry of **2** was reproduced in the optimized structure of **2a**^{dis}. Figure 2 illustrates important natural orbitals of the distorted complex **2a**^{dis}. The orbital occupancy values given in parentheses were evaluated by broken symmetry DFT calculations. Five of the seven d electrons are found in metal-localized orbitals as unpaired [B (d_{yz}, 1e), C (d_{xz}, 1e), D ($d_{x^2-y^2}$, 1e)] and paired electrons [F (d_{xy}, 2e)], respectively. The other two electrons are accommodated in the highly delocalized orbitals A and E, formed by antibonding and bonding interactions between the π^* (bpep) and d_{z^2} (Fe) orbitals, with orbital occupancies of 0.24 and 1.76, respectively. Although the orbital symmetry between π^* and d_{z^2} may be considered inconsistent, the distorted trigonal monopyramidal geometry, in which the iron atom is lifted significantly off the PNP plane (∠P−Fe−P = 132.5°), enables effective interaction between these orbitals. The total spin density of the iron was estimated as 3.33, which is in accordance with the Fe(I) center of **2**. The Mössbauer isomer shift for **2a**^{dis} was estimated as $\delta = 0.64$ mm/s.
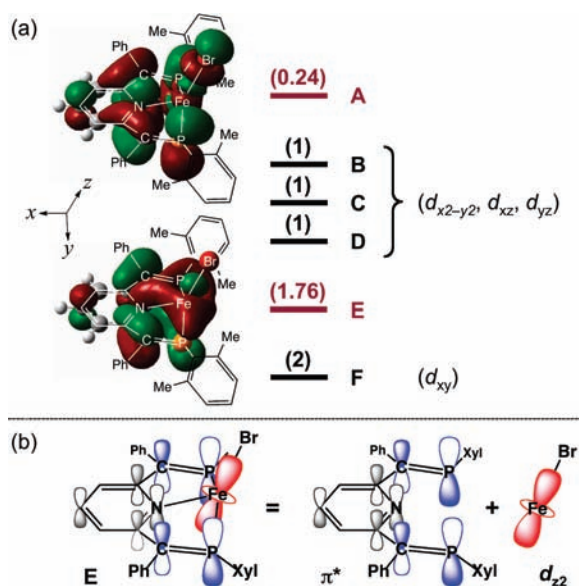
Figure 2. (a) Natural orbital diagram for a model compound with distorted trigonal monopyramidal geometry (**2a**^{dis}). The values in parentheses represent orbital occupancy. (b) A schematic view of the orbital interaction between bpep and iron in molecular orbital E.

The electronic structure of the square planar complex **2a**^{sp} was examined in a similar fashion. The optimized structure of **2a**^{sp} was 15.9 kcal/mol higher in energy than that of **2a**^{dis}. Interestingly, **2a**^{sp} had a sextet ground state ($S = 5/2$), which would be regarded as consisting of a high-spin Fe(II) center ($S = 2$) and a ligand-localized radical ($S = 1/2$). The Fe−P bonds were elongated by 0.11 Å, and the Mayer's bond order decreased accordingly, compared with **2a**^{dis}. Thus the weaker bonding interaction between Fe and P in **2a**^{sp} than in **2a**^{dis} was evidenced.

In conclusion, we succeeded in synthesizing a coordinatively unsaturated complex with a formal Fe(I) center (**2**), using BPEP as a PNP pincer-type phosphaalkene ligand. The complex adopts a distorted trigonal monopyramidal configuration, which enables an effective bonding interaction between the d_{z^2} orbital of iron and the π^* orbital of BPEP. Mössbauer spectroscopy and theoretical calculations revealed the electronic structure that is assignable to a high-spin Fe(I) complex. These features are remarkably different from those of **3**, which contains ^iPrPDI, a nitrogen analogue of BPEP: **3** adopts a square planar configuration and has an Fe(II) center.[5] It is likely that the presence of an extremely low-lying π^* orbital,[12] which is characteristic of phosphaalkene ligands, is responsible for the unique geometry and electronic structure of **2**. The reactivity of this novel 15-electron iron system is currently under investigation.

Supporting Information Available: Experimental procedures and crystallographic data of **1** and **2**; computational methods and data for DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Note that the structure of **2** is significantly distorted from the ideal trigonal monopyramidal geometry, owing to the rigid pincer-type ligand structure of BPEP.

(11) The possibility of the hydrido structure [FeH(Br)(BPEP)] was excluded for the following reasons. (a) No notable absorption was observed in the metal hydride region of the IR spectrum (1700−2200 cm^{-1}). (b) Complex **2** readily combined with PhCN to form the five-coordinate complex [FeBr(PhCN)(BPEP)] (see Supporting Information).

(12) The π^* orbital of a truncated model of bpep (3,5-(HP=CH)$_2$C$_5$H$_3$N) was located 0.78 eV lower than that of pdi (3,5-(HN=CH)$_2$C$_5$H$_3$N) by DFT calculations.

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