High-spin and low-spin iron(II) complexes with facially-coordinated borohydride ligands†

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Rare examples of monometallic high-spin and low-spin $L_3Fe(H_3BH)$ complexes have been characterized, where the two L_3 ligands are $[Tp^{Ph_2}]$ and $[PhBP_3]$ ($[Tp^{Ph_2}] = [HB(3,5-Ph_2pz)_3]^-$ and $[PhBP_3] = [PhB(CH_2PPh_2)_3]^-$). The structures are reported wherein the borohydride ligand is facially coordinated to the iron center in each complex. Density functional methods have been employed to explain the bonding in these unusual iron(II) centers. Despite the differences in spin states, short Fe–B distances are observed in both complexes and there is significant theoretical evidence to support a substantial bonding interaction between the iron and boron nuclei. In light of this interaction, we suggest that these complexes can be described as $(L_3)Fe(\eta^4-H_3BH)$ complexes.

Introduction

Paramagnetic iron hydrides have been invoked as intermediates in the catalytic cycle of hydrogenases and nitrogenases.¹ Particularly noteworthy is a recent study by Hoffman and co-workers giving evidence for an iron hydride intermediate during nitrogenase turnover.² On the basis of their biophysical ENDOR studies, a high-spin iron hydride intermediate is observed which may correspond to either E2 or E4 in the Thorneley–Lowe kinetic scheme.³ Diamagnetic iron hydrides have been extensively studied by several laboratories.⁴ We decided to explore the coordination chemistry of borohydride anions as a possible route to paramagnetic iron hydrides, since in some instances, late transition metal borohydride adducts can serve as precursors to metal hydrides.⁵

Transition metal and lanthanide tetrahydridoborate complexes with varying degrees of stability and reactivity have been reported,⁶ including recent reports of a nickel tetrahydridoborate complex⁷ and a Mo–Fe cluster with terminal borohydride anions.⁸ Although low-spin hexahydridoborate-bridged diiron(II) complexes were recently reported,⁹ mononuclear iron tetrahydridoborate complexes are rare.^{10,11} Prior attempts to isolate the homoleptic borohydride $Fe(BH_4)_2$ were hindered by complex product mixtures due to the thermal instability of the product(s).¹¹ These homoleptic complexes have not been structurally characterized.

Sterically hindering ligands can lend kinetic stability to reactive inorganic species, and replacement of one BH_4^- unit with a more sterically encumbering tridentate borate ligand results in a marked increase in the stability of iron(II) borohydride derivatives. To the best of our knowledge, only one structurally characterized, monometallic Fe^{II} -borohydride complex has been reported, $[FeH(H_2BH_2)\{CH_3C(CH_2PPh_2)_3\}]$.¹⁰

We give an account herein of the synthesis of mononuclear $(L_3)Fe^{II}(BH_4)$ complexes that are stable at room temperature. The borohydride ligand is facially coordinated to the iron center in both the high-spin complex ($L_3 = [Tp^{Ph_2}]$) and the low-spin complex ($L_3 = [PhBP_3]$). The literature precedent has been to describe these interactions as tridentate or η^3 -complexes of borohydride.^{6,12} In general, borohydrides give rise to interesting structural features, and their three-centered two-electron bonding can lead to a variety of hapticities for the borohydride ligand.¹² Here, a combination of structural, spectroscopic and theoretical methods is used to probe the nature of these species and to address their different spin-states. On the basis of these calculations, we suggest it may be more accurate to describe the binding as an η^4 interaction.

Experimental

General

All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Nonhalogenated solvents were tested with a standard purple solution of benzophenone ketyl in tetrahydrofuran to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Elemental analyses were performed either by Atlantic Microlab, Norcross, GA, or by Desert Analytics, Tucson, AZ. Varian 300 MHz spectrometers were used to record the 1H NMR and ^{31}P NMR

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spectra at ambient temperature. ^1H chemical shifts were referenced to residual solvent, while ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4 at δ 0 ppm. ^{11}B NMR were acquired on a JEOL 400 MHz spectrometer, and the chemical shifts were referenced to neat $\text{BF}_3\cdot\text{OEt}_2$ at δ 0 ppm. IR measurements were taken on **1** as KBr pellets using an Avatar 320 FTIR spectrometer controlled by EZ Omnic software set at 4 cm^{-1} resolution, or in the case of **2** were obtained with a KBr solution cell using a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Bio-Rad Merlin Software (v. 2.97) set at 4 cm^{-1} resolution.

Magnetic measurements on **1** were recorded using a Quantum Designs SQUID magnetometer running Magnetic Property Measurement System Rev. 2 software. Data were recorded at 5000 G. The sample was suspended in the magnetometer in a plastic straw sealed under nitrogen with Lilly No. 4 gel caps. Loaded samples were centered within the magnetometer using the DC centering scan at 35 K and 5000 G. Data were acquired at 4–30 K (one data point every 2 K) and 30–300 K (one data point every 5 K). The magnetic susceptibility was adjusted for diamagnetic contributions using the constitutive corrections of Pascal's constants. The molar magnetic susceptibility (χ_m) was calculated by converting the calculated magnetic susceptibility (χ) obtained from the magnetometer to a molar susceptibility (using the multiplication factor $\{(\text{molecular weight})/[(\text{sample weight})(\text{field strength})]\}$). The mass used for **1** was the unsolvated neutral complex. Effective magnetic moments were calculated using eqn (1).

$$\mu_{\text{eff}} = (7.997\chi_m T)^{1/2} \quad (1)$$

Metal complex syntheses

[Tp^{Ph2}]Fe(H₃BH), 1. A solution of $\text{Fe}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.20 g, 0.5 mmol) in CH_3CN (5 mL) was added dropwise to a mixture of the Tp^{Ph2} ligand¹³ (0.35 g, 0.5 mmol) and KBH_4 (0.027 g, 0.5 mmol). The resulting white suspension was stirred overnight at RT. The solvent was then removed *in vacuo* and the crude white powder was dissolved in 5 mL CH_2Cl_2 . The solution was filtered and the filtrate was kept for slow vapor diffusion of ether. After standing unperturbed overnight an off-white crystalline solid was collected. Yield: 0.12 g (33%). Anal. Calc. for **1**, $\text{C}_{45}\text{H}_{38}\text{B}_2\text{FeN}_6$: C, 73.01; H, 5.17; N, 11.35. Found: C, 72.25; H, 5.09; N, 11.26; Cl, 1.12%. Trace chloride is always observed in the elemental analysis despite repeated attempts to further purify the sample.

[PhBP₃]Fe(H₃BH), 2. This compound was synthesized by metathesis of the previously reported iron chloride complex $[\text{PhBP}_3]\text{FeCl}^{14}$ (0.10 g, 0.13 mmol) with a large excess (30 $\times$) of NaBH_4 (0.15 g, 3.9 mmol) in THF (5 mL) at room temperature. After stirring overnight, the solution was filtered and the volatiles were removed under reduced pressure. The resultant dark red solid was taken up in benzene and crystallized from vapor diffusion of petroleum ether (bp 35–60 °C) into the solution. Yield: 0.095 g, (97%). Anal. Calc. for **2**, $\text{C}_{45}\text{H}_{55}\text{B}_2\text{FeP}_3$: C, 71.47; H, 6.00. Found: C, 71.07; H, 6.09%. ^1H NMR (300 MHz, C_6D_6): δ 8.10 (d, $J = 7.5$ Hz, 2H); 7.69 (t, $J = 7.5$ Hz, 2H); 7.49 (br s, 12H); 7.45 (overlaps with resonance at 7.49 ppm, t, $J = 7.5$ Hz, 1H); 6.72 (m, 18H); 1.54 (s, 6H); –11.8 (br s, 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6): δ 76.2 (s). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.3 MHz, C_6D_6): δ 22.2 (br s,

BH_4^-); –12.9 (s, $\text{PhB}(\text{CH}_2\text{PPh}_2)_3^-$). IR (KBr/ C_6H_6): 2603 cm^{-1} (w); 2575 cm^{-1} (m).

X-Ray diffraction analysis

$[\text{Tp}^{\text{Ph}_2}]\text{Fe}(\text{H}_3\text{BH})$ (**1**) was characterized using X-ray diffraction at the X-ray Crystallographic Laboratory at the University of Minnesota. A crystal of **1** was attached to the tip of a glass capillary on a Siemens SMART Platform CCD diffractometer for data collection at 173(2) K using graphite-monochromated Mo-K α ($\lambda = 0.71073\text{ \AA}$). X-Ray diffraction studies on $[\text{PhBP}_3]\text{Fe}(\text{H}_3\text{BH})$ (**2**) were carried out in the Beckman Institute Crystallographic Facility at Caltech on a Bruker Smart 1000 CCD diffractometer. The crystal was mounted on a glass fiber with Paratone N oil. A summary of the crystallographic details for both **1** and **2** is given in Table 1. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms except those attached to boron atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydride atoms were found from the E-map and refined independently. The final full matrix least squares refinement converged to $R1 = 0.0281$ and $wR2 = 0.0648$ for **1** and $R1 = 0.0515$ and $wR2 = 0.0838$ for **2**.

CCDC reference numbers: 250211 for **1** and 250212 for **2**.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509580h

Computational methods

Models for **1** and **2** in which the phenyl rings on the ligands were replaced by H atoms were fully optimized at the *m*PWPW91 level¹⁵ of density functional theory.¹⁶ A basis set was employed that combined the CEP-31G effective core potential and associated basis functions on Fe¹⁷ with the polarized McLean–Chandler basis set on P¹⁸ and the 6-311G(d,p) basis set¹⁹ on all other atoms (for a total of 421 and 301 basis functions, respectively, for the simplified analogs of **1** and **2**). The optimized Kohn–Sham determinantal wave functions were used for the computation of Mayer bond orders²⁰ and in the depiction of molecular orbitals.

Table 1 Summary of crystallographic data for $[\text{Tp}^{\text{Ph}_2}]\text{Fe}(\text{H}_3\text{BH})$, (**1**) and $[\text{PhBP}_3]\text{Fe}(\text{H}_3\text{BH})$, (**2**)

	1	2
Chemical formula	$\text{C}_{45}\text{H}_{38}\text{B}_2\text{FeN}_6$	$\text{C}_{45}\text{H}_{55}\text{B}_2\text{FeP}_3$
M_r	740.28	756.19
Space group	$R3c$	$C2/c$
$a/\text{\AA}$	16.185(1)	39.226(4)
$b/\text{\AA}$	16.185(1)	13.006(1)
$c/\text{\AA}$	25.833(3)	16.141(2)
$a/^\circ$	90	90
$\beta/^\circ$	90	110.695(4)
$\gamma/^\circ$	120	90
$V/\text{\AA}^3$	5860.7(9)	7703.1(1)
Z	6	8
$D_c/\text{g cm}^{-3}$	1.258	1.304
T/K	173(2)	100(2)
μ/cm^{-1}	4.26	5.48
$R1/wR2^a$ ($I > 2\sigma(I)$)	0.0281/0.0621	0.0515/0.0785
$R1/wR2$ (all data)	0.0357/0.0648	0.0971/0.0838

^a $R1 = \sum \|F_o\| - \|F_c\| / \sum F_o$, $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ where $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$.

Results and discussion

Treatment of iron(II) perchlorate with the scorpionate ligand, potassium hydrotris(3,5-diphenylpyrazol-1-yl)borate $\text{K}[\text{Tp}^{\text{Ph}_2}]$ and KBH_4 in acetonitrile results in the formation of an off-white solid, which upon recrystallization from methylene chloride–diethyl ether gives rise to clear colorless blocks of $[\text{Tp}^{\text{Ph}_2}]\text{Fe}(\text{BH}_4)$ (**1**). Metathesis of $[\text{PhBP}_3]\text{FeCl}^{14}$ with an excess of NaBH_4 in THF results in the formation of a deep red solution. After removal of the sodium salts, recrystallization of the crude red powder affords ruby red crystals of $[\text{PhBP}_3]\text{Fe}(\text{BH}_4)$ (**2**). Unlike the reported synthesis of $[\text{FeH}(\text{H}_2\text{BH}_2)]\{\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3\}$, we do not observe an intermediate dinuclear μ_3 -trihydride in either synthesis.¹⁰ In contrast to $\text{Fe}(\text{BH}_4)_2$,¹¹ both **1** and **2** are thermally stable at room temperature.

Single-crystal X-ray diffraction studies confirmed **1** and **2** to be $(\text{L}_3)\text{Fe}^{\text{II}}(\text{BH}_4)$ complexes (Fig. 1, Table 2), with the absence of counterions in both structures providing support for the iron(II) oxidation state assignment. Both the monoanionic ancillary ligand ($[\text{Tp}^{\text{Ph}_2}]$ or $[\text{PhBP}_3]$) and the BH_4^- anion are coordinated facially to the iron center in each complex, generating an effective C_3 -axis of symmetry that contains the ligand boron atom, the iron atom, and the boron atom of the borohydride in each case. The Tp^{Ph_2} complex **1**, in fact, lies on a crystallographic three-fold axis, making only a third of the molecule crystallographically unique. Additionally, the iron centers of both **1** and **2** can be described as having a trigonally distorted octahedral geometry (for **1**: B2-Fe-N11 $126.10(4)^\circ$ and $\text{N11-Fe-N11}'$ $88.81(5)^\circ$; for **2**: $\text{B2-Fe-P}_{\text{av}}$ $125.09(5)^\circ$, $\text{P}_{\text{av}}\text{-Fe-P}_{\text{av}}$ $90.21(2)^\circ$).

The Fe–N11 bond length in **1** ($2.106(1)$ Å) is comparable to those found for $[\text{Tp}^{\text{Ph}_2}]\text{Fe}(\kappa^2\text{-O}_2\text{CPh})$ (Fe– N_{av} $2.111(1)$ Å),²¹ consistent with a high-spin iron(II) center. On the other hand, the Fe– P_x bond lengths of **2** (Fe– P_{av} $2.2061(4)$ Å) are comparable to the Fe– P_x distances in either the low-spin pseudo-tetrahedral imide $\{[\text{PhBP}_3]\text{Fe}^{\text{II}}\equiv\text{NAd}\}^-$ (Fe– P_{av} $2.142(6)$ Å) or the low-spin octahedral species $\{[\text{PhBP}_3]\text{Fe}(\text{NCCH}_3)_3\}$ (FeCl_4) (Fe– P_{av} $2.280(1)$ Å).^{22,23} Accordingly the BH_4^- ligand in each case is structurally distinct. The Fe–H3 distance of $1.99(2)$ Å in **1** is significantly longer than the average Fe–H distance of $1.60(2)$ Å in **2**.

Fig. 1 ORTEP plot of $[\text{Tp}^{\text{Ph}_2}]\text{Fe}(\text{H}_3\text{BH})$ (**1**) and $[\text{PhBP}_3]\text{Fe}(\text{H}_3\text{BH})$ (**2**) showing 50% probability thermal ellipsoids and the labelling scheme for selected atoms. All hydrogen atoms, except those attached to boron atoms, as well as a one 3-phenyl group on **1** and all but the *ipso*-carbons of the phenyl rings on **2** have been omitted for clarity.

Table 2 Selected bond distances and angles for $[\text{Tp}^{\text{Ph}_2}]\text{Fe}(\text{H}_3\text{BH})$, (**1**), and $[\text{PhBP}_3]\text{Fe}(\text{H}_3\text{BH})$, (**2**)

Complex 1			
Fe–B2	2.084(4)	B2–Fe–N11	126.10(4)
Fe–H3	1.99(2)	N11–Fe–N11'	88.81(5)
B2–H3	1.16(2)	B2–Fe–H3	33.1(7)
B2–H2	0.98(5)	Fe–B2–H3	69(1)
Fe–N11	2.106(1)	Fe–B2–H2	180.000(3)
		H3–B2–H2	111(1)
Complex 2			
Fe–B2	1.855(2)	B2–Fe–P1	124.24(5)
Fe–H47	1.57(2)	B2–Fe–P2	126.54(5)
Fe–H48	1.62(2)	B2–Fe–P3	124.50(5)
Fe–H49	1.61(2)	P1–Fe–P2	92.06(2)
B2–H47	1.20(2)	P2–Fe–P3	89.03(2)
B2–H48	1.18(2)	P3–Fe–P1	89.53(2)
B2–H49	1.26(2)	B2–Fe–H47	39.9(7)
B2–H46	1.07(2)	B2–Fe–H48	39.0(5)
Fe–P1	2.2119(4)	B2–Fe–H49	41.9(6)
Fe–P2	2.2088(4)	Fe–B2–H47	57.2(8)
Fe–P3	2.1977(4)	Fe–B2–H48	59.5(7)
		Fe–B2–H49	58.7(7)
		Fe–B2–H46	178.6(9)
		H46–B2–H47	124(1)
		H46–B2–H48	121(1)
		H46–B2–H49	120(1)

Solid-state magnetic susceptibility data for **1** were obtained from 4–300 K by SQUID magnetometry (Fig. 2). The plot of $\chi_m T$ vs. temperature is consistent with a high-spin iron(II) ($S = 2$) center. Curie–Weiss behavior was verified by a plot of χ_m^{-1} vs. T (inset). From 10 to 300 K the average value of μ_{eff} is $5.07 \mu_B$. This value unambiguously establishes the high-spin character of the iron(II) center in **1**. Not surprisingly the value deviates from the spin-only value of $4.899 \mu_B$, as expected for an electronic configuration with a spin–orbit coupling contribution.

Interestingly, the Fe–B2 distances in both complexes are rather short. The Fe–B2 distance in **1** of $2.084(4)$ Å is less than the Fe–N11 distance. The geometry observed in the high-spin iron(II) complex **1** is closely related to that observed in $[\text{Tp}^*]\text{Ni}(\text{H}_3\text{BH})$ which also has a short Ni–B distance of $2.048(5)$ Å.⁷ These nickel and iron

Fig. 2 SQUID magnetometry data for **1** plotted as $\chi_m T$ vs. T . The inset shows the same data plotted as χ_m^{-1} vs. T (slope = 0.311 , intercept = 0.025 , $R^2 = 0.9999$).

complexes exhibit similar distortions of the borohydride anion. In both cases the coordinated borohydride is essentially tetrahedral, showing only a slight elongation of the B–H bonds that bridge the boron and iron nuclei. The corresponding Fe–B2 distance in **2** is 1.855(2) Å, consistent with the expected decrease in ionic radius for a low-spin metal center. To the best of our knowledge, the closest structural analogues to these complexes are $[\{\text{Fe}(\text{PET}_3)_3\}_2(\mu\text{-H})_6\text{B}]^+$ and $[(\text{triphos})\text{Fe}(\text{H}_3\text{BH}_3)\text{Fe}(\text{triphos})]^+$.⁹ These low-spin complexes exhibit similarly short Fe–B bond distances (1.903(3), 1.913(3) and 1.912(1) Å, respectively). A table comparing the other bond distances and angles of these complexes is included in the ESI.†

One of the key features in determining the hapticity of borohydride anion binding to transition metal ions has been the vibrational features of the ligated borohydride.⁶ IR analysis of **1** (Fig. 3(A)) shows a number of interesting features. The feature observed at 2603 cm^{−1} is insensitive to deuteration of the borohydride and therefore has been assigned to the $\nu(\text{B-H})$ of the $[\text{Tp}^{\text{Ph}_2}]$ ligand. A broad band observed at 2430 cm^{−1} is sensitive to isotopic substitution. The deuterated species exhibits a reproducible broad feature near 1824 cm^{−1} under a number of other vibrational bands in the Fe(D₃BD) complex. This broad band also appears in the difference spectrum. This mode has been tentatively assigned to the $\nu(\text{B-H})_{\text{distal}}$, and is in good agreement with published $\nu(\text{B-H})$ vibrations and theory. Hooke's law predicts a $\nu(\text{B-D})/\nu(\text{B-H})$ ratio of 0.74 and we observe a ratio of 0.75 for this mode. Another broad band appears at 2088 cm^{−1} which we ascribe to the $\nu(\text{B-H})_{\text{proximal}}$ mode. Using the ratio determined for the terminal B–H stretch, the $\nu(\text{B-D})_{\text{proximal}}$ for $[\text{Tp}^{\text{Ph}_2}]\text{Fe}(\text{D}_3\text{BD})$ is estimated to lie near 1540 cm^{−1}, a region obscured by strong ligand vibrations. Literature precedent suggests that for a tridentate binding of BH_4^- , three A_1 bands should be observed (between 2450–2600, 2100–2200 and 1200–1250 cm^{−1}, respectively).⁶ We do not observe the lowest energy mode for **1** and believe it is obscured

by vibrational modes of the ancillary ligand. The higher energy bands appear at the low end of the given frequency range. This may have to do with the open-shell nature of **1**. The low-spin borohydride adduct **2** shows three vibrations at 2606, 2367 and 1296 cm^{−1}. These modes respond to isotopic substitution of the borohydride ligand. The highest energy band shifts to 1939 cm^{−1} while the other two vibrations are lost in the peaks observed for the $[\text{PhBP}_3]$ ligand framework. The assignments are analogous to those reported in the literature⁶ and consistent with a facially coordinated BH_4^- ligand.

There are several ways to imagine the Fe–(H_3BH) interaction. For instance, it may be viewed as arising from three separate three-centered, two-electron interactions between each iron center and the B–H bonds, isolobal with η^5 -cyclopentadienide, halide and oxide.²⁴ Given the short Fe–B distances and the convention of describing the hapticity as $\eta^3\text{-BH}_4$ group,⁶ it was unclear to us whether the B atom was involved in bonding with the metal center in either **1** or **2**. Alternatively, it may not interact with the boron center at all, simply utilizing the hydrides to bridge the two nuclei (consistent with the η^3 designation previously used). To gain additional insight into the nature of the bonding between the iron and borohydride moiety, *m*PWPW91 density functional calculations were undertaken for simplified models of high-spin **1** and low-spin **2**. All of the phenyl rings in both **1** and **2** were replaced with hydrogen atoms for these computational studies. Structures having C_{3v} and C_3 symmetry, respectively, were found as minima, with structural parameters generally in good agreement with the experimental data (Table 3). Bond orders were computed by the method of Mayer²⁰ using the optimized density matrices for these structures (Table 3). This method has previously been shown to be robust for the description of multicordinate bonding between transition metals and associated ligands.²⁵

Analysis of the Kohn–Sham molecular orbitals rationalizes the computed bond orders in the two systems (Fig. 4). The highest energy doubly occupied orbital in both **1** and **2** belongs to the totally symmetric irreducible representation and mixes the Fe d_{z^2} with both a boron hybrid and all four of the hydrogenic 1s orbitals. Bonding interactions in this orbital contribute to the significant Fe– $\text{H}_{\text{proximal}}$ bond orders. The orbital we show has an antibonding interaction between the boron and iron centers, albeit a weak one. (There is an almost perfect cancellation of the two orbitals magnitudes so that the B–Fe part appears almost non-bonding.) The bonding interaction appears significantly lower in the orbital manifold and has positive overlap of the boron p with the iron d_{z^2} orbital. The four singly occupied orbitals in quintet **1** constitute two degenerate sets each belonging to the e irreducible representation. In singlet **2**, the energy separation

Fig. 3 IR spectra of (A) $[\text{Tp}^{\text{Ph}_2}]\text{Fe}(\text{H}_3\text{BH})$ and (B) $[\text{PhBP}_3]\text{Fe}(\text{H}_3\text{BH})$. The natural abundance spectra are shown in black and the spectra of the BD_4^- complexes are shown in red.

Table 3 Theoretical bond lengths and Mayer bond orders

	Bond length/Å		Bond order	
	1 ^a	2 ^a	1	2
Fe–B2	2.052 (2.084)	1.840 (1.855)	0.56	0.88
Fe– $\text{H}_{\text{proximal}}$	1.978 (1.99)	1.688 (1.60)	0.31	0.46
Fe–N/Fe–P	2.100 (2.106)	2.206 (2.212)	0.40	0.96
B– $\text{H}_{\text{proximal}}$	1.262 (1.16)	1.331 (1.21)	0.69	0.50
B– H_{distal}	1.200 (0.98)	1.190 (1.07)	0.93	0.93

^a Observed crystallographic distances in parentheses.

Fig. 4 Frontier DFT MOs (the a symmetry HOMO and highest energy *e* set) and a qualitative splitting diagram for **1** (orbitals for **2** are qualitatively very similar). Note that the orientation of the model in the lowest orbital is somewhat different from the other two in order to improve clarity.

between these two orbital sets is larger (because of the stronger ligand field enforced by the phosphine donors as opposed to the pyrazole donors) and the orbitals of the lower energy set are doubly occupied while those of the higher energy set are empty. The members of the higher energy set, also depicted in Fig. 4, are dominated by π^* antibonding interactions between the d_{xz} and d_{yz} orbitals and *s* orbitals on the borohydride H atoms towards which they are directed. The singly occupied nature of these orbitals in **1** compared to **2**, where they are empty, explains the substantially greater Fe–H_{proximal} bond order seen in the latter. Not surprisingly, this difference in Fe–H bond orders is balanced by a smaller B–H_{proximal} bond order in **2** than in **1**. This analysis is also consistent with the closer approach of the borohydride, and especially its proximal H atoms, to Fe in **2** compared with **1**. The remaining two singly occupied orbitals in **1**, which are doubly occupied in **2**, are not depicted: the Fe d_{xy} and $d_{x^2-y^2}$ AOs contribute to these MOs and show no particular interactions with the borohydride ligand (which is incapable of δ bonding). Rather, these orbitals are π^* antibonding between Fe and the ligand nitrogen atoms in **1**, but π bonding between Fe and the ligand phosphorus atoms in **2**. This in part explains the lower Fe–P/Fe–N bond orders seen for **1** compared to **2**. Theory is thus consistent with designating the interaction as an Fe– η^4 -borohydride coordination.

In conclusion, we have demonstrated that borohydride adducts of iron can be generated and isolated. The spin state of the iron center can be controlled *via* the ancillary ligand. Alteration of the ligand field results in compensatory changes in the observed bond distances as well as the theoretical bond orders for the (L_3)Fe(η^4 -H₃BH) complex. Studies are underway to examine the effect of spin state on the reactivity of these novel complexes, as paramagnetic iron hydrides are postulated to be reactive intermediates in the catalytic cycles of nitrogenases and hydrogenases.^{1–3}

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