LETTER

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Expanding metallaborane chemistry: an octahedral BH_6 moiety supported through M–H–B bridges

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The X-ray crystal structure of the complex [(triphos)Fe($\mu,\eta^4:\eta^4$-BH_6)Fe(triphos)]$^+$ in conjunction with spectroscopic data reveals a central unit formally described as BH_6^{3-}; DFT calculations show why this ligand is stable for iron but not for the ruthenium analogue.

Since the pioneering work of Alfred Stock a century ago,[1] boron hydrides have fascinated and confounded chemists in equal measure. Established rules of valency and bonding had to be recast to accommodate these non-classical systems. In addition to the BH_4^- ion, which has a rich and diverse coordination chemistry in its own right, higher boron hydrides act as ligands to a variety of transition-metal centres.[2] Preparation of BH_4^- complexes generally proceeds by metathesis, either by the replacement of one or more CO ligand by a neutral borane moiety, or else by reaction of BH_4^- with a transition-metal chloro complex.[2] We report here an alternative route to a novel type of metallaborane, in which condensation of two hydride–borohydride molecules produces a hypervalent BH_6 moiety supported between two metal centres.

Reaction of $[Fe(H_2O)_6](BF_4)_2$ with triphos [$MeC(CH_2PPh_2)_3$; 'P_3'] and 8 eq. of $NaBH_4$ in THF–EtOH affords the known complex [$P_3Fe(H)(\eta^2$-$BH_4)$] **1**.[3a] However, if the reaction mixture is allowed to stand for *ca.* 12 h, the novel cationic complex [$P_3Fe(\mu,\eta^4:\eta^4$-$BH_6)FeP_3]^+$ **2** is produced (ESI-MS 1377.37, M^+). If only 1.5 eq. of borohydride is added, the known trihydride [$P_3Fe(\mu$-$H)_3FeP_3]^+$ is formed.[3b] The ^1H NMR spectrum of **2** displays a single feature in the hydride region (−10.2 ppm; 6H) which sharpens on ^{11}B decoupling. The $^{31}P\{^1H\}$ spectrum reveals a singlet at 63.4 ppm, while the ^{11}B spectrum displays a broad feature at 55.1 ppm ($\nu_{\frac{1}{2}} = 1500$ Hz), close to chemical shifts reported for transition-metal boryl complexes.[4] The IR spectrum shows broad features at 1899 (ν_{M-H-B}; $\nu_H/\nu_D = 1.32$) and 1080 cm^{-1} (δ_{M-H-B}), characteristic of tridentate metal borohydride complexes.[5] The ^{57}Fe Mössbauer spectrum of **2** reveals an isomer shift of −0.016(39) and quadrupole splitting of 0.639(63) mm s^{-1}, consistent with two low-spin Fe^{II} centres, leaving the central BH_6 moiety with a formal charge of −3. Variable-temperature NMR experiments over the range 190–310 K produced no significant changes in the ^1H, ^{31}P and ^{11}B spectra, and failed to resolve any B–H coupling. Complex **2** gave a relaxation time, ($T_{1\ min}$), value of 118.5 ms at 250 K; short for a classical hydride, but much longer than values found for H_2 ligands.

A yellow single crystal of [$P_3Fe(\mu,\eta^4:\eta^4$-$BH_6)FeP_3]^+[X]^-$ **2***was characterised by X-ray diffraction,† with the result shown in Fig. 1. The structure reveals a high symmetry (locally D_{3d} around the core) geometry for the cation **2**, with an almost octahedral BH_6 moiety; the boron atom lying at a centre of inversion.‡ Note that the inversion symmetry of the entire structure is inconsistent with a tetrahedral BH_4^- bridge even if disordered. At 1.91 Å, the Fe–B distances are shorter than the sum of the respective van der Waals radii (2.05 Å), and imply a direct metal–boron bonding interaction, hence our description of the coordination as η^4. The Fe–H and B–H distances are equivalent within 2 esd's. The Fe–H bonds are intermediate between the terminal and bridging Fe–H moieties in the hydride-borohydride complex **1**,[4] and the B–H distances are longer than for M–H_b–B moieties found in other metal borohydride complexes (1.0–1.4 Å).[5] All Fe–P distances are statistically equivalent, implying a comparable *trans* influence of all three BH moieties, in contrast to **1** and the ruthenium analogue of **2**.[3a,6] The P–Fe–Fe–P dihedral angles of 60° indicate a highly symmetrical cation.

This remarkable coordination environment for boron appears to be a consequence of the elongated B–H bonds, which are supported by the stable and well-known *fac*-P_3FeH_3 fragment on either side of the boron atom. During the course of this research, the similar complex [$(Et_3P)_3Fe(BH_6)Fe(PEt_3)_3]^+$ was reported by Berke *et al.*[7] However, the ruthenium analogue of **2** appears as the more

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† CCDC reference number for **2***: 224893. See http://www.rsc.org/suppdata/nj/b4/b401442c/ for crystallographic data in .cif or other electronic format.

‡ The nature of the anion in **2*** is ambiguous and appears to represent a highly disordered average of borohydride solvolysis products with average composition $B(OH)_2(OEt)_2^-$. Independent evidence for this assignment comes from elemental analysis, and spectroscopic features at −1.2 ppm (^{11}B NMR); 1.7, 1.6 and 1.1 ppm (^1H NMR); and a ν_{OH} mode (IR). The cationic nature of **2** is confirmed by preparation of the BPh_4^- salt, which unfortunately did not produce X-ray quality crystals.

Crystal data for **2***: $C_{86}H_{96}B_2Fe_2O_4P_6$, $M = 1512.77$, yellow block, $0.20 \times 0.20 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.4208(9)$, $b = 12.6840(12)$, $c = 14.2246(15)$ Å, $\alpha = 97.844(5)$, $\beta = 115.241(5)$, $\gamma = 104.180(5)°$, $V = 1889.7(3)$ $Å^3$, $Z = 1$, $D_c = 1.329$ g $/cm^{-3}$, $F_{000} = 796$, Nonius KappaCCD, MoKα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 50.0°$, 10 749 reflections collected, 6567 unique ($R_{int} = 0.1103$). Final GooF = 1.318, $R1 = 0.1341$, $wR2 = 0.2043$, R indices based on 5129 reflections with $I > 2\sigma(I)$ (refinement on F^2), 489 parameters, 24 restraints. Lp and absorption corrections applied, $\mu = 0.563$ mm^{-1}.

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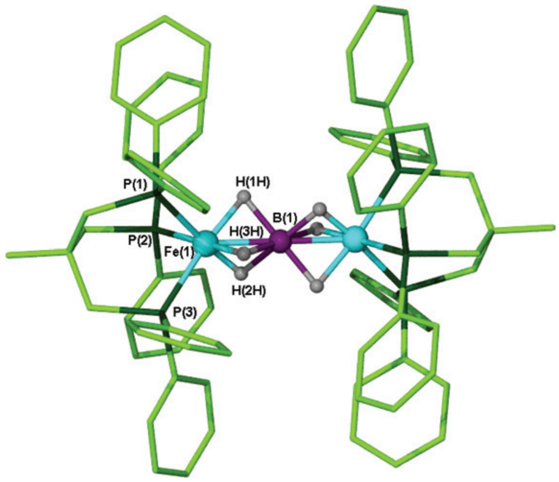

Fig. 1 X-Ray crystal structure of $[(\text{triphos})Fe(BH_6)Fe(\text{triphos})]^+$ (**2**). Selected bond lengths (in Å): Fe–P 2.181(2)–2.186(2), Fe–H 1.34(9)–1.56(10), B–H 1.40(10)–1.48(10), Fe–B 1.9122(11). Selected angles (in degrees): H(1)–Fe–H(2) 85(4), H(1)–Fe–H(3) 81(5), H(2)–Fe–H(3) 75(6), Fe–B–H(1) 53(4), Fe–B–H(2) 44(4), Fe–B–H(3) 45(4), Fe–B–Fe 180.00(12).

conventional hydride–borohydride isomer $[P_3Ru(H)(\mu,\eta^2{:}\eta^2\text{-}BH_4)(H)RuP_3]^+$ **3**.[6] The inversion symmetry of the heavy-atom skeleton in the structure of **2** is in direct contrast to the geometry observed for **3** imposed by the tetrahedral BH_4^-. In order to explore the reasons for this difference, we carried out DFT calculations§ on the model complexes $[(PH_3)_3Fe(BH_6)Fe(PH_3)_3]^+$ **2′** and $[(PH_3)_3Ru(BH_6)Ru(PH_3)_3]^+$ **3′** to ascertain the relative energies of the BH_4-bridged (**a**) and BH_6-bridged (**b**) isomers in each case. In spite of the use of PH_3 in these calculations, full geometry optimisations in D_{3d} symmetry faithfully reproduced the experimental skeletal and core geometries of **2** and **3**, and showed them to be the ground state in each case. The two isomers of the model Fe system **2′** are almost isoenergetic, in contrast to the Ru system **3′**, for which **3a′** is 24 kJ mol^{-1} more stable than its BH_6-bridged counterpart **3b′**.

Analysis of the molecular orbitals for the BH_4- and BH_6-bridged version of **2′** and **3′** (Fig. 2, top) reveals significant changes in the B–H bonding region between the isomers **a** and **b**. The 15a and 16a orbitals of **2a′** and **3a′** and the corresponding $4a_{1g}$ and $4a_{2u}$ orbitals of **2b′** and **3b′** (Fig. 2, bottom) are all $B\text{–}H_b\text{–}M$ σ-bonding in nature. In the model Fe complex **2′** they are not significantly affected energetically in the transition from the BH_4-bridged to the BH_6-bridged form: 16a increases by a negligible 0.04 eV, while 15a is destabilised by a modest 0.15 eV. In contrast, in the Ru complex **3′**, there is very significant destabilisation of both these orbitals (0.44 and 0.83 eV respectively) on going from the BH_4-bridged to the BH_6-bridged form. This clear difference is also reflected in the calculated structural parameters for **2′** and **3′**, which reveal that the $B\text{–}H_b$ bonds lengthen significantly—from 1.36 Å in both **2a′** and **3a′** to 1.52 Å in **2b′** and 1.66 Å in **3b′**—on going from the BH_4-bridged to the BH_6-bridged isomer. This lengthening permits the boron centre to attain the remarkably high coordination number of six—or eight if the close M–B contacts are taken into account. The extra lengthening in **3′** may arise from the higher energy of the Ru 4d orbitals in comparison with Fe 3d (relativistic AO energies −5.379 and −7.742 eV, respectively), which renders the Ru centre a stronger donor. The $B\text{–}H_b$ bonding presumably cannot accommodate such drastic lengthening in **3**, and consequently the $B\text{–}H_b\text{–}Ru$ molecular orbitals are destabilised, favouring the BH_4-bridged isomer **3a** as observed experimentally.

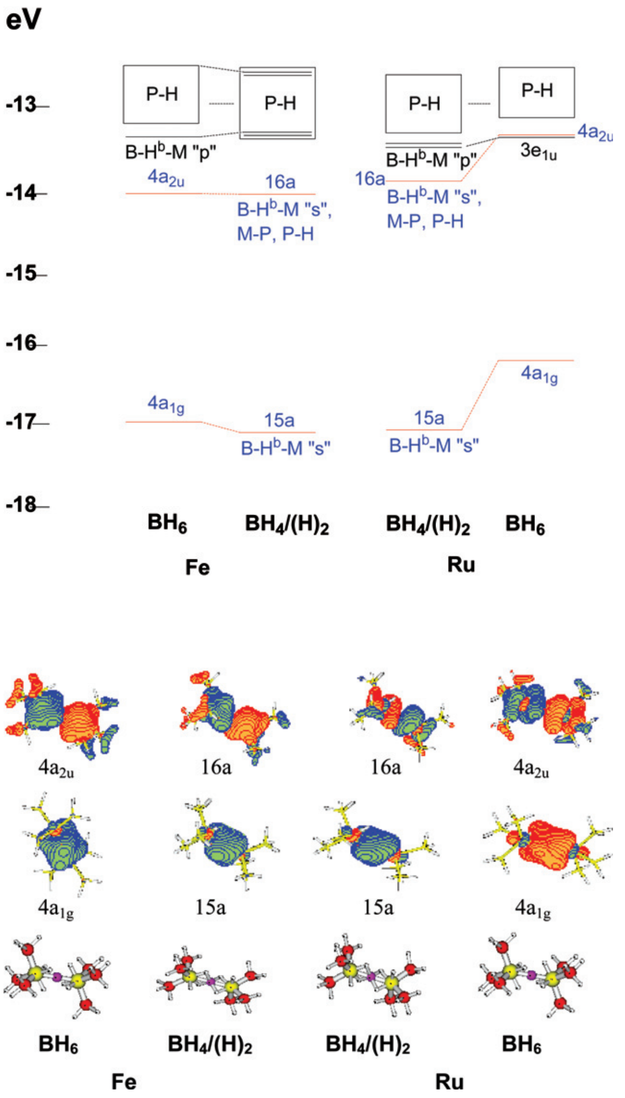

Fig. 2 Top: MO energy level diagram for the BH_4- (**a**) and BH_6-bridged (**b**) isomers of $[(H_3P)_3Fe(BH_6)Fe(PH_3)_3]^+$ **2′** and $[(H_3P)_3Ru(BH_6)Ru(PH_3)_3]^+$ **3′**. Bottom: 15a and 16a orbitals of **2a′** and **3a′** and the corresponding $4a_{1g}$ and $4a_{2u}$ orbitals of **2b′** and **3b′**.

The computational results also help to explain some of the spectroscopic properties of **2**. Our failure to observe B–H coupling in the NMR spectra was perplexing, especially given the high-symmetry boron environment. However, the B–H bonds in **2** are long and weak, and such coupling may be intrinsically smaller than the natural linewidths of the ^1H and ^{11}B resonances. Rapid quadrupolar spin–lattice relaxation may still be responsible for the lack of observed coupling, and in fact no B–H and P–H coupling is observed for the BH_4 moiety in **1**. As noted earlier, the ^{11}B chemical shift of **2** is consistent with a transition-metal boryl moiety,[4] and the depiction in Fig. 2 may represent the bonding in the complex more closely than

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§ Calculations were performed using the Amsterdam Density Functional (ADF) program suite (version 2002).[8] The basis sets employed were uncontracted, valence-only, Slater type functions of triple zeta quality. One polarisation function was included for all atoms; p for H, d for B and P, and f for Fe and Ru. Scalar relativistic corrections were included *via* the ZORA to the Dirac equation.[9] The frozen core approximation was employed (Ru.3d, Fe.2p, P.2p and B.1s). The local density parameterisation of Vosko, Wilk and Nusair was used,[10a] in conjunction with Becke's gradient correction[10b] to the exchange part of the potential and the correlation correction due to Perdew.[10c] Calculations on the BH_6-bridged species were run in D_{3d} symmetry, while no symmetry restrictions were employed for the BH_4-bridged systems. The ADF numerical integration factor was set to 4.5 in all cases, and geometries were optimised such that the maximum gradient was 0.001 H/au or less.

does that in Fig. 1. Berke *et al.* reported comparable spectroscopic data for $[(Et_3P)_3Fe\text{-}(BH_6)Fe(PEt_3)_3]^+$, and interpreted them in a similar way.[7]

The synthesis of **2** from **1** represents a novel departure in metallaborane chemistry, in that terminal M–H moieties are drawn into the expanded coordination sphere of the boron atom on coupling of the two metal centres. Synthetic strategies including hydride–borohydride precursors thus hold out the prospect of novel hydrogen-rich metallaborane complexes containing hypervalent or hypercoordinate boron centres. Transition-metal M–H moieties are unique in the variety of secondary interactions which they display with other ligands in the metal coordination sphere.[11] These include intramolecular hydrogen bonding and inter-ligand hypervalent interactions; and dihydrogen and other σ-bond complexes can also be described in such a way. The boron centre in **2** may turn out to be a stage on the reaction coordinate of yet another sub-class of such behaviour.

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