# Rapid intramolecular heterolytic dihydrogen activation by a four-membered heterocyclic phosphane–borane adduct†

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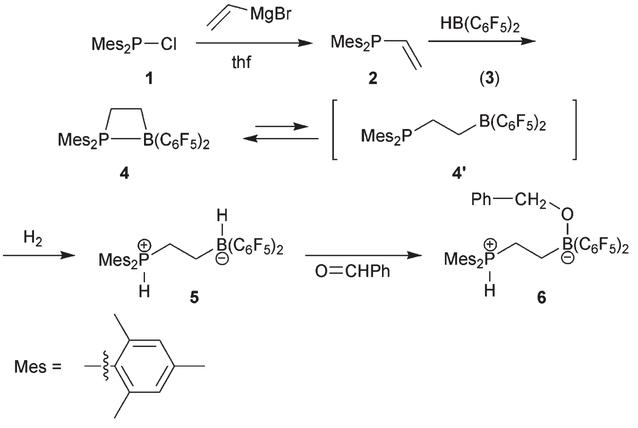
*Received (in Cambridge, UK) 10th July 2007, Accepted 13th September 2007*
*First published as an Advance Article on the web 2nd October 2007*
**DOI: 10.1039/b710475h**

**A four-membered cyclic intramolecular phosphane–borane adduct activates dihydrogen to yield the respective ethylene-bridged zwitterionic phosphonium–hydridoborate system, which reduces benzaldehyde.**

Heterolytic dihydrogen cleavage has been shown to be of importance in enzymatic reaction cycles involving metal-containing hydrogenases.[1] Related heterolytic dihydrogen cleavage and usage has been observed in a great variety of molecular transition metal complexes[2] and catalysts.[3] In contrast, very few examples are known where the $H_2$ molecule is split into a proton and a hydridic component in a completely metal-free environment, solely by means of reagents containing main group elements.[4,5] Stephan *et al.* have recently described such a hydrogen activation, occurring by means of phosphane/borane combinations that were specially designed to avoid efficient Lewis acid/Lewis base self-quenching.[4] The $R_3P/BR'_3$ examples tested reacted rapidly (and reversibly) with dihydrogen to give the corresponding $[R_3PH^+][HBR'_3{}^-]$ salts.[5] We have now prepared the first cyclic alkylene-bridged system of this type and observed its rapid hydrogen uptake to give a zwitterionic salt, which is shown to exhibit hydridic reactivity towards an organic carbonyl compound.[6] Some of the details of this pertinent study will be described in this account.

Chlorodimesitylphosphane (**1**)[7] was reacted with vinyl magnesium bromide to yield vinyldimesitylphosphane [**2**; 48% isolated after chromatographic purification; $^{31}$P NMR ($d_6$-benzene): $\delta$ −22.0; $^1$H NMR: $\delta$ 6.98 (1H) and 5.35/5.29 (=$CH_2$); $^{13}$C NMR: $\delta$ 129.4 and 121.8 (–CH=$CH_2$)] (Scheme 1). Subsequent treatment with $HB(C_6F_5)_2$ (**3**)[8] (1 equiv.) in pentane resulted in a clean anti-Markovnikov addition to yield **4** (75%). The spectroscopic data of **4** indicate the formation of a four-membered boraphospha heterocycle, exhibiting a P–B interaction.¶ $^1$H NMR resonances of the [P]–$CH_2$–$CH_2$–[B] moiety occur at $\delta$ 2.87 ($^2J_{PH}$ = 8 Hz) and 2.29 ($^3J_{PH}$ = 42 Hz), respectively. The compound's spectroscopic studies also included $^{19}$F [$\delta$ −128.8 (*o*-), −157.0 (*p*-) and −163.6 (*m*-$C_6F_5$)], $^{11}$B ($\delta$ 8.5) and $^{31}$P NMR data ($\delta$ + 20.6), which indicate internal adduct formation.



Scheme 1

This was supported by the results of a DFT calculation (Fig. 1).[9] Compound **4** features a calculated gas phase structure that contains a close to planar four-membered ring with a calculated P–B distance of 2.21 Å.[10] A very prominent structural feature of **4** is the parallel arrangement of one P–mesityl ring with one B–$C_6F_5$ group. The resulting π–π donor–acceptor interaction between these spatially close aryl π-systems seems to contribute to the stability of the unusual four-membered heterocyclic structure of **4**.[11] The DFT calculation localizes two isomeric open chain local minima of **4** (*gauche*-**4′**, *trans*-**4′**), which are both only *ca.* 7 kcal mol$^{-1}$ above the cyclic (π-stacking stabilized) ground state of **4**. We assume that the open isomers are responsible for the observed $H_2$-activation (see below).

A solution of compound **4** in pentane was stirred in a dihydrogen atmosphere (1.5 bar) at room temperature. Within 15 min, a large amount of a white precipitate had formed, which was isolated (60% yield) and subsequently identified as the inner phosphonium-borate salt $Mes_2PH^+CH_2CH_2BH^-(C_6F_5)_2$ (**5**).

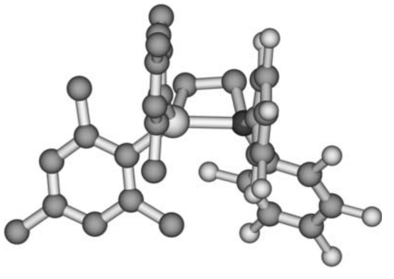


**Fig. 1** DFT-calculated structure of **4** featuring π-stacking stabilization.

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† Electronic supplementary information (ESI) available: Experimental section and details of the quantum chemical calculations. See DOI: 10.1039/b710475h

‡ X-Ray crystal structure analyses.

§ Quantum chemical calculations.

Compound **5** shows a PH unit in the $^{31}$P NMR spectrum at $\delta$ −6.5 as a doublet with a coupling constant $^1J_{\mathrm{PH}} \approx 490$ Hz. The corresponding $^1$H NMR P*H* resonance was located at $\delta$ 7.87 (dt, $^1J_{\mathrm{PH}}$ = 486 Hz, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 1H). The $^{19}$F NMR spectrum features a set of typical borate $C_6F_5$ resonances at $\delta$ −133.4 (*o*), −165.8 (*p*) and −168.0 (*m*), and the $^{11}$B NMR signal is split into a doublet by coupling with the directly-bonded hydrogen [$\delta$ −20.1 (d, $^1J_{\mathrm{BH}}$ = 88 Hz)]. The analogous reaction of **4** with $D_2$ generated the corresponding product **5-D$_2$**, which features a 1 : 1 : 1 intensity $^{31}$P NMR triplet resonance at $\delta$ −6.97. We located the broad $^2$H NMR [B]-D resonance at $\delta$ 2.94 and the [P]-D resonance as a doublet at $\delta$ 7.87 (d, $^1J_{\mathrm{PD}}$ = 75 Hz; in THF).

Compound **5** was characterized by X-ray diffraction (single crystals were obtained by diffusion of pentane vapor into a THF solution of **5**).¶ In the crystal, the zwitterion **5** features the bulky $\mathrm{Mes_2PH^+}$ and $\mathrm{HB(C_6F_5)_2^-}$ substituents in an antiperiplanar orientation at the central $\mathrm{–CH_2–CH_2–}$ bridging unit [P1–C1 1.811(2), C1–C2 1.530(3) and C2–B1 1.631(3) Å; $\theta_{\mathrm{P1–C1–C2–B1}}$ 179.0(1)°]. The bond angles at P1 [C21–P1–C11 114.9(1), C21–P1–C1 107.6(1) and C11–P1–C1 118.7(1)°] and B1 [C31–B1–C2 110.1(2), C31–B1–C41 108.1(2) and C41–B1–C2 114.1(2)°] indicate pseudo-tetrahedral coordination geometries at both the phosphorus and boron atoms in **5** (see Fig. 2).

The borohydride moiety in **5** transfers a hydride anion to a suitable receptor. The reaction of **5** with benzaldehyde in THF solution at ambient temperature resulted in hydride addition to the carbonyl carbon, with the formation of the respective zwitterionic [B]–$\mathrm{OCH_2Ph}$ product **6** [$^{11}$B NMR: $\delta$ −0.3 (br s); $^{19}$F NMR: $\delta$ −133.7 (*o*), −164.3 (*p*) and −167.4 (*m*); $^{31}$P NMR: $\delta$ −4.8 (d); $^1$H NMR: $\delta$ 7.86 (dt, $^1J_{\mathrm{PH}}$ = 492 Hz, $^3J_{\mathrm{HH}}$ = 7.6 Hz, PH) and 4.09 (s, 2H); $^{13}$C NMR: $\delta$ 65.6 (O*C*H$_2$Ph)]. The formation of **6** was confirmed by an X-ray crystal structure analysis (single crystals obtained from THF/pentane by the diffusion method).¶ It features a distorted antiperiplanar arrangement of the central P1–C2–C3–B4 core ($\theta$ = 151.4(7)°), with the attachment of the newly formed $\mathrm{–OCH_2Ph}$ substituent at the tetravalent, pseudotetrahedral boron center (see Fig. 3) (average C–P–C angle at P1 = 113.6°, average angle at B1 = 107.8°).

Our work shows that heterolytic dihydrogen splitting and activation can be readily achieved under metal-free conditions starting from an intramolecular phosphane–borane adduct. The resulting borohydride moiety features the typical ability to serve as a reducing agent, here shown by its facile reaction with benzaldehyde. These observations are likely to represent interesting and useful steps towards the utilization of dihydrogen in the absence of metals, and in the development of novel active “organohydrogenation” systems,[12] here having the useful feature of an easily modifiable organic bridging group between phosphorus and boron.

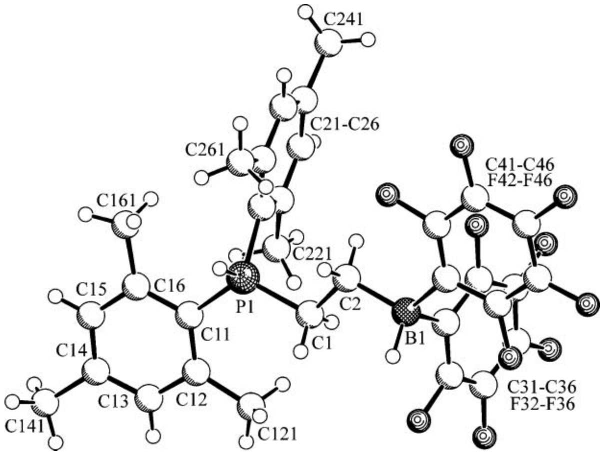

**Fig. 2** A view of the molecular structure of the zwitterionic dihydrogen addition product **5**.

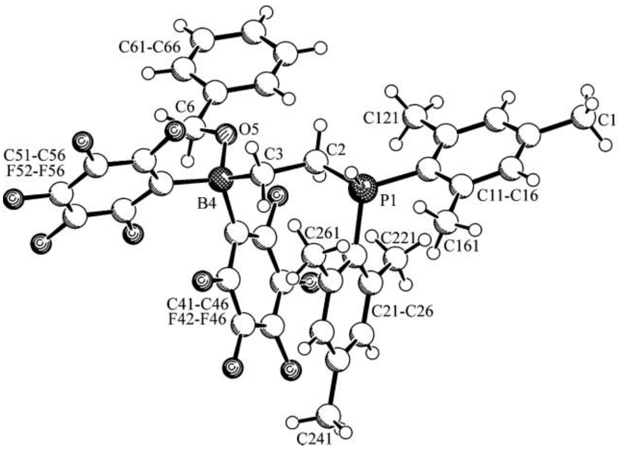

**Fig. 3** A view of the molecular structure of product **6**.

## Notes and references

¶ Compounds **4**, **5** and **6** were isolated and characterized by elemental analysis, and by $^1$H, $^2$H, $^{11}$B, $^{13}$C, $^{31}$P and $^{19}$F NMR spectroscopy. In addition, compounds **5** and **6** were characterized by X-ray crystal structure analyses.

Crystal data for **5**: $C_{32}H_{28}BF_{10}P$, $M$ = 644.32, monoclinic, space group $P2_1/c$ (no. 14), $a$ = 12.3680(3), $b$ = 18.5413(5), $c$ = 13.1716(1) Å, $\beta$ = 96.361(2)°, $V$ = 3001.90(13) Å$^3$, $D_c$ = 1.426 g cm$^{-3}$, $\mu$ = 1.572 mm$^{-1}$, $Z$ = 4, $\lambda$ = 1.54178 Å, $T$ = 223(2) K, 21035 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 5312 independent ($R_{\mathrm{int}}$ = 0.060) and 4566 observed reflections [$I \geqslant 2\sigma(I)$], 411 refined parameters, $R$ = 0.050, w$R^2$ = 0.144. CCDC 650365.

Crystal data for **6**: $C_{39}H_{34}BF_{10}OP$, $M$ = 750.44, triclinic, space group $P\bar{1}$ (no. 2), $a$ = 12.1089(8), $b$ = 12.7662(10), $c$ = 12.8752(8) Å, $\alpha$ = 104.669(3), $\beta$ = 100.577(5), $\gamma$ = 100.279(3)°, $V$ = 1839.0(2) Å$^3$, $D_c$ = 1.355 g cm$^{-3}$, $\mu$ = 1.385 mm$^{-1}$, $Z$ = 2, $\lambda$ = 1.54178 Å, $T$ = 223(2) K, 20114 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 6171 independent ($R_{\mathrm{int}}$ = 0.078) and 4081 observed reflections [$I \geqslant 2\sigma(I)$], 479 refined parameters, $R$ = 0.077, w$R^2$ = 0.227. CCDC 650366.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710475h

1 A. I. Krasna and D. Rittenberg, *J. Am. Chem. Soc.*, 1954, **76**, 3015; A. I. Krasna, *Methods Enzymol.*, 1978, **53**, 296; B. J. Lemon and J. W. Peters, *Handbook of Metalloproteins*, ed. A. Messerschmidt, R. Huber, T. Poulos and K. Wieghardt, Wiley, New York, 2001, vol. **2**, pp. 738; M. Frey, J. C. Fontecilla-Camps and A. Volbeda, *Handbook of Metalloproteins*, ed. A. Messerschmidt, R. Huber, T. Poulos and K. Wieghardt, Wiley, New York, 2001, vol. **2**, pp. 880.
2 X.-Y. Lin, K. Vankatesan, H. W. Schmalle and H. Berke, *Organometallics*, 2004, **23**, 3153 and references cited therein. See also: M. P. Magee and J. R. Norton, *J. Am. Chem. Soc.*, 2001, **123**, 1778.
3 R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97; R. Noyori, M. Kitamura and T. Ohkuma, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 5356; C. P. Casey, G. A. Bikzhanova and I. A. Guzei, *J. Am. Chem. Soc.*, 2006, **128**, 2286 and references cited in therein.
4 G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124.

5 G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880.

6 For remotely related systems, see, *e.g.*: T. J. Clark, C. A. Russell and I. Manners, *J. Am. Chem. Soc.*, 2006, **128**, 9582; M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, 12048; Y. Jian and H. Berke, *Chem. Commun.*, 2007, 3571, and references cited therein.

7 H. Goldwhite, J. Kaminski, G. Millhauser, J. Ortiz, M. Vargas and L. Vertal, *J. Organomet. Chem.*, 1986, **310**, 21; R. A. Bartlett, M. M. Olmstead, P. P. Power and G. A. Sigel, *Inorg. Chem.*, 1987, **26**, 1941; J. B. Lambert and J.-H. So, *J. Org. Chem.*, 1991, **56**, 5960.

8 W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345.

9 S. Grimme, *J. Comput. Chem.*, 2004, **25**, 1463; S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787; S. Grimme, J. Antony, T. Schwabe and C. Mück-Lichtenfeld, *Org. Biomol. Chem.*, 2007, **1**, 741.

10 For comparison, $d_{P-B}$ in $Ph_3P–B(C_6F_5)_3$ = 2.180(6) Å. See: H. Jacobsen, H. Berke, S. Döring, G. Kehr, G. Erker, R. Fröhlich and O. Meyer, *Organometallics*, 1999, **18**, 1724.

11 J. H. Williams, *Acc. Chem. Res.*, 1993, **26**, 593; S. L. Cockroft, C. A. Hunter, K. R. Lawson, J. Perkins and C. J. Urch, *J. Am. Chem. Soc.*, 2005, **127**, 8594; Y. El-Azizi, A. Schmitzer and S. K. Collins, *Angew. Chem.*, 2006, **118**, 982, (*Angew. Chem., Int. Ed.*, 2006, **45**, 968) and references cited therein.

12 Recent non-bridged examples: P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem.*, 2007, **119** (early view); P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, DOI: 10.1002/anie.200702908.