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# Facile dihydrogen release from phosphino-borinate ester Lewis pairs†

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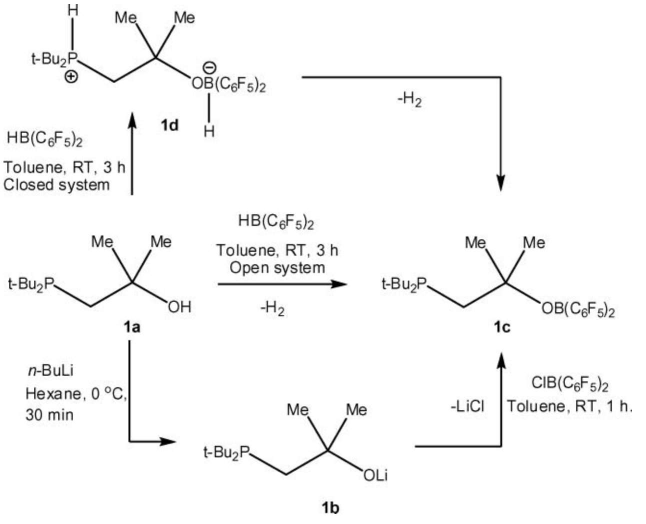
**New phosphino-borinate ester Lewis pairs of the type $^t\mathrm{Bu_2PCH_2C(R)_2OB(C_6F_5)_2}$ (R = Me or $CF_3$) are synthesised from the corresponding phosphino-alcohol and $HB(C_6F_5)_2$. Dihydrogen release from the zwitterionic $^t\mathrm{Bu_2PHCH_2C(R)_2OBH(C_6F_5)_2}$ is facile.**

Solution phase combinations of sterically hindered ('frustrated') Lewis acid–Lewis base pairs have been the subject of much recent interest, not least because the high latent reactivity of such species in, for example, the reversible heterolytic cleavage of hydrogen. Stephan and co-workers have demonstrated that the precise balance of sterics and electronics between simple tertiary phosphine–borane frustrated pairs plays a pivotal role in the reversibility of this particular reaction. The same group showed that the $P(Mes)_3$–$B(C_6F_5)_3$ pair reacts cleanly with hydrogen at room temperature and the resulting ion-pair is stable at temperatures up to 150 °C.[1] In a subsequent study,[2] the combination of P(*o*-tol)$_3$ with the modified borane B(*p*-$C_6F_4H$)$_3$ was also shown to cleave hydrogen at room temperature but the resulting ion-pair decomposed slowly under ambient conditions over nine days, releasing hydrogen and reforming the starting materials. In the context of hydrogen storage using such materials, facile release of dihydrogen is clearly crucial and yet in all other examples,[3–5] release is very slow and requires heating to 60 °C or more. In most cases, a reduction in Lewis acidity relative to $B(C_6F_5)_3$ seems to be beneficial in creating a reversible system.‡

In related work, Britovsek and co-workers[6] synthesised $(C_6F_5)_2B(OC_6F_5)$ and $(C_6F_5)B(OC_6F_5)_2$ in order to compare the effect that successive substitution of a -$C_6F_5$ group with -$OC_6F_5$ has on the Lewis acidity. Interestingly, they found that the experimental Lewis acidity depended on which NMR method was employed (Guttman[7] or Childs[8]); $B(OC_6F_5)_3$ appears to be a stronger Lewis acid than $B(C_6F_5)_3$ using Gutmann's methodology but a much weaker Lewis acid when using the method of Childs. They concluded that substitution of a -$C_6F_5$ groups for -$OC_6F_5$ makes the boron centre a progressively harder Lewis acid. With this in mind, we sought about designing and investigating the reactivity of novel frustrated Lewis pairs featuring a borinate ester as the Lewis acid component, reasoning that the harder Lewis acid in such species would give rise to modified reactivity and a method to tune dihydrogen activation and release.

Phosphino-alcohol synthons (**1a**,**b**) may be synthesised *via* the facile and highly selective ring opening of 2,2-disubstituted oxarines using a modified literature procedure (Scheme 1).[9]



**Scheme 1** Synthesis of **1a–1d**.

Compound **1c** was prepared by reaction of the preformed lithium phosphino-alkoxide **2a** with $ClB(C_6F_5)_2$ or by reaction of **1a** with $HB(C_6F_5)_2$. The second route proved more practical since the only by-product in an open system is hydrogen; removal of solvent gave **1c** as a highly moisture and oxygen sensitive, colourless oil in analytical purity.

The $^{31}P$ {$^1H$} NMR spectrum of **1c** exhibits a sharp singlet at 24.5 ppm suggesting little or no P–B interaction. The absence of this interaction is further supported by the broad singlet at 35 ppm in the $^{11}B$ {$^1H$} and characteristic pentafluorophenyl resonances in 4 : 2 : 4 ratio, with $\Delta\delta$ (*m*-F, *p*-F) separation of 11 ppm, typical of trigonal planar boron and in good agreement with the related borinate ester *n*-$BuOB(C_6F_5)_2$.[10] The VT NMR spectrum of **1c** reveals a shift in the $^{31}P$ resonance upon cooling to −80 °C from 24.5 to 48 ppm along with a simultaneous decrease in the $\Delta\delta$ (*m*-F, *p*-F) separation. This observation is consistent with the formation of a P–B interaction at lower temperatures. Preliminary DFT calculations reveal that this is best explained by an intermolecular process rather than intramolecular; concentration studies are underway to verify this.

We originally postulated that **1c** may form *via* loss of dihydrogen from the zwitterionic product **1d**. However, no NMR signals attributable to **1d** were observed unless the reaction is performed in a sealed system. In such instances, analytically pure **1d** precipitates from the reaction medium in varying quantities, but is not observed in the supernatant. A further observed product is $[H_2B(C_6F_5)_2]^-$, suggesting dihydrogen activation by the Lewis pair formed between $HB(C_6F_5)_2$ and the phosphine moiety of **1a**. The isolable $^t\mathrm{Bu_3P{-}BH(C_6F_5)_2}$ adduct and its subsequent reaction with 1 bar hydrogen at 80 °C has been previously reported.[11]

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† Electronic supplementary information (ESI) available: Experimental details. CCDC reference numbers 764587 and 764588. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00513d

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In a closed system, X-ray quality crystals of **1d** formed (Fig. 1). The structure is very much as expected.§ A point of note is the orientation of H1 with regard to O1 suggesting a possible interaction, which is not possible with a purely hydrocarbon backbone structure.

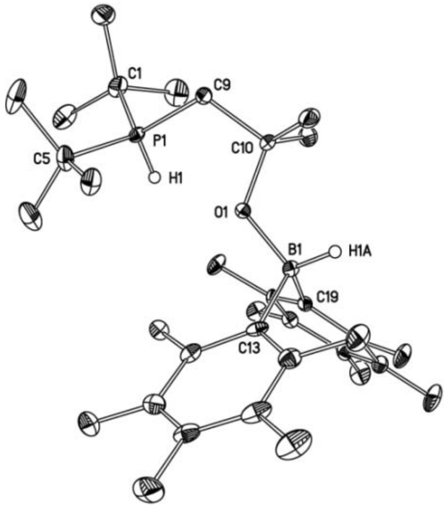
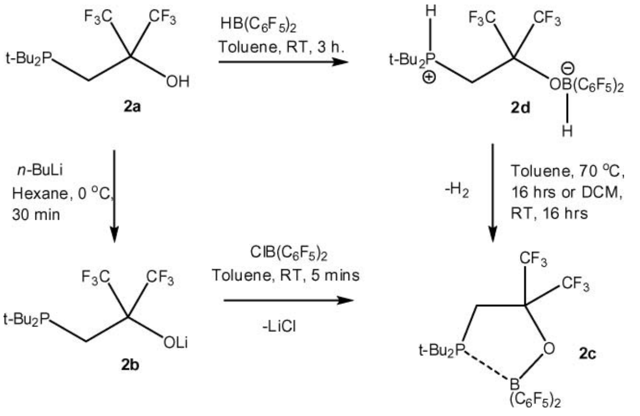


**Fig. 1** Molecular structure of **1d**. Thermal ellipsoids are shown at 30% probability, and most hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C9 1.802(6), P1–C1 1.838(6), P1–C5 1.850(7), O1–C10 1.422(7), O1–B1 1.481(7), B1–C13 1.657(9), B1–C19 1.674(8), C9–P1–C5 113.6(3), C9–P1–C1 110.1(3), C5–P1–C1 116.6(3), O1–B1–C13 107.3(5), O1–B1–C19 113.3(4), C13–B1–C19 109.1(4).

Upon dissolution of **1d** in $CD_2Cl_2$, decomposition to **1c** over the course of several hours was observed. After *ca.* 7 h no **1d** could be detected by NMR spectroscopy. Monitoring the loss of **1d** and the formation of **1c** by $^{31}P$ NMR revealed smooth first order kinetics with a half life of 140 min. Attempts to form **1d** by direct hydrogenation of toluene solutions of **1c** in high pressure NMR tubes (6 bar hydrogen, 80 °C) failed. A similar lack of reactivity was observed by Erker *et al.*[12] for *trans*-alkenyl linked FLPs, only giving the hydrogenated product after 3 h at 60 bar hydrogen. However, attempts to hydrogenate **1c** under more forcing conditions (35 bar for 4 days at ambient temperature) resulted in a mixture of products of which 10% could be assigned to **1d** on the basis of NMR spectroscopy. In a further attempt to probe the reactivity of **1c** towards dihydrogen, a preformed sample of **1c** in $d_8$-toluene was exposed to 1 bar of a 1 : 1 $H_2$–$D_2$ mixture, and after standing at room temperature for 12 h, HD was visible in the $^1H$ NMR spectrum (~25% based on relative integration of $H_2$ resonance). This clearly indicates that the FLPs described here will indeed cleave dihydrogen under mild conditions, even if the formation of zwitterionic products is not favourable in this case. A similar observation was made by Bercaw *et al.*[13] using the weak Lewis acid $^tBuCH_2CH_2B(C_8H_{14})$, in conjunction with the bulky phosphazene base $^tBuNP(pyrrolidinyl)_3$.

In an analogous synthetic procedure with a more fluorinated derivative, **2a** reacts with $HB(C_6F_5)_2$ in toluene at ambient temperatures to precipitate almost quantitative yields of **2d** after *ca.* 5 min (Scheme 2). It seems that the increased Lewis acidity at boron that arises from the replacement of the methyl groups in **1c** with trifluoromethyl groups in **2c** results in a greater driving force to form the zwitterionic product. After 46 h in $CD_2Cl_2$ solution **2d** decomposes to **2c**, as well as two as-yet unidentified species. Hydrogen loss and similar side-products are observed in identical NMR spectra obtained by warming a slurry of **2d** in toluene to 70 °C for *ca.* 16 h. Independent synthesis of **2c** was achieved from **2b** and $ClB(C_6F_5)_2$.



**Scheme 2** Synthesis of **2a–2d**.

In stark contrast to **1d**, the X-ray crystal structure¶ confirms the presence of a P–B interaction in the solid state (Fig. 2). The persistence of this interaction in solution is supported by the broad $^{31}P$ resonance at 46 ppm, and a relatively sharp $^{11}B$ resonance at 5 ppm. Furthermore, a $\Delta\delta$ (*m*-F, *p*-F) separation of 6.4 ppm is consistent with a tetrahedral boron centre. Interestingly, the *ortho*-F and *meta*-F resonances appear as broad singlets at room temperature, but resolve at elevated temperatures suggestive of restricted rotation about the B–C bonds. Also noteworthy was the persistence of chemical shift, $\Delta\delta$ (*m*-F, *p*-F) separation, and by implication P–B interaction at temperatures up to 105 °C.

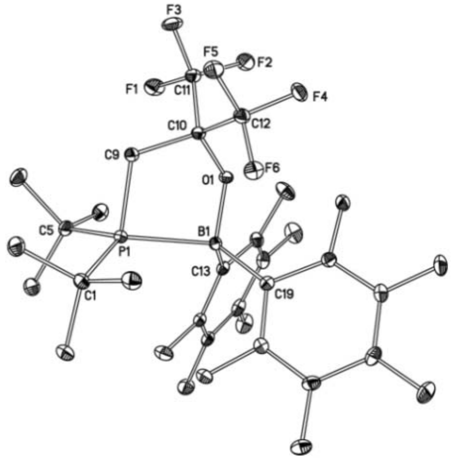


**Fig. 2** Molecular structure of **2c**. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.891(2), P1–C9 1.845(2), P1–C5 1.901(2), O1–C10 1.381(2), O1–B1 1.463(2), B1–C13 1.631(2), B1–C19 1.652(2), C9–P1–C5 104.9(1), C9–P1–C1 102.9(1), C5–P1–C1 111.6(2), O1–B1–C13 107.9(2), O1–B1–C19 114.1(2), C13–B1–C19 105.5(2).

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Hydrogenation of **2c** was attempted under the same range of conditions as **2d** but was unsuccessful. This is not surprising given the persistent P–B interaction in this compound.

In conclusion, we have demonstrated a new synthetic strategy to access linked phosphino-borinate frustrated Lewis pairs and investigated their reactivity towards hydrogen. Whilst heterolytic hydrogen cleavage to yield the corresponding zwitterions does not appear to be favourable, the isotopic scrambling of mixtures of $H_2$ and $D_2$ caused by **1c** suggests that reversible hydrogen activation is occurring but, in solution at least, the equilibrium is heavily biased towards the hydrogen-free pair.[13] From this it fits that the reverse reaction (hydrogen release) is by some margin the most facile to date. We suggest that a combination of the modified Lewis acidity and the possible proton-shuttle effect of the oxygen linker are responsible for this modified reactivity. Modification of the Lewis acidity of the boron centre by fluorination of the backbone linker structure has a drastic effect not least in the formation of a much stronger P–B interaction.

## Notes and references

‡ It is noted that the corresponding zwitterion formed from the 1,8-bis(diphenylphosphino)naphthalene–$B(C_6F_5)_3$ pair and hydrogen reported by Erker and co-workers[3] releases hydrogen at 60 °C.

§ *Crystal data*: **1d**: $C_{24}H_{28}BF_{10}OP$, $M = 564.24$, triclinic, $a = 15.722(1)$, $b = 16.265(1)$, $c = 21.551(1)$ Å, $\alpha = 89.298(2)$, $\beta = 68.628(2)$, $\gamma = 88.040(2)°$, $V = 5128.9(4)$, $T = 100(2)$, space group $P\bar{1}$, $Z = 8$, $\mu = 0.196$ mm$^{-1}$, $R_{int} = 0.0266$ (for 111 428 measured reflections), $R_1 = 0.1216$ [for 21 001 unique reflections with $>2\sigma(I)$], $wR_2 = 0.2732$ (for all 23 552 unique reflections).

¶ *Crystal data*: **2c**: $C_{24}H_{20}BF_{16}OP$, $M = 670.18$, monoclinic, $a = 9.8156(4)$, $b = 14.9264(6)$, $c = 17.6266(8)$ Å, $\beta = 90.736(3)°$, $V = 2582.29(19)$, $T = 100(2)$, space group $P2_1/n$, $Z = 4$, $\mu = 0.242$ mm$^{-1}$, $R_{int}$ n/a (non-merohedral twin), 5988 measured reflections, $R_1 = 0.0323$ [for 5083 unique reflections with $>2\sigma(I)$], $wR_2 = 0.0802$ (for all 5988 unique reflections).

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

2 A. J. Lough and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 52.

3 H. Wang, R. Fröhlich, G. Kehr and G. Erker, *Chem. Commun.*, 2008, 5966.

4 G. C. Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124.

5 V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskela, T. Repo, P. Pyykko and B. Rieger, *J. Am. Chem. Soc.*, 2008, **130**, 14117.

6 G. J. P. Britovsek, J. Ugolotti and A. J. P. White, *Organometallics*, 2005, **24**, 1685.

7 U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 135; V. Gutmann, *Coord. Chem. Rev.*, 1976, **18**, 225.

8 R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, 1982, **60**, 809.

9 S. M. Baxter and P. T. Wolczanski, *Organometallics*, 1990, **9**, 2508.

10 D. J. Parks, E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492.

11 C. Jiang, O. Blacque and H. Berke, *Organometallics*, 2009, **28**, 5233.

12 P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Frohlich and G. Erker, *Angew. Chem., Int. Ed.*, 2008, **47**, 7543.

13 A. J. M. Miller, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2010, **132**, 3301.

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