Heterolytic dihydrogen activation with the 1,8-bis(diphenylphosphino)-naphthalene/B(C$_6$F$_5$)$_3$ pair and its application for metal-free catalytic hydrogenation of silyl enol ethers†‡

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The "frustrated Lewis pair" 1,8-bis(diphenylphosphino)-naphthalene/B(C$_6$F$_5$)$_3$ reversibly activates dihydrogen; it serves as an active catalyst for the hydrogenation of silyl enol ethers under mild reaction conditions.

Wittig, Tochtermann and others[1] observed that some bulky borane/phosphane pairs (and related systems) are hindered toward the usual Lewis acid/Lewis base neutralization reaction. Tochtermann called such systems "antagonistische Paare". They were used *e.g.* in the addition reaction to benzyne to yield *ortho*-phenylene-bridged zwitterionic phosphonium/borate compounds. Much later Stephan *et al.* observed that "frustrated" borane/phosphane Lewis pairs, whose direct interaction was inhibited by steric bulk, added ethene (and other simple alkenes) between them to yield similarly structured alkylene-bridged zwitterions.[2] More importantly, "frustrated Lewis pairs",[3] such as *e.g.* (mesityl)$_3$P/B(C$_6$F$_5$)$_3$ (1) were shown by Stephan *et al.* to rapidly activate dihydrogen at ambient conditions to yield the respective phosphonium/hydridoborate salts, *e.g.* (mesityl)$_3$PH$^+$/HB(C$_6$F$_5$)$_3^-$ (2).[4–6] These systems were shown to act as imine hydrogenation catalysts at elevated temperature.[7] We had recently described the H$_2$-activation reaction by the weakly interacting intramolecular Lewis pair 3 to yield the zwitterion 4 (see Scheme 1).[8] The 3/4 system was shown to actively catalyze the hydrogenation reaction of a variety of enamines and of some bulky imines under very mild conditions at room temperature.[9] We have now found a unique "frustrated" P/B pair, that evaded a deactivating interaction by its special

conformative features and studied its ability for heterolytic H$_2$-activation and its catalytic hydrogenation properties.

When 1,8-bis(diphenylphosphino)naphthalene (5)[10] and B(C$_6$F$_5$)$_3$ were stoichiometrically mixed in d$_8$-toluene, the ^{31}P, ^{19}F and ^{11}B NMR spectra remained practically unchanged, suggesting no Lewis adduct was formed. This is in sharp contrast to the parent triphenylphosphine, which forms a classical Lewis adduct when mixed with B(C$_6$F$_5$)$_3$.[11] Consequently, the 1 : 1 mixture of 5 and B(C$_6$F$_5$)$_3$ reacted smoothly with dihydrogen (2 bar) at room temperature in toluene. We isolated the mono-phosphonium/hydridoborate salt (6) as a white solid in 80% yield (see Scheme 2). The formation of the [HB(C$_6$F$_5$)$_3^-$] anion was confirmed by its typical ^{19}F NMR spectrum featuring signals at δ −132.0 (*o*-), δ −163.7 (*p*-) and δ −166.4 (*m*-C$_6$F$_5$) in a 6 : 3 : 6 intensity ratio and a ^{11}B NMR doublet at δ −22.8 ($^1J_{BH}$ = 84 Hz; corresponding B*H* ^{1}H NMR resonance at δ 4.49 in d$_6$-benzene). The ^{31}P and ^{1}H NMR spectra of the (previously described)[12] 5-H$^+$ mono-cation are dynamic. The broad doublet observed in the ^{31}P NMR spectrum at 25 °C in d$_2$-dichloromethane decoalesces upon lowering the temperature to feature a doublet of doublets at δ 10.0 ($^1J_{PH}$ ≈ 557 Hz, J_{PP} = 110 Hz) for the −Ph$_2$PH$^+$ unit (^{1}H NMR P*H* signal at δ 10.1) and a doublet at δ −18.8 of the adjacent neutral −PPh$_2$ substituent at the naphthalene *peri*-positions. The analogous reaction of the 5/B(C$_6$F$_5$)$_3$ pair with D$_2$ gave the corresponding salt 5-D$^+$/[D-B(C$_6$F$_5$)$_3^-$] (6-D$_2$). In the ^{2}H NMR spectrum at 25 °C, it shows a broad [B]–D resonance at δ 4.34 and it features a broad ^{2}H NMR triplet at δ 9.73 with an exchange averaged coupling constant of J_{PD} ≈ 40 Hz.

The salt 6 was characterized by an X-ray crystal structure analysis (single crystals were obtained from pentane–dichloromethane by the diffusion method). The [HB(C$_6$F$_5$)$_3^-$] anion exhibits an averaged set of C–B–C angles of 112.8(3)° (B–C(C$_6$F$_5$) bond lengths between 1.626(5) Å and 1.630(5) Å). The corresponding cation shows a neutral −PPh$_2$ substituent at the naphthalene framework that features typical angles of a
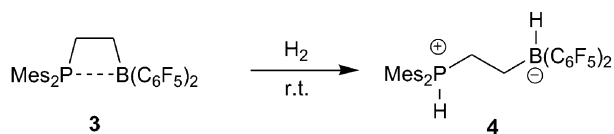
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† Electronic supplementary information (ESI) available: Experimental section and details of the quantum chemical calculations. CCDC 697210. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b813286k
‡ Dedicated to Professor Manfred T. Reetz on the occasion of his 65th birthday.
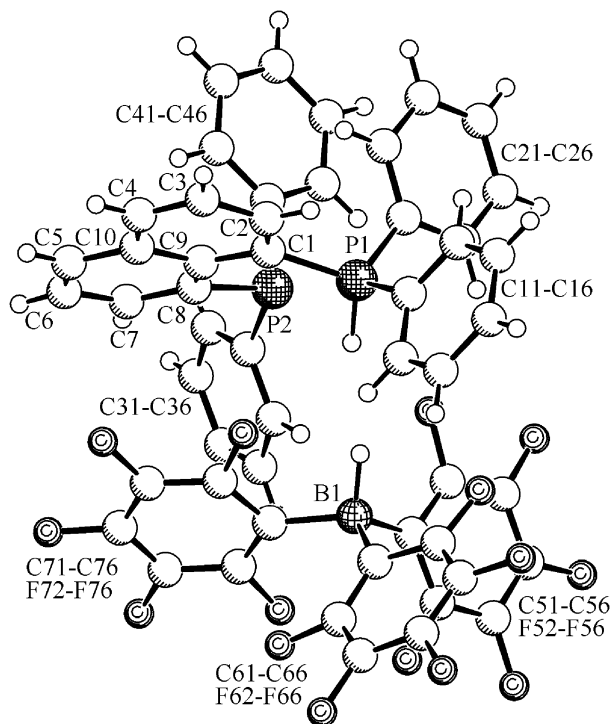§ X-Ray crystal structure analysis.

Scheme 1

Scheme 2
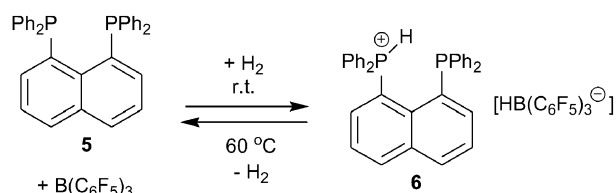
Fig. 1 A view of the molecular structure of the phosphonium/hydridoborate salt **6** featuring a weak P–H···H–B contact in the crystal.[14]

three-coordinate phosphane [C8–P2–C31 105.00(12)°, C8–P2–C41 102.14(13)°, C31–P2–C41 102.51(12)°; corresponding bond lengths P2–C41 1.824(3) Å, P2–C8 1.826(3) Å, P2–C31 1.826(3) Å]. The adjacent cationic –Ph$_2$PH$^+$ substituent shows markedly larger angles [C1–P1–C11 108.61(12)°, C1–P1–C21 113.60(14)°, C11–P1–C21 107.70(13)°, corresponding bond lengths P1–C21 1.788(3) Å, P1–C11 1.800(3) Å, P1–C1 1.805(3) Å]].

An exceptional feature of the structure of salt **6** is the observed weak P–H···H–B interaction[13] between the phosphonium cation and the hydridoborate anion (see Fig. 1) with a H···H distance of 2.08 Å.

The H$_2$-activation process by **5**/B(C$_6$F$_5$)$_3$ is reversible. Heating a solution of the salt **6** in d$_6$-benzene at 60 °C resulted in a practically quantitative formation of **5** and B(C$_6$F$_5$)$_3$, indicating stoichiometric loss of H$_2$. We note that the **5**/B(C$_6$F$_5$)$_3$/H$_2$ ⇌ **6** system is one of the rare examples of an observed reversible uptake/release of dihydrogen at a "frustrated Lewis pair".[4]

The facile manner of H$_2$ release from the salt **6** prompted us to explore the possibility of applying the **5** + B(C$_6$F$_5$)$_3$/**6** system as a hydrogenation catalyst. We chose a series of silyl enol ethers (**7**) as substrates for the hydrogenation reaction
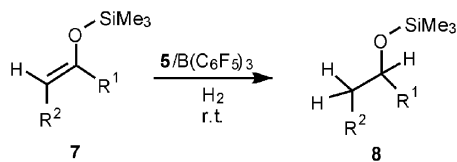
Scheme 3

Table 1 Hydrogenation of silyl enol ethers (**7**) catalyzed by **5**/B(C$_6$F$_5$)$_3^a$

Substrate	Product	Conversion^b (%)
7a	**8a**	>99 (93)
7b	**8b**	>99 (89)
7c	**8c**	>99 (86)
7d	**8d**	>99 (85)
7e	**8e**	16/>99^c

^{a} 20 mol% of **5**/B(C$_6$F$_5$)$_3$ in C$_6$D$_6$ under 2 bar H$_2$ at room temperature for 20 h. ^{b} Conversion was determined via ^{1}H NMR analysis and isolated yields are given in parentheses. ^{c} 20 mol% of **5**/B(C$_6$F$_5$)$_3$ in C$_6$D$_6$ under 60 bar H$_2$ at room temperature for 3 h.

(see Scheme 3)—to the best of our knowledge this was the first time that this class of compounds has been employed in such a metal-free catalytic hydrogenation. For the systems **7a–7d** (see Table 1) quantitative hydrogenation was achieved with 20 mol% of the **5** + B(C$_6$F$_5$)$_3$ catalyst system under mild conditions (2 bar H$_2$, room temperature). Under these conditions the hydrogenation of the least hindered substrate (**7e**) was only close to stoichiometric but a complete conversion to **8e** was achieved under more forcing conditions at 60 bar H$_2$ pressure.

We have shown that the 1,8-bis(diphenylphosphino)-naphthalene/B(C$_6$F$_5$)$_3$ pair reversibly activates dihydrogen under metal-free conditions with an unprecedentedly low temperature gap between absorption and release of H$_2$. Although this bis-phosphine at the naphthalene *peri*-positions does not act as a proton sponge,[15] it seems to favour a conformational orientation of the pair of –PPh$_2$ groups that prevents a direct P/B adduct formation. This system serves as an active catalyst for alkene hydrogenation in silyl enol ether substrates. Our approach to use a conformationally restricted

bifunctional bis-phosphine and $B(C_6F_5)_3$ to heterolytically activate dihydrogen extends the concept of "antagonistic/frustrated Lewis pairs" and will be useful for the development of novel catalyst systems[16] and potential hydrogen storage materials.

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