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PAPER

Reversible, metal-free hydrogen activation by frustrated Lewis pairs†

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The Lewis acid cyclohexylbis(pentafluorophenyl)boron **1**, which exhibits about 15% lower Lewis acidity in comparison with $B(C_6F_5)_3$, activates H_2 in the presence of the bulky Lewis bases 2,2,6,6-tetramethylpiperidine (**TMP**), 1,2,2,6,6-pentamethylpiperidine (**PMP**), tri-*tert*-butylphosphine (t-Bu_3P) leading in facile reactions at room temperature to heterolytic splitting of dihydrogen and formation of the salts [**TMP**H][$CyBH(C_6F_5)_2$] **2**, [**PMP**H][$CyBH(C_6F_5)_2$] **3** and [t-Bu_3PH][$CyBH(C_6F_5)_2$] **4**, which could be dehydrogenated at higher temperatures. The related Lewis acid 1-phenyl-2-[bis-(pentafluorophenyl)boryl]ethane **5** exhibiting about 10% lower Lewis acidity than $B(C_6F_5)_3$ is also capable of splitting H_2 in a heterolytic fashion in the presence of **TMP**, **PMP** and t-Bu_3P yielding [**TMP**H][$PhC_2H_4BH(C_6F_5)_2$] **6**, [**PMP**H][$PhC_2H_4BH(C_6F_5)_2$] **7** and [t-Bu_3PH][$PhC_2H_4BH(C_6F_5)_2$] **8**. Under comparable conditions as for **2–4**, the dehydrogenations of **6–8** were much slower. **4b** and **6** were characterized by single crystal X-ray diffraction studies.

Introduction

Dehydrogenation and hydrogenation processes are potential "fuelling" and "refuelling" reactions of a chemical storage system.[1,2] These reactions could occur as 1,2-eliminations/additions from/to a(n) saturated/unsaturated substrate or as binuclear activation processes. Both reactions should be reversible and facile, *i.e.* possessing low kinetic barriers. This is usually the case when the involved H atoms bear opposite polarizations.[3] Among the compounds with lighter main group elements, which were considered suitable for the given purpose, ammonia borane became a major research focus.[4–9] In recent years respective studies emphasized the dehydrogenation occuring as a 1,2-elimination process. As yet the system is irreversible partly due to thermodynamics, but also due to kinetic short-comings mainly caused by too strong bonds involved. Apparently compounds with heavier main group elements involving generally weaker E–H bonds allow dehydrogenation/hydrogenation reactions with lower barriers. Early model studies on homopolar hydrogenations were carried out in vapor phase with the heavier group 13 elements by trapping intermediates in frozen matrices.[10–12] Similarly, Power and co-workers reported that the highly unsaturated model compound "digermyne" can directly react with H_2 affording a mixture of digermene, digermane and germane.[13] One might speculate that the process takes the course of a direct 1,2-addition processes with simultaneous addition and splitting of the H_2 molecule or with bicentered radical type additions.[3] The mentioned reversible heteropolar binuclear activation pathway of H_2 as introduced by the work of Stephan and his co-workers established a new so-called "metal-free" way of hydrogenation/dehydrogenation. Frustrated Lewis pairs (FLPs), which are main group element "unquenched" Lewis acid–base pairs. The constituents stay remote by steric hindrance forming encounter complexes.[14–16] For instance, the addition of H_2 to the intramolecular Lewis pair $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ resulted in a zwitterionic phosphonium borate salt $(C_6H_2Me_3)_2PH^+(C_6F_4)B^-H(C_6F_5)_2$, thus activating H_2 in a heteropolar fashion at two reaction centers.[17] Due to their high molecular weights, such FLP compounds are certainly not suited for H_2 storage. But the given low energy pathways for H_2 activation may show new directions to develop efficient storage materials. In particular we thought it necessary to acquire more insights into the conditions for reversibility of the underlying chemical processes.

Following the pioneering work of Stephan, an increasing number of FLPs were studied exploring the chemical influence of the Lewis base.[18–38] It was found that the Lewis base function is not limited to phosphine centers, but could be extended to sterically demanding amines, imines, or N-heterocyclic carbenes. In contrast, the influence of the Lewis acid was studied much less. In the majority of FLPs $B(C_6F_5)_3$ was used. To extend the series of functional Lewis acids, our group has explored the role of 1,8-bis(dipentafluorophenyl)naphthalene, $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ in the activation of H_2 with bulky Lewis bases.[39,40] The hydrogenation process was found to proceed in a facile manner, but reversibility of the conversions could not be achieved. Tuning the Lewis acidity it was found that $B(p\text{-}C_6F_4H)_3$ with about 5% less acidity compared to $B(C_6F_5)_3$ (Gutmann–Beckett's method[41–44]) and presumably due to the changed electronics the FLP with $(o\text{-}C_6H_4Me)_3P$ enabled reversible activation of H_2 at room temperature.[28] Since in this case the change in the sterics and electronics of the Lewis acid was not much, we thought that

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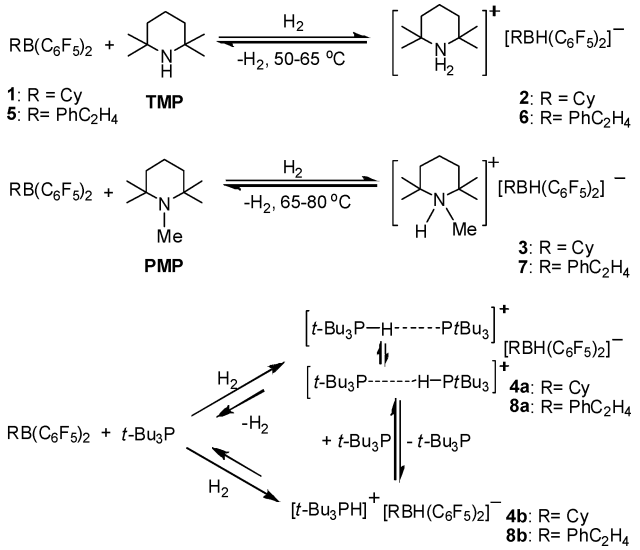
related variations of the $B(C_6F_5)_3$ master compound might not only lead to reversibly activating systems, but also to a conceptual conclusion of how to steer FLPs toward reversibility.

Results and discussion

With regard to reversible release of H_2, we aimed at the exploration of the Lewis acids cyclohexylbis(pentafluorophenyl)-boron **1** ($CyB(C_6F_5)_2$) and 1-phenyl-2-[bis(pentafluorophenyl)-boryl]ethane **5** ($PhC_2H_4B(C_6F_5)_2$) as FLP components modified for reduced Lewis acidity with respect to $B(C_6F_5)_3$. According to Gutmann–Beckett's method[41–44] these Lewis acids showed reduced acidities by about 15% and 10%. They were tested for reversible H_2 up-take in the presence of various bulky N,P-Lewis bases as shown in Scheme 1.



Scheme 1

To prepare $CyB(C_6F_5)_2$ (**1**), $HB(C_6F_5)_2$ was treated in a hydroboration reaction with 1 equiv. of cyclohexene in toluene, which afforded **1** as a white solid in 92% yield. The ^1H NMR spectrum showed signals for the cyclohexyl group at 2.04 (m, 1H, CH), 1.67 (m, 4H, CH_2), 1.20 ppm (m, 6H, CH_2). The ^{19}F NMR spectrum [δ –132.0 (*o*-), –149.9 (*p*-), –162.2 (*m*-C_6F_5) (C_6D_6)] was consistent with the presence of a three-coordinate boron atom ($\Delta\delta_{m,p} = 12.3$). We reckoned that the steric congestion of **1** would still be close to that of $B(C_6F_5)_3$ and any difference in the FLP reactivity of **1** was expected to originate from an electronic effect, *i.e.* its lower Lewis acidity, which was thought to be translated into a considerably weaker *B–H* bond of the tetracoordinate borate species with concomitant higher propensity for dehydrogenation.

Exposure of a toluene solution of the stoichiometric mixture of **1** and 2,2,6,6-tetramethylpiperidine (**TMP**) to an atmosphere of H_2 (1000 mbar) for 30 min afforded the H_2 cleaved ionic product [**TMP**H][$HBCy(C_6F_5)_2$] **2** (Scheme 1), which was isolated as a white solid in 76% yield. In the ^1H NMR spectrum **2** displayed a broad B*H* resonance at 2.67 ppm and a N*H* resonance at 4.74 ppm. The ^{19}F NMR spectrum featured a set of typical C_6F_5-borate resonances at δ –132.7 (*o*-), –164.6 (*p*-) and –167.1 (*m*-C_6F_5) ppm. The ^{11}B NMR signal was found to be split into a doublet at –15.5 ppm with a $^1J_{HB}$ coupling of 88 Hz supporting the presence of a boron bound H atom. Interestingly, **2** was quite unstable in solution indeed gradually releasing H_2 at room temperature. The H_2 liberation became accelerated when the solution was heated to 50 °C. The dehydrogenation reaction of **2** proceeded then so quickly that within 30 min the yield of free $CyB(C_6F_5)_2$ and **TMP** amounted to more than 80% (Fig. 1, curve 1). This is indeed one of the rare examples of a B,N FLP reversibly activating H_2 in solution, but apparently also in the solid state at room temperature, where **2** showed also slow release of H_2.

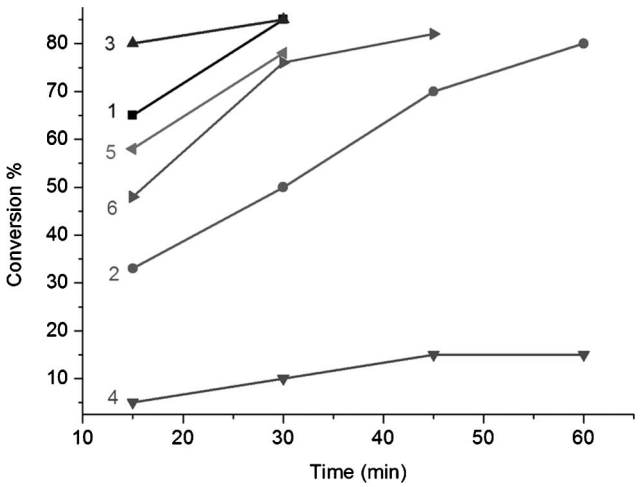


Fig. 1 Dehydrogenation of **2**, **3**, **6** and **7** in C_6D_6 at various temperatures. Curve 1: **2** at 50 °C, curve 2: **3** at 65 °C, curve 3: **3** at 80 °C, curve 4: **6** at 50 °C, curve 5: **6** at 65 °C, curve 6: **7** at 80 °C.

Modifying also the base component we then studied the H_2 reaction of the FLP **PMP**$\cdots BCy(C_6F_5)_2$ (**PMP** = 1,2,2,6,6-pentamethyl piperidine) according to Scheme 1 by exposure of a toluene solution of the stoichiometric mixture of **PMP** and $BCy(C_6F_5)_2$ to an atmosphere of H_2 (1000 mbar) for 1 h at room temperature. The reaction observed resulted in the formation of the ionic product [**PMP**H][$HBCy(C_6F_5)_2$] **3** isolated as an analytically pure, white solid in 72% yield (Scheme 1). In the ^1H NMR spectrum **3** featured broad N*H* and *BH* resonances at 5.42 and 2.70 ppm and in the ^{11}B NMR spectrum a signal at –15.7 ppm with a $^1J_{BH}$ coupling of 80 Hz. The reaction with H_2 turned out to be reversible, as well, occurring, however, at the somewhat elevated temperature of about 65 °C. The maximum conversion rate in a closed system was found to be about 80% within 1 h (Fig. 1. curve 2). At 80 °C, the maximum conversion was 85% within 30 min (Fig. 1, curve 3).

When the FLP *t*-$Bu_3P\cdots Cy(C_6F_5)_2$ containing a phosphorus Lewis base, was reacted with H_2 at room temperature, a white product was isolated in 74% yield after work-up. The NMR pursuit of the reaction mixture revealed in the ^{11}B NMR spectrum a broad signal located at –22.2 ppm. Surprisingly, in the ^1H NMR spectrum (C_6D_6) two P*H* resonances appeared at 4.61 (**4a**) and 5.71 ppm (**4b**) with $^1J_{HP}$ couplings of 438 and 453 Hz and in the ^{31}P NMR spectrum the corresponding resonances were found at 56.4 and 52.2 ppm (Fig. 2). The MAS ^{31}P NMR of solid **4** also exhibited two signals at 66.7 (broad) and 59.2 (sharp) ppm. Especially based on the relatively large chemical shift difference these could be attributed to the presence of a crystal mixture of **4a** and **4b**.

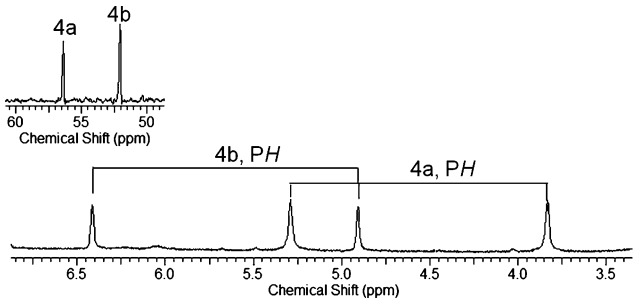


Fig. 2 31P{^{1}H} NMR (insert) and ^{1}H NMR spectrum of **4** in C_6D_6 at r.t.

It is interesting to note that when the FLP t-$Bu_3P\cdots CyB(C_6F_5)_2$ was reacted with D_2, the ^{1}H NMR spectrum also gave two P*H* resonances at 5.52 and 4.44 ppm, and the ^{31}P NMR spectrum exhibited four resonances at 56.8 (s, *P*H), 55.8 (t, *P*D), 52.9 (s, *P*H), 52.0 (t, *P*D) (Fig. 3). This observation suggested an exchange reaction between D and H. One assumption was that the reaction was initiated by the release of the *tert*-butyl cation from the generated $[t\text{-}Bu_3PD]^+$ cation. The relatively stable carbocation $[(CH_3)_3C]^+$ became then deprotonated by another molecule of t-Bu_3P to generate isobutylene $CH_2{=}C(CH_3)_2$, which then inserted into the intermediate [t-Bu_2PD] compound to generate a D-labelled t-Bu_3P. The release of isobutene and t-Bu_2PH from the cation $[t\text{-}Bu_3PH]^+$ has also been put forward for the $[t\text{-}Bu_3PH][HB(p\text{-}C_6F_4H)_3]$ case published by Stephan's group.[45] Also in this case evidence for the appearance of free $CH_2{=}C(CH_3)_2$ could not be provided, even in presence of a great excess of t-Bu_3P. We assumed the isobutylene insertion reaction was approximately as fast as the isobutylene generation, a circumstance, which naturally is expected to prevent detection of the free olefin. Once the isobutylene generated, it quickly inserts (Scheme 2).

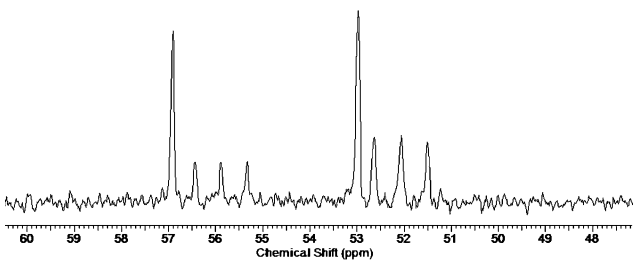
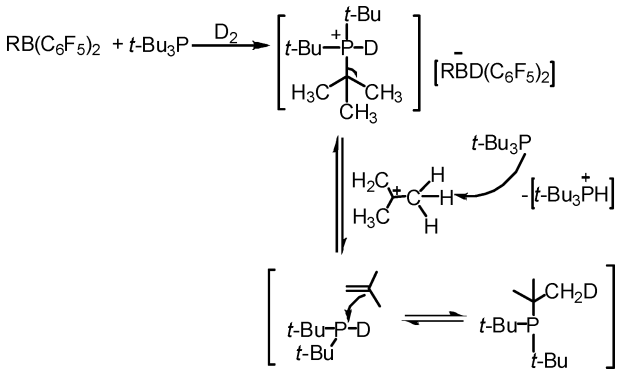


Fig. 3 31P{^{1}H} NMR spectrum of the FLP t-$Bu_3P\cdots CyB(C_6F_5)_2$ to react with D_2 in C_6D_6 at r.t.

The products of the reactions of the FLP t-$Bu_3P\cdots CyB(C_6F_5)_2$ with H_2 or D_2 in benzene were two species coexisting in solution and in solid state. One product should be the expected ionic product $[t\text{-}Bu_3PH][CyBH(C_6F_5)_3]$ **4b**, which is consistent with the NMR spectra (^{1}H NMR: 5.71 ppm; ^{31}P{^{1}H} NMR: 52.2 ppm) and the X-ray diffraction analysis, in which the anion and the cation are oriented "face-to-face" to each other with a non-bonding H1$\cdots$H2 distance of 2.63 Å (Fig. 4).[46] For the other species, several assumptions are given. One assumption was the Coulombic ion pair of **4a**, in which the cation and the anion were anticipated to be held together additionally by multiple, but generally weak, CH$\cdots$F, PH$\cdots$F or BH$\cdots$HP dihydrogen bonding interactions. These weak interactions of the hydrogen or dihydrogen bonding type were not detectable by NMR spectroscopy. T_1(min) or NOE



Scheme 2

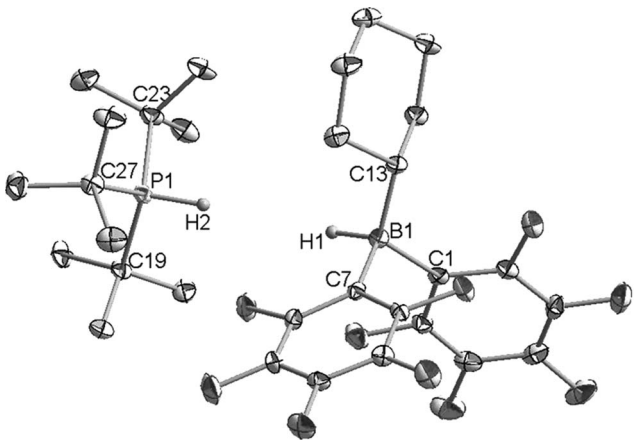


Fig. 4 Molecular structure of the ion pair **4b**, 30% probability thermal ellipsoids are shown. Hydrogen atoms except for the P*H* and B*H* are omitted for clarity. Selected bond lengths [Å]: B1–H1 1.205(12) B1–C1 1.651(2), B1–C7 1.653(2), B1–C13 1.630(2), P1–C19 1.8684(14), P1–C23 1.8748(15), P1–C27 1.8663(15), P1–H2 1.298(13). Selected bond angles [°] C13–B1–C1 116.93(12), C13–B1–C7 111.01(12), C1–B1–C7 106.27(11), C13–B1–H1 108.2(6), C1–B1–H1 105.7(6), C7–B1–H1 108.3(6), C27–P1–C19 114.50(7), C27–P1–C23 114.37(7), C19–P1–C23 113.90(7), C27–P1–H2 103.1(6), C19–P1–H2 105.8(6), C23–P1–H2 103.4(6).

measurements did not provide any hint for correlation effects between the cation and the anion. Another proposal for the structure of **4a** was the formation of $[t\text{-}Bu_2PH_2][CyBH(C_6F_5)_3]$ (or $[t\text{-}Bu_2PHD][CyBH(C_6F_5)_3]$), based on the generation of t-Bu_2PH during the H-D (H) exchange reaction. But no J(HD) J(PD) coupled resonances were observed in the ^{1}H NMR or the ^{31}P NMR spectrum and a ^{31}P NMR resonance was also not detected expected for the phosphonium cation $[t\text{-}Bu_2PH_2]^+$ at 26 ppm.[45] So this proposal could not be verified by appropriate spectroscopic compliance, as well.

Based on the fact that the isolated product mixture dissolved in the non-polar solvent C_6D_6 giving two different species, but in the polar solvent $CDCl_3$ only one species, we first of all reckoned that both compounds are structurally related. We suspected the unusual hydrogen bonded species $[t\text{-}Bu_3P\text{–}H\cdots PtBu_3][CyBH(C_6F_5)_2]$ to be **4a** (Scheme 1). The structure is assumed to possess a double minimum potential. A dynamic process could lead to exchange of the binding modes of the two P atoms. A dynamic process could not be "frozen" out even at

-80 °C. The ground state structures of a dynamic or a static P-H···P binding situation have only one strong covalent P–H contact, which leads, in both cases, to detectable doublet coupling in the ^{1}H NMR spectrum. In order to prove this assumption, we then varied the ratios of *t*-Bu_3P to $CyB(C_6F_5)_2$ in the reaction with H_2 and monitored the reaction course. The ratio of the products **4a** or **4b** turned out to be sensitive with respect to the applied amount of *t*-Bu_3P, only if *t*-Bu_3P was in great excess. For instance in the cases of the 1 : 2 or 1 : 1 ratios with respect to $CyB(C_6F_5)_2$, the majority of the product is **4b** [*t*-Bu_3PH][$CyBH(C_6F_5)_3$] and **4a** is formed in small amounts only. But when the *t*-Bu_3P to $CyB(C_6F_5)_2$ ratio was increased to 2 : 1, **4a** became the predominant product and **4b** could not be detected at all when *t*-Bu_3P was present in great excess (*t*-Bu_3P: $CyB(C_6F_5)_2$ = 5 : 1). This observation suggested that **4a** is formed from **4b** in an equilibrium reaction *via* the addition of *t*-Bu_3P (Scheme 1). **4a** featured a P*H* resonance at 4.61 ppm in ^{1}H NMR spectrum with a $^1J_{HP}$ coupling of 438 Hz. The lower *J*(HP) coupling of the P*H* signal of **4a** compared to **4b** of 453 Hz could indeed be related to [P–H···P] hydrogen bonding, since the hydrogen bonding of P(*t*Bu)$_3$ is expected to withdraw electron densities from the P–H bond and decrease its bond order. Additional experiments showed that both **4a** and **4b** were not stable in solution and gradually underwent dehydrogenation reactions. According to ^{1}H NMR and ^{31}P NMR pursuits, the P*H* signals of **4a** disappeared first at room temperature accompanied by the appearance of signals for free H_2 located at 4.45 ppm and of free *t*-Bu_3P. **4b** seemed somewhat more stable in this process, but it disappeared also at elevated temperatures.

Further investigations demonstrated that the dehydrogenation reaction of the mixture of **4** is quite temperature dependent. At room temperature and based on NMR spectroscopy, the conversion was about 30% within 3 h in C_6D_6 solution (Fig. 5, curve 1). While at 50 °C, the conversion reached 60% (Fig. 5, curve 2), and at the higher temperature of 80 °C more than 80% of free *t*-Bu_3P and $CyB(C_6F_5)_3$ were regenerated within 1 h (Fig. 5, curve 3).

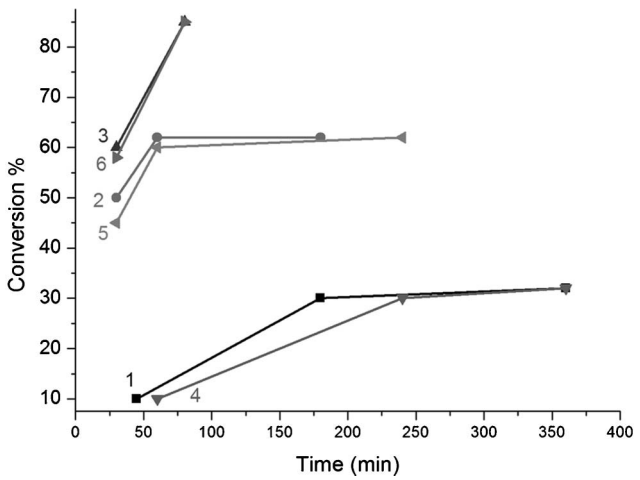


Fig. 5 Dehydrogenations of **4** and **8** in C_6D_6 at various temperatures pursued by ^{1}H NMR. Curve 1: **4** at r.t., curve 2: **4** at 50 °C, curve 3: **4** at 80 °C, curve 4: **8** at r.t., curve 5: **8** at 50 °C, curve 6: **8** at 80 °C.

The series of FLP combinations applied up to now, showed that the Lewis acidity of the Lewis acid is a crucial factor to achieve reversibility in the H_2 splitting. In addition it was found earlier that H_2 can be heterolytically cleaved by the *t*-$Bu_3P···B(C_6F_5)_3$, **TMP**$···B(C_6F_5)_3$ or **PMP**$···B(C_6F_5)_3$ FLPs, but none of the corresponding salts [*t*-Bu_3PH][$HB(C_6F_5)_3$], [**TMPH**][$HB(C_6F_5)_3$] and [**PMPH**][$HB(C_6F_5)_3$][47] could release H_2 even at higher temperatures. This inability was prevailingly attributed to a too high B–H bond strength in the $[HB(C_6F_5)_3]^-$ anion related to the higher Lewis acidity of $B(C_6F_5)_3$.

In order to further substantiate the given assumption of the Lewis acidity influence, we selected the Lewis acid $PhCH_2CH_2B(C_6F_5)_2$ **5** with a Lewis acidity between those of $BCy(C_6F_5)_2$ **1** and $B(C_6F_5)_3$. **5** was then applied in FLPs in combination with the same Lewis bases as for **1**. As expected, the FLPs **TMP**$···PhCH_2CH_2B(C_6F_5)_2$ and **PMP**$···PhCH_2CH_2B(C_6F_5)_2$ induced heterolytic splitting of H_2 at room temperature to form white solids of the ionic products [**TMPH**][$PhCH_2CH_2BH(C_6F_5)_2$] **6** and [**PMPH**][$PhCH_2CH_2BH(C_6F_5)_2$] **7** in 85% and 83% yield. Both of these ionic compounds featured in the ^{1}H NMR signals of the N*H* resonances with chemical shifts at 4.52 and 5.49 ppm in C_6D_6 similar to those of **2** and **3** indicating the presence of the same cationic species. In addition, the ^{19}F NMR resonances of **6** (–133.7 (*o*-), –164.3 (*p*-), –166.9 (*m*-C_6F_5) ppm) and **7** (–133.6 (*o*-), –164.1 (*p*-), –167.0 (*m*-C_6F_5) ppm) are comparable to those of **2** and **3**. As anticipated, both compounds **6** and **7** released H_2 under mild conditions, but the rates were not quite as high as in the $BCy(C_6F_5)_2$ cases. After 1 h at 50 °C, the conversion of **6** was only 15% (Fig. 1, curve 4), while for **2** it had reached more than 80% under the same conditions. In order to accomplish the same yields in the dehydrogenation process as for **2**, **6** required temperatures of about 65 °C. Due to the higher Lewis acidity of $PhCH_2CH_2B(C_6F_5)_2$, **5** was supposed to generate a stronger B–H bond in the hydrido borate anion than $BCy(C_6F_5)_2$ consequently requiring more severe conditions in dehydrogenation batches.

Single-crystals of **6** were grown from a toluene–hexane solution at 243 K and analyzed by X-ray diffraction. After refinement of the NH_2 and B*H* hydrogens a close B–H···H–N bonding contact of 1.88 Å could be extracted,[48] consistent with strong dihydrogen bonding (Fig. 6). Similar dihydrogen bonding was observed in the X-ray crystal structure of [*t*-$BuNH_2$-CH_2Ph][$HB(C_6F_5)_3$], in which the distance between one of the NH_2 protons and the B–*H* hydride was 1.87(3) Å.[49] Despite this close contact, no evidence was found for spontaneous dehydrogenation or dehydrogenation taking place at elevated temperatures. **6**, however, released H_2 at 65 °C was quite fast. This again provided evidence that reformation of H_2 from a [LBH][LAH] pair (LB: Lewis base; LA: Lewis acid) is mainly correlated with the strength of the B–H bond rather than with a kinetically feasible short contact between the protonic and hydridic hydrogen atoms.

The FLP *t*-$Bu_3P···BPhCH_2CH_2(C_6F_5)_2$ also enabled heterolytic activation of H_2 in the same way as the *t*-$Bu_3P···CyB(C_6F_5)_2$ system. The isolated product exhibited again two different P*H* resonances at 5.34 (**8b**, [*t*-Bu_3P–H···P*t*Bu_3][$PhCH_2CH_2BH(C_6F_5)_2$]) and at 4.13 ppm (**8a**, [*t*-Bu_3P–H][$PhCH_2CH_2BH(C_6F_5)_2$]) in the ^{1}H NMR spectrum in C_6D_6 solution with $^1J_{HP}$ coupling constants of 447 and 432 Hz and in the ^{31}P NMR spectrum also two signals were located at 53.5 (**8b**) and 57.4 ppm (**8a**). The solid state ^{31}P NMR also gave two different resonances of 59.3 (sharp, **8b**) and 64.0 (broad, **8a**) ppm indicating that both compounds are co-crystallizing. A similar observation

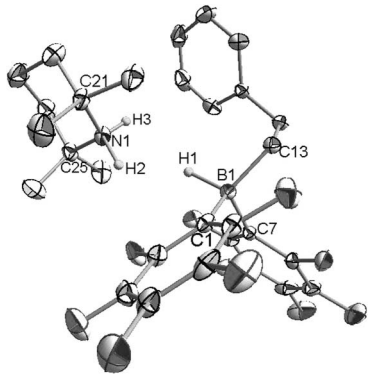


Fig. 6 Molecular structure of **6**, 30% probability thermal ellipsoids are shown. Hydrogen atoms except for the N*H* and B*H* are omitted for clarity. Selected bond lengths [Å]: B1–H1 1.283(18), B1–C1 1.643(2), B1–C7 1.639(2), B1–C13 1.634(2), N1–C21 1.542(2), N1–C25 1.528(2), N1–H2 0.98(2), N1–H3 0.89(2). Selected bond angles [°]: C25–N1–C21 120.63(12), C25–N1–H2 110.7(12), C21–N1–H2 104.9(12), C25–N1–H3 104.6(13), C21–N1–H3 109.1(13), H2–N1–H3 106.1(18), C13–B1–C7 109.27(12), C13–B1–C1 116.23(13), C7–B1–C1 108.43(12), C13–B1–H1 108.0(8), C7–B1–H1 110.6(8), C1–B1–H1 104.3(8).

was made as for **4**: when **8** was dissolved in the more polar solvent $CDCl_3$, only one species could be observed which was attributed to the structure of the solvated ions of **8b**.

By analogy to **4** we assume that there are two coexisting ion pairs **8a** and **8b** in benzene solution, and in the solid state we suppose in analogy to **4** the presence of a crystalline mixture of **8a** and **8b** (Scheme 1). Moreover, the ion pair **8a** seemed to be quite unstable in solution accompanied by fast H_2 loss, while **8b** in $CDCl_3$ was found to be more stable. At the elevated temperature of 80 °C, the conversion of the dehydrogenation of the mixture of **8** also increased to more than 80% (Fig. 4, curve 6).

Conclusions

In a tuning effort the two Lewis acids $CyB(C_6F_5)_2$ **1** and $PhC_2H_4B(C_6F_5)_2$ **5** were applied as FLPs in combination with the bulky Lewis bases **TMP**, **PMP** and *t*-Bu_3P to split dihydrogen heterolytically. In comparison with the known chemistry of the "parent" Lewis acid $B(C_6F_5)_3$, reversibility of the H_2 uptake was achieved for $CyB(C_6F_5)_2$ and $PhC_2H_4B(C_6F_5)_2$. Based on Gutmann's method, the relative Lewis acidities of the fluorinated boron Lewis acids are as follows: $B(C_6F_5)_3$ > $B(p\text{-}C_6F_4H)_3$ > $PhC_2H_4B(C_6F_5)_2$ > $CyB(C_6F_5)_2$. Changes in the Lewis bases turned out to be of secondary importance for hydrogenation/dehydrogenation reversibility. The main factor for reversible activation of H_2 was found to be the diminished Lewis acidity with regard to $B(C_6F_5)_3$ accomplished in this work by variation of one of the boron substituents.

Experimental

General

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze–thaw cycles prior to use. All organic reagents were purchased from Aldrich and used without further purification. $HB(C_6F_5)_2$ was synthesized according to the literature,[50,51] cyclohexene and styrene were dried before use. ^{1}H NMR, ^{19}F NMR and ^{11}B{^{1}H} NMR ^{31}P{^{1}H} NMR data were recorded on a Varian Gemini-300 spectrometer. Chemical shifts are expressed in parts per million (ppm) referenced to deuterated solvent used. ^{19}F NMR, ^{11}B{^{1}H} NMR and ^{31}P{^{1}H} NMR were referenced to $CFCl_3$, $BF_3{\cdot}OEt_2$ and 85% H_3PO_4, respectively. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with Mo-Kα radiation, λ = 0.71073 Å).[52] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, absorption correction and data reduction were performed with the Oxford program suite *CrysAlisPro*.[53] The structures were solved with direct methods (*SHELXS-97*) and were refined by full-matrix least-squares methods on F^2 (*SHELXL-97*).[54] All programs used during the crystal structure determination processes are included in the *WINGX* software.[55] The program *PLATON*[56] was used to check the result of the X-ray analyses.

Synthesis of $CyB(C_6F_5)_2$ 1 and $PhC_2H_4B(C_6F_5)_2$ 5. These two compounds were prepared in a similar fashion and thus for only one is the preparation detailed. $HB(C_6F_5)_2$ (0.346 g, 1 mmol) and cyclohexene (0.1 g, 1.2 mmol) were dissolved in 5 mL of toluene. The slurry turned clear after 5 min, the solution was stirred for an additional 30 min. Then the solvent was removed *in vacuo* to obtain **1** as a white solid which was washed by hexane and dried *in vacuo*.

$CyB(C_6F_5)_2$ 1. Yield: 92%. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 2.04 (m, 1H, CH), 1.67 (m, 4H, CH_2), 1.20 ppm (m, 6H, CH_2). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ –132.0 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), –149.9 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), –162.2 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5).

$PhC_2H_4B(C_6F_5)_2$ 5. Yield: 95%. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.12 (d, 2H, $^3J_{HH}$ = 6 Hz, Ph-*H*), 7.02 (m, 3H, Ph-*H*), 2.70 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 2.22 ppm (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ –131.6 (d, 4F, $^3J_{FF}$ = 20 Hz, *o*-C_6F_5), –148.4 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), –162.3 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5).

Lewis acidity tests according to the Gutmann–Beckett method in $CDCl_3$. *$^{31}P\{^1H\}$ NMR*: $Ph_3P{=}O$ reference: δ = 29.5. $(Ph_3P{=}O)B(C_6F_5)_3$ reference addcut: δ = 45.5. Reference shift: $\Delta\delta$ = 16.0. $(Ph_3P{=}O)B(Cy)(C_6F_5)_2$ reference adduct: δ = 42.0. Reference shift: $\Delta\delta$ = 12.5. Lewis-acidity relative to $B(C_6F_5)_3$: 78.1%. $(Ph_3P{=}O)B(PhCH_2CH_2)(C_6F_5)_2$ reference adduct: δ = 42.3. Reference shift: $\Delta\delta$ = 12.8. Lewis-acidity relative to $B(C_6F_5)_3$: 80.0%. $Et_3P{=}O$ reference: δ = 52.8. $(Et_3P{=}O)B(C_6F_5)_3$ reference adduct: δ = 76.3. Reference shift: $\Delta\delta$ = 23.5. $(Et_3P{=}O)B(Cy)(C_6F_5)_2$ reference adduct: δ = 72.8. Reference shift: $\Delta\delta$ = 20.0. Lewis-acidity relative to $B(C_6F_5)_3$: 85.1%. $(Et_3P{=}O)B(PhCH_2CH_2)(C_6F_5)_2$ reference adduct: δ = 74.4. Reference shift: $\Delta\delta$ = 21.6. Lewis-acidity relative to $B(C_6F_5)_3$: 91.9%. ***Gutmann–Beckett* in C_6D_6.**

$^{31}P\{^{1}H\}$ NMR: $Ph_3P{=}O$ reference: $\delta = 25.3$. $(Ph_3P{=}O)B(C_6F_5)_3$ reference adduct: $\delta = 45.6$. Reference shift: $\Delta\delta = 20.3$. $(Ph_3P{=}O)B(Cy)(C_6F_5)_2$ reference adduct: $\delta = 42.1$. Reference shift: $\Delta\delta = 16.8$. Lewis-acidity relative to $B(C_6F_5)_3$: 82.8%. $(Ph_3P{=}O)B(PhCH_2CH_2)(C_6F_5)_2$ reference adduct: $\delta = 42.3$. Reference shift: $\Delta\delta = 17.0$. Lewis-acidity relative to $B(C_6F_5)_3$: 83.7%. $Et_3P{=}O$ reference: $\delta = 46.0$. $(Et_3P{=}O)B(C_6F_5)_3$ reference adduct: $\delta = 75.8$. Reference shift: $\Delta\delta = 29.8$. $(Et_3P{=}O)B(Cy)(C_6F_5)_2$ reference adduct: $\delta = 72.5$. Reference shift: $\Delta\delta = 26.5$. Lewis-acidity relative to $B(C_6F_5)_3$: 88.9%. $(Et_3P{=}O)B(PhCH_2CH_2)(C_6F_5)_2$ reference adduct: $\delta = 74.2$. Reference shift: $\Delta\delta = 28.2$. Lewis-acidity relative to $B(C_6F_5)_3$: 94.6%.

Preparation of [TMPH][CyBH(C_6F_5)$_2$] 2, [PMPH][CyBH(C_6F_5)$_2$] 3, [*t*-Bu_3PH][CyBH(C_6F_5)$_2$] 4, [TMPH][$PhC_2H_4BH(C_6F_5)_2$] 6, [PMPH][$PhC_2H_4BH(C_6F_5)_2$] 7, [*t*-Bu_3PH][$PhC_2H_4BH(C_6F_5)_2$] 8. **2–4** and **6–8** were all prepared in the same way. Their preparations are described in general form (LA = Lewis acid. LB = Lewis base). Stoichiometric amounts of LA (0.2 mmol) and LB (0.2 mmol) were dissolved in 5 mL of toluene, giving a colorless solution. The reaction vessel was filled with 1000 mbar of H_2 and the solution was stirred at room temperature for 1 h. The reaction mixture was then concentrated to half of its volume, and hexane was added to induce precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*.

Compound 2. $CyB(C_6F_5)_2$ (0.0856 g, 0.2 mmol) and **TMP** (0.0283 g, 0.2 mmol). **2** was obtained as a white solid, yield 76%. Anal. Calcd for $C_{27}H_{32}BF_{10}N$: C, 56.76; H, 5.65; N, 2.45. Found: C, 56.51; H, 5.60; N, 2.50. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 4.74 (br, 2H, N*H*), 2.67 (br, 1H, B*H*), 2.03 (m, 4H, CH_2), 1.70 (m, 4H, CH_2), 1.48 (m, 1H, CH), 1.18 (m, 2H, CH_2), 0.72 (overlap, 18H, CH_2, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ –132.7 (d, 4F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), –164.6 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), –167.1 (t, 4F, $^3J_{FF}$ = 21 Hz, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (C_6D_6, 96 MHz, 298 K): δ –15.5 ppm (br).

Compound 3. $CyB(C_6F_5)_2$ (0.0856 g, 0.2 mmol) and PMP (0.034 g, 0.2 mmol). **3** was obtained as a white solid, yield 72%. Anal. Calcd for $C_{28}H_{34}BF_{10}N$: C, 57.45; H, 5.85; N, 2.39. Found: C, 57.07; H, 5.47; N, 2.04. ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ 5.42 (br, 1H, N*H*), 2.70 (br, 1H, B*H*), 2.12 (m, 3H, Cy-H), 1.83 (d, 3H, $^3J_{HH}$ = 6 Hz, N-CH_3), 1.45 (m, 2H, Cy-H), 1.26 (m, 6H, Cy-H), 1.04 (m, 2H, CH_2), 0.90 (m, 4H, CH_2), 0.76 (s, 6H, CH_3), 0.34 (s, 6H, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ –132.5 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), –164.9 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), –167.3 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (C_6D_6, 96 MHz, 293 K): δ –15.7 ppm (br).

Compounds 4a and 4b. $CyB(C_6F_5)_2$ (0.0856 g, 0.2 mmol) and *t*-Bu_3P (0.04 g, 0.2 mmol). **4a** and **4b** were obtained as a white solid, yield 74%. Anal. found: C, 56.77; H, 6.51. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 5.71 (d, $^1J_{HP}$ = 453 Hz, P*H*, **4b**), 4.61 (d, $^1J_{HP}$ = 438 Hz, P*H*, **4a**), 3.16 (br, 1H, B*H*), 2.23 (m, 1H, CH), 1.97 (m, 4H, CH_2), 1.76 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 0.85 (d, 27H, $^3J_{H-P}$ = 15 Hz, P{(C(CH_3)$_3$}). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ –132.1 (overlap, *o*-C_6F_5), –165.9 (t, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5, **4b**), –166.8 (t, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5, **4a**), –167.9 (t, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5, **4b**), –168.4 ppm (t, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5, **4a**). $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz, 298 K): δ 56.4 (**4a**), 52.2 (**4b**) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6, 96 MHz, 298 K): δ –22.2 ppm (br).

Compound 6. $PhCH_2CH_2B(C_6F_5)_2$ (0.09 g, 0.2 mmol) and **TMP** (0.0283 g, 0.2 mmol). **6** was obtained as a white solid, yield 85%. Anal. Calcd. for $C_{29}H_{30}BF_{10}N$: C, 58.70; H, 5.10; N, 2.36. Found: C, 58.42; H, 5.02; N, 2.23. ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ 7.38 (d, 2H, $^3J_{HH}$ = 6 Hz, Ph–*H*), 7.18 (t, 2H, $^3J_{HH}$ = 6 Hz, Ph–*H*), 7.03 (t, 1H, $^3J_{HH}$ = 6 Hz, Ph–*H*), 4.52 (br, 2H, N*H*), 2.85 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 1.75 (br, 2H, CH_2), 0.89 (m, 2H, CH_2), 0.78 (m, 2H, CH_2), 0.69 (s, 12H, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ –133.7 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), –164.3 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), –166.9 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (C_6D_6, 96 MHz, 293 K): δ –18.8 ppm (br).

Compound 7. $PhCH_2CH_2B(C_6F_5)_2$ (0.09 g, 0.2 mmol) and **PMP** (0.034 g, 0.2 mmol). **7** was obtained as a white solid, yield 83%. Anal. Calcd. for $C_{30}H_{32}BF_{10}N$: C, 59.32; H, 5.31; N, 2.31. Found: C, 59.53; H, 5.41; N, 2.33. ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ 7.42 (d, 2H, $^3J_{HH}$ = 6 Hz, Ph-*H*), 7.26 (t, 2H, $^3J_{HH}$ = 6 Hz, Ph–*H*), 7.13 (t, 1H, $^3J_{HH}$ = 6 Hz, Ph–*H*), 5.49 (br, 1H, N*H*), 2.80 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 1.77 (m, 2H, CH_2), 1.61 (d, 3H, $^3J_{HH}$ = 6 Hz, N-CH_3), 1.23 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 0.79 (m, 4H, CH_2), 0.65 (s, 6H, CH_3), 0.18 ppm (s, 6H, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ –133.6 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), –164.1 (t, 3F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), –167.0 (t, 6F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (C_6D_6, 96 MHz, 293 K): δ –18.6 ppm (br).

Compounds 8a and 8b. $PhCH_2CH_2B(C_6F_5)_2$ (0.09 g, 0.2 mmol) and *t*-Bu_3P (0.04 g, 0.2 mmol). **8a** was obtained as a white solid, yield 78%. Anal. Calcd. for $C_{32}H_{38}BF_{10}P$: C, 58.73; H, 5.85. Found: C, 58.59; H, 5.72. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.49, 7.25, 7.10 (Ph–*H*), 5.34 (d, $^1J_{HP}$ = 447 Hz, P*H*, **8b**), 4.13 (d, $^1J_{Hp}$ = 432 Hz, P*H*, **8a**), 3.00, 2.81, 1.88, 1.58, 1.22 (CH_2), 0.74 (d, 27H, $^3J_{H-P}$ = 15 Hz P{(C(CH_3)$_3$}). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ –133.1 (overlap, *o*-C_6F_5), –165.6 (t, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5, **8b**), –166.7 (t, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5, **8a**), –167.7 (t, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5, **8b**), –168.3 (t, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5, **8a**). $^{31}P\{^1H\}$NMR (C_6D_6, 121 MHz, 298 K): δ 57.4 (**8a**), 53.5 (**8b**).$^{11}B\{^1H\}$ NMR (C_6D_6, 96 MHz, 298 K): δ –18.5 ppm (br).

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