Metal-free dihydrogen activation chemistry: structural and dynamic features of intramolecular P/B pairs†‡

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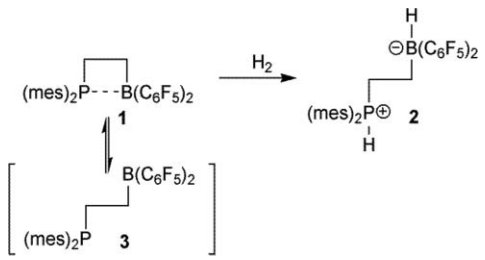
Hydroboration of allyl(dimesityl)phosphane with $HB(C_6F_5)_2$ gives the intramolecular five-membered P–B Lewis pair **7**, that was characterized by X-ray diffraction. Similarly, $HB(C_6F_5)_2$ addition to the substrates $(mesityl)_2P–CR{=}CH_2$ (R = CH_3, Ph) yield the corresponding $(mesityl)_2P(\mu\text{-}CHRCH_2)B(C_6F_5)_2$ products **9a** (R = CH_3) and **9b** (R = Ph) that show a weak intramolecular P···B interaction. The activation energy of the (reversible) P···B cleavage of these substrates was determined by dynamic ^{19}F NMR spectroscopy (**9a**: $\Delta G^{\neq}_{inv}$ (280 K) = 11.7 ± 0.4 kcal mol^{-1}). Compounds **9b** and **9c** show similar values. Compound **9c** was prepared by $HB(C_6F_5)_2$ addition to $(mesityl)_2P–CH{=}CHSiMe_3$. Compound **9a** reacts rapidly with dihydrogen (2.5 bar) at room temperature in pentane to give the zwitterionic H_2-activation product $(mesityl)_2PH^+(\mu\text{-}CHMeCH_2)BH^-(C_6F_5)_2$ (**11**).

Introduction

Following the pioneering work by Stephan *et al.*[1] an increasing number of metal-free heterolytic hydrogen splitting systems based on "frustrated"[2] (or "antagonistic")[3] Lewis pairs are beginning to appear in the literature.[4,5] We have contributed a remarkable early example.[6] The system **1** contains a weakly intramolecularly interacting phosphane Lewis base/borane Lewis acid pair that splits dihydrogen rapidly at room temperature and low H_2 pressure to yield the ethylene-linked phosphonium–hydridoborate zwitterion **2**. The betaine **2** transfers (Scheme 1) the activated H^+/H^- pair under very mild conditions to a variety of unsaturated compounds. The **1**–**2** pair serves as an efficient hydrogenation catalyst[7] for a variety of substrates, such as enamines, bulky imines and (less efficiently) silyl enol ethers.[8,9]



Scheme 1

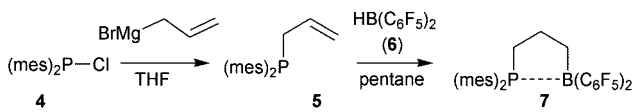
So far the intramolecular Lewis pair **1** has not been structurally characterized by X-ray diffraction due to the lack of suitable single crystals. However, a state of the art DFT calculation has revealed some interesting structural features of **1**[6] such as a π–π stacking interaction between a mesityl group at phosphorus and a parallel pentafluorophenyl substituent at boron,[10] which actually contributes a substantial fraction of the total phosphane–borane interaction energy of this intramolecular Lewis pair. S. Grimme's DFT calculation[6] has also revealed that this Lewis pair is easily cleaved: two conformationally different open local isomeric minima (**3**) were found to be both just *ca.* 7 kcal mol^{-1} in energy above the global minimum (**1**).

In this study, we have prepared a close structural model of **1** with regard to the π–π stacking interaction of the aryl substituents along the P···B vector.[10] In addition, we have gained some experimental evidence for the rapid endothermic **1** ⇄ **3** equilibration by preparing suitably substituted derivatives of **1** and investigating their dynamic features.

Results and discussion

Hydroboration of allyl(dimesityl)phosphane

The reaction of chlorodimesitylphosphane (**4**)[11] with allylmagnesium bromide in THF gave allyldimesitylphosphane (**5**) in 60% yield. This was then treated with an equimolar amount of $HB(C_6F_5)_2$ (**6**).[12] A clean regioselective hydroboration reaction took place at ambient conditions in pentane. We isolated the trimethylene-bridged phosphane/borane product (**7**) in *ca.* 70% yield as a white solid (Scheme 2).



Scheme 2

Compound **7** features three ^1H NMR CH_2 multiplets at δ 2.73, 1.77 and 1.72 ppm with corresponding ^{13}C NMR signals at δ 27.0 ($^1J_{PC}$ = 39.8 Hz), 24.6 (broad) and 21.9 ppm ($^2J_{PC}$ = 12.7 Hz). The ^{31}P NMR signal is at δ 20.8 ppm and the ^{11}B NMR resonance was located at δ –2.7 ppm (in [D_6]benzene). Compound **7** features a

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† Electronic supplementary information (ESI) available: Lineshape analysis of **9a** and error calculations of kinetic parameters. CCDC reference number 701817 for compound **7**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b815832k

‡ Dedicated to Professor Hans-Joachim Galla on the occasion of his 60th birthday.

set of ^{19}F NMR signals at δ −127.4 (*o*), −158.4 (*p*) and −164.4 ppm (*m*-F of C_6F_5). The $\Delta\delta$ (*m*-F)–(*p*-F) separation is consistent with a tetracoordinate boron situation, but we note that it is slightly larger at $\Delta\delta = 6$ ppm than typically observed of classical $RB(C_6F_5)_3$ borate examples.[13]

Compound **7** was characterized by an X-ray crystal structure analysis (single crystals from ether). In the crystal, the system **7** exhibits a cyclic framework that consists of three carbon atoms, the phosphorus and the boron center. These make up a core of the molecule that features a slightly distorted cyclopentane-like envelope conformation (see Fig. 2).[14] The carbon atoms C1, C2, C3 and the phosphorus atom P1 are arranged almost co-planar (dihedral angle −11.3(6)°). The boron atom marks the "tip" of the envelope structure (dihedral angles C2–C1–P1–B1 −18.2(5)°, C1–P1–B1–C3 39.5(4)°). In this characteristic conformation the C31–C36 C_6F_5 group at boron and the C11–C16 mesityl substituent at phosphorus come into an arrangement (see Fig. 1) that indicates some potential π–π stacking interaction (dihedral angle C11–P1–B1–C31 44.5(5)°, C16 ··· C36 separation 3.213(9) Å).

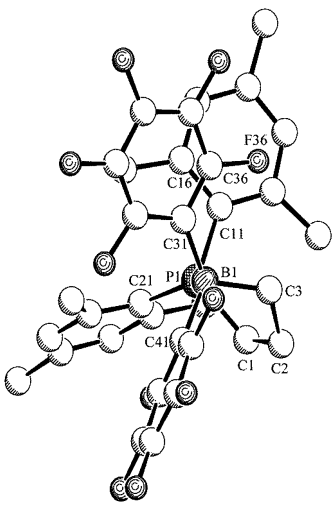


Fig. 1 A view of the molecular geometry of compound **7** (hydrogen atoms omitted for clarity): selected bond lengths (Å) and angles (°): P1–B1 2.092(7), P1–C1 1.827(6), P1–C11 1.848(7), P1–C21 1.856(6), C1–C2 1.563(8), C2–C3 1.541(9), C3–B1 1.615(9), B1–C31 1.641(10), B1–C41 1.651(9); B1–P1–C1 93.8(3), B1–P1–C11 106.0(3), B1–P1–C21 131.8(3), C1–P1–C11 113.6(3), C1–P1–C21 103.4(3), C11–P1–C21 107.5(3), P1–C1–C2 107.5(4), C1–C2–C3 110.1(5), C2–C3–B1 108.9(5), C3–B1–P1 91.5(4), C3–B1–C31 117.7(5), C3–B1–C41 105.8(5), C31–B1–C41 112.8(5).

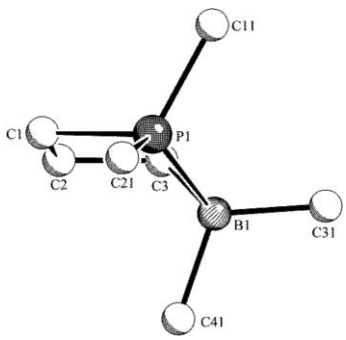


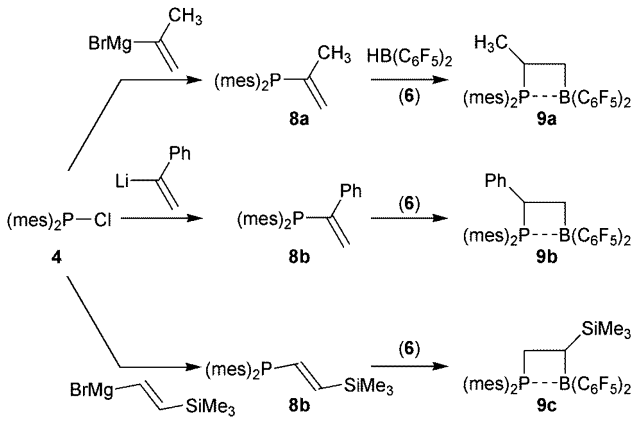
Fig. 2 A projection of the envelope-shaped core of compound **7**.

The angles inside the five-membered heterocycle are small (*e.g.* C1–P1–B1 93.8(3)°, C3–B1–P1 91.5(4)°). The P1–B1 bond length is 2.092(7) Å. This is slightly longer as compared to the related reference compounds $[Ph_2P(CH_2)_3B(C_6F_5)_2]$ (2.060(2) Å) or $[Ph_2P(CH_2)_4B(C_6F_5)_2]$ (2.021(3) Å) that we had previously described.[14,15]

Hydroboration of alkenyl(dimesityl)phosphanes

Three differently substituted alkenyl(dimesityl)phosphanes were prepared by the reactions of Mes_2PCl (**4**) with the respective alkenyl Grignard or alkenyl lithium reagents. Compound **8a** was thus obtained in 49% yield from the reaction of the substrate **4** with 2-propenylmagnesiumbromide. α-Lithiostyrene was generated by treatment of α-bromostyrene with *n*-butyl lithium. Its subsequent reaction with **4** then gave the alkenylphosphane **8b** (21% isolated). Eventually, we treated **4** with *E*-(2-TMS-vinyl)MgBr and isolated the corresponding trimethylsilyl-substituted alkenyl phosphane product **8c** in 26% yield after chromatographic purification.

Each of the three alkenylphosphanes (**8**) was then subjected to the hydroboration reaction with $HB(C_6F_5)_2$ (**6**) in pentane at ambient reaction conditions. The corresponding alkylene-bridged phosphane/borane products **9a–9c** were isolated as off-white solids in 64–96% yield (Scheme 3).



Scheme 3

The products **9** were characterized by C, H elemental analysis and by NMR spectroscopy. In $[D_6]$benzene at 298K, compound **9a** features a very typical set of NMR signals of the central P–$CH(CH_3)CH_2$ unit. It shows a ^{1}H NMR dd of the methyl substituent at carbon atom C1 at δ 0.87 ppm ($^3J_{PH} = 15.5$ Hz, $^3J_{HH} = 6.8$ Hz, 3H). The bridge CH_2 unit features diastereotopic hydrogens (δ 2.96 and 1.69 ppm), one of which shows a very large $^3J_{PH} = 106.9$ Hz coupling constant.[16] The ^{31}P NMR resonance of **9a** appears at δ 33.2 ppm and the ^{11}B NMR signal is observed at δ 3.2 ppm. The mesityl substituents at P are diastereotopic. We monitor two mesityl *m*-CH ^{1}H NMR signals at δ 6.56 and 6.35 ppm, each of 2H intensity.

The ^{19}F NMR spectrum of compound **9a** is strongly temperature dependent. In $[D_8]$toluene at 323K, we observe a set of only three signals at δ −128.8 (br. 4F, *o*), −157.2 (2F, *p*) and −163.5 ppm (4F, *m*-C_6F_5). Upon lowering the temperature we monitor a series of decoalescing signals indicating the presence of a combination of three dynamic processes that become subsequently frozen out

on the NMR time scale (^{19}F, 564 MHz). Upon cooling, the single (averaged) *p*-C_6F_5 resonance rapidly broadens and decoalesces to a 1 : 1 intensity pair (T_{coal} = 280 K) with a separation of $\Delta\nu$ = 1015 Hz at 233 K. This feature is probably due to the reversible opening process of the P–B linkage in **9a**, resulting in a symmetry equivalence of the pair of C_6F_5 substituents at the trigonally planar coordinated boron center at the stage of the alleged equilibrating acyclic isomeric intermediate.

The analogous process can be followed by the line shape analysis of the *o*- and *m*-C_6F_5 ^{19}F NMR resonances. The decoalescence behaviour of the *o*-C_6F_5 signal at δ –128.8 ppm is complicated by the overlapping of the freezing of two different dynamic processes within the same temperature range. Consequently, the δ –128.8 ppm signal splits into three signals upon lowering the temperature to 253 K, namely a 1 : 1 intensity pair at δ –123.7 and –137.0 ppm ($\Delta\nu$ = 7557 Hz) and a broad singlet at δ –127.7 ppm of 2F relative intensity (see Fig. 3). This latter *o*-C_6F_5 ^{19}F NMR resonance splits into another 1 : 1 pair of resonances (δ –123.2 and –132.0 ppm $\Delta\nu$ = 5076 Hz) upon further lowering the monitoring temperature. The pair of *m*-C_6F_5 resonances analogously decoalesces upon further lowering the temperature eventually to a tight group of four resonances, each of 1F relative intensity.

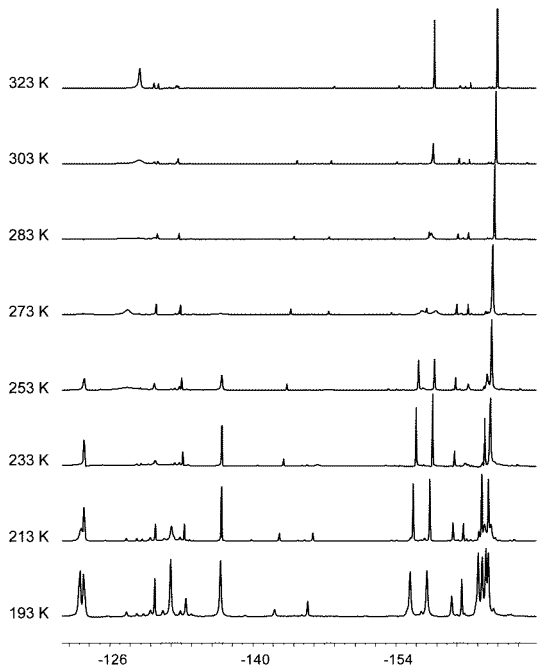


Fig. 3 Temperature-dependent dynamic ^{19}F NMR spectra of compound **9a** (in [D8]toluene, 564 MHz).

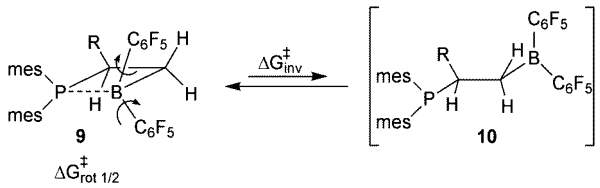
We assume that the decoalescence process of the *p*-C_6F_5 signal corresponds to the ring opening process of the four-membered heterocyclic framework structure of **9a** by cleavage of the phosphorus boron linkage (**9** ⇄ **10**) (see Scheme 4). From the lineshape analysis[17] (for details see the ESI†) we have calculated a Gibbs activation energy of $\Delta G^{\neq}_{inv}$ (280 K) = 11.7 ± 0.4 kcal mol^{-1}. For the temperature range between 333–233 K this led to values of $\Delta H^{\neq}$ = 15.9 kcal mol^{-1} and $\Delta S^{\neq}$ = 15.0 cal Grd.$^{-1}$ mol^{-1}. The additional decoalescence processes that we have observed are likely to correspond to freezing the rotation of the B–C_6F_5 linkages.[18]

Table 1 Gibbs activation energies of the P–B cleavage of the complexes **9** ($\Delta G^{\neq}_{inv}$) and energy barriers of the B–C_6F_5 rotational processes ($\Delta G^{\neq}_{rot}$)[a]

Compound	**9a** (1-CH_3)	**9b** (1-Ph)	**9c** (2-$SiMe_3$)
$\Delta G^{\neq}_{inv}$ (T/K)	11.7 (280)	12.6 (303)	11.8 (298)
$\Delta G^{\neq}_{rot1}$ (T/K)	11.2 (295)	11.9 (313)	9.6 (248)
$\Delta G^{\neq}_{rot2}$ (T/K)	9.1 (238)	9.7 (253)	9.5 (248)

[a] $\Delta G^{\neq}$ values ± 0.4 kcal mol^{-1}, $T_{coal.}$ in K, for details see the ESI†.

For the $B(C_6F_5)_2$ pair we have found two rather different Gibbs activation energy barriers of $\Delta G^{\neq}_{rot\,1}$ (295 K) = 11.2 ± 0.4 kcal mol^{-1} and $\Delta G^{\neq}_{rot\,2}$ (238 K) = 9.1 ± 0.4 kcal mol^{-1}.



Scheme 4

Compound **9b** features similar NMR data [^{31}P: δ 40.3 ppm; ^{11}B: δ 2.5 ppm; ^{1}H: δ (CH_2) = 3.19 ppm ($^3J_{PH}$ = 110.1 Hz), 2.30 ppm]. The ^{19}F NMR spectrum is again dynamic. From the decoalescence of the respective *o*- and *p*-C_6F_5 resonances we have calculated the set of three Gibbs activation energies of **9b**, which were in a similar range as found for **9a** (see Table 1 and Fig. 4).

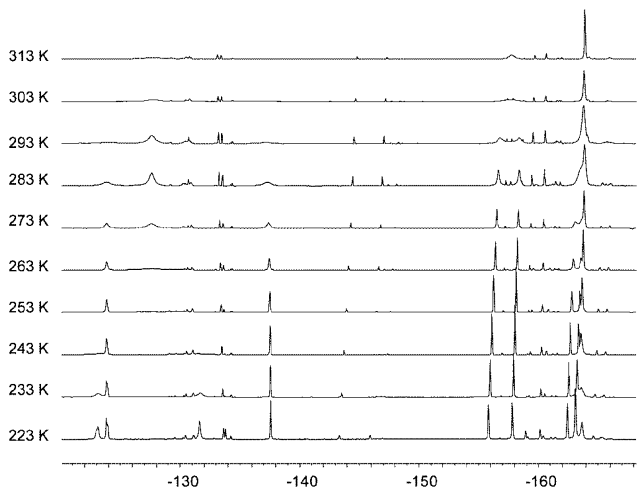


Fig. 4 Dynamic ^{19}F NMR spectra (564 MHz) of compound **9b** (in [D_8]toluene).

Compound **9c** features the $SiMe_3$ substituent at the β-carbon atom of the bridge, adjacent to the boron center. This gives rise to a ^{1}H NMR trimethylsilyl singlet at δ –0.14 ppm. Again, the almost temperature invariant ^{13}C NMR spectrum features signals of a pair of diastereotopic mesityl substituents at phosphorus [δ 22.7/22.6 (*o*-CH_3) and δ 20.7/20.3 ppm (*p*-CH_3)]. Compound **9c** also shows temperature dependent dynamic ^{19}F NMR spectra (see Fig. 5). From the decoalescence of the *p*-F resonance of the $B(C_6F_5)_2$ unit we have obtained the barrier of the P–B dissociation of compound **9c** and the analysis of the complex decoalescence of the corresponding *o*-F resonance gave us the barrier of rotation about the B–C_6F_5 vectors in **9c** (see Table 1 and Fig. 5).

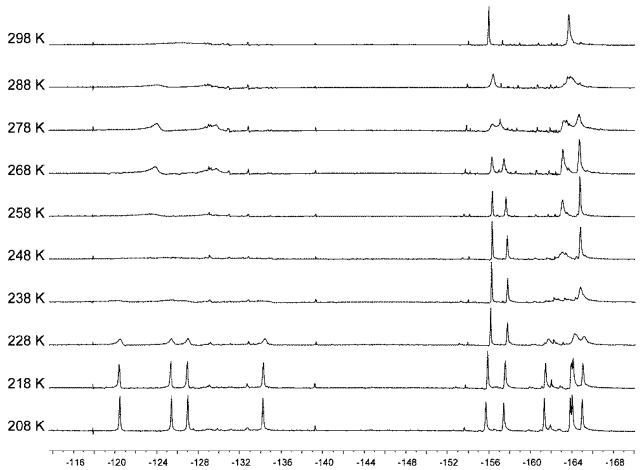
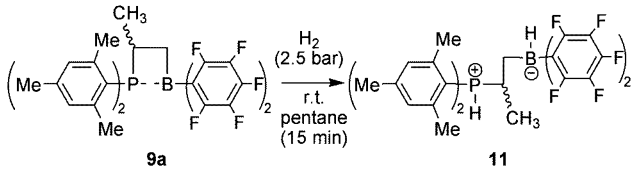


Fig. 5 Dynamic ^{19}F NMR spectra (564 MHz) of compound **9c** (in [D_8]toluene).

Reaction with dihydrogen

We did not observe a reaction of the compounds **7**, **9b** and **9c** with dihydrogen under our typical reaction conditions (*i.e.* ambient temperature in pentane or toluene at 2.5 bar or 60 bar H_2 pressure). In contrast, the α-methyl-substituted derivative **9a** splits the dihydrogen molecule heterolytically[19] under mild reaction conditions. Stirring of a solution of **9a**, *in situ* generated in pentane, at room temperature under an atmosphere of dihydrogen (2.5 bar) produced a white precipitate of the zwitterionic phosphonium/hydridoborate product **11** (49% isolated) (Scheme 5).



Scheme 5

Product **11** contains a prochiral phosphorus and prochiral boron center in addition to the chiral α-carbon center in the bridge. Consequently, we observed the NMR signals of a pair of diastereotopic mesityl groups at phosphorus (*e.g.* featuring a 1 : 1 pair of ^{1}H NMR *m*-resonances at δ 7.12 and 7.10 ppm) and of a pair of diastereotopic C_6F_5 substituents at boron [*e.g.* showing marginally separated ^{19}F NMR resonances of the *o*-F (δ –132.8 ppm, 4F), *p*-F (δ –165.6/–165.9 ppm, 1F each) and *m*-F (δ –167.8/–168.1 ppm, 2F each) pairs. The ^{1}H NMR spectrum of compound **11** features a PH resonance at δ 7.66 ppm (dd, 1H). It shows a very typical large PH coupling constant of $^1J_{PH}$ = 475.8 Hz[16] and a smaller $^3J_{HH}$ of 10.9 Hz. We observed the ^{1}H NMR BH resonance at δ 3.01 ppm (1 : 1 : 1 : 1 q, broadened by beginning relaxation).[20] The corresponding ^{31}P NMR signal of **11** is found at δ 2.3 ppm and the ^{11}B NMR resonance at δ –21.7 ppm. The protons of the $CH(CH_3)$–CH_2 bridge give rise to a broad ABX-type ^{1}H NMR pattern with a sharp dd resonance of the methyl group at δ 1.42 ppm ($^3J_{PH}$ = 23.7 Hz, $^3J_{HH}$ = 7.1 Hz) (for further details see Fig. 6 and the Experimental).

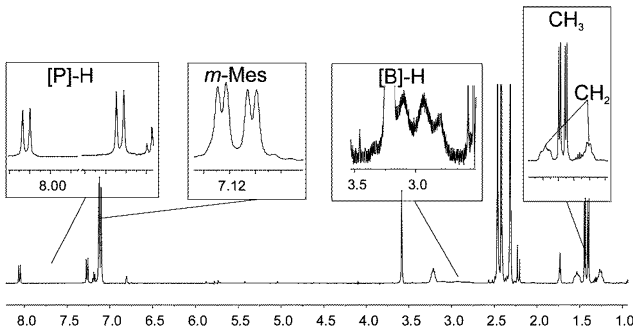


Fig. 6 ^{1}H NMR spectrum of the zwitterion **11** (in [D_8]THF).

Conclusions

We recently described the metal-free hydrogen activation system **1**, which probably is one of the most active system of its kind at present.[6,7] The **1**–**2** system is a very active catalyst for the hydrogenation of enamines and of bulky imines under very mild conditions and it transfers the H^+/H^- pair catalytically to other acceptors. The state of the art DFT analysis[6,21] of **1** has revealed its characteristic bonding features—it is described as an almost planar four-membered heterocycle containing a rather weak P···B linkage. One pair of mesityl and C_6F_5 substituents at P/B, arranged close to parallel to each other at the framework, is in an orientation to support the weak P···B contact by an energetically favourable π–π-stacking interaction between an electron-rich and an electron-poor arene system.

The calculation has also revealed a potential equilibration of the cyclic system **1** with an open isomer (**3**). Two almost isoenergetic local minima of open isomers were found in the calculation, both being *ca.* 7 kcal mol^{-1} higher in energy than the global minimum structure **1**. The calculated isomers of **3** only differed in their conformational arrangement of the bulky substituents at the μ-C_2-bridge (idealized: *gauche* and anti-periplanar). The present experimental study was aimed at confirming the facile ring opening of the P···B linkage in the system **1** or suitable derivatives of **1**, respectively. The attachment of a single substituent at the C_2-bridge has introduced an element of central chirality into systems **9**. In the cyclic, closed form the presence of a single element of chirality makes the hydrogen atoms at the adjacent CH_2 group diastereotopic as well as the pairs of mesityls at phosphorus and the C_6F_5 groups at boron. Cleavage of the P···B linkage (to generate the not directly observable isomers **10**) would, of course, leave the CH_2 hydrogens diastereotopic. This process would also leave the mesityl groups at P diastereotopic since the resulting tricoordinate phosphane in the alleged structure of **10** remains a stereogenic center, *i.e.* it features a persistent non-planar coordination geometry at the heavy group 15 element. Consequently, the ^{1}H NMR mesityl features of the systems **9** remain almost temperature invariant in the high temperature regime indicating the presence of a pair of persistently diastereotopic mesityl substituents in the respective temperature range.

The situation at boron is distinctively different. Cleaving the P–B linkage changes the coordination geometry at boron from pseudotetrahedral to planar-tricoordinate. The loss of the prochiral character of the R–B(C_6F_5)$_2$ moiety makes the pair of C_6F_5 groups symmetry equivalent. This consequently results in a coalescence of the corresponding pairs of ^{19}F NMR signals in

the high temperature regime. In all three examples investigated (*i.e.* **9a–9c**) we have observed the respective pairs of *p*-F ^{19}F NMR resonances to coalesce to a single averaged signal at high temperature. From this coalescence behaviour of the *p*-F NMR signals we have calculated the activation energies of the P···B dissociation process (see Table 1) [*e.g.* **9a**: $\Delta G^{\neq}_{inv}$ (280 K) = 11.7 ± 0.4 kcal mol^{-1}]. The obtained positive activation entropy [$\Delta S^{\neq}_{inv}$ = 15.0 cal Grd.$^{-1}$ mol] of this example is consistent with the observation of a bond breaking reaction by this NMR experiment.

The behaviour of the *o*- and *m*-F NMR signals is more complicated. Coincidence of the P···B bond breaking process (leading to C_6F_5 inversion at boron) with freezing the B–C_6F_5 rotation results in more complicated spectra. Thus, for compound **9a**, the energy barrier of P···B dissociation ($\Delta G^{\neq}_{inv}$) is almost the same as the rotational energy barrier of one of the B–C_6F_5 units ($\Delta G^{\neq}_{rot\,1}$). The barrier of rotation of the remaining B–C_6F_5 moiety ($\Delta G^{\neq}_{rot\,2}$) is lower. So consequently, if we increase the temperature in the monitoring of the *o*-^{19}F NMR signals from 233 K we first observed the coalescence of the δ −123.0/−132.0 ppm pair of *o*-F NMR resonances [$\Delta G^{\neq}_{rot\,2}$ (238 K) ≈ 9.1 kcal mol^{-1}]. Above *ca.* 263 K we begin to observe the coalescence of the second *o*-F pair (δ −123.4/−136.8 ppm), but this process [$\Delta G^{\neq}_{rot\,1}$ (295 K) ≈ 11.2 kcal mol^{-1}] overlaps with the $(C_6F_5)_2B$ "inversion" process, originating from the reversible P···B bond cleavage, which has a very similar activation energy barrier (see above). Complex **9b** (R = α-phenyl) shows an analogous behaviour and consequently features very similar temperature dependent ^{19}F NMR spectra. Complex **9c** (R = β-$SiMe_3$) features two almost identical B–C_6F_5 rotational barriers and a markedly higher activation energy of P···B dissociation.

The observed kinetic features of all three compounds **9** fit very well with the (calculated) thermodynamic properties of **1** with regard to their thermally induced ring opening process and equilibration with the respective (not directly observed) acyclic isomers (**3**, **10**). It is remarkable that all three examples studied here, namely **9a**, **9b** and **9c**, show similar activation barriers of ring opening. Nevertheless, only the compound **9a** was found to be an active system for heterolytic H_2-splitting under our typical reaction conditions. This indicates that P···B bond cleavage seems not to be a limiting factor, at least not in the systems **1** and **9**, for H_2-activation, however, steric interactions may play a significant role, as the results from our investigation of this series of compounds suggest.

Experimental

General

All reactions involving air or moisture-sensitive compounds were carried out under an inert gas using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. Unless otherwise noted, starting materials were prepared according to literature procedures. Commercially available starting compounds were used without further purification. The following instruments were used for physical characterisation of the compounds: melting points, DSC 2010 TA-instruments; elemental analyses, Foss–Heraeus CHNO-Rapid; NMR, Bruker ARX 300 (^{1}H = 300 MHz; ^{13}C = 75 MHz, ^{31}P = 121.5 MHz; ^{19}F = 282.4 MHz), Varian UNITY plus NMR spectrometer (^{1}H = 599.9 MHz; ^{13}C = 150.8 MHz; ^{31}P = 242.8 MHz; ^{19}F = 564.2 MHz). X-Ray crystal structure determination, data set was collected with Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski and W. Minor, *Methods in Enzymol.*, 1997, **276**, 307–326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33–37; R. H. Blessing, *J. Appl. Crystallogr.* 1997, **30**, 421–426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr., Sect. A*, 2003, **59**, 228–234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

General procedure for the preparation of compounds 5, 8a and 8c. Chlorodimesitylphosphane (**4**) (1 equiv.) was dissolved in THF (50 mL) and the respective Grignard reagent was added carefully at room temperature. After stirring the solution for one hour at ambient temperature, the solvent was removed *in vacuo* and the obtained residue was extracted with pentane. The crude product was purified by chromatography after removing pentane.

Compound 5. The reaction of chlorodimesitylphosphane (**4**) (5.00 g, 16.4 mmol) and allylmagnesium bromide (1.7 M solution in THF) yielded after chromatography (silicagel; CH_2Cl_2–cyclohexane 3 : 10, R_f = 0.26) the product as a colourless oil (3.03 g, 60%). mp 59°C. ESI$^+$MS (*m*/*z* for $C_{21}H_{28}P^+$): calcd: 311.1923, found: 311.1926. ^{1}H-NMR (400 MHz, 300 K, benzene-d_6) δ/ppm: 6.67 (4H, m, $^4J_{PH}$ = 2.3 Hz, *m*-Mes), 5.67 (1H, m, CH=), 4.86 (2H, m, =CH_2), 3.24 (2H, m, $^2J_{PH}$ = 7.5 Hz, ^{P}CH_2), 2.30 (12H, s, *o*-CH_3^{Mes}), 2.07 (6H, s, *p*-CH_3^{Mes}). ^{13}C{^{1}H}-NMR (101 MHz, 300 K, benzene-d_6) δ/ppm: 142.0 (d, $^2J_{PC}$ = 13.5 Hz, *o*-Mes), 137.5 (*p*-Mes), 134.5 (d, $^2J_{PC}$ = 11.4 Hz, CH=), 133.6 (d, $^1J_{PC}$ = 24.7 Hz, *i*-Mes), 130.3 (d, $^3J_{PC}$ = 2.6 Hz, *m*-Mes), 117.1 (d, $^3J_{PC}$ = 11.5 Hz, =CH_2), 33.6 (d, $^1J_{PC}$ = 17.8 Hz, CH_2), 23.4 (d, $^3J_{PC}$ = 13.2 Hz, *o*-CH_3^{Mes}), 20.9 (*p*-CH_3^{Mes}). ^{31}P{^{1}H}-NMR (162 MHz, 298 K, benzene-d_6) δ/ppm: −23.4 ($\nu_{1/2}$ = 3 Hz).

Compound 8a. The reaction of chlorodimesitylphosphane (**4**) (5.60 g, 18.4 mmol) and (2-propenyl)magnesium bromide (0.5 M solution in THF) (37.0 mL, 16.0 mmol) after chromatography (silicagel; CH_2Cl_2–cyclohexane 2 : 10) yielded the product as a colourless oil (2.81 g, 9.01 mmol, 49%). mp 66°C. Anal. calcd for $C_{21}H_{27}P$ (310.41 g mol^{-1}), C 81.25, H 8.77, found: C 80.99, H 8.78. ^{1}H-NMR (400 MHz, 300 K, benzene-d_6) δ/ppm: 6.73 (4H, dm, $^4J_{PH}$ = 2.4 Hz, *m*-Mes), 5.29 (1H, dm, $^3J_{PH,trans}$ = 18.4 Hz, =$CH_{2(trans)}$), 5.12 (1H, $^3J_{PH,cis}$ = 7.6 Hz, =$CH_{2(cis)}$), 2.42 (12H, s, *o*-CH_3^{Mes}), 2.08 (6H, s, *p*-CH_3^{Mes}), 2.04 (3H, dm, $^3J_{PH}$ = 12.4 Hz, CH_3). ^{13}C{^{1}H}-NMR (101 MHz, 300 K, benzene-d_6) δ/ppm: 143.4 (d, $^2J_{PC}$ = 15.6, *o*-Mes), 143.4 (d, $^1J_{PC}$ = 18.0 Hz, *i*-Mes), 138.2 (*p*-Mes), 130.3 (d, $^1J_{PC}$ = 18.3 Hz, ^{P}C=), 130.3 (d, $^3J_{PC}$ = 3.9 Hz, *m*-Mes), 120.8 (d, $^2J_{PC}$ = 10.6 Hz, =CH_2), 23.9 (d, $^2J_{PC}$ = 34.8 Hz, CH_3), 22.5 (d, $^3J_{PC}$ = 15.7 Hz, *o*-CH_3^{Mes}), 20.9 (*p*-CH_3^{Mes}). ^{31}P{^{1}H}-NMR (162 MHz, 298 K, benzene-d_6) δ/ppm: −17.4 ($\nu_{1/2}$ = 5 Hz).

Compound 8c. *Trans*-[2-(trimethylsilyl)vinyl]magnesium bromide solution in THF (0.5 M) was freshly prepared by addition of *trans*-[2-(trimethylsilyl)vinyl]bromide (5.80 g, 32.4 mmol)–THF (20 mL) solution to a suspension of magnesium turnings (780 mg,

32.1 mmol) in THF (50 mL). Subsequently, the reaction of chlorodimesitylphosphane (**4**) (5.10 g, 16.7 mmol) with *trans*-[2-(trimethylsilyl)vinyl]-magnesium bromide solution (0.5 M in THF, 34.0 mL, 16.7 mmol) after chromatography (silicagel; CH_2Cl_2–cyclohexane 3 : 10, $R_f = 0.55$) gave the product as a white solid (1.61 g, 4.34 mmol, 26%). mp 75 °C. Anal. calcd for $C_{23}H_{33}PSi$ (368.57 g mol^{-1}) C 74.95, H 9.02, found: C 74.79, H 9.01. ^{1}H-NMR (400 MHz, 300 K, benzene-d$_6$) δ/ppm: 7.42 (1H, dd, $^2J_{PH} = 34.3$ Hz, $^3J_{HH} = 19.8$ Hz, ^{P}CH=), 6.71 (4H, d, $^4J_{PH} = 2.7$ Hz, *m*-Mes), 6.14 (1H, dd, $^3J_{HH} = 19.8$ Hz, $^3J_{PH} = 15.8$ Hz, =CH^{TMS}), 2.40 (12H, s, *o*-CH$_3^{Mes}$), 2.06 (6H, s, *p*-CH$_3^{Mes}$), 0.00 (9H, s, $^2J_{SiH} = 6.8$ Hz, (CH$_3$)$_3$Si). ^{13}C{^{1}H}-NMR (101 MHz, 300 K, benzene-d$_6$) δ/ppm: 145.5 (d, $^1J_{PC} = 24.2$ Hz, ^{P}CH=), 142.8 (d, $^2J_{PC} = 14.4$ Hz, *o*-Mes), 138.1 (*p*-Mes), 137.1 (d, $^2J_{PC} = 4.5$ Hz, =CH^{TMS}), 131.2 (d, $^1J_{PC} = 17.3$ Hz, *i*-Mes), 130.3 (d, $^3J_{PC} = 3.4$ Hz, *m*-Mes), 23.3 (d, $^3J_{PC} = 14.0$ Hz, *o*-CH$_3^{Mes}$), 20.9 (*p*-CH$_3^{Mes}$), –1.53 (d, $^4J_{PC} = 1.5$ Hz, $^1J_{SiC} = 52.2$ Hz, (CH$_3$)$_3$Si). ^{31}P{^{1}H}-NMR (162 MHz, 298 K, benzene-d$_6$) δ/ppm: –16.1 ($\nu_{1/2} = 2$ Hz).

Preparation of compound 8b. *n*-Butyllithium (1.6 M in hexane) was added to a pre-cooled solution (–78 °C) of α-bromostyrene (3.90 g, 2.90 mL, 21.2 mmol) in THF (80 mL). After stirring the reaction mixture for 30 min at –78 °C, a solution of chlorodimesitylphosphane (**4**) (6.49 g, 21.2 mmol) in THF (20 mL) was added. Stirring was continued overnight. Then the solvent was removed, the obtained residue was extracted with pentane (200 mL) and after removing pentane *in vacuo* the crude product was purified by chromatography (silicagel; CH_2Cl_2–cyclohexane 3 : 10, $R_f = 0.66$). Compound **8b** was obtained as a colourless oil (1.65 g, 4.43 mmol, 21%). mp 98 °C. Anal. calcd for $C_{26}H_{29}P$ (372.48 g mol^{-1}) C 83.84, H 7.85, found: C 83.65, H 8.00. ^{1}H-NMR (300 MHz, 300 K, benzene-d$_6$) δ/ppm: 7.90 (2H, m, Ph), 7.06 (3H, m, Ph), 6.68 (4H, d, $^4J_{PH} = 2.8$ Hz, *m*-Mes), 5.75 (1H, dd, $^3J_{PH,trans} = 11.6$ Hz, $^2J_{HH} = 1.4$ Hz, =CH$_{2(trans)}$), 5.23 (1H, dd, $^3J_{PH,cis} = 4.7$ Hz, $^2J_{HH} = 1.4$ Hz,=CH$_{2(cis)}$), 2.39 (12H, s, *o*-CH$_3^{Mes}$), 2.04 (6H, s, *p*-CH$_3^{Mes}$). ^{13}C{^{1}H}-NMR (76 MHz, 300 K, benzene-d$_6$) δ/ppm: 146.8 (d, $^2J_{PC} = 18.8$ Hz, *i*-Ph), 143.6 (d, $^2J_{PC} = 15.9$ Hz, *o*-Mes), 142.5 (d, $^1J_{PC} = 26.7$ Hz, *i*-Mes), 138.4 (*p*-Mes), 130.4 (d, $^3J_{PC} = 4$ Hz, *m*-Mes), 130.1 (d, $^1J_{PC} = 15.8$ Hz, ^{P}C=), 128.8 (d, $^4J_{PC} = 1.7$ Hz, *m*-Ph), 128.1 (d, $^5J_{PC} = 2.0$ Hz, *p*-Ph) [observed in DEPT-135], 127.4 (d, $^3J_{PC} = 15.9$ Hz, *o*-Ph), 120.1 (d, $^2J_{PC} = 6.1$ Hz, =CH$_2$), 22.7 (d, $^3J_{PC} = 15.4$ Hz, *o*-CH$_3^{Mes}$), 20.9 (*p*-CH$_3^{Mes}$). ^{31}P{^{1}H}-NMR (122 MHz, 300 K, benzene-d$_6$) δ/ppm: –24.2 ($\nu_{1/2} = 1$ Hz).

General procedure for the preparation of compounds 7, 9a and 9b. The respective phosphane (1 equiv.) and HB(C$_6$F$_5$)$_2$ (1 equiv.) were dissolved in pentane (10 mL) and stirred for 10 min at ambient temperature. The resulting yellow solution was evaporated to dryness *in vacuo*.

Compound 7. The reaction of allyldimesitylphosphane (**5**) (83.0 mg, 0.27 mmol) and HB(C$_6$F$_5$)$_2$ (**6**) (93.0 mg, 0.27 mmol) yielded **7** (124 mg, 0.19 mmol, 70%) as a white solid. mp 184 °C. Anal. calcd for $C_{33}H_{28}BF_{10}P$ (656.34 g mol^{-1}) C 60.39, H 4.30, found: C 59.54, H 4.73. ^{1}H-NMR (600 MHz, 298 K, benzene-d$_6$) δ/ppm: 6.42 (4H, br., *m*-Mes), 2.73 (2H, br., ^{P}CH$_2$), 2.05 (12H, br., *o*-CH$_3^{Mes}$), 1.91 (6H, s, *p*-CH$_3^{Mes}$), 1.77 (2H, br., CH$_2^B$), 1.72 (2H, br., CH$_2$). ^{13}C{^{1}H}-NMR (151 MHz, 298 K, benzene-d$_6$) δ/ppm: 149.0 (dm, $^1J_{FC} = 240$ Hz, C$_6$F$_5$), 142.5 (*o*-Mes), 141.0 (*p*-Mes), 139.4 (dm, $^1J_{FC} = 248$ Hz, *p*-C$_6$F$_5$), 137.3 (dm, $^1J_{FC} = 244$ Hz, C$_6$F$_5$), 131.2 (*m*-Mes), 120.8 (br., *i*-C$_6$F$_5$), n.o. (*i*-Mes), 27.0 (d, $^1J_{PC} = 39.8$ Hz, ^{P}CH$_2$), 24.6 (br., CH$_2^B$), 23.3 (*o*-CH$_3^{Mes}$), 21.9 (d, $^2J_{PC} = 12.7$ Hz, CH$_2$), 20.4 (*p*-CH$_3^{Mes}$). ^{31}P{1H}-NMR (122 MHz, 300 K, benzene-d$_6$) δ/ppm: 20.8 ($\nu_{1/2} = 40$ Hz). ^{19}F-NMR (282 MHz, 300 K, benzene-d$_6$) δ/ppm: –127.4 (br., 4F, *o*-C$_6$F$_5$), –158.4 (2F, *p*-C$_6$F$_5$), –164.4 (br., 4F, *m*-C$_6$F$_5$). ^{11}B{^{1}H}-NMR (96 MHz, 300 K, benzene-d$_6$) δ/ppm: –2.7 ($\nu_{1/2} = 400$ Hz).

Crystal data for $C_{33}H_{28}BF_{10}P$: $M = 656.33$ g mol^{-1}, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.0881(5)$, $b = 10.3454(5)$, $c = 24.1019(12)$ Å, $\beta = 101.884(3)°$, $V = 2949.5(2)$ Å^3, $D_c = 1.478$ g cm^{-3}, $\mu = 1.612$ mm^{-1}, $Z = 4$, $\lambda = 1.54178$ Å, $T = 223(2)$ K, 20 597 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 5064 independent ($R_{int} = 0.062$) and 2801 observed reflections [$I \geq 2\sigma(I)$], 412 refined parameters, $R = 0.084$, w$R_2 = 0.228$.

Compound 9a. The reaction of dimesityl(2-propenyl)-phosphane (**8a**) (70.0 mg, 0.23 mmol) and HB(C$_6$F$_5$)$_2$ (**6**) (78.0 mg, 0.23 mmol) yielded **9a** (96.0 mg, 0.15 mmol, 64%) as a yellow solid. mp 160 °C (decomp.). Anal. calcd for $C_{33}H_{28}BF_{10}P$ (656.34 g mol^{-1}) C 60.39, H 4.30, found: C 59.37, H 4.43. ^{1}H-NMR (600 MHz, 298 K, benzene-d$_6$) δ/ppm: 6.56 (2H, br. s, *m*-Mes), 6.35 (2H, br. s, *m*-Mes′), 3.82 (1H, oct, $^3J_{HH(anti)} = 13.5$ Hz, $^3J_{HH(syn)} \approx {}^2J_{PH} = 8.2$ Hz, $^3J_{HH(Me)} = 6.8$ Hz, CH), 2.96 (1H, ddd, $^3J_{PH} = 106.9$ Hz, $^2J_{HH} = 13.5$ Hz, $^3J_{HH(syn)} = 8.3$ Hz, ^{B}CH$_{anti}$), 1.96, 1.91 (br., s, CH$_3^{Mes}$), 1.69 (1H, td, $^2J_{HH} \approx {}^3J_{HH(anti)} = 13.5$ Hz, $^2J_{PH} = 9.7$ Hz, ^{B}CH$_{syn}$), 0.87 (3H, dd, $^3J_{PH} = 15.5$ Hz, $^3J_{HH} = 6.8$ Hz, CH$_3$) [coupling constants from ^{1}H{^{1}H} and ^{1}H{^{31}P} decoupling NMR experiments and simulation of the spin system]. ^{13}C{^{1}H}-NMR (151 MHz, 298 K, benzene-d$_6$) δ/ppm: 148.0 (br., dm, $^1J_{FC} = 243$ Hz, C$_6$F$_5$), 142.9 (d, $^3J_{PC} = 7.4$ Hz, *o*-Mes), 141.1 (br., *o*-Mes′), 141.1 (d, $^4J_{PC} = 2.5$ Hz, *p*-Mes), 140.8 (d, $^4J_{PC} = 2.5$ Hz, *p*-Mes′), 140.2 (br. dm, $^1J_{FC} = 254$ Hz, *p*-C$_6$F$_5$), 137.6 (dm, $^1J_{FC} = 260$ Hz, C$_6$F$_5$), 131.2 (d, $^3J_{PC} = 7.1$ Hz, *m*-Mes), 130.7 (d, $^3J_{PC} = 8.9$ Hz, *m*-Mes′), 125.9 (d, $^1J_{PC} = 19.5$ Hz, *i*-Mes′), 124.0 (d, $^1J_{PC} = 24.2$ Hz, *i*-Mes), 119.5 (br., *i*-C$_6$F$_5$), 38.1 (d, $^1J_{PC} = 31.2$ Hz, CH), 29.5 (br., ^{B}CH$_2$), 23.6 ($J_{PC} = 6.5$ Hz), 23.1 (br.), 20.6, 20.5 (CH$_3^{Mes}$), 18.3 (d, $^2J_{PC} = 4.8$ Hz, CH$_3$). ^{31}P{^{1}H}-NMR (122 MHz, 300 K, benzene-d$_6$) δ/ppm: 33.2 ($\nu_{1/2} = 19$ Hz). ^{31}P-NMR (122 MHz, 300 K, benzene-d$_6$) δ/ppm: 33.2 (d, $^3J_{PH} = 106.9$ Hz). ^{19}F-NMR (282 MHz, 300 K, benzene-d$_6$) δ/ppm: –128.8 (br., 4F, *o*-C$_6$F$_5$), –157.4 (2F, *p*-C$_6$F$_5$), –163.5 (4F, *m*-C$_6$F$_5$). ^{11}B{^{1}H}-NMR (96 MHz, 300 K, benzene-d$_6$) δ/ppm: 3.2 ($\nu_{1/2} = 500$ Hz).

Compound 9b. The reaction of dimesityl(1-phenylvinyl)-phosphane (**8b**) (90.0 mg, 0.24 mmol) and HB(C$_6$F$_5$)$_2$ (**6**) (84.0 mg, 0.24 mmol) yielded **9b** (116 mg, 0.16 mmol, 67%) as a yellow solid. mp 219 °C (decomp.). Anal. calcd for $C_{38}H_{30}BF_{10}P$ (718.41 g mol^{-1}) C 63.53, H 4.21, found: C 63.19, H 4.72. ^{1}H-NMR (300 MHz, 300 K, benzene-d$_6$) δ/ppm: 6.91 (m), 6.83 (m), 6.69 (m), 6.37 (br.) (Σ9H, Ph, *m*-Mes), 5.08 (1H, dt, $^3J_{HH(anti)} = 14.7$ Hz, $^3J_{HH(syn)} \approx {}^2J_{PH} = 8.1$ Hz, CH^P), 3.19 (1H, dm, $^3J_{PH} = 110.1$ Hz, ^{B}CH$_{2anti}$), 2.30 (m, ^{B}CH$_{2syn}$), 2.07, 1.91, 1.90 (br., s, CH$_3^{Mes}$). ^{31}P{^{1}H}-NMR (122 MHz, 300 K, benzene-d$_6$) δ/ppm: 40.3 ($\nu_{1/2} = 17$ Hz). ^{31}P-NMR (122 MHz, 300 K, benzene-d$_6$) δ/ppm: 40.3 (d, $^3J_{PH} = 110.1$ Hz). ^{19}F-NMR (282 MHz, 300 K, benzene-d$_6$) δ/ppm: –124.0, –127.1, –135.6 (br., Σ4F, *o*-C$_6$F$_5$), –157.0 (br., 2F, *p*-C$_6$F$_5$), –163.1 (br., 4F, *m*-C$_6$F$_5$). ^{11}B{^{1}H}-NMR (96 MHz, 300 K,

benzene-d_6) δ/ppm: 2.5 ($\nu_{1/2}$ = 600 Hz). UV-vis (pentane): λ_{max} = 434 nm, $c = 1.7 \times 10^{-3}$mmol cm^{-3}, d = 1 cm, ε = 118 cm^2 mmol^{-1}.

Preparation of compound 9c. Dimesityl(*trans*-2-(trimethylsilyl)vinyl)phosphane (**8c**) (150 mg, 0.41 mmol) and HB(C_6F_5)$_2$ (**6**) (141 mg, 0.41 mmol) were dissolved in toluene (10 mL) and stirred at 80 °C for 25 min. Then the solvent was removed *in vacuo* and the obtained residue was dissolved in pentane (5 mL). The resulting yellow solution was evaporated to dryness *in vacuo* to yield **9c** as a yellow solid (280 mg, 0.39 mmol, 96%). mp 56 °C. Anal. calcd for $C_{33}H_{34}BF_{10}PSi$ (714.50 g mol^{-1}) C 58.83, H 4.80, found: C 58.33, H 4.85. ^{1}H-NMR (400 MHz, 300 K, benzene-d_6) δ/ppm: 6.55 (2H, d, $^4J_{PH}$ = 2.7 Hz, *m*-Mes), 6.39 (2H, d, $^4J_{PH}$ = 2.9 Hz, *m*-Mes′), 2.90 (2H, br. m, ^{P}CH$_2$, CH^{TMS}), 2.62 (1H, m, ^{P}CH$_2$′), 2.29 (6H, s, *o*-CH$_3^{Mes}$), 2.15 (6H, s, *o*-CH$_3^{Mes'}$), 1.97 (3H, s, *p*-CH$_3^{Mes}$), 1.92 (6H, s, *p*-CH$_3^{Mes'}$), –0.14 (9H, s, TMS). ^{13}C{^{1}H}-NMR (101 MHz, 300 K, benzene-d_6) δ/ppm: 147.9 (dm, $^1J_{FC}$ = 232 Hz, C_6F_5), 142.5 (d, $^2J_{PC}$ = 8.5 Hz, *o*-Mes), 142.4 (d, $^2J_{PC}$ = 9.0 Hz, *o*-Mes′), 140.7 (dm, $^1J_{FC}$ = 242 Hz, *p*-C_6F_5), 140.4 (d, $^4J_{PC}$ = 1.4 Hz, *p*-Mes), 140.2 (d, $^4J_{PC}$ = 1.9 Hz, *p*-Mes′), 137.8 (dm, $^1J_{FC}$ = 246 Hz, C_6F_5), 131.3 (d, $^4J_{PC}$ = 6.8 Hz, *m*-Mes′), 130.2 (d, $^4J_{PC}$ = 5.6 Hz, *m*-Mes), n.o. (*i*-Mes), 120.1 (br., *i*-C_6F_5), 27.1 (d, $^1J_{PC}$ = 21.5 Hz, ^{P}CH$_2$), 22.7, 22.6 (each d, each $^3J_{PC}$ = 7.9 Hz, *o*-CH$_3^{Mes}$), 22.2 (br., CH^{TMS}), 20.7, 20.3 (*p*-CH$_3^{Mes}$), –1.6 (TMS). ^{31}P{^{1}H}-NMR (122 MHz, 300 K, benzene-d_6) δ/ppm: 15.9 ($\nu_{1/2}$ = 27 Hz). ^{19}F-NMR (282 MHz, 300 K, benzene-d_6) δ/ppm: –126.8 (br., 4F, *o*-C_6F_5), –155.6 (br., 2F, *p*-C_6F_5), –163.5 (br., 4F, *m*-C_6F_5). ^{19}F-NMR (564 MHz, 198 K, toluene-d_8) δ/ppm: –120.6, –125.6, –127.1, –134.4 (each 1F, *o*-C_6F_5), –155.8, –157.5 (each 1F, *p*-C_6F_5), –161.4, –163.9, –164.1, –165.1 (each 1F, *m*-C_6F_5). ^{11}B{^{1}H}-NMR (96 MHz, 300 K, toluene-d_8) δ/ppm: 23.2 ($\nu_{1/2}$ = 700 Hz). UV-vis (pentane): λ_{max} = 368 nm, $c = 1.8 \times 10^{-3}$mmol cm^{-3}, d = 1 cm, ε = 514 cm^2 mmol^{-1}.

Preparation of Compound 11. Dimesityl(2-propenyl)-phosphane (**8a**) (660 mg, 2.13 mmol) and HB(C_6F_5)$_2$ (**6**) (736 mg, 2.13 mmol) were suspended in pentane (10 mL) and stirred for 5 min at ambient temperature. The resulting yellow solution was stirred under a hydrogen atmosphere (2.5 bar) for 15 min. During this time a white precipitate was formed. It was collected by filtration, washed with pentane (10 mL) and dried *in vacuo*. The product **11** (645 mg, 1.03 mmol, 49%) was obtained as a white solid. mp 94 °C. Anal. calcd for $C_{33}H_{30}BF_{10}P$ (627.39 g mol^{-1}) C 60.20, H 4.59, found: C 59.47, H 4.46. ^{1}H-NMR (600 MHz, 298 K, THF-d_8) δ/ppm: 7.66 (1H, dd, $^1J_{PH}$ = 475.8 Hz, $^3J_{HH}$ = 10.9 Hz, PH), 7.12 (2H, d, $^4J_{PH}$ = 3.9 Hz, *m*-Mes), 7.10 (2H, d, $^4J_{PH}$ = 4.1 Hz, *m*-Mes′), 3.21 (1H, m, ^{P}CH^{Me}), 3.01 (1H, br. 1 : 1 : 1 : 1 q [partially relaxed $^1J_{BH}$], $^1J_{BH}$ ≈ 95 Hz, BH), 2.46 (6H, s, *o*-CH$_3^{Mes}$), 2.42 (6H, s, *o*-CH$_3^{Mes'}$), 2.32 (s, 3H, *p*-CH$_3^{Mes}$), 2.31 (s, 3H, *p*-CH$_3^{Mes'}$), 1.53 (1H, br. m, ^{B}CH$_2$), 1.42 (3H, dd, $^3J_{PH}$ = 23.7 Hz, $^3J_{HH}$ = 7.1 Hz, CH$_3$), 1.25 (1H, br. m, ^{B}CH$_2$′). ^{13}C{^{1}H}-NMR (151 MHz, 298 K, THF-d_8) δ/ppm: 149.1 (dm, $^1J_{FC}$ = 261 Hz, C_6F_5), 146.0 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes), 145.8 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes′), 144.7 (d, $^2J_{PC}$ = 8.5 Hz, *o*-Mes′), 144.5 (d, $^2J_{PC}$ = 9.0 Hz, *o*-Mes), 137.3 (dm, $^1J_{FC}$ = 249 Hz, C_6F_5), 132.4 (d, $^3J_{PC}$ = 6.9 Hz, *m*-Mes), 132.3 (d, $^3J_{PC}$ = 6.9 Hz, *m*-Mes′), n. o. (*p*-, *i*-C_6F_5), 115.0 (d, $^1J_{PC}$ = 67.4 Hz, *i*-Mes), 114.0 (d, $^1J_{PC}$ = 76.7 Hz, *i*-Mes′), 33.5 (d, $^1J_{PC}$ = 30.0 Hz, ^{P}CH^{Me}), 26.3 (br., ^{B}CH$_2$), 22.31 (d, $^3J_{PC}$ = 6.2 Hz, *o*-CH$_3^{Mes}$), 22.27 (d, $^3J_{PC}$ = 6.0 Hz, *o*-CH$_3^{Mes'}$), 21.12 (*p*-CH$_3^{Mes}$), 21.09 (*p*-CH$_3^{Mes'}$), 17.5 (CH$_3$). ^{31}P{^{1}H}-NMR (122 MHz, 300 K, THF-d_8) δ/ppm: = 2.3 ($\nu_{1/2}$ = 40 Hz). ^{31}P-NMR (122 MHz, 300 K, THF-d_8) δ/ppm: 2.3 (dm, $^1J_{PH}$ = 476 Hz). ^{19}F-NMR (282 MHz, 300 K, THF-d_8) δ/ppm: –132.8 (4F, *o*-C_6F_5), –165.6, –165.9 (each 1F, *p*-C_6F_5), –167.8, –168.1 (each 2F, *m*-C_6F_5). ^{11}B{^{1}H}-NMR (96 MHz, 300 K, THF-d_8) δ/ppm: –21.7 ($\nu_{1/2}$ = 65 Hz). ^{11}B-NMR (96 MHz, 300 K, THF-d_8) δ/ppm: –21.7 (d, $^1J_{BH}$ ≈ 95 Hz).

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