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Structure and Dynamic Features of an Intramolecular Frustrated Lewis Pair

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Abstract: Di(mesityl)cyclohexenylphosphine undergoes hydroboration with Piers' borane $[HB(C_6F_5)_2]$ to yield the cyclohexylene-anellated frustrated Lewis pair **5**. This P/B pair splits H_2 with the formation of the product **4** and adds to the C=O double bond of phenyl isocyanate to yield **6**. In the crystal, compound **5** features a puckered four-membered heterocyclic core structure with a long P–B bond (av. 2.197(5) Å). The activation energy of the P–B cleavage of the frustrated Lewis pair **5** was determined by dynamic ^{19}F NMR spectroscopy at $\Delta G^{\neq}(298\,K) = 12.1 \pm 0.3\,kcal\,mol^{-1}$.

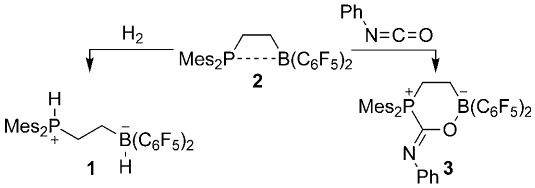
Keywords: boron · frustrated Lewis pairs · hydrogen · phosphorus

Introduction

Bulky substituents prevent the effective quenching of reactive Lewis acids and Lewis bases. These "frustrated Lewis pairs"[1] can undergo remarkable reactions with a variety of organic or inorganic substrates, among them the heterolytic cleavage of dihydrogen and the utilization of this activation process in some metal-free catalytic hydrogenation reactions.[2,3] Frustrated Lewis pairs cooperatively add to a variety of unsaturated substrates, such as alkenes and alkynes,[4] carbonyl compounds,[5] and they may add even to carbon dioxide[6] or N_2O.[7]

Frustrated Lewis pairs used in the activation of small molecules do exhibit some interaction between the acid and base antagonists. This follows from recent state of the art DFT calculations[8] and from preliminary experimental studies.[9] Herein we describe the structural features of an intramolecular frustrated Lewis pair with directly adjacent interacting phosphine and borane functional groups and qualitatively correlate them with the measured dissociation activation energy of the pair.

We recently described the synthesis and properties of the intramolecular frustrated Lewis pair **2**.[10] DFT calculations suggested a four-membered cyclic structure. The system **2** is one of the most active P/B pairs so far in H_2 splitting (to yield **1**). It is an active metal-free hydrogenation catalyst[3e] and it adds to CO_2[6c] and typically to phenyl isocyanate[5] (to yield **3**) (see Scheme 1). Unfortunately, compound **2** could so far not be structurally determined by X-ray diffraction due to the lack of suitable single crystals. The available described information about **2** comes from DFT calculations.[10]



Scheme 1. Dihydrogen activation and addition of phenyl isocyanate to the P/B pair **2**.

Results and Discussion

We have now reacted di(mesityl)cyclohexenylphosphine (prepared from Mes_2PCl and cyclohexenyllithium) with Piers' borane $[HB(C_6F_5)_2]$.[11] The system undergoes a clean *syn*-hydroboration reaction to yield the *trans*-1,2-P/B-substituted cyclohexane derivative **5**. Compound **5** shows typical frustrated Lewis pair properties.[1] It splits dihydrogen heterolytically to yield the phosphonium–hydroborate zwitterion **4** and it reacts rapidly with phenyl isocyanate at ambient conditions to cleanly yield the bicyclic addition product **6** (74 % isolated; Scheme 2).

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X-ray crystal structure analyses

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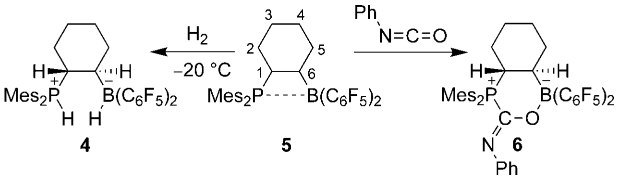


Scheme 2. Reaction of the P/B pair **5** with dihydrogen and with phenyl isocyanate.

The product **4** was characterized by X-ray diffraction (single crystals were obtained from heptane; see Figure 1). In the crystal, the compound shows a *trans*-1,2-disubstituted cyclohexane framework in a chair conformation, with both the bulky (mesityl)$_2$PH- and the -BH(C$_6$F$_5$)$_2$ substituents occupying adjacent equatorial positions (P1−C1 1.835(3), B1−C6 1.666(4) Å). These substituents are rotated such that both hydrogens are oriented toward an “inside” position facing each other at a distance of only about 2.15 Å (the corresponding P1−B1 distance is 3.167 Å).

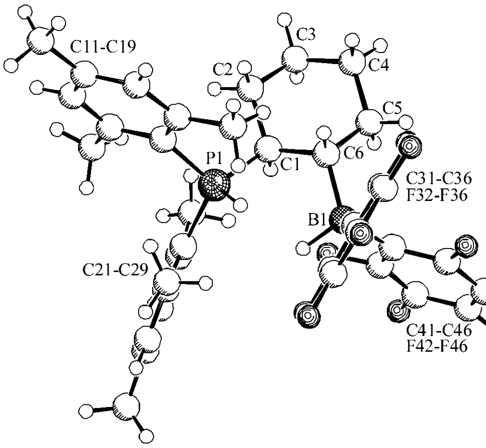


Figure 1. Molecular structure of the dihydrogen activation product **4**. Selected bond lengths [Å] and angles [°]: P1−C1 1.835(3), P1−C11 1.819(3), P1−C21 1.802(3), B1−C6 1.666(4), B1−C31 1.641(5), B1−C41 1.634(5), C1−C2 1.543(4), C1−C6 1.537(4), C6−C5 1.541(4); C1-P1-C11 115.1(1), C1-P1-C21 115.8(1), C11-P1-C21 113.3(1), C6-B1-C31 110.7(2), C6-B1-C41 115.1(3), C31-B1-C41 113.6(2), P1-C1-C2 111.4(2), P1-C1-C6 110.5(2), B1-C6-C1 112.7(2), B1-C6-C5 115.2(3), C2-C1-C6 113.9(2), C1-C6-C5 108.3(3); P1-C1-C6-B1 51.9(3).

The NMR spectra of **4** at 193 K show typical phosphonium signals [^{31}P: δ =−4.5 ppm ($^1J_{\mathrm{PH}}$ ≈496 Hz) with a corresponding ^{1}H NMR signal at δ=7.94 ppm] and hydroborate resonances [^{11}B: δ=−19.7 ($^1J_{\mathrm{BH}}$ ≈70 Hz) and ^{1}H: δ= 3.35 ppm (broad)], respectively. In **4** both the mesityl groups at phosphorus and the C$_6$F$_5$ substituents at boron are diastereotopic (for details see the Supporting Information).

The product **6** features a typical phosphonium ^{31}P NMR resonance at δ=+8.5 ppm and a borate ^{11}B NMR signal at δ=+1.4 ppm. The chiral product features pairwise diastereotopic mesityl groups at phosphorus and C$_6$F$_5$ groups at boron. The latter show very small $\delta_{p,m}$ differences of the ^{19}F NMR C$_6$F$_5$ resonances ($\Delta\delta_{p,m}$ is 4.1/4.7), typical of a tetracoordinate borate structure.[12] Compound **6** was also characterized by X-ray diffraction (see Figure 2). It shows a *trans*-fused heterodecalin-type structure with typical bond lengths of P1−C1 1.854(2) Å and B1−C6 1.629(2) Å (for details see the Supporting Information).[13]

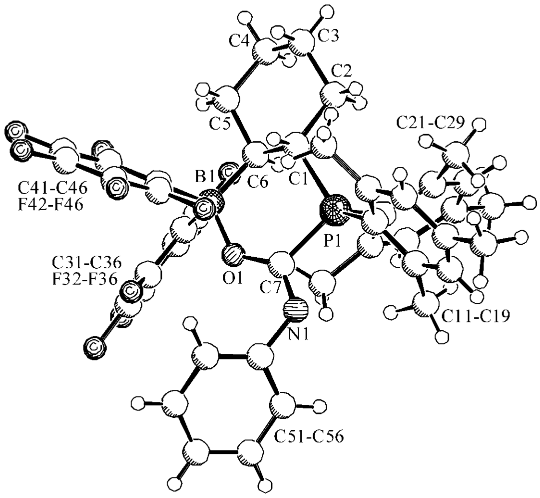


Figure 2. Molecular structure of compound **6**. Selected bond lengths [Å] and angles [°]: P1−C1 1.854(2), P1−C7 1.858(2), P1−C11 1.821(2), P1−C21 1.831(2), B1−C6 1.629(2), B1−O1 1.522(2), B1−C31 1.660(2), B1−C41 1.666(2), C1−C2 1.541(2), C1−C6 1.558(2), C6−C5 1.548(2), C7−O1 1.298(2), C7−N1 1.272(2), N1−C51 1.423(2); C1-P1-C7 103.4(1), C1-P1-C11 120.0(1), C1-P1-C21 105.9(1), C7-P1-C11 105.6(1), C7-P1-C21 113.6(1), C11-P1-C21 108.7(1), O1-B1-C6 113.5(1), O1-B1-C31 100.8(1), O1-B1-C41 104.7(1), C6-B1-C31 115.3(1), C6-B1-C41 113.0(1), C31-B1-C41 108.5(1), P1-C1-C2 112.3(1), P1-C1-C6 107.2(1), P1-C7-O1 120.1(1), P1-C7-N1 114.1(1), B1-O1-C7 131.4(1), B1-C6-C1 114.8(1), B1-C6-C5 109.7(1), C2-C1-C6 112.0(1), C1-C6-C5 108.5(1), O1-C7-N1 125.8(2), C7-N1-C51 120.0(1); P1-C1-C6-B1 62.7(2), P1-C7-O1-B1 −1.6(2).

Single crystals of the frustrated Lewis pair **5** suitable for X-ray diffraction were obtained by slow evaporation of solvent from a solution of the compound in heptane. The X-ray crystal structure analysis of **5** (see Figure 3) revealed the presence of a cyclohexane chair with an anellated four-membered heterocycle. The P1−C1 [1.850(4) Å for molecule **A**, 1.841(4) Å for **B**] and B1−C2 [(1.644(6) Å (**A**), 1.623(6) Å (**B**)] bonds are *trans*-attached at the cyclohexylene subunit. The four-membered ring is markedly puckered [angle between the P1-C1-C2 and P1-B1-C2 planes: 45.8° (**A**)], which results in favorable distortions of vicinal bond vectors and substituents from coplanarity [dihedral angles P1-C1-C2-B1 39.6(3)° (**A**)/38.3(3)° (**B**); molecule **A**: C41-B1-P1-C11 37.7(4)°, C31-B1-P1-C21 57.7(4)°]. The P1−B1 distance in **5** amounts to 2.188(5) Å (independent molecule **A**) and 2.206(5) Å (molecule **B**), respectively. These values are at the very long end of P−B bond lengths for phosphine−B(C$_6$F$_5$)$_2$R adducts. In the series of selected reference compounds (**7**–**10**, see Scheme 3) the observed P−B bond lengths cover a range from 1.972(2) Å to 2.180(6) Å; they show a marked dependency on the steric bulk of the substituents at boron and phosphorus.

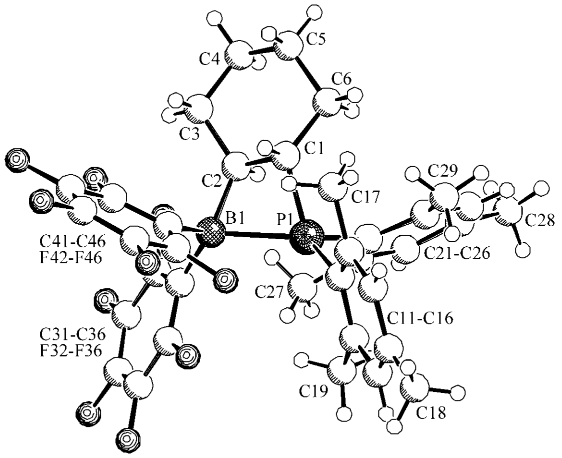
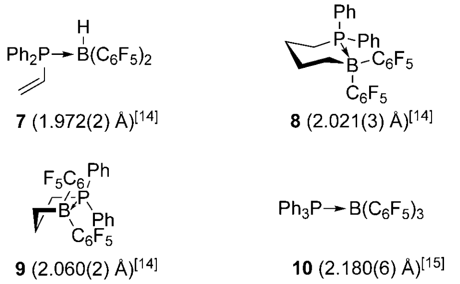


Figure 3. A view of the molecular structure of the frustrated Lewis pair **5**. Selected bond lengths [Å] and angles [°] (molecule A): P1−B1 2.188(5), P1−C1 1.850(4), P1−C11 1.823(4), P1−C21 1.864(4), B1−C2 1.644(6), B1−C31 1.602(6), B1−C41 1.639(6), C1−C2 1.543(5), C1−C6 1.536(6), C2−C3 1.528(5); B1-P1-C1 73.2(2), B1-P1-C11 126.4(2), B1-P1-C21 123.1(2), C1-P1-C11 122.9(2), C1-P1-C21 102.4(2), C11-P1-C21 104.1(2), P1-B1-C2 77.4(2), P1-B1-C31 121.2(3), P1-B1-C41 111.7(3), C2-B1-C31 124.9(4), C2-B1-C41 112.5(3), C31-B1-C41 106.8(3), P1-C1-C2 91.1(2), P1-C1-C6 126.2(3), B1-C2-C1 98.8(3), B1-C2-C3 125.7(3), C2-C1-C6 113.6(3), C1-C2-C3 110.3(3); P1-C1-C2-B1 39.6(3).

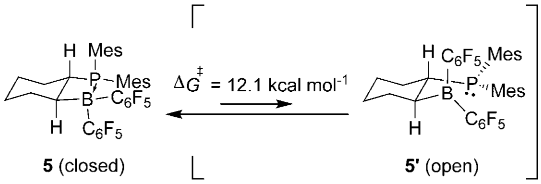


Scheme 3. P−B bond lengths of the reference compounds **7**–**10**.

The NMR spectra also indicate decreased phosphonium (^{31}P: $\delta = +23.5$ ppm) and borate (^{11}B: $\delta = +12.6$ ppm, ^{19}F (C_6F_5), $\Delta\delta_{p,m} = 6.7$) character of **5** relative to that of **4** and **6**.

The question remained whether the long (and potentially weak) P−B bond in **5** would correspond to a low bond dissociation energy. This is difficult to measure but the determination of the activation barrier of the P−B bond cleavage is easy; it provides an upper limit of E_{diss} and a valuable parameter of describing the reactivity of the frustrated pair.

Equilibration of the favored P-B four membered ring structure **5** (closed) with its P/B cleaved isomer **5′** (open) of higher energy content would interconvert the *pseudo*-tetrahedral geometry at phosphorus into another nonplanar prochiral P-geometry (Scheme 4). Since both feature diastereotopic mesityl groups, ring opening would not result in temperature-dependent changes at the -P(mesityl)$_2$ side. This is different on the boron side: here the open form features a trigonal-planar and thus non-stereogenic coordination geometry at boron. Therefore, equilibration between **5** (closed) with the **5′** (open) high energy isomer could result in coalescence of the NMR C_6F_5 signals. That is actually observed. At low temperature (233 K) we monitor four ^{1}H NMR *m*-H (mesityl) signals and two pairs of corresponding ^{1}H NMR *o*-CH_3 (mesityl) resonances, indicating "frozen" rotation of a pair of diastereotopic mesityl substituents at phosphorus in **5**. Increasing the monitoring temperature from 233 K (500 MHz) rapidly leads to pairwise coalescence of these signals by onset of aryl group rotation around the P−C(mesityl) vector, but the mesityl groups at the phosphorus atom in the frustrated pair **5** remain diastereotopic in the whole investigated temperature range. The behavior at the boron atom is different. At low temperature we observe the typical ^{19}F NMR signals of a pair of diastereotopic C_6F_5 groups. Upon increasing the temperature we observe pairwise coalescence of the *o*, *m*, and *p* fluorine resonances to eventually give a single set of the ^{19}F NMR C_6F_5 signals (the spectra are depicted in the Supporting Information). From the coalescence behavior of the pair of the ^{19}F NMR *o*-C_6F_5 signals we have determined the Gibbs activation energy of the P−B bond cleavage of **5** as $\Delta G^{\neq}$ (298 K) = 12.1 ± 0.3 kcal mol^{-1}.



Scheme 4. P−B bond cleavage of **5**.

Conclusion

This experimental study has revealed the presence of the heterocyclic four-membered intramolecular P/B adduct structure of the 1,2-cyclohexylene-anellated frustrated Lewis pair **5**, similar to that predicted by the DFT calculations for the parent ethylene-bridged system **2** and we have characterized its structural details. The P−B bond in **5** is rather long and apparently weak: it requires an activation energy of about 12 kcal mol^{-1} to cleave it. The results indicate that Lewis acid/Lewis base adducts can serve as reactive substrates in frustrated Lewis pair chemistry, provided their dissociation occurs at reasonable reaction conditions. We assume that these findings will render a variety of additional Lewis acid/base adducts as candidates of frustrated Lewis pair behavior.

Experimental Section

General remarks: All reactions were carried out under an argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds. Elemental analyses: Elementar Vario ELIII. NMR: Bruker AC 200 P (^{1}H, 200 MHz; ^{11}B, 64 MHz; ^{31}P, 81 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz; ^{13}C, 126 MHz; ^{11}B, 160 MHz; ^{31}P, 202 MHz; ^{19}F, 470 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{11}B, 192 MHz; ^{31}P, 242 MHz; ^{19}F, 564 MHz). Assignments of the resonances were supported by 2D experiments and chemical shift calculations. ^{11}B NMR spectra were referenced to an external $Et_2O{\cdot}BF_3$ (neat) sample; ^{31}P NMR spectra were referenced to an external H_3PO_4 sample (85 % solution in water); ^{19}F NMR spectra were referenced to an external $CFCl_3$ (neat) sample. X-ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN[16] and PLATON,[17] absorption correction Denzo,[18] structure solution SHELXS-97,[19] structure refinement SHELXL-97,[20] graphics SCHAKAL.[21] CCDC-781886 (**4**), CCDC-781887 (**6**), and CCDC-781888 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 4: Di(mesityl)cyclohexenylphosphine (53 mg, 0.15 mmol) and bis(pentafluorophenyl)borane (52 mg, 0.15 mmol) were mixed in heptane (2 mL). The mixture was stirred for 30 min at room temperature until a clear transparent yellow solution was obtained. The resulting yellow solution was transferred into a Schlenk flask, which was charged with 1.5 bar of dihydrogen at −20 °C and then placed into a freezer at −20 °C and kept there for 2 h. The product precipitated as colorless crystals. Heptane was removed by using a syringe, and the precipitate was dried in vacuo at −20 °C to give the product **4** as a white solid (74 mg, 71 %). At 25 °C, compound **4** was unstable in solution and decomposed. Crystals suitable for X-ray crystal structure analysis were obtained from a heptane solution at −20 °C. ^{1}H NMR (500 MHz, 193 K, [D$_8$]toluene) [all signals are broad, **4**:heptane ca. 10:6]: $\delta = 7.94$ (br d, $^{1}J_{PH} \approx 496$ Hz, 1 H, PH), 6.33 (br s, 1 H, *m*-Mes^{A}), 6.23 (br s, 1 H, *m*-Mes^{B}), 6.12 (br s, 1 H, *m*′-Mes^{A}), 6.06 (br s, 1 H, *m*′-Mes^{B}), 3.49 (br, 1 H, CH^{P}), 3.35 (br, 1 H, BH), 2.41, 2.06, 1.67, 1.49 (each br s, each 3 H, *o*-CH$_3^{Mes}$), 2.14, 1.42 (each br, each 1 H, CH$_2^{Cy}$), 1.82 (br s, 6 H, *p*-CH$_3^{Mes(A)}$, *p*-CH$_3^{Mes(B)}$), 1.74 (br, 1 H, CH^{B}), 1.63, 1.17 (each br, each 1 H, CH$_2^{Cy}$), 1.54, 1.16 (each br, each 2 H, CH$_2^{Cy}$), 1.41, 1.22 ppm (each br, each 2 H, CH$_2^{Cy}$); ^{13}C{^{1}H} NMR (126 MHz, 193 K, [D$_8$]toluene) [all signals are broad, key resonances are listed using the ghsqc experiment]: $\delta = 131.8$ (*m*-Mes^{A}), 131.6 (*m*′-Mes^{B}), 130.9 (*m*′-Mes^{A}, *m*-Mes^{B}), 42.7 (br d, $^{1}J_{PC} \approx 41$ Hz, CH^{P}), 36.2 (br, CH^{B}), 34.1, 30.4, 27.9, 27.1 (CH$_2^{Cy}$), 23.7, 22.5, 21.3, 20.6 (br, *o*-CH$_3^{Mes}$), 20.7 ppm (br, *p*-CH$_3^{Mes(A)}$, *p*-CH$_3^{Mes(B)}$); ^{11}B{^{1}H} NMR (160 MHz, 193 K, [D$_8$]toluene): $\delta = -19.7$ ppm ($\nu_{1/2} \approx 130$ Hz); ^{11}B NMR (160 MHz, 193 K, [D$_8$]toluene): $\delta = -19.7$ ppm (d, $^{1}J_{BH} \approx 70$ Hz); ^{31}P{^{1}H} NMR (202 MHz, 193 K, [D$_8$]toluene) $\delta = -4.5$ (85 %, $\nu_{1/2} \approx 40$ Hz), [−13.6 (unidentified product, 15 %, $\nu_{1/2} \approx 70$ Hz), −95.0 ppm (traces of Mes$_2$PH, $\nu_{1/2} \approx 5$ Hz)]; ^{31}P NMR (202 MHz, 193 K, [D$_8$]toluene): $\delta = -4.5$ (85 %, d, $^{1}J_{PH} = 496$ Hz), [−13.6 (unidentified product, 15 %, d, $^{1}J_{PH} = 496$ Hz), −95.0 ppm (traces of Mes$_2$PH, d, $^{1}J_{PH} = 235$ Hz)]; ^{19}F NMR (470 MHz, 193 K, [D$_8$]toluene): $\delta = -129.4$ (br, *o*-C$_6$F$_5$), −130.3 (br, *o*-C$_6$F$_5$), −161.3 (br, *p*-C$_6$F$_5$), −164.4 ppm (br, *m*-C$_6$F$_5$); elemental analysis calcd (%) for $C_{36}H_{34}BF_{10}P{\cdot}0.6\,C_7H_{16}$: C 63.65, H 5.79; found: C 63.43, H 5.67.

X-ray crystal structure analysis of 4: Formula $C_{36}H_{34}BF_{10}P$, $M_r = 698.41$, colorless crystal $0.20 \times 0.15 \times 0.05$ mm, $a = 11.0288(9)$, $b = 12.2541(8)$, $c = 15.3222(10)$ Å, $\alpha = 68.595(3)$, $\beta = 89.107(3)$, $\gamma = 85.844(6)°$, $V = 1922.7(2)$ Å^3, $\rho_{calcd} = 1.206$ g cm^{-3}, $\mu = 1.265$ mm^{-1}, empirical absorption correction ($0.786 \leq T \leq 0.940$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and ϕ scans, 22 913 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 6451 independent ($R_{int} = 0.087$) and 4401 observed reflections [$I \geq 2\sigma(I)$], 445 refined parameters, $R = 0.070$, $wR^2 = 0.207$, max. (min.) residual electron density 0.24 (−0.25) e Å^{-3}, hydrogen atoms at P and B from difference Fourier calculations, others calculated and refined as riding atoms, disordered solvent molecules couldn't be assigned, therefore SQUEEZE was used.

Synthesis of 5: Bis(pentafluorophenyl)borane (98 mg, 0.28 mmol) was added to a solution of di(mesityl)cyclohexenylphosphine (100 mg, 0.28 mmol) in [D$_6$]benzene (1 mL). After the reaction mixture had been stirred for 30 min at room temperature, all volatiles were evaporated in vacuo to give the product as a bright yellow solid (190 mg, 100 %). Crystals suitable for the X-ray crystal structure analysis were obtained by a slow evaporation of a heptane solution at −30 °C. ^{1}H NMR (500 MHz, 298 K, [D$_8$]toluene): $\delta = 6.48$ (br, 2 H, *m*-Mes^{A}), 6.43 (br, 2 H, *m*-Mes^{B}), 2.95 (dt, $^{3}J_{HH} = 14.4$ Hz, $^{3}J_{HH} = 3.6$ Hz, 1 H, CH^{P}), 2.35, 1.40 (each m, each 1 H, 5-H), 2.10 (br, 6 H, *o*-CH$_3^{Mes(B)}$), 1.95, 0.99 (each m, each 1 H, 2-H), 1.94 (m, 1 H, CH^{P}), 1.92 (s, 6 H, *p*-CH$_3^{Mes(A)}$ and *p*-CH$_3^{Mes(B)}$), 1.91 (br, 6 H, *o*-CH$_3^{Mes(A)}$), 1.57, 0.97 (each m, each 1 H, 4-H), 1.48, 1.11 ppm (each m, each 1 H, 3-H); ^{13}C{^{1}H} NMR (126 MHz, 298 K, [D$_8$]toluene): $\delta = 147.5$ (dm, $^{1}J_{CF} \approx 242$ Hz, C$_6$F$_5$), 143.8 (br d, $^{2}J_{PC} = 6.5$ Hz, *o*-Mes$^{A(t)}$), 141.0 (br d, $^{2}J_{PC} = 8.2$ Hz, *o*-Mes$^{B(t)}$), 140.8 (d, $^{4}J_{PC} = 2.3$ Hz, *p*-Mes$^{A(t)}$), 140.3 (dm, $^{1}J_{CF} \approx 252$ Hz, C$_6$F$_5$), 140.1 (d, $^{4}J_{PC} = 2.5$ Hz, *p*-Mes$^{B(t)}$), 137.6 (dm, $^{1}J_{CF} \approx 252$ Hz, C$_6$F$_5$), 131.1 (br d, $^{3}J_{PC} = 7.8$ Hz, *m*-Mes^{A}), 130.5 (d, $^{3}J_{PC} = 7.8$ Hz, *m*-Mes^{B}), 130.1 (br d, $^{1}J_{PC} = 12.1$ Hz, *i*-Mes^{B}), 124.9 (d, $^{1}J_{PC} = 26.6$ Hz, *i*-Mes^{A}), 119.8 (br, *i*-C$_6$F$_5$), 46.0 (d, $^{1}J_{PC} = 27.0$ Hz, CH^{P}), 37.6 (br, CH^{B}), 32.9 (d, $^{3}J_{PC} = 49.0$ Hz, C-5), 29.9 (d, $^{2}J_{PC} = 7.0$ Hz, C-2), 27.2 (C-4), 27.0 (d, $^{3}J_{PC} = 8.4$ Hz, C-3), 24.3 (br, *o*-CH$_3^{Mes(A)}$), 22.7 (br, *o*-CH$_3^{Mes(B)}$), 20.7 (d, $^{5}J_{PC} = 1.1$ Hz, *p*-CH$_3^{Mes(B)}$), 20.5 ppm (d, $^{5}J_{PC} = 1.1$ Hz, *p*-CH$_3^{Mes(A)}$) [(t): tentative assignment]; ^{31}P{^{1}H} NMR (202 MHz, 298 K, [D$_8$]toluene): $\delta = 23.5$ ppm (m, $\nu_{1/2} \approx 30$ Hz); ^{11}B{^{1}H} NMR (160 MHz, 298 K, [D$_8$]toluene): $\delta = 12.6$ ppm ($\nu_{1/2} \approx 670$ Hz); ^{19}F NMR (470 MHz, 298 K, [D$_8$]toluene): $\delta = -127.5$ (br, 2F, *o*-C$_6$F$_5$), −156.9 (1F, *p*-C$_6$F$_5$), −163.6 ppm (2F, *m*-C$_6$F$_5$); elemental analysis calcd (%) for $C_{36}H_{32}PBF_{10}$: C 62.09, H 4.63; found: C 63.02, H 4.02.

X-ray crystal structure analysis of 5: Formula $C_{36}H_{32}BF_{10}P$, $M_r = 696.40$, colorless crystal $0.15 \times 0.10 \times 0.07$ mm, $a = 18.9773(7)$, $b = 17.4327(6)$, $c = 22.5078(8)$ Å, $\beta = 91.729(2)°$, $V = 7442.8(5)$ Å^3, $\rho_{calcd} = 1.243$ g cm^{-3}, $\mu = 1.307$ mm^{-1}, empirical absorption correction ($0.828 \leq T \leq 0.914$), $Z = 8$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and ϕ scans, 53 357 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 13 044 independent ($R_{int} = 0.124$) and 7343 observed reflections [$I \geq 2\sigma(I)$], 877 refined parameters, $R = 0.072$, $wR^2 = 0.208$, max. (min.) residual electron density 0.24 (−0.36) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, disordered solvent molecules couldn't be assigned, therefore SQUEEZE was used.

Synthesis of 6: Di(mesityl)cyclohexenylphosphine (100 mg, 0.28 mmol) and bis(pentafluorophenyl)borane (99 mg, 0.28 mmol) were mixed in pentane (8 mL). The mixture was stirred for 15 min. After addition of phenyl isocyanate (155 μL, 1.4 mmol), the reaction mixture was stirred for 3.5 h. The resulting white precipitate was isolated by cannula filtration from the suspension and washed three times with pentane (3 mL). Removal of all volatiles in vacuo yielded the product **6** as a white powder (170 mg, 74 %). Crystals suitable for the X-ray crystal structure analysis were obtained by gas diffusion of heptane into a benzene solution of **6**. ^{1}H NMR (600 MHz, 298 K, CD$_2$Cl$_2$): $\delta = 7.30$ (m, 2 H, *o*-Ph), 7.22 (m, 2 H, *m*-Ph), 7.07 (m, 1 H, *p*-Ph), 7.05 (d, $^{4}J_{PH} = 4.2$ Hz, 2 H, *m*-Mes^{A}), 6.97 (d, $^{4}J_{PH} = 4.1$ Hz, 2 H, *m*-Mes^{B}), 3.54 (m, 1 H, CH^{P}), 2.44 (s, 6 H, *o*-CH$_3^{Mes(B)}$), 2.36 (s, 3 H, *p*-CH$_3^{Mes(A)}$), 2.32 (s, 3 H, *p*-CH$_3^{Mes(B)}$), 2.20 (br s, 6 H, *o*-CH$_3^{Mes(A)}$), 2.15, 1.58 (each br m, each 1 H, 2-H), 1.84, 1.11 (each br m, each 1 H, 5-H), 1.76, 1.27 (each m, each 1 H, 3-H), 1.70 (br m, 1 H, CH^{B}), 1.62, 1.11 ppm (each m, each 1 H, 4-H); ^{13}C{^{1}H} NMR (151 MHz, 298 K, CD$_2$Cl$_2$): $\delta = 150.3$ (d, $^{1}J_{PC} = 122.1$ Hz, C^{N}), 148.3 (dm, $^{1}J_{CF} \approx 238$ Hz, C$_6$F$_5$), 147.6 (dm, $^{1}J_{CF} \approx 231$ Hz, C$_6$F$_5$), 145.9 (d, $^{3}J_{PC} = 21.8$ Hz, *i*-Ph), 144.7 (d, $^{2}J_{PC} = 9.1$ Hz, *o*-Mes^{A}), 144.1 (d, $^{4}J_{PC} = 2.9$ Hz, *p*-Mes^{A}), 144.0 (d, $^{4}J_{PC} = 3.0$ Hz, *p*-Mes^{B}), 143.9 (br, *o*-Mes^{B}), 139.2 (dm, $^{1}J_{CF} \approx 250$ Hz, 2 × C$_6$F$_5$), 137.2 (dm, $^{1}J_{CF} \approx 248$ Hz, 2 × C$_6$F$_5$), 132.6 (d, $^{3}J_{PC} = 7.0$ Hz, *m*-Mes^{A}), 132.5 (d, $^{3}J_{PC} = 7.5$ Hz, *m*-Mes^{B}), 128.5 (*m*-Ph), 125.7 (*p*-Ph), 125.1 (*o*-Ph), 122.8 (br, 2 × *i*-C$_6$F$_5$), 121.6 (d, $^{1}J_{PC} = 73.4$ Hz, *i*-Mes^{B}), 115.2 (d, $^{1}J_{PC} = 74.1$ Hz, *i*-Mes^{A}), 42.5 (d, $^{1}J_{PC} = 34.3$ Hz, CH^{P}), 30.0 (d, $^{3}J_{PC} = 13.1$ Hz, C-5), 29.5 (d, $^{2}J_{PC} = 4.0$ Hz, C-2), 29.4 (br, CH^{B}), 27.0 (C-4), 26.8 (d, $^{3}J_{PC} = 13.2$ Hz, C-3), 24.6 (d, $^{3}J_{PC} = 4.2$ Hz, *o*-CH$_3^{Mes(A)}$), 24.5 (br, *o*-CH$_3^{Mes(B)}$), 21.1 (*p*-CH$_3^{Mes(A)}$), 20.9 ppm (*p*-CH$_3^{Mes(B)}$); ^{11}B{^{1}H} NMR (160 MHz, 298 K, CD$_2$Cl$_2$): $\delta = 1.4$ ppm ($\nu_{1/2} \approx 340$ Hz); ^{31}P{^{1}H} NMR (202 MHz, 298 K, CD$_2$Cl$_2$): $\delta = 8.5$ ppm ($\nu_{1/2} \approx 25$ Hz); ^{19}F NMR (470 MHz, 298 K, CD$_2$Cl$_2$): $\delta = -130.0$, −133.8 (each br, each 2F, *o*-C$_6$F$_5$), −160.9 (1F, *p*-C$_6$F$_5^{A}$), −161.0 (1F, *p*-C$_6$F$_5^{B}$), −165.0 (2F, *m*-C$_6$F$_5^{A}$), −165.7 ppm (2F, *m*-C$_6$F$_5^{B}$); elemental analysis calcd (%) for $C_{43}H_{37}BF_{10}NOP$: C 63.33, H 4.57, N 1.72; found: C 62.60, H 4.49, N 1.77.

X-ray crystal structure analysis of 6: Formula $C_{43}H_{37}BF_{10}NOP{\cdot}1.5\,C_6H_6$, $M_r = 932.68$, colorless crystal $0.40 \times 0.35 \times 0.15$ mm, $a = 11.6750(4)$, $b =$

13.5520(5), $c=15.0991(6)$ Å, $\alpha=81.138(2)$, $\beta=75.048(2)$, $\gamma=87.483(2)°$, $V=2280.51(15)$ Å^3, $\rho_{calcd}=1.358$ g cm^{-3}, $\mu=1.235$ mm^{-1}, empirical absorption correction ($0.638 \leq T \leq 0.836$), $Z=2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda=1.54178$ Å, $T=223(2)$ K, ω and ϕ scans, 28550 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.60$ Å^{-1}, 7966 independent ($R_{int}=0.041$) and 7212 observed reflections [$I \geq 2\sigma(I)$], 601 refined parameters, $R=0.044$, $wR^2=0.118$, max. (min.) residual electron density 0.26 (−0.39) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

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