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Noninteracting, Vicinal Frustrated P/B-Lewis Pair at the Norbornane Framework: Synthesis, Characterization, and Reactions

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Supporting Information

ABSTRACT: Hydroboration of dimesitylnorbornenylphosphane with Piers' borane [$HB(C_6F_5)_2$] gave the frustrated Lewis pair (FLP) **4** in good yield. It has the $-PMes_2$ Lewis base attached at the 2-endo position and the $-B(C_6F_5)_2$ group 3-exo oriented at the norbornane framework. The vicinal FLP **4** was shown by X-ray diffraction and by spectroscopy to be a rare example of an intramolecular noninteracting pair of a Lewis acid and Lewis base functionality. The FLP **4** rapidly splits dihydrogen heterolytically at ambient temperature to yield the phosphonium/hydrido borate zwitterion **5**. It adds to the carbonyl group of benzaldehyde and to carbon dioxide to yield the adducts **6** and **7**, respectively. Compounds **5**–**7** were characterized by X-ray diffraction. Compound **4** adds to the S═O function of sulfur dioxide to give a pair of diastereomeric heterocyclic six-membered ring products due to the newly formed sulfur chirality center, annulated with the norbornane skeleton, which were investigated by $^{31}P/^{11}B$ single and double resonance solid state NMR experiments. Compound **8** was also characterized by X-ray diffraction. The FLP **4** undergoes a clean *N*,*N*-addition to nitric oxide (NO) to give a norbornane annulated five-membered heterocyclic persistent FLP-NO aminoxyl radical **12** (characterized, e.g., by X-ray diffraction and EPR spectroscopy). Additionally, the FLP radical was characterized by ^{1}H solid state NMR spectroscopy. The radical **12** undergoes a H-atom abstraction reaction with 1,4-cyclohexadiene to yield the respective diamagnetic FLP-NOH product **13**, which was also characterized by X-ray diffraction and solid state NMR spectroscopy.

INTRODUCTION

Frustrated Lewis Pairs (FLPs), that is, pairs of reactive but sufficiently bulky Lewis acids and Lewis bases that avoid neutralizing strong adduct formation, have been shown to react with a variety of small molecules.[1] Activation of dihydrogen by heterolytic splitting and utilization of the resulting FLP bound H^+/H^- pair in metal free catalytic hydrogenation is one prominent feature,[2,3] but FLPs were also shown to bind to alkenes and alkynes,[4] to various carbonyl compounds,[5] to nitrogen oxides (N_2O,[6] NO[7]), and even to CO_2[8] or SO_2.[9]

Reactions of intermolecular FLPs with small molecules must find a way to avoid the "termolecularity trap". DFT calculations indicated that combinations of such bulky Lewis bases and acids as, for example, the often used $^tBu_3P/B(C_6F_5)_3$ pair form "encounter complexes" by van der Waals interaction that preorient the FLP for the essential reaction with, for example, H_2 or CO_2, etc.[10,11] Intramolecular FLPs avoid any termolecularity problem by having the active Lewis acid and Lewis base components tied together by a suitable linker. Many such systems were described in recent years and many of them were shown to exhibit very high reactivity toward activation of small molecules.[12−14] Avoiding termolecularity by formation of the intramolecular FLP is achieved at the expense of a potentially increased tendency of intramolecular Lewis acid−Lewis base adduct formation. Although it is seldom if at all observed for geminal FLPs,[13,15] internal adduct formation is found for many vicinal FLPs[12,16−18] and systems with longer bridges.[19] We could show by dynamic NMR spectroscopy that a variety of vicinal P/B and N/B FLPs undergo rapid ring opening by reversible P−B or N−B bond cleavage to equilibrate with their not directly observed open isomers of higher energy content. These then were thought to be the reactive forms of the intramolecular FLPs to achieve small molecule activation.[10,12] The **1** ⇆ **1′** equilibrium is a typical example (see Chart 1). The P−B bond cleavage in this system

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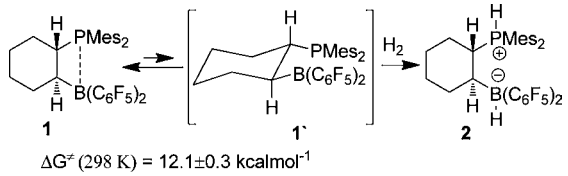
Chart 1



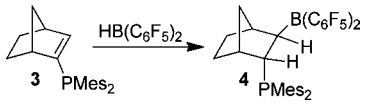
has an activation barrier of $\Delta G^{\ddagger}(298\ \mathrm{K}) \approx 12.1 \pm 0.3$ kcal mol^{-1}, that is, it occurs very rapidly even at low temperature. Consequently, compound **1** was shown to rapidly cleave dihydrogen heterolytically even at −20 °C to form the zwitterion **2** in high yield. This reaction is thought to proceed through the open isomer **1′** featuring the C−P and C−B vectors in gauche orientation at the cyclohexane framework.[10,20]

It is probably this kinetically facile generation of the nonquenched reactive intermediates (e.g., **1′**) that makes many interacting P/B (or N/B)[16,19] vicinal FLPs still good for small molecule activation. It may, however, be a disadvantage that the actual reactive open FLP forms (e.g., **1′**) are only available in minute quantities from the closed/open equilibrium (e.g., **1** ⇆ **1′**). It might be better if it were possible to directly prepare analogues of the open forms and prevent their internal P/B adduct formation geometrically. That we have done by using a rigid norbornane derived framework to which we have attached a $-PMes_2$ Lewis base and a $-B(C_6F_5)_2$ Lewis acid component stereoselectively such that direct P−B formation was inhibited. In this account, we shall discuss the formation of this vicinal noninteracting P/B FLP, present the results of its structural and spectroscopic characterization, and show a selected series of FLP reactions this system undergoes.

RESULTS AND DISCUSSION

Synthesis of the Vicinal Frustrated Lewis Pair. Norbornene can rather selectively be deprotonated by using "Schlosser's base".[21] Consequently, we used a related procedure for the synthesis of 2-dimesitylphosphinonorbornene (**3**). Bicyclo[2.2.1]heptene was treated with a 1:1 mixture of potassium tert-butoxide and *n*-butyllithium in THF. The resulting norbornenyl carbanion was then quenched with chlorodimesitylphosphane. Workup including sequential chromatographic separation eventually gave the starting material **3** for our FLP synthesis in 13% yield. This was acceptable since we needed only one additional step to arrive at our target molecule **4** (see Scheme 1). For this purpose, the phosphane **3**

Scheme 1



(^{31}P NMR: δ = −37.7) was treated with Piers' borane $[HB(C_6F_5)_2]$[22] in dichloromethane at room temperature. A clean hydroboration reaction took place and we isolated the frustrated Lewis pair **4** as a yellow solid in 96% yield.

Single crystals of compound **4** for the X-ray crystal structure analysis (see Figure 1 and Tables 2 and 3) were obtained by slow evaporation of solvent from a pentane solution at −35 °C. Compound **4** selectively features the $-B(C_6F_5)_2$ Lewis acid

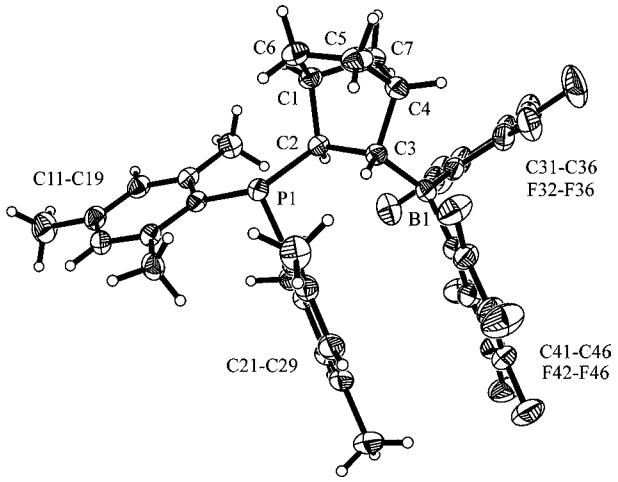


Figure 1. View of the molecular structure of compound **4** (thermal ellipsoids are shown with 30% probability).

substituent in the exo-orientation at carbon atom C3 and the $-PMes_2$ Lewis base substituent in the endo position at C2. The defined cis-1,2-addition stereochemistry of the hydroboration reaction has thus brought these two functional groups in a fixed vicinal orientation at the rigid norbornyl framework (dihedral angle P1−C2−C3−B1 110.7(2)°). The resulting P···B separation is large at 3.878(1) Å, precluding any direct Lewis acid/Lewis base interaction within this pair of heteroatoms. Consequently, the coordination geometry at boron is trigonal planar with a sum of C−B−C angles of 359.7° (individual values: C3−B1−C31 121.7(2)°, C3−B1−C41 121.6(2)°, C31−B1−C41 116.4(2)°). The phosphorus atom attains the usual distorted pseudotetrahedral coordination geometry, characterized by a sum of C−P1−C angles of 320.5°. We note that compound **4** features a conformational orientation of the bulky aryl groups at phosphorus and at boron that brings a mesityl π-system and a C_6F_5 π-system facing each other (shortest distance between the C21−C29 and the C41−C46 planes: 3.65 Å). This might indicate the presence of a weak π-stacking interaction[23] between the $-PMes_2$ and $-B(C_6F_5)_2$ groups at the norbornane framework in **4**.

Compound **4** was characterized by ^{11}B and ^{31}P solid state NMR spectroscopy. The ^{11}B Hahn echo MAS NMR spectrum of **4** (see Figure 2) reveals a resonance at δ_{CS} = 75.2 ppm (in good agreement with the broad ^{11}B resonance at δ_{CS} = 75.0 ppm observed in solution typical for a planar-tricoordinate R-B$(C_6F_5)_2$ boron Lewis acid[22]) which is strongly influenced by second order quadrupolar effects. Line shape analysis reveals a quadrupolar coupling constant C_Q of 4.7 MHz and an asymmetry parameter η_Q of 0.22. For obtaining the best agreement between the experimental and the simulated spectrum, also Chemical Shielding Anisotropy (CSA) parameters are included within those simulations (see Table 1). The experimental values are in excellent agreement with DFT calculations in the gas phase for both, the electric field gradient (EFG) and the magnetic shielding tensors, for the first using a GGA DFT (B97-D[24]) and for the latter a hybrid DFT (B3-LYP[25,26]) level of theory (for details see Table 1 and the Supporting Information). The extraordinarily large C_Q value and the η_Q parameter close to zero both point to a highly symmetric, nearly perfectly planar three-coordinated boron species. Together with the strongly positive isotropic chemical shift value, all the ^{11}B NMR parameters indicate that there is no

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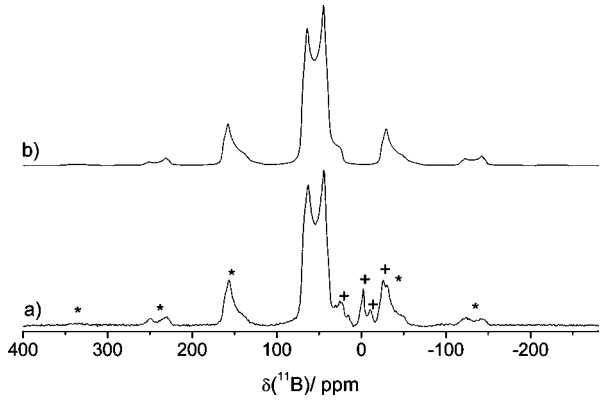


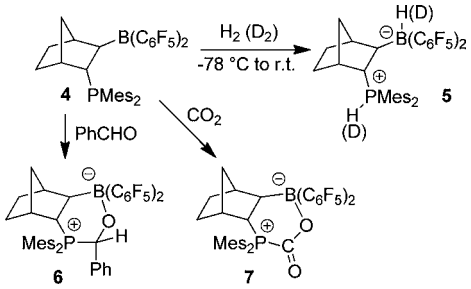
Figure 2. (a) ^{11}B Hahn echo MAS NMR spectrum of FLP **4** acquired at 11.74 T with a spinning frequency of 15.0 kHz and (b) corresponding line shape simulation based on the NMR parameters given in Table 1. + marks impurities and * marks spinning sidebands.

electronic interaction between the two Lewis centers. This result contrasts sharply with those obtained for most of the other vicinal P/B FLPs investigated so far,[17c,18] where significant covalent interactions result in much lower values for both ^{11}B δ_{CS} and C_Q values, and where these NMR parameters could be correlated with intramolecular B···P distances and catalytic activities.[17c,18] Also, the ^{31}P chemical shifts (δ = −22.4 ppm in the solid state, −21.8 ppm in solution) highlight the special character of **4** in comparison to the other vicinal FLPs, for which chemical shifts in-between 24.5 and 14.5 ppm are observed, which is typical for the presence of Lewis acid/base interactions. These results are further supported by our DFT calculations of Wiberg bond order indices for the B···P interaction[27] of 0.014 in the CAO basis and 0.008 in the NAO basis (in contrast to values near 0.8 in the NAO basis previously described for a series of related vicinal P/B compounds that show a phosphane/borane interaction[17c,18]).

FLP Reactions of 4 with Small Molecules. Compound **4** is a reactive frustrated Lewis pair. It splits dihydrogen under mild conditions. In a typical experiment we exposed the FLP **4** to a 2.5 bar H_2 atmosphere in *n*-pentane at −78 °C. Warming to r.t. resulted in the formation of a white precipitate of the product of heterogeneous splitting of dihydrogen, the phosphonium/hydridoborate zwitterion **5** that we isolated in 67% yield (see Scheme 2).

In solution compound **5** features the typical ^{1}H and ^{13}C NMR signals of the disubstituted norbornane framework. It shows the ^{1}H NMR resonance of the −PH function as a dd at δ = 7.22 with the typical large $^1J_{PH}$ ~ 467 Hz coupling constant ($^3J_{PH}$ ~ 9 Hz). The ^{31}P NMR spectrum shows a respective dd

Scheme 2



at δ = −7.4. The −BH unit exhibits a ^{11}B NMR feature at δ = −19.6 (d, $^1J_{BH}$ ~ 90 Hz). Compound **5** is chiral. Consequently it features the NMR signals of a pair of diastereotopic mesityl substituents at phosphorus and of a pair of diastereotopic $-C_6F_5$ groups at boron (for details see the Supporting Information).

The H_2-splitting product **5** was characterized by X-ray diffraction (see Figure 3, Table 2 and Table 3). The structure of

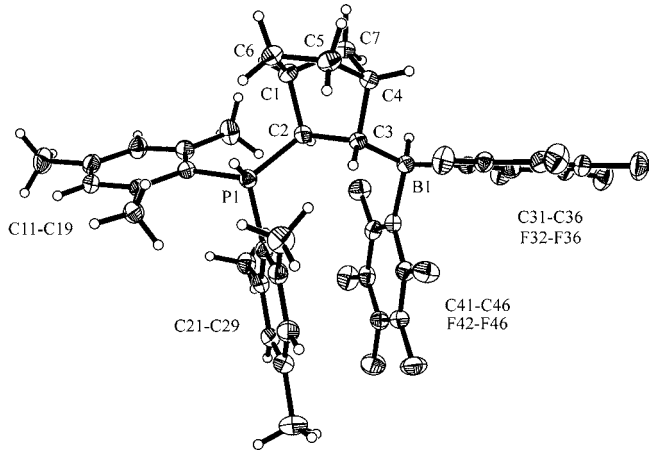


Figure 3. Projection of the molecular structure of the phosphonium hydridoborate zwitterion **5** (thermal ellipsoids are shown with 30% probability).

5 confirms the formation of a $-PHMes_2^+$ phosphonium and a $-BH(C_6F_5)_2^-$ hydridoborate pair of substituents at the FLP's norbornane framework. The P−H and B−H vectors point to different directions.[3b] The sum of C−B−C angles confirms the formation of a tetracoordinate borate center. The P···B separation is large, but the system shows a conformation in the crystal that might indicate a mesityl/C_6F_5 π-stacking

Table 1. ^{11}B Solid-state NMR Parameters of 4 and 8

	δ_{CS}/ ppm ± 0.5 ppm	C_Q/ MHz ± 5%	η_Q ± 0.1	Δσ/ppm ± 20 ppm	η_σ ± 0.1
4	75.2[a] (74.0[b])	4.66[a] (4.77[b])	0.22[a] (0.23[b])	122.5[a] (130.3[b])	0.60[a] (0.58[b])
8	2.4/−0.2 (−0.9[b,c]/−4.1[b,d])	2.15/1.71 (2.04[b,c]/1.89[b,d])	0.47/0.38 (0.41[b,c]/0.44[b,d])		

[a]Extracted by line shape simulation of the MAS NMR spectrum shown in Figure 2. Euler angles of α = 0°, β = 15° and γ = 45° for relating the CSA with the EFG tensor were used within the simulations. [b]DFT-calculated values in the gas-phase (EFG values were calculated on a B97-D/def2-TZVP[28] (mod.) (for the full AO basis set see the Supporting Information) and CSA values on a B3-LYP/def2-TZVP level of theory). [c]Structure of **8**-eq. [d]Structure of **8**-ax.

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Table 2. Selected Bond Lengths[a] of the FLP 4 and its Reaction Products 5−8, 12 and 13

	C2−C3	C2−P1	C3−B1	X−P1	Y−B1
4	1.581(2)	1.876(2)	1.567(3)		
5	1.577(3)	1.810(2)	1.636(3)	[b]	[b]
6[f]	1.575(4)	1.824(3)	1.633(4)	1.976(3)[c]	1.499(4)[c]
7[g]	1.571(4)	1.813(3)	1.609(4)	1.907(3)[c]	1.554(4)[c]
8[h]	1.589(5)	1.819(4)	1.621(6)	2.404(2)[d]	1.573(5)[d]
12[i]	1.570(4)	1.790(3)	1.620(4)	1.744(2)[e]	1.617(4)[e]
13[j]	1.569(3)	1.809(3)	1.631(4)	1.646(2)[e]	1.587(4)[e]

[a]Bond length in Å [b]X = Y = H. [c]C8(X), O1(Y). [d]S1(X), O1(Y). [e]X = Y = N1. [f]C8−O1 1.376(3) Å, C8−C51 1.517(4) Å. [g]C8−O1 1.289(3) Å, C8−O2 1.205(3) Å. [h]S1−O1 1.545(3) Å, S1−O2 1.367(4) Å, S1−O2A 1.310(8) Å. [i]N1−O1 1.291(3) Å. [j]N1−O1 1.430(3) Å.

interaction[23] in the periphery of the pair of the heteroatom bonded substituents (see Figure 3 and Tables 2 and 3).

Table 3. Selected Structural Parameters of the FLP 4 and its Reaction Products 5−8, 12 and 13[a]

	Σ C′−P1−C[b]	Σ C′−B1−C[c]	Σ Z−X−Y
4	320.5	359.7	
5	344.9	335.7	
6	335.7	336.2	327.8[d]
7	340.0	338.4	360.0[e]
8	340.4	339.7	312.3[f]
12	340.1	339.5	360.0[g]
13	337.6	337.9	360.1[g]

[a]Bond angles in deg. [b]C′/C: C2, C11, C21. [c]C′/C: C3, C31, C41. [d]C8(X), Z/Y: P1, O1, C51. [e]C8(X), Z/Y: P1, O1, O2. [f]S1(X), Z/Y: P1, O1, O2 (O2A: 344.1°). [g]N1(X), Z/Y: B1, P1, O1.

Compound **4** undergoes typical FLP reactions with carbonyl compounds under very mild conditions.[5] This was shown by exposure of **4** to benzaldehyde. Mixing of a solution of PhCHO with a solution of FLP **4** in *n*-pentane at ambient temperature resulted in the instantaneous formation of a white precipitate of the P/B 1,2-addition product **6** (see Scheme 2). It was isolated in 85% yield.

The FLP **4** contains a total of four chirality centers within the unsymmetrically substituted norbornane framework. These are of course not independent of each other. The addition of **4** to the prochiral benzaldehyde molecule generates a fifth carbon chirality center. Therefore, one might expect the formation of a mixture of two product diastereoisomers. However, we have observed that this FLP reaction is highly diastereoselective and we have only found a single diastereoisomer (**6**) within the limits of detection. This could have the phenyl substituent at the newly formed annulated heterocyclic six-membered ring oriented toward the norbornane exo- or endo side. The X-ray crystal structure analysis of compound **6** has revealed that we have here obtained the exo-oriented isomer (see Figure 4). The structure of **6** features the newly formed heterocyclic six-membered ring system exo/endo annulated with the norbornane framework. It shows the newly formed P1−C8 (1.976(3) Å) and B1−O1 (1.499(4) Å) single bonds (C8−O1: 1.376(3) Å). The six-membered heterocycle in **6** is formed in a distorted chair conformation. It has the phenyl substituent at C8 oriented in an equatorial position in a cis-arrangement to the C1−H vector at the norbornane junction, that is, pointing to the exoface of the norbornane framework.

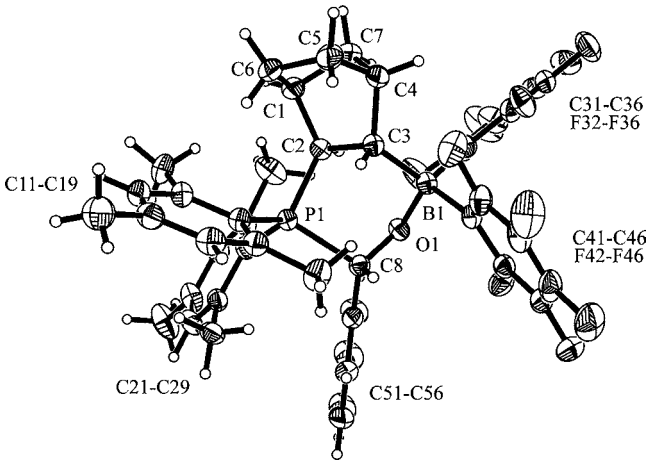

Figure 4. View of the molecular structure of the benzaldehyde addition product **6** (thermal ellipsoids are shown with 30% probability).

In solution, rotation of the bulky mesityl substituents around the P−C(aryl) vectors (299 K) and the bulky $-C_6F_5$ substituents around the respective B−C(aryl) vectors (213 K) is frozen on the NMR time scale. Consequently we have observed a total of six separate mesityl CH_3 ^{1}H NMR resonances and four mesityl C−H proton resonances of the pair of diastereotopic mesityl substituents at phosphorus and a total of ten ^{19}F NMR signals of the pair of diastereotopic C_6F_5 groups at boron (the spectra are depicted in the Supporting Information). The ^{11}B NMR signal of **6** occurs at δ = 0.2 in a typical borate range and the ^{31}P NMR signal of **6** was found at δ = +38.9.

The open FLP **4** reacts readily with carbon dioxide. We exposed the P/B pair to CO_2 (3 bar) at −78 °C and warmed the reaction mixture to r.t. Workup gave the CO_2 addition product **7** in 78% yield. The compound was characterized by X-ray diffraction. The structure features the newly formed six-membered heterocycle in a distorted half-chair conformation annulated with the supporting rigid norbornane framework. The phosphorus Lewis base of **4** was added to the carbonyl carbon atom of the CO_2 molecule and the boron Lewis acid was attached to a CO_2 oxygen atom.[8] The resulting exocyclic C8−O2 linkage is in the C═O double bond range at 1.205(3) Å whereas the endocyclic C8−O1 bond is longer (1.289(3) Å). The coordination geometry at the bound CO_2 carbon atom C8 in **7** is trigonal planar with a sum of bond angles of 360.0° (P1−C8−O2 116.3(2)°, P1−C8−O1 119.6(2)°, O1−C8−O2 124.1(3)°) (see Figure 5 and Tables 2 and 3).

The CO_2 addition product **7** features a ^{13}C NMR carbonyl signal at δ = 160.7 with a coupling constant of $^1J_{PC}$ = 88.0 Hz. The corresponding carbonyl stretching frequency observed in the IR spectrum was found at 1704 cm^{-1}. We find hindered rotation of the pairs of bulky diastereotopic aryl groups at boron and at phosphorus at the very rigid bicyclic skeleton of **7**. Consequently, we have observed four *o*-F, two *p*-F and four *m*-F ^{19}F NMR signals of compound **7** in solution at 213 K and a total of six mesityl CH_3 ^{1}H NMR signals and four CH- mesityl resonances. The ^{31}P NMR spectrum of the FLP/CO_2 adduct **7** shows a resonance at δ = 13.7.

We had recently shown that FLPs can also react with sulfur dioxide. We had isolated and described a small series of [P]−S(O)−O−[B] type addition products.[9] These compounds featured a strongly nonplanar coordination geometry at sulfur

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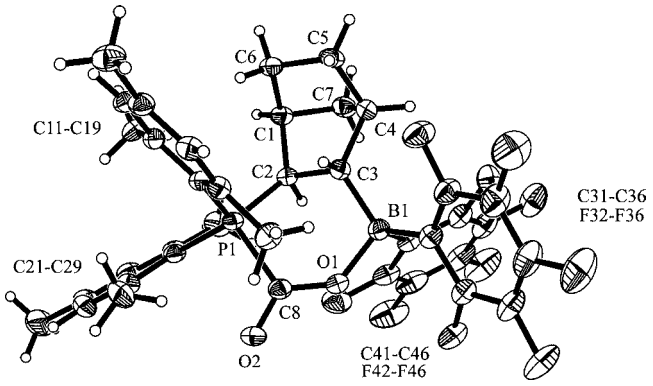
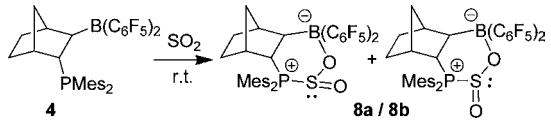


Figure 5. Molecular structure of the FLP/CO_2 addition product **7** (thermal ellipsoids are shown with 30% probability).

which makes the sulfur atoms in these FLP/SO_2 addition products chiral centers. The FLP **4** was treated with SO_2 gas (2 bar) for five minutes at room temperature in *n*-pentane. During this time a white precipitation of the SO_2 adduct **8** was formed and isolated as a colorless solid (see Scheme 3).

Scheme 3



We expected the formation of a pair of epimeric SO_2 addition products that were distinguished only by their relative configuration at the chiral sulfur atom. The two possible diastereoisomers were then distinguished as having the relative configuration of *rac*-(1R,2S,3R,4S,^{S}S) (i.e., **8a**) and *rac*-(1R,2S,3R,4S,^{S}R) (i.e., **8b**). Indeed we have found that the obtained product contained a mixture of two diastereoisomers in a ca. 5:2 molar ratio. They are characterized in solution by ^{31}P NMR signals at δ = 59.5 (major) and δ = 53.6 (minor isomer), respectively. For the major isomer of **8** we have monitored a set of four *o*-C_6F_5 ^{19}F NMR signals, two *p*-C_6F_5 and some overlapping *m*-C_6F_5 resonances. The minor isomer of **8** features a similar series of four *o*-C_6F_5 and two *p*-C_6F_5 signals.

We obtained single crystals of compound **8** (see Figure 6). The structure shows the chair-shaped six-membered heterocycle annulated with the norbornane framework. The six-membered ring FLP SO_2 adduct **8** was formed by means of P−S and B−O bond formation (see Figure 6 and Tables 2 and 3). The oxygen atom O2 is disordered over two positions (ca. 5 : 2). In the crystal the major isomer of the FLP/SO_2 adduct **8** features the exocyclic oxygen (S1−O2:1.367(4) Å) in a pseudoequatorial site at the newly formed six-membered ring. The coordination geometry at sulfur is trigonal-pyramidal with the sum of the three bond angles of 312.2° (P1−S1−O2 104.4(2)°, P1−S1−O1 95.1(1)°, O1−S1−O2 112.8(2)°).

The SO_2 activation product **8** was additionally investigated by solid-state NMR spectroscopy for a more thorough characterization of the two diastereomers formed in this reaction. The ^{31}P{^{1}H} CPMAS NMR spectrum (see Figure 7, bottom) reveals two resonances at 57.8 and 56.6 ppm in an intensity ratio of ca. 3:2 (see the Supporting Information) most probably resulting from the two [B]−O−S(O)−[P] epimers. In close agreement with these findings, also two ^{11}B resonances

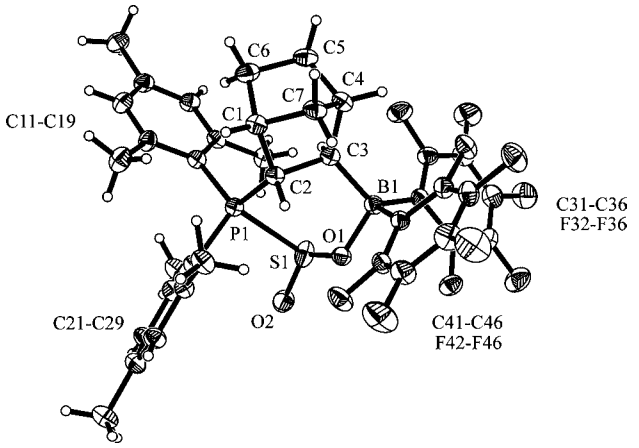


Figure 6. Molecular structure of the FLP/SO_2 addition product **8a** (thermal ellipsoids are shown with 30% probability).

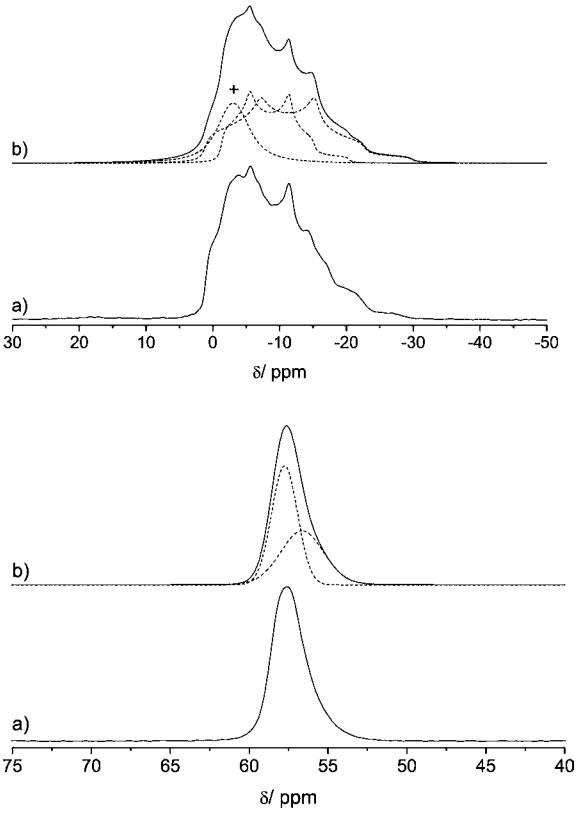


Figure 7. (Top) (a) ^{11}B{^{1}H} MAS NMR spectrum of **8** acquired at 7.05 T with a rotation frequency of 14.0 kHz and (b) corresponding line shape simulation. (Bottom) (a) ^{31}P{^{1}H} CPMAS NMR spectrum of **8** acquired at 7.05 T with a spinning frequency of 10.0 kHz and (b) line shape simulation.

are found in a ^{11}B{^{1}H} MAS NMR spectrum (see Figure 7, top) with only slightly differing quadrupolar coupling parameters (see Table 1). These parameters are in close agreement with the DFT-calculated ones for the [B]−O−S(O)−[P] epimers.

For further proving the hypothesis of the formation of epimers, we performed {^{1}H}→^{31}P{^{11}B} cross-polarization-rotational echo adiabatic passage double resonance (CP-REAPDOR) experiments (see Figure 8a) which allow a B···P distance determination through recoupling of the heteronuclear

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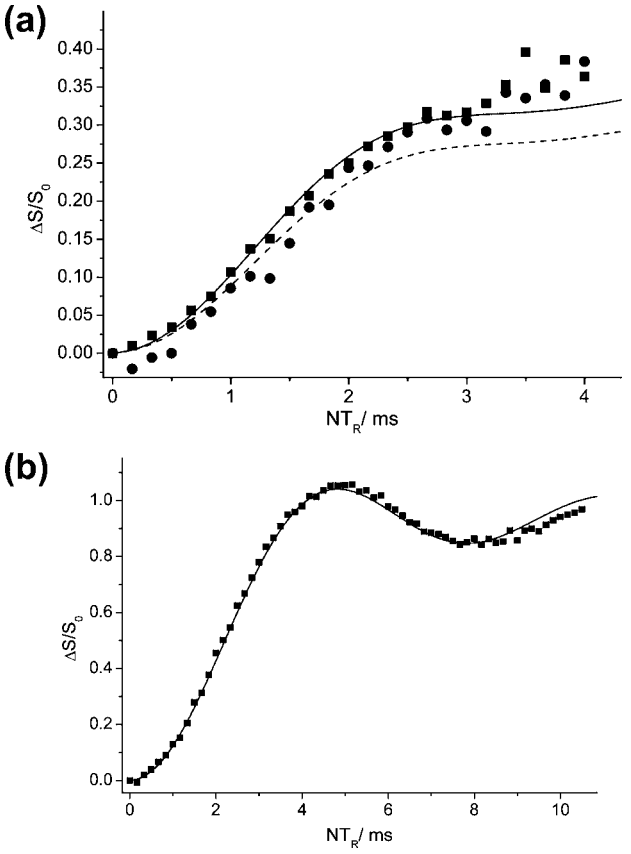
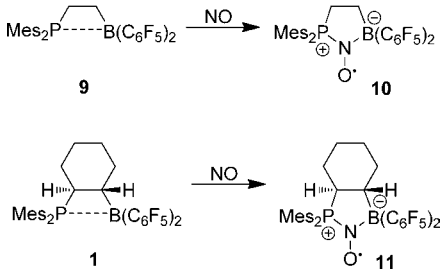


Figure 8. (a) $\{^1H\}\rightarrow{}^{31}P\{^{11}B\}$ CP-REAPDOR experiment of **8** performed at 7.05 T with a spinning frequency of 12.0 kHz. The dephasing curves for the resonances at 57.8 ppm (■) and 56.6 ppm (●) are shown. The SIMPSON simulations are based on the crystallographic B···P distance and quadrupolar coupling parameters of C_Q = 1.71 MHz, η_Q = 0.38 (solid curve) and C_Q = 2.15 MHz, η_Q= 0.47 (dashed curve). (b) $\{^1H\}\rightarrow{}^{11}B\{^{31}P\}$ CP-REDOR experiment of **8** performed at 7.05 T with a spinning frequency of 12.0 kHz and ^1H decoupling during the evolution and data acquisition time. The SIMPSON simulation (straight curve) is based on the crystallographic B···P distance of 3.54 Å.

B···P dipolar interaction under MAS conditions.[29] As illustrated by Figure 8a the two phosphorus moieties show very similar REAPDOR dephasing curves close to the numerical simulation on the basis of the crystallographic B···P distance of 3.54 Å and experimental quadrupolar coupling parameters. These experiments suggest that both epimers have the same B···P distance within experimental error, while the slight differences observed between the two REAPDOR curves arise from the difference in the corresponding ^{11}B-C_Q values and/or experimental uncertainties. These results are confirmed by the $\{^1H\}\rightarrow{}^{11}B\{^{31}P\}$ CP-rotational echo double resonance (REDOR)[17c,30] curve shown in Figure 8b. The clear oscillatory behavior signifies the presence of isolated two-spin systems with identical (within experimental error), extremely well-defined internuclear distances for both epimers present.

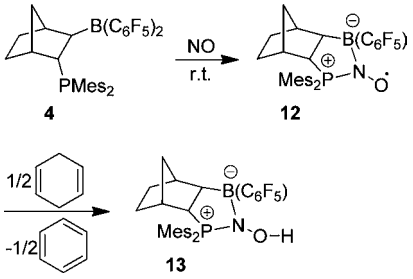
Reaction with Nitric Oxide. We had recently shown that the ethylene bridged P/B FLP **9** reacted under mild conditions with nitric oxide (NO).[7] The reaction took place by N,N-addition of the P/B pair to yield the five membered heterocyclic product **10**. The paramagnetic compound **10** is chemically related to the large compound class of the aminoxyl radicals. Compound **10** is a persistent radical. It is the parent compound of the new class of FLP-NO aminoxyl radicals (see Scheme 4). The FLP **1** also adds NO. The resulting FLP-NO nitroxide product **11** shows a variety of typical features of persistent aminoxyl radical species.[7]

Scheme 4



The open FLP **4** reacts rapidly with NO in *n*-pentane solution in the temperature range between −78 °C to r.t. A solid formed quickly upon exposure of the reactive FLP to a NO atmosphere at low temperature and we isolated the FLP *N,N*-addition product **12** as a pale turquoise solid in 87% yield (Scheme 5). Single crystals of **12** suitable for X-ray structure analysis (see Figure 9 and Tables 2 and 3) were obtained from dichloromethane/*n*-pentane at −35 °C by the diffusion method.

Scheme 5



The X-ray crystal structure analysis of compound **12** has confirmed that the phosphorus Lewis base and the boron Lewis acid have both added to the nitrogen atom of the nitric oxide reagent (see Figure 9). The resulting five-membered heterocycle is found annulated to the norbornane framework in a 2-

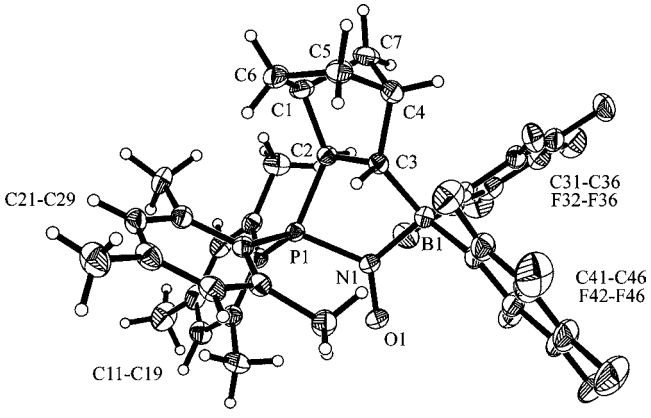


Figure 9. Molecular structure of the persistent FLP-NO aminoxyl radical **12** (thermal ellipsoids are shown with 30% probability).

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endo (C2−P1: 1.790(3) Å), 3-exo (C3−B1: 1.620(4) Å) fashion. The nitrogen atom in the aminoxyl radical **12** features a trigonal-planar coordination geometry with a sum of its three bond angles being 360.0° with individual angles of 126.1(2)° (O1−N1−B1), 118.9(2)° (O1−N1−P1) and 115.0(2)° (B1−N1−P1). The B1−N1 bond length (1.617(4) Å) is unexceptional. The P1−N1 bond is very long at 1.744(2) Å, clearly being in a phosphorus-nitrogen single bond range. The O1−N1 bond is rather short at 1.291(3) Å which indicates a considerable delocalization of the unpaired electron between the aminoxyl oxygen and nitrogen atoms.[7]

The EPR spectrum of **12** in fluorobenzene at room temperature displays a multiline pattern centered at g = 2.0078 (Figure 10). As previously seen in other P/B FLP-NO

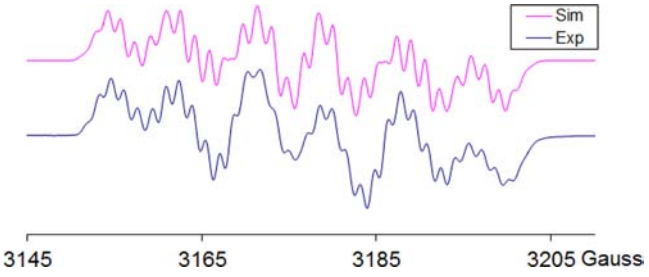

Figure 10. X-band EPR spectrum and simulation of **12** in fluorobenzene at room temperature.

adducts, coupling to the ^{14}N [$A(^{14}N)$ = 19.8 MHz], ^{31}P [$A(^{31}P)$ = 49.7 MHz], and $^{11}B/^{10}B$ [$A(^{11}B)$ = 9.5 MHz] nuclei is observed. While the magnitudes of these hyperfine coupling constants are almost identical to those in the related P/B FLP-NO adduct **11** [$A(^{14}N)$ = 20.4 MHz, $A(^{31}P)$ = 50.5 MHz, $A(^{11}B)$ = 8.9 MHz], a sharper EPR spectrum is seen for **12** that possesses more fine structure, perhaps due to the extremely rigid nature of the tricyclic **12**. Satisfactory simulation required consideration of the four *o*-^{19}F nuclei of the B-C_6F_5 groups ($A(^{19}F)$ = 4.0 MHz) as well as the two ^{1}H nuclei within the P/B−NO five-membered ring [$A(^{1}H)$ = 3.3 MHz].

UV−vis spectroscopy of **12** in fluorobenzene at room temperature reveals an absorbance centered at λ_{max} = 682 nm (ε = 6.8 $M^{-1}\,cm^{-1}$, Figure 11). Vibrational fine structure is present with an average spacing of 1093(36) cm^{-1} that corresponds to the N-O stretch in the electronic excited state of **12** expected to possess a lower N−O bond order.[7] This compares well to the value of 1097(24) cm^{-1} for the vibronic

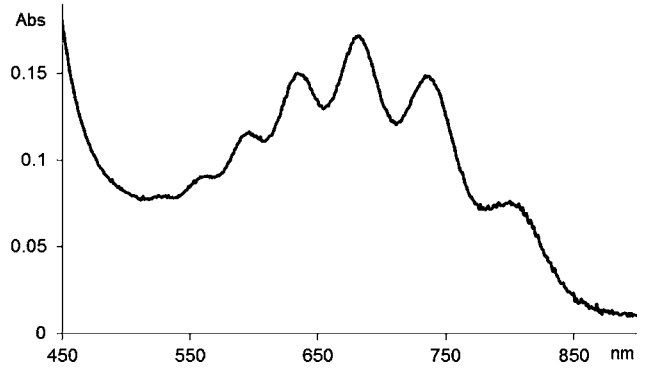

Figure 11. UV−vis spectrum of **12** in fluorobenzene at room temperature.

fine structure seen in the UV−vis spectrum of **11** [λ_{max} = 708 nm (ε = 5.0 $M^{-1}cm^{-1}$)].

Additionally, the radical **12** represents the first example for this class of compounds to be characterized by solid-state NMR spectroscopy. Since state-of-the-art liquid-state NMR experiments suffer from the presence of strongly pronounced paramagnetic relaxation enhancement effects between the free electron and the nuclei[31] leading in a lot of cases to undetectable, extremely broad resonances, this effect is often reduced in the solid-state, owing to the absence of molecular reorientation dynamics. Figure 12 shows the ^{1}H MAS NMR

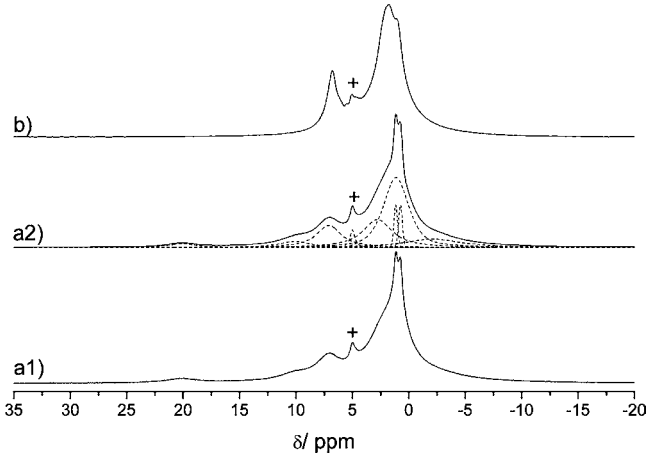

Figure 12. ^{1}H Hahn echo MAS NMR spectra of (a1) **12** and (b) **13** acquired at 11.74 T with a rotation frequency of 28.0 kHz. (a2) Line shape simulation for the spectrum of **12** is additionally shown. + marks an impurity.

spectra of **12** and **13.** The electron-spin-carrying molecule **12** shows strongly high-frequency shifted resonances at chemical shift values of about 20 and 10 ppm which have their origin most probably in pseudoscalar hyperfine interactions. Line shape simulation and integration reveals that three resonances of the norbornyl-backbone are shifted to higher frequencies. With the help of DFT calculations of Mulliken spin density populations (see the Supporting Information) we assign the resonances at around 10 ppm to H2 and H3 (attached to C2 and C3, respectively), while a resonance at about 20 ppm most probably results from the hydrogen atom attached to C5 (H5B). The crystal structure of **12** suggests that this H atom has a rather close intermolecular contact with the unpaired electron density situated at the terminal O atom of the nitroxide moiety and DFT calculations of the Mulliken spin density populations for a dimer of **12** (thereby taking into account also intermolecular interactions) yield also significant spin populations for this particular proton species (see the Supporting Information).

It was also possible to record ^{11}B and ^{31}P MAS NMR spectra of the solid material containing **12** (see the Supporting Information). The spectral parameters obtained from these spectra closely resemble those of **13**, however, and are also inconsistent with the sizable ^{11}B and ^{31}P magnetic hyperfine coupling constants extracted from the liquid state EPR spectra. Furthermore, an absolute quantification experiment indicated that the ^{31}P nuclei detected correspond only to 2−3% of the total number of spins present in these samples. Therefore, we conclude that the spectra observed here do not belong to

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molecules of **12** but rather to molecules of **13** forming a solid solution with the radical species.

Additionally demonstrating the radical character of **12** in the solid state, the magnetic susceptibility was measured (for more details see the Supporting Information). As typical for radicals the compound exhibits Curie−Weiss behavior and the effective magnet moment was determined to 1.60(1) μ_B (the slight deviation from the theoretically expected spin-only value of 1.73 for one unpaired electron is attributed to a small amount of diamagnetic impurities).

Many persistent aminoxyl radicals undergo hydrogen atom abstraction (HAA) reactions,[32] and so does our FLP-NO nitroxide radical **12**. Exposure of a benzene solution of the paramagnetic compound **12** to 1,4-cyclohexadiene at r.t. resulted in a rapid loss of the green color. The diamagnetic compound **13** was obtained as a colorless crystalline solid in 96% yield. Compound **13** shows a ^{31}P NMR resonance at δ = 40.8 and a ^{11}B NMR signal at δ = −6.7. The [N]OH ^{1}H NMR signal is found at δ = 4.66. The chiral compound **13** shows the typical set of six separate CH_3 ^{1}H NMR signals and the separate set of four separate mesityl CH resonances of the pair of diastereotopic mesityl substituents at phosphorus in addition to the typical ^{1}H NMR signals of the norbornane derived residue. The ^{19}F NMR spectrum of the FLP-NOH compound **13** shows the signals of a pair of diastereotopic C_6F_5 groups at boron. At 299 K the rotation around the B−C vectors are "frozen" on the NMR time scale. This leads to the observation of a total of four *o*-C_6F_5 ^{19}F NMR signals. Three of these are in the usual chemical shift range (ca. δ = −130 to δ = −133) whereas one *o*-C_6F_5 signal is shifted markedly to a more negative δ-value (δ = −144) (see Figure 13). We assume that this indicates the presence of a [N]O−H···F−C(aryl) interaction.[33] Consequently, we monitor J_{HF} coupling in the ^{1}H NMR spectrum of **13**.

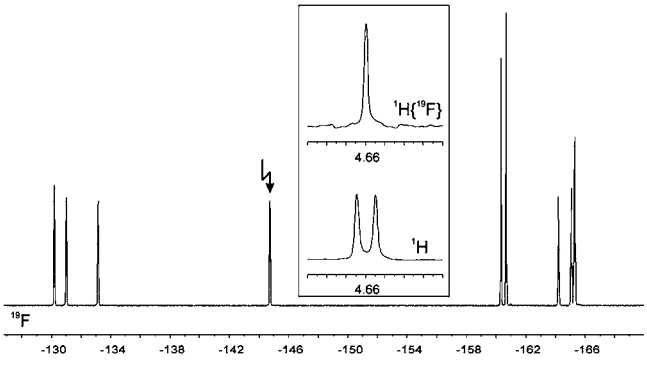


Figure 13. ^{19}F NMR (564 MHz, 253K, CD_2Cl_2) spectrum of compound **13** with ^{1}H NMR (600 MHz, 253K, CD_2Cl_2) and ^{1}H{^{19}F} NMR (selectively decoupled ^{19}F at δ = −144.8) spectra of the [N]O^{1}H resonance featuring a [N]OH···F−C(aryl) interaction.

Compound **13** was characterized by X-ray diffraction (see Figure 14 and Tables 2 and 3). The structure is composed of the five-membered heterocyclic ring that is 2-endo, 3-exo annulated with the supporting norbornane framework. The system now contains an [N]O−H moiety. Its formation has resulted in a marked elongation of the N1−O1 bond length from 1.15 Å in NO itself,[34] and 1.291(3) Å for the FLP-NO radical **12** to 1.430(3) Å in **13** which is a typical value of a FLP-NOH compound. The N1−B1 bond in **13** (1.587(4) Å) has become slightly shorter than in the radical. The P1−N1 bond

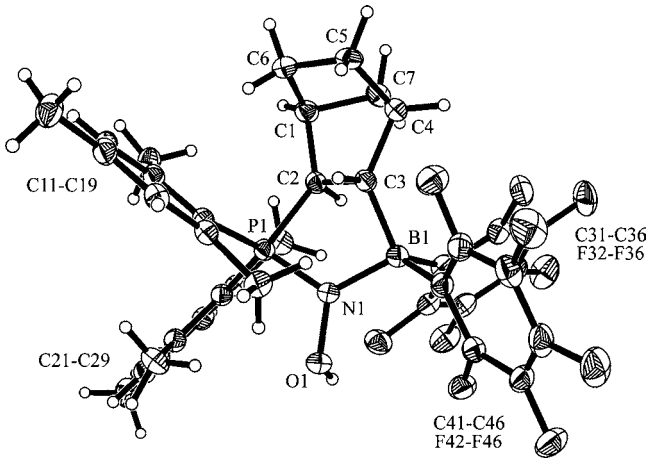
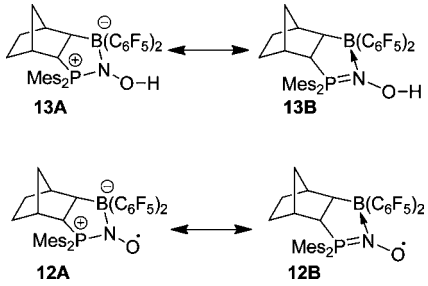


Figure 14. Molecular structure of the compound **13** (thermal ellipsoids are shown with 30% probability).

length in **13** is found at 1.646(2) Å. This is by ca. 0.1 Å shorter than the corresponding P−N linkage in the FLP-NO radical **12**. This probably indicates some participation of a mesomeric phosphinimine type structure [35] (**13B**, see Scheme 6). In contrast the FLP-NO radical seems to be best described by a σ-structure (**12A**) featuring single bonds between the heteroatoms inside the ring.

Scheme 6



Interestingly we find the [N]O−H group in the FLP-NOH compound **13** oriented toward the C32−F32 vector of a C_6F_5 group at boron (O1−H01···F32: 2.13 Å). This may serve as a further indication for the occurrence of a weak O−H···F−C contact in **13** (see above).

We also carried out two competition experiments. We treated a mixture of the parent vicinal P/B FLP **9** and our new FLP **4** with NO (ca. 0.5 molar equiv.). Subsequent treatment with 1,4-hexadiene converted the resulting FLP-NO radicals to their diamagnetic products. In this experiment the FLP **4** reacted ca. 3.6 times faster than **9**. However, the relative reactivity seems to be strongly reagent dependent. In a similar competition experiment of the **9**/**4** mixture with benzaldehyde it was the FLP **9** that reacted preferentially by a factor of 2.3 (for details see the Supporting Information).

Reaction with Ethylene. The FLP **4** appears quite robust in all these reactions. However, we eventually found some evidence that its formation by the hydroboration reaction might be reversible under some suitable conditions. This was found when we treated **4** with ethylene. For this purpose we prepared the FLP **4** in situ by treatment of dimesityl-2-norbornenylphosphane (**3**) with $HB(C_6F_5)_2$ in *n*-pentane for 30 min at room temperature. The resulting yellow solution of the FLP **4**

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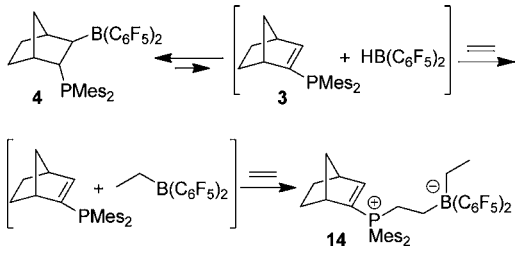
was then without any workup subjected to an ethylene atmosphere (3 bar) at r.t. The reaction between **4** and $CH_2{=}CH_2$ was apparently slow, it required ca. 2 d for the typical yellow color to disappear. During this time, colorless crystals of a product (**14**) had formed that were isolated in 68% yield (see Scheme 7).

Scheme 7



The X-ray crystal structure analysis (see Figure 15) revealed that two equivalents of ethylene had been taken up. The

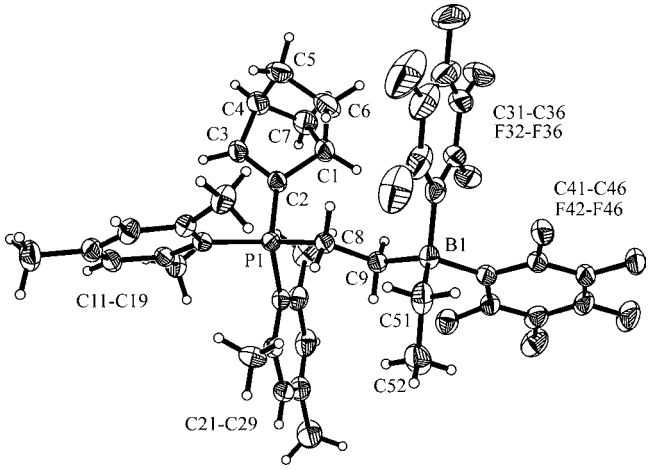


Figure 15. Projection of the molecular structure of compound **14** (thermal ellipsoids are shown with 30% probability).

compound shows a norbornene framework with a phosphorus substituent at C2 (C2–C3 1.340(4) Å, C2–P1 1.782(3) Å). The boron atom has become removed from C3. It now has an ethyl substituent attached to it (B1–C51: 1.637(5) Å) and it is connected with the $-PMes_2$ substituent at the norbornene framework by an ethylene bridge.

Apparently, the P/B addition reaction of the FLP **4** to ethylene is sufficiently slow to allow for the observation of an alternative competing pathway. The formation of the product **14** may be rationalized by the following hypothetical reaction course: slow retro-hydroboration of **4** might generate a small quantity of **3** and $HB(C_6F_5)_2$ in an endothermic equilibrium situation from which the borane was then rapidly trapped by its hydroboration of ethylene. The resulting ethyl-$B(C_6F_5)_2$ product then can be considered forming a new intermolecular frustrated Lewis pair with **3**,[36] which then eventually traps a further equivalent of ethylene in a typical FLP olefin addition reaction to form **14**. This hypothetical reaction pathway would explain the formation of the observed product straightforwardly but it needs further experimental evidence to be confirmed.

CONCLUSIONS

It is likely that many intermolecular frustrated Lewis pairs feature weak bonding interactions between the Lewis acid and Lewis base components that enable them to react with added small molecules.[10,11,17,37] Those LA/LB interactions seem to effectively eliminate the "termolecularity trap" of such three-component-reactions. A variety of intramolecular FLPs were also shown to exhibit interactions between their Lewis acid and Lewis base components. For several examples these interactions were quantified either by experimental work (e.g., liquid and solid-state NMR) or by quantum chemical calculations.[12,16−18,20] There were only a few examples of geminal or vicinal FLPs known where any direct LA/LB interaction was absent mainly in cases of very weak Lewis base components, having, for example, strongly electron withdrawing C_6F_5 substituents at phosphorus.[13−15] For vicinal FLPs having "normal" substituents at the Lewis base component and using the ubiquitous $-B(C_6F_5)_2$ Lewis acid site, to the best of our knowledge, most published examples feature some degree of LA/LB interaction. This posed the question of whether such weak LA/LB interaction might actually be necessary in order to observe typical FLP reactions and reaction modes toward small molecule binding or activation.

The properties and the observed reactions of FLP **4** described in this study indicate that such LA/LB interaction seems not to be necessary. There is good indication from the spectroscopic features, including the solid state NMR experiments and structural properties that **4** is a rare example of a noninteracting intramolecular frustrated Lewis pair. Nevertheless, it effects rapid heterolytic cleavage of dihydrogen and it adds rapidly to CO_2, to benzaldehyde, to SO_2 and even to NO. This encompasses almost the full range of known small molecule reactions of FLPs. This behavior indicates that intramolecular frustrated Lewis pairs probably activate themselves (at least in many cases) by cleaving their moderately strong or weak interactions. The open forms, available from this preceding equilibrium must probably be considered the active species in many of such FLP reactions. Future design efforts of new FLPs may take this effect into account in order to generate highly active new main group systems of this type for advanced small molecule activation.

EXPERIMENTAL SECTION

General Procedures. All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glovebox) under an atmosphere of argon. Solvents were dried with the procedure according to Grubbs[38] or were distilled from appropriate drying agents and stored under an argon atmosphere. NMR spectra were recorded on a *Bruker* AV 300 (^{1}H 300 MHz, ^{13}C 76 MHz, ^{31}P 122 MHz, ^{11}B 96 MHz, ^{19}F 282 MHz), a *Varian* Inova 500 (^{1}H 500 MHz, ^{13}C 126 MHz, ^{19}F 470 MHz, ^{11}B 160 MHz, ^{31}P 202 MHz) and on a *Varian* UnityPlus 600 (^{1}H 600 MHz, ^{13}C 151 MHz, ^{19}F 564 MHz, ^{11}B 192 MHz, ^{31}P 243 MHz). ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\bullet}Et_2O$ (external reference), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (external reference). NMR assignments were supported by additional 2D NMR experiments. IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). HRMS was recorded on GTC Waters Micromass (Manchester, UK). X-Ray crystal structure analyses. Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT;[39] data reduction Denzo-SMN;[40] absorption correction, Denzo;[41] structure solution SHELXS-97;[42] structure refinement

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SHELXL-97[43] and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Synthesis of the Dimesitylnorbornenylphosphane (3). ^{t}BuOK (2.02 g, 18.00 mmol) was weighed in a well dried Schlenk flask, dissolved in THF (20.0 mL) and cooled to −78 °C. A precooled solution (−78 °C) of bicyclo[2.2.1]hept-2-ene (5.15 g, 54.69 mmol) in THF (10.0 mL) was transferred to the precooled solution of ^{t}BuOK via a syringe. *n*-BuLi (1.6 M, 11.2 mL, 17.92 mmol) was added slowly to the above reaction mixture at −78 °C. The reaction mixture was stirred for 30 min at −78 °C then warmed up to −60 °C and the temperature was maintained between −60 °C and −50 °C for 90 min. The reaction mixture was cooled again to −78 °C and a precooled (−60 °C) solution of Mes_2PCl (6.53 g, 21.42 mmol) in THF (10 mL) was added to it. The reaction mixture was allowed to warm to r.t. and the solvent was evaporated under vacuum to get a brown residue. The residue was dissolved in *n*-pentane (100 mL) and filtered over Celite. The filtrate was concentrated under vacuum to give a brown oily residue. The residue was dissolved in a minimum amount of *n*-pentane, loaded onto an alumina column (basic, activity III) and eluted with *n*-pentane which gave the compound **3** as colorless oil in impure form. Further chromatography on a silica gel column (CH_2Cl_2/*n*-pentane, 3:7) gave the compound **3** in pure form (R_F = 0.31, 1.011 g, 13% yield). ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 6.84 (s, 2H, *m*-Mes^A), 6.82 (s, 2H, *m*-Mes^B), 5.45 (m, 1H, H-3), 3.13 (br s, 1H, H-1), 2.82 (br s, 1H, H-4), 2.35 (s, 6H, *o*-CH_3^{MesB}), 2.26 (s, 6H, *p*-$CH_3^{MesA,B}$), 2.22 (s, 6H, *o*-CH_3^{MesA}), 1.73/0.97 (each m, each 1H, H-5), 1.71/1.22 (each m, each 1H, H-6), 1.57/1.31 (each br m, each 1H, H-7). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 144.0 (d, $^1J_{PC}$ = 12.6 Hz, C-2), 143.8 (d, $^2J_{PC}$ = 14.7 Hz, *o*-Mes^A), 141.8 (d, $^2J_{PC}$ = 15.2 Hz, *o*-Mes^B), 139.5 (d, $^2J_{PC}$ = 3.1 Hz, C-3), 138.8, 137.4 (*p*-$CH_3^{MesA,B}$), 132.1 (d, $^1J_{PC}$ = 20.0 Hz, *i*-Mes^B), 130.5 (d, $^1J_{PC}$ = 8.2 Hz, *i*-Mes^A), 130.1 (d, $^3J_{PC}$ = 2.7 Hz, *m*-Mes^B), 129.8 (d, $^3J_{PC}$ = 4.7 Hz, *m*-Mes^A), 48.4 (d, $^2J_{PC}$ = 30.8 Hz, C-1), 45.9 (d, $^3J_{PC}$ = 2.0 Hz, C-7), 43.6 (d, $^3J_{PC}$ = 2.4 Hz, C-4), 27.8 (d, $^4J_{PC}$ = 2.0 Hz, C-5), 25.6 (C-6), 22.8 (d, $^3J_{PC}$ = 13.5 Hz, *o*-CH_3^{MesB}), 22.3 (d, $^3J_{PC}$ = 16.6 Hz, *o*-CH_3^{MesA}), 21.1 (*p*-CH_3^{MesA}), 20.9 (*p*-CH_3^{MesB}). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ = −37.7 ($\nu_{1/2} \approx$ 2 Hz). HRMS: calcd for $C_{25}H_{32}P$ $[M + H]^+$: 363.22361. Found: 363.22233. IR (KBr): ν/cm^{-1} = 3023 (w), 2961 (s), 2862 (s), 2360 (w), 1602 (w), 1549 (w), 1447 (s).

Synthesis of Compound 4. Dimesitylnorbornenylphosphane (25 mg, 0.069 mmol) and $HB(C_6F_5)_2$ (24 mg, 0.069 mmol) were weighed together and dissolved in CD_2Cl_2 (0.7 mL) to give a yellow solution. NMR data was collected after 30 min which showed the formation of compound **4**, admixed with ca. 5% (detected in ^{1}H NMR spectrum) of a compound not identified yet. The solvent was removed under vacuum to give a yellow solid (47 mg, 96% yield). Crystals of compound **4** suitable for X-ray crystal structure analysis were obtained by slow evaporation of its solution in *n*-pentane at −35 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 6.75 (d, $^4J_{PH}$ = 2.6 Hz, 2H, *m*-Mes^A), 6.52 (d, $^4J_{PH}$ = 2.3 Hz, 2H, *m*-Mes^B), 4.06 (br m, 1H, PCH), 2.76/1.50 (each m, each 1H, H-6), 2.72 (br m, 1H, H-1), 2.37 (br m, 1H, H-4), 2.34 (br s, 12H, *o*-$CH_3^{MesA,B}$), 2.19 (s, 3H *p*-CH_3^{MesA}), 2.03 (s, 3H, *p*-CH_3^{MesB}), 2.01 (dd, $^3J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, BCH), 1.69/1.52 (each m, each 1H, H-5), 1.42/1.26 (each m, each 1H, H-7), $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 144.9 (d, $^3J_{PC}$ = 15.6 Hz, *o*-Mes^B), n.o. (*o*-Mes^A), 139.4 (d, $^4J_{PC}$ = 1.5 Hz, *p*-Mes^B), 137.2 (d, $^4J_{PC}$ = 1.0 Hz, *p*-Mes^A), 133.1 (d, $^1J_{PC}$ = 33.4 Hz, *i*-Mes^A), 131.9 (d, $^1J_{PC}$ = 20.9 Hz, *i*-Mes^B), 130.6 (br, *m*-Mes^A), 129.4 (d, $^3J_{PC}$ = 4.5 Hz, *m*-Mes^B), 49.3 (br d, $^2J_{PC}$ = 17.5 Hz, BCH), 42.1 (d, $^2J_{PC}$ = 21.6 Hz, C-1), 41.3 (d, $^3J_{PC}$ = 2.6 Hz, C-4), 40.7 (d, $^3J_{PC}$ = 5.0 Hz, C-7), 39.5 (d, $^1J_{PC}$ = 18.7 Hz, PCH), 32.9 (C-5), 24.4 (d, $^3J_{PC}$ = 31.8 Hz, C-6), 23.06 (d, $^3J_{PC}$ = 15.9), 23.01 (d, $^3J_{PC}$ = 13.5) (*o*-$CH_3^{MesA,B}$), 20.7 (*p*-CH_3^{MesA}), 20.6 (*p*-CH_3^{MesB}). [C_6F_5 not listed.] $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 99 K): δ = 75.0 ($\nu_{1/2} \approx$ 1500 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ = −21.8 ($\nu_{1/2} \approx$ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −130.3 (m, 2F, *o*-C_6F_5), −151.2 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), −162.1 (m, 4F, *m*-C_6F_5). HRMS: calcd for $C_{37}H_{33}PBF_{10}$ $[M + H]^+$: 709.22478. Found: 709.22337. IR (KBr): ν/cm^{-1} = 2936 (s), 2863 (s), 2362 (w), 1647 (s), 1604 (w), 1521 (s), 1474 (vs). X-ray crystal structure analysis of compound **4**: formula $C_{37}H_{32}BF_{10}P$, M = 708.41, colorless crystal, 0.40 × 0.25 × 0.13 mm, a = 20.4305(4), b = 14.7348(5), c = 11.0389(3) Å, β = 90.088(2)°, V = 3323.14(16) Å^3, ρ_{calc} = 1.416 g cm^{-3}, μ = 1.474 mm^{-1}, empirical absorption correction (0.590 ≤ T ≤ 0.831), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 16319 reflections collected (±h, ± k, ± l), [(sinθ)/λ] = 0.60 Å^{-1}, 5559 independent (R_{int} = 0.032) and 5162 observed reflections [$I > 2\sigma(I)$], 448 refined parameters, R = 0.045, wR^2 = 0.119, max. (min.) residual electron density 0.25 (−0.24) e Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Synthesis of Compound 5-H. $HB(C_6F_5)_2$ (80 mg, 0.231 mmol) and the norbornenyl-phosphane **3** (82 mg, 0.226 mmol) were weighed together, dissolved in *n*-pentane (10 mL) and stirred for 30 min. at r.t. to give a yellow solution of compound **4**. The solution was degassed by freeze−pump−thaw cycles (×2) and cooled to −78 °C. H_2 gas was pressed (2.5 bar) over the solution and the solution was allowed to warm to r.t. The solution was stirred at r.t. for further 10 min. Formation of a colorless precipitate was observed. The solvent was decanted off, the residue washed with *n*-pentane (3 mL) and dried in vacuum to give a slightly yellow solid. The compound was crystallized from CH_2Cl_2 to give compound **5-H** as thin colorless needles (108 mg, 67% yield). The obtained crystals were suitable for X-ray crystal structure analysis. ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.22 (dd, $^1J_{PH}$ = 466.9 Hz, $^3J_{PH}$ = 9.2 Hz, 1H, HP), 7.04 (br, 2H), 6.96 (br, 1H), 6.81 (br, 1H) (*m*-Mes), 3.20 (br, 1H, PCH), 2.75, 2.26 (each br, each 1H, H-1,4), 2.10/1.28, 1.74/1.42, 1.42/1.23 (each m, each 1H, CH_2), 2.58 (very br), 2.50 (br), 2.41 (very br), 2.26 (br) (Σ18H, *o*-CH_3^{Mes}), 2.32, 2.29 (each s, each 3H, *p*-CH_3^{Mes}), 1.86 (br d, $^3J_{PH}$ = 27.6 Hz, 1H, BCH). $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2): δ = 145.6, 145.4 (*p*-Mes), n.o. (*o*-Mes), 132.4, 132.0, 131.8, 131.4 (each br, *m*-Mes), 114.8 (d, $^1J_{PC}$ = 69.8 Hz), 113.7 (d, $^1J_{PC}$ = 79.2 Hz) (*i*-Mes), 43.6 (d, J_{PC} = 5.9 Hz), 41.6 (d, $^2J_{PC}$ = 2.2 Hz) (C-1,4), 43.5 (br, BCH), 42.9 (d, $^1J_{PC}$ = 35.0 Hz, PCH), 38.9 (d, J_{PC} = 15.0 Hz), 32.7, 25.4 (d, J_{PC} = 10.5 Hz) (CH_2), 23.0, 22.5 (each br, *o*-CH_3^{Mes}), 21.3, 21.1 (*p*-CH_3^{Mes}), [C_6F_5 not listed]. ^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = −19.6 (d, $^1J_{BH} \sim$ 90 Hz). ^{31}P NMR (243 MHz, CD_2Cl_2, 299 K): δ = −7.4 (br dd, $^1J_{PH}$ = 467.5 Hz, $^3J_{HH}$ = 28.8 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −131.8 (br m, 2F, *o*-$C_6F_5^A$), −133.0 (br, 2F, *o*-$C_6F_5^B$), −163.2 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-$C_6F_5^A$), −164.6 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-$C_6F_5^B$), −165.4 (m, 2F, *m*-$C_6F_5^A$), −167.2 (m, 2F, *m*-$C_6F_5^B$). HRMS: calcd for $C_{37}H_{33}PBF_{10}$ $[M - H]^+$: 709.22478. Found: 709.22413. IR (KBr): ν/cm^{-1} = 2966 (s), 2929 (s), 2967 (m), 2370(s, PH/BH), 1636 (w), 1604 (m), 1509 (s), 1457 (vs). Elemental analysis: calc. for $C_{37}H_{34}PBF_{10}$: C, 62.55; H, 4.82. Found: C, 61.76; H, 4.75. X-ray crystal structure analysis of compound **5**: formula $C_{37}H_{34}BF_{10}P$, M = 710.42, colorless crystal, 0.25 × 0.05 × 0.03 mm, a = 17.5236(5), b = 18.1897(6), c = 20.2976(3) Å, V = 6469.8(3) Å^3, ρ_{calc} = 1.459 g cm^{-3}, μ = 1.515 mm^{-1}, empirical absorption correction (0.703 ≤ T ≤ 0.956), Z = 8, orthorhombic, space group *P*bca (No. 61), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 33268 reflections collected (±h, ± k, ± l), [(sinθ)/λ] = 0.60 Å^{-1}, 5632 independent (R_{int} = 0.056) and 5632 observed reflections [$I > 2\sigma(I)$], 456 refined parameters, R = 0.045, wR^2 = 0.114, max. (min.) residual electron density 0.23 (−0.26) e Å^{-3}, hydrogen atoms at P1 and B1 were refined freely, other hydrogen atoms calculated and refined as riding atoms.

Synthesis of Compound 5-D. A solution of the compound **4** (243 mg, 0.343 mmol) in *n*-pentane was cooled (−60 °C) and degassed. D_2 gas (1.2 bar) was pressed over the solution for 3 min and the cooling bath was removed. After stirring the reaction mixture for 30 min at r.t. the solvent was decanted off and the residual yellowish precipitate was washed with *n*-pentane (1 × 4 mL). Crystallization from CH_2Cl_2 gave the compound **5-D** as a colorless crystalline solid (132 mg, 54% yield). ^{2}H NMR (92 MHz, CD_2Cl_2, 299 K): δ = 7.24 (d, $^1J_{PD}$ = 71.7 Hz, 1D, DP), 2.55 (br, 1D, DB). ^{11}B NMR (160 MHz, CD_2Cl_2, 299 K): δ = −19.8 ($\nu_{1/2} \approx$ 80 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = −8.0 (1:1:1 t, $^1J_{PD}$ = 71.7 Hz).

Synthesis of Compound 6. $HB(C_6F_5)_2$ (96 mg, 0.277 mmol) and dimesitylnorbornenylphosphane (100 mg, 0.276 mmol) were

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weighed together, dissolved in *n*-pentane (15 mL) and stirred for 30 min. at r.t. to give a yellow solution. Then a solution of benzaldehyde (40.0 mg, 0.377 mmol) in *n*-pentane (2.0 mL) was added to the solution of the FLP **4** and instantaneous formation of a colorless precipitate was observed. The reaction mixture was stirred at r.t. for 15 min. The volatiles were removed under vacuum. The obtained residue was washed with *n*-pentane (3 mL) and dried under vacuum overnight to give compound **6** as a colorless solid (166 mg, 85% yield). There is about 5% of an unidentified compound present which could not be separated even by crystallization (^{31}P NMR: δ = 30.7). Crystals of compound **6** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane to a solution of compound **6** in CH_2Cl_2 at −35 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.05 (br m, 1H, *m*-Mes^A), 7.04 (m, 1H, *p*-Ph), 7.00 (m, 2H, *o*-Ph), 6.99 (s, 1H, *m*-Mes^B), 6.92 (m, 2H, *m*-Ph), 6.84 (br s, 1H, *m*′-Mes^A), 6.46 (d, $^2J_{PH}$ = 13.5 Hz, CHO), 6.20 (br s, 1H, *m*′-Mes^B), 3.63 (m, 1H, PCH), 2.90 (s, 3H, *o*-CH_3^{MesB}), 2.88 (s, 3H, *o*-CH_3^{MesA}), 2.80 (br s, 1H, H-1), 2.43 (br s, 1H, H-4), 2.30 (s, 3H, *p*-CH_3^{MesA}), 2.18 (s, 3H, *p*-CH_3^{MesB}), 1.91 (s, 3H, *o*′-CH_3^{MesA}), 1.64 (dd, $^3J_{PH}$ = 23.9 Hz, $^3J_{HH}$ = 11.9 Hz, BCH), 1.39/1.01 (each m, each 1H, H-5), 1.13/0.78 (each m, each 1H, H-7), 0.95 (s, 3H, *o*′-CH_3^{MesB}), 1.09/0.75 (each m, each 1H, H-6). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 144.6 (d, $^2J_{PC}$ = 4.4 Hz, *o*′-Mes^A), 143.8 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Mes^A), 143.0 (d, $^4J_{PC}$ = 3.2 Hz, *p*-Mes^B), 142.5 (d, $^2J_{PC}$ = 7.5 Hz, *o*-Mes^B), 142.0 (d, $^2J_{PC}$ = 11.7 Hz, *o*-Mes^A), 141.9 (d, $^2J_{PC}$ = 8.6 Hz, *o*′-Mes^B), 138.5 (d, $^3J_{PC}$ = 3.3 Hz, *i*-Ph), 132.7 (d, $^3J_{PC}$ = 11.8 Hz, *m*-Mes^A), 132.4 (d, $^3J_{PC}$ = 10.7 Hz, *m*-Mes^B), 132.0 (d, $^3J_{PC}$ = 8.4 Hz, *m*′-Mes^A), 131.4 (d, $^3J_{PC}$ = 10.1 Hz, *m*′-Mes^B), 128.4 (br d, $^3J_{PC}$ = 5.9 Hz, *o*-Ph), 128.3 (d, $^5J_{PC}$ = 3.3 Hz, *p*-Ph), 127.2 (d, $^4J_{PC}$ = 1.8 Hz, *m*-Ph), 121.6 (d, $^1J_{PC}$ = 45.1 Hz, *i*-Mes^A), 120.9 (d, $^1J_{PC}$ = 53.4 Hz, *i*-Mes^B), 87.6 (d, $^1J_{PC}$ = 22.6 Hz, CHO), 42.5 (d, $^2J_{PC}$ = 6.2 Hz, C-1), 41.6 (d, $^3J_{PC}$ = 16.8 Hz, C-7), 40.3 (d, $^1J_{PC}$ = 36.6 Hz, PCH), 38.8 (br d, $^3J_{PC}$ = 7.4 Hz, C-4), 35.1 (br, BCH), 34.1 (C-5), 27.0 (*o*-CH_3^{MesA}), 25.1 (d, $^3J_{PC}$ = 5.6 Hz, *o*′-CH_3^{MesB}), 24.2 (d, $^3J_{PC}$ = 4.9 Hz, *o*′-CH_3^{MesA}), 24.0 (br, *o*-CH_3^{MesB}), 22.4 (C-6), 21.1 (d, $^5J_{PC}$ = 1.4 Hz, *p*-CH_3^{MesA}), 20.8 (d, $^5J_{PC}$ = 1.3 Hz, *p*-CH_3^{MesB}). [C_6F_5 not listed]. ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = 0.2 ($\nu_{1/2} \approx$ 150 Hz). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = 38.9 ($\nu_{1/2} \approx$ 5 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 213 K): δ = −130.2, −133.5, −134.2, −134.8 (each m, 1F each, *o*-C_6F_5), −160.5 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), −160.8 (t, $^3J_{FF}$ = 21.6 Hz, 1F, *p*-C_6F_5), −164.3 (m, 1F, (m, 1F, *m*-C_6F_5), −165.1, (m, 2F, *m*-C_6F_5), −165.8, (m, 1F, *m*-C_6F_5). IR (KBr): ν/cm^{-1} = 2953 (vs), 2875 (s), 2361 (w), 2339 (w), 1640 (m), 1606 (m), 1512 (s), 1456 (vs). Elemental analysis: calc. for $C_{44}H_{38}PBF_{10}O$: C, 64.88; H, 4.70. Found: C, 63.20; H, 4.50. X-ray crystal structure analysis of compound **6**: formula $C_{44}H_{38}BF_{10}OP$, M = 814.52, colorless crystal, 0.37 × 0.20 × 0.10 mm, a = 11.3261(2), b = 11.4019(2), c = 18.0739(4) Å, α = 80.106(4), β = 86.398(7), γ = 67.178(8)°, V = 2119.31(7) Å^3, ρ_{calc} = 1.276 g cm^{-3}, μ = 0.141 mm^{-1}, empirical absorption correction ($0.949 \le T \le 0.986$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 16980 reflections collected ($\pm h, \pm k, \pm l$), [(sinθ)/λ] = 0.59 Å^{-1}, 7239 independent (R_{int} = 0.037) and 6197 observed reflections [$I > 2\sigma(I)$], 520 refined parameters, R = 0.067, wR^2 = 0.199, max. (min.) residual electron density 0.35 (−0.30) e Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Synthesis of Compound 7. $HB(C_6F_5)_2$ (97 mg, 0.280 mmol) and the dimesitylnorbornenylphosphane (100 mg, 0.276 mmol) were weighed together, dissolved in *n*-pentane (70 mL) and stirred for 2 h. at r.t. to give a yellow solution. The solution was cooled to −78 °C and degassed by applying vacuum. CO_2 gas was pressed (3.0 bar) onto the solution. The cooling bath was removed and the solution was allowed to warm to r.t. Formation of a precipitate was observed. The reaction mixture was cooled to −78 °C and the solvent was removed via a filter canula. The residue was washed with precooled *n*-pentane (1 × 3 mL) and dried under vacuum to get compound **7** as a colorless solid (162 mg, 78% yield). Crystals of the compound **7** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane to a solution of compound **7** in CH_2Cl_2 at −35 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): δ = 7.03 (d, $^4J_{PH}$ = 3.9 Hz, 2H, *m*-Mes^{A,B}), 6.94 (br, 1H, *m*′-Mes^A), 6.91 (d, $^4J_{PH}$ = 3.8 Hz, 1H, *m*′-Mes^B), 3.08 (br d, $^3J_{PH}$ = 12.0 Hz, 1H, PCH), 2.83 (br s, 1H, H-1), 2.63 (s, 3H, *o*-CH_3^{MesA}), 2.50 (br, 1H, H-4), 2.38 (s, 3H, *o*-CH_3^{MesB}), 2.30 (s, 3H, *p*-CH_3^{MesB}), 2.28 (s, 3H, *p*-CH_3^{MesA}), 1.83 (s, 3H, *o*′-CH_3^{MesB}), 1.74 (s, 3H, *o*′-CH_3^{MesA}), 1.61 (br dd, $^3J_{PH}$ = 21.6 Hz, $^3J_{HH}$ = 12.0 Hz, 1H, BCH), 1.31/0.92 (each br m, each 1H, H-5), 1.23/1.01 (each br m, each 1H, H-6), 1.17/0.61 (each br m, each 1H, H-7). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 213 K): δ = 160.7 (d, $^1J_{PC}$ = 88.0 Hz, CO), 144.9 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Mes^B), 144.13 (d, $^2J_{PC}$ = 12.6 Hz, *o*′-Mes^A), 144.10 (d, $^2J_{PC}$ = 2.2 Hz, *p*-Mes^A), 143.1 (d, $^2J_{PC}$ = 9.8 Hz, *o*′-Mes^B), 142.9 (d, $^2J_{PC}$ = 8.5 Hz, *o*-Mes^B), 140.9 (d, $^2J_{PC}$ = 12.4 Hz, *o*-Mes^A), 132.5 (d, $^3J_{PC}$= 11.1 Hz, *m*′-Mes^A), 132.1 (d, $^3J_{PC}$ = 12.5 Hz, *m*-Mes^A), 131.9 (d, $^3J_{PC}$ = 10.6 Hz, *m*-Mes^B), 131.0 (d, $^3J_{PC}$ = 10.5 Hz, *m*′-Mes^B), 118.0 (d, $^1J_{PC}$ = 68.3 Hz, *i*-Mes^A), 114.3 (d, $^1J_{PC}$ = 69.1 Hz, *i*-Mes^B), 42.7 (d, $^1J_{PC}$ = 21.8 Hz, PCH), 42.6 (d, $^2J_{PC}$ = 7.3 Hz, C-1), 40.8 (d, $^3J_{PC}$ = 17.7 Hz, C-7), 38.2 (br, C-4), 33.7 (br, BCH), 33.3 (br, C-5), 24.1 (d, $^3J_{PC}$ = 3.5 Hz, *o*′-CH_3^{MesA}), 23.9 (d, $^3J_{PC}$ = 7.6 Hz, *o*′-CH_3^{MesB}), 23.3 (br, *o*-CH_3^{MesA}), 22.9 (d, $^3J_{PC}$ = 4.6 Hz, *o*-CH_3^{MesB}), 21.2 (br, C-6), 21.0 (*p*-CH_3^{MesB}), 20.7 (*p*-CH_3^{MesA}). [C_6F_5 not listed] ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 213 K): δ = 13.7 ($\nu_{1/2} \approx$ 4 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 213 K): δ = −129.6 (m, 1F, *o*-$C_6F_5^A$), −131.4 (m, 1F, *o*-$C_6F_5^B$), −136.2 (m, 1F, *o*′-$C_6F_5^B$), −137.8 (m, 1F, *o*′-$C_6F_5^A$), −158.8 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*-$C_6F_5^A$), −159.1 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*-$C_6F_5^B$), −163.1 (m, 1F, *m*-$C_6F_5^A$), −163.4 (m, 1F, *m*′-$C_6F_5^A$), −164.1 (m, 1F, *m*-$C_6F_5^B$), −164.8 (m, 1F, *m*′-$C_6F_5^B$). HRMS: calcd for $C_{38}H_{33}PBO_2F_{10}$ [M + H − CO_2]$^+$: 709.22478. Found: 709.22578. CO_2 seems to be released under the applied conditions. IR (KBr): ν/cm^{-1} = 2957(s), 2878 (m), 2360 (w), 2338 (m), 1704 (s, CO), 1642 (m), 1605 (m), 1513 (m), 1458 (vs). X-ray crystal structure analysis of **7**: formula $C_{38}H_{32}BF_{10}P$ * CH_2Cl_2, M = 837.34, colorless crystal, 0.15 × 0.10 × 0.05 mm, a = 10.4235(10), b = 17.0105(9), c = 21.3930(20) Å, V = 3793.2(5) Å^3, ρ_{calc} = 1.466 gcm^{-3}, μ = 2.691 mm^{-1}, empirical absorption correction ($0.688 \le T \le 0.877$), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 20986 reflections collected ($\pm h, \pm k, \pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 6556 independent (R_{int} = 0.040) and 5989 observed reflections [$I > 2\sigma(I)$], 515 refined parameters, R = 0.041, wR^2 = 0.097, max. (min.) residual electron density 0.16 (−0.22) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. Flack parameter was refined to 0.01(2).

Synthesis of Compound 8. $HB(C_6F_5)_2$ (43 mg, 0.123 mmol) and the dimesitylnorbornenylphosphane (40.0 mg, 0.121 mmol) were weighed together, dissolved in *n*-pentane (6.0 mL) and stirred for 30 min. at r.t. to give a yellow solution of the compound **4**. The solution was degassed by applying some vacuum and SO_2 gas was pressed (2.0 bar) over the solution which resulted in the formation of a colorless precipitate. The reaction mixture was stirred at r.t. for 5 min., the reaction flask was flushed with argon and the solvent was decanted off. The residue was washed with *n*-pentane (1 × 3 mL) and dried under vacuum to give **8a** and **8b** as a colorless solid (68 mg, 80% yield). The two diastereoisomers were obtained in a ratio of ca.5:2 (determined by NMR spectroscopy). *Major isomer* (ca. 65%): ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.16 (br s, 1H, *m*-Mes^A),7.09 (br d, $^4J_{PH}$ = 4.5 Hz, 1H, *m*-Mes^B), 6.94 (s, 2H, *m*′-Mes^{A,B}), 3.54 (br m, 1H, PCH), 2.88 (br, 1H, H-1), 2.74 (br d, $^3J_{PH}$ = 1.7 Hz, 3H, *o*-CH_3^{MesA}), 2.65 (s, 3H, *o*-CH_3^{MesB})^t, 2.42 (br, 1H, H-4), 2.35 (s, 3H, *p*-CH_3^{MesA})^t, 2.34 (s, 3H, *p*-CH_3^{MesB})^t, 2.06 (s, 3H, *o*′-CH_3^{MesB})^t, 1.82 (br dd, $^3J_{PH}$ = 24.4 Hz, $^3J_{HH}$ = 10.6 Hz, BCH), 1.69 (s, 3H, *o*′-CH_3^{MesA}), 1.40/1.02 (each br m, each 1H, H-5), 1.13/0.83 (each br m, each 1H, H-6), 1.13/0.69 (each br m, each 1H, H-7). [^{t} tentatively assigned]. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K) [selected resonances]: δ = 121.4 (d, $^1J_{PC}$ = 35.4 Hz, *i*-Mes^B), 116.5 (d, $^1J_{PC}$ = 44.5 Hz, *i*-Mes^A), 43.1 (d, J_{PC} = 12.6 Hz, C-1), 41.3 (d, $^1J_{PC}$ = 15.2 Hz, PCH), 40.6 (d, $^3J_{PC}$ = 15.6 Hz, C-7), 39.5 (br m, C-4), 35.6 (br, BCH), 33.3 (C-5), 22.7 (br, C-6). ^{31}P NMR (202 MHz, CD_2Cl_2, 299 K): δ = 59.5 (dm, $^3J_{PH}$ = 24.7 Hz. ^{19}F NMR (470 MHz, CD_2Cl_2, 213 K): δ = −130.4, −132.3, −134.9, −135.5 (each m, each 1F, *o*-C_6F_5), −158.6, −158.9 (each t, each $^3J_{FF}$ = 20.6 Hz, each 1F, *p*-C_6F_5), −163.6, −164.06, 164.11, −164.9 (each m, each 1F, *m*-C_6F_5). *Minor isomer* (ca. 35%): ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.14 (br s, 1H, *m*-Mes^A), 7.11 (br d, $^4J_{PH}$ = 4.0

Hz, 1H, *m*-Mes^{B}), 6.96 (br s, 1H, *m*′-Mes^{A}), 6.89 (br s, 1H, *m*′-Mes^{B}), 3.11 (br d, $^{1}J_{PH}$ = 10.5 Hz, 1H, PCH), 2.79 (br, 1H, H-1), 2.70 (s, 3H, *o*-CH_3^{MesA}), 2.67 (d, $^{3}J_{PH}$ = 1.9 Hz, 3H, *o*-CH_3^{MesB}), 2.66 (br, 1H, H-4), 2.35 (s, 3H, *p*-CH_3^{MesA})^{t}, 2.32 (s, 3H, *p*-CH_3^{MesB})^{t}, 2.06 (s, 3H, *o*′-CH_3^{MesB}), 1.97 (s, 3H, *o*′-CH_3^{MesA}), 1.90 (br ddm, $^{3}J_{PH}$ = 22.4, $^{3}J_{PH}$ = 11.0, 1H, BCH), 1.47/1.19 (each br m, each1H, H-5), 1.12/0.54 (each br m, each 1H, H-7), 1.12/0.80 (each br m, each 1H, H-6)^{t}. [^{t} tentatively assigned] $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 299 K) [selected resonances]: δ = 124.5 (d, $^{1}J_{PC}$ = 22.1 Hz, *i*-Mes^{B}), 121.7 (d, $^{1}J_{PC}$ = 50.2 Hz, *i*-Mes^{A}), 43.1 (d, J_{PC} = 12.6, C-1), 41.0 (d, $^{1}J_{PC}$ = 11.5 Hz, PCH), 40.1 (d, $^{3}J_{PC}$ = 15.1, C-7), 38.5 (br, C-4), 33.4 (C-5), 29.9 (br, BCH), 22.7 (C-6)^{t}. [^{t} tentatively assigned]. ^{31}P NMR (202 MHz, CD_2Cl_2, 299 K): δ = 53.6 (dm, $^{3}J_{PH}$ = 23.3 Hz). . ^{19}F NMR (470 MHz, CD_2Cl_2, 213K): δ = −129.9, −134.0, −135.5, −136.6 (each m, each 1F, *o*-C_6F_5), −159.1, −160.0 (each t, each $^{3}J_{FF}$ = 20.6 Hz, each 1F, *p*-C_6F_5), −163.8, −164.0, −165.0, −165.1 (each m, each 1F, *m*-C_6F_5). *Data from the mixture*: HRMS: calcd for $C_{37}H_{33}PBSO_2F_{10}$ [M + H − SO_2]$^{+}$: 709.22478. Found: 709.22578. SO_2 seems to be released under the applied conditions. IR (KBr): ν/cm^{-1} = 2957 (s), 2928 (s), 2880 (s), 2361 (m), 2341 (m), 1641 (m), 1606 (m), 1559 (w), 1515 (s), 1457 (vs). X-ray crystal structure analysis of compound **8**: formula $C_{37}H_{32}BF_{10}O_2PS$, M = 772.47, colorless crystal, 0.10 × 0.07 × 0.02 mm, a = 16.4556(7), b = 16.7148(6), c = 24.6103(8) Å, V = 6769.1(4) Å^3, ρ_{calc} = 1.516 g cm^{-3}, μ = 2.107 mm^{-1}, empirical absorption correction (0.817 ≤ T ≤ 0.959), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 36959 reflections collected (±h, ± k, ± l), [(sinθ)/λ] = 0.60 Å^{-1}, 5779 independent (R_{int} = 0.112) and 3593 observed reflections [$I > 2\sigma(I)$], 456 refined parameters, R = 0.057, wR^2 = 0.144, max. (min.) residual electron density 0.26 (−0.50) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Synthesis of Compound 12. $HB(C_6F_5)_2$ (345 mg, 1.00 mmol) and the norbornenylphosphane **3** (360.0 mg, 1.00 mmol) were weighed together, dissolved in *n*-pentane (70 mL) and stirred for 30 min. at r.t. to give a yellow solution. The solution was cooled to −78 °C and degassed by applying vacuum. NO gas was pressed (2.0 bar) onto the solution and quick formation of a precipitate was observed. The cooling bath was removed and the reaction mixture was stirred at r.t. for further 10 min. The reaction flask was flushed with argon and the solvent was removed under vacuum. The residue was washed with *n*-pentane (1 × 10 mL) and dried under vacuum to give compound **12** as a turquoise solid (643 mg, 87% yield). Crystals of compound **12** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane to a solution of compound **12** in CH_2Cl_2 at −35 °C. HRMS: calcd for $C_{37}H_{32}PBF_{10}NONa$ [M + Na]$^{+}$: 761.20535. Found: 761.20330. IR (KBr): ν/cm^{-1} = 2951 (s), 2883 (m), 1641 (w), 1606 (m), 1513 (s), 1463 (vs). Elemental analysis: calc. for $C_{37}H_{32}PBF_{10}NO$: C, 60.18; H, 4.37; N, 1.90. Found: C, 60.53; H, 4.70; N, 1.75. X-ray crystal structure analysis of compound **12**: formula $C_{37}H_{32}BF_{10}NOP$ * CH_2Cl_2, M = 823.34, pale green crystal, 0.35 × 0.25 × 0.10 mm, a = 10.5699(3), b = 17.6128(6), c = 10.9505(5) Å, β = 113.061(2)°, V = 1875.70(12) Å^3, ρ_{calc} = 1.458 g cm^{-3}, μ = 2.679 mm^{-1}, empirical absorption correction (0.452 ≤ T ≤ 0.774), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 10974 reflections collected (±h, ± k, ± l), [(sinθ)/λ] = 0.60 Å^{-1}, 5757 independent (R_{int} = 0.039) and 5666 observed reflections [$I > 2\sigma(I)$], 521 refined parameters, R = 0.039, wR^2 = 0.105, max. (min.) residual electron density 0.48 (−0.28) e Å^{-3}, hydrogen atoms were calculated and refined as riding atoms. Flack parameter was refined to 0.03(2).

Synthesis of Compound 13. The nitroxide adduct **12** (95 mg, 0.129 mmol) was dissolved in benzene (7.0 mL) to give a green solution. 1,4-Cyclohexadiene (0.1 mL, 1.057 mmol) was added to the solution and stirred at r.t for 5 min. to give a colorless solution. The volatiles were evaporated *in vacuo*, the obtained residue was washed with *n*-pentane (2 × 5 mL) and dried under vacuum to give compound **13** as colorless crystalline solid (91 mg, 96% yield). Crystals of compound **13** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane to a solution of compound **13** in CH_2Cl_2 at −35 °C. ^{1}H NMR (600 MHz, CD_2Cl_2, 233 K): δ = 7.05 (d, $^{4}J_{PH}$ = 4.2 Hz, 1H, *m*-Mes^{A}), 6.90 (br, 1H, *m*-Mes^{B}), 6.86 (br, 1H, *m*′-Mes^{A}), 6.74 (d, $^{4}J_{PH}$ = 4.8 Hz, 1H, *m*′-Mes^{B}), 4.66 (d, J_{FH} = 11.6 Hz, 1H, OH), 2.71 (br m, 1H, H-1), 2.61 (br m, 1H, H-4), 2.60 (m, 1H, PCH), 2.55 (s, 3H, *o*-CH_3^{MesA}), 2.41 (s, 3H, *o*-CH_3^{MesB}), 2.28 (s, 3H, *p*-CH_3^{MesA}), 2.24 (s, 3H, *p*-CH_3^{MesB}), 1.93 (s, 3H, *o*′-CH_3^{MesA}), 1.92 (s, 3H, *o*′-CH_3^{MesB}), 1.54 (m, 1H, BCH), 1.31/1.04 (each m, each 1H, H-5), 1.24/0.81 (each m, each 1H, H-7), 1.13/0.51 (each m, each 1H, H-6). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 233 K): δ = 144.5 (d, $^{2}J_{PC}$ = 8.3 Hz, *o*′-Mes^{A}), 144.2 (d, $^{2}J_{PC}$ = 5.9 Hz, *o*-Mes^{B}), 143.3 (d, $^{4}J_{PC}$ = 2.6 Hz, *p*-Mes^{A}), 142.7 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-Mes^{B}), 140.7 (d, $^{2}J_{PC}$ = 12.1 Hz, *o*-Mes^{A}), 139.4 (d, $^{2}J_{PC}$ = 16.3 Hz, *o*′-Mes^{B}), 131.5 (d, $^{3}J_{PC}$ = 11.2 Hz, *m*′-Mes^{A}), 131.4 (d, $^{3}J_{PC}$ = 10.4 Hz, *m*-Mes^{B}), 131.3 (d, $^{3}J_{PC}$ = 12.2 Hz, *m*-Mes^{A}), 130.0 (d, $^{3}J_{PC}$ = 11.5 Hz, *m*′-Mes^{B}), 123.1 (d, $^{1}J_{PC}$ = 80.3 Hz, *i*-Mes^{B}), 119.9 (d, $^{1}J_{PC}$ = 88.7 Hz, *i*-Mes^{A}), 49.8 (d, $^{1}J_{PC}$ = 63.8 Hz, PCH), 42.3 (d, $^{3}J_{PC}$ = 18.7 Hz, C-7), 41.4 (br, BCH), 40.3 (d, $^{2}J_{PC}$ = 2.1 Hz, C-1), 37.7 (m, C-4), 35.4 (C-5), 24.3 (br, *o*-CH_3^{MesA}), 23.2 (d, $^{3}J_{PC}$ = 3.8 Hz, *o*′-CH_3^{MesA}), 21.2 (d, $^{3}J_{PC}$ = 8.6 Hz, *o*′-CH_3^{MesB}), 20.9 (d, $^{5}J_{PC}$ = 1.2 Hz, *p*-CH_3^{MesB}), 20.8 (d, $^{5}J_{PC}$ = 1.2 Hz, *p*-CH_3^{MesA}), 20.5 (br, C-6), 20.2 (d, $^{3}J_{PC}$ = 4.1 Hz, *o*-CH_3^{MesB}). [C_6F_5 not listed. $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 233 K): δ = −6.7 ($\nu_{1/2}$ ≈ 400 Hz). $^{31}P\{^{1}H\}$ NMR (242 MHz, CD_2Cl_2, 233 K): δ = 40.8 ($\nu_{1/2}$ ≈ 5 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 233 K): δ = −130.2, (m, 1F, *o*-$C_6F_5^{A}$), −131.1, (m, 1F, *o*-$C_6F_5^{B}$), −133.2 (m, 1F, *o*′-$C_6F_5^{A}$), −144.8 (m, 1F, *o*′-$C_6F_5^{B}$), −160.1 (t, $^{3}J_{FF}$ = 20.9 Hz, 1F, *p*-$C_6F_5^{A}$), −160.5 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-$C_6F_5^{A}$), −164.0 (m, 1F, *m*-$C_6F_5^{B}$), −164.8 (m, 1F, *m*′-$C_6F_5^{B}$), −165.1 (m, 2F, *m*-, *m*′-$C_6F_5^{A}$). HRMS: calcd for $C_{37}H_{33}PBF_{10}NONa$ [M + Na]$^{+}$: 762.21318. Found: 762.21269. IR (KBr): ν/cm^{-1} = 3532 (s, OH), 2954 (s), 2874 (s), 1640 (m), 1606 (m), 1512 (s), 1458 (vs). Elemental analysis: calc. for $C_{37}H_{33}PBF_{10}NO$: C, 60.10; H, 4.50; N, 1.89. Found: C, 59.62; H, 4.53; N, 1.69. X-ray crystal structure analysis of compound **13**: formula $C_{37}H_{33}BF_{10}NOP$, M = 739.42, colorless crystal, 0.17 × 0.13 × 0.07 mm, a = 9.0382(2), b = 13.0849(2), c = 15.5601(3) Å, α = 113.879(2), β = 96.700(1), γ = 93.957(1)°, V = 1657.44(5) Å^3, ρ_{calc} = 1.482 g cm^{-3}, μ = 0.173 mm^{-1}, empirical absorption correction (0.971 ≤ T ≤ 0.988), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 17726 reflections collected (±h, ± k, ± l), [(sinθ)/λ] = 0.60 Å^{-1}, 5725 independent (R_{int} = 0.041) and 4939 observed reflections [$I > 2\sigma(I)$], 470 refined parameters, R = 0.053, wR^2 = 0.126, max. (min.) residual electron density 0.22 (−0.22) e Å^{-3}, hydrogen atom at O1 was refined freely, other hydrogen atoms were calculated and refined as riding atoms.

Synthesis of Compound 14. $HB(C_6F_5)_2$ (49 mg, 0.142 mmol) and the dimesitylnorbornenylphosphane **3** (50 mg, 0.138 mmol) were weighed together, dissolved in *n*-pentane (5.0 mL) and stirred for 30 min. at r.t. to give a yellow solution of compound **4**. The solution was degassed by freeze−pump−thaw cycles (× 2), cooled to −78 °C. Ethylene gas was pressed (3.0 bar) over the solution and the reaction mixture allowed to warm to r.t. The reaction mixture was kept at r.t. for 2 days without stirring. The color of the solution almost disappeared and colorless crystals were formed. The solvent was decanted off and the residue was washed with *n*-pentane (1 × 3 mL) to give **14** as a colorless crystalline solid (71 mg, 68% yield). Crystals of compound **14** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of compound **14** in CH_2Cl_2 at −35 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 6.95 (d, $^{4}J_{PH}$ = 4.5 Hz, 2H, *m*-Mes^{A}), 6.94 (d, $^{4}J_{PH}$ = 4.5 Hz, 2H, *m*-Mes^{B}), 6.72 (dm, $^{3}J_{PH}$ = 12.2 Hz, 1H, =CH), 3.62 (br s, H-1), 3.11 (br s, H-4), 2.65, 2.42 (each m, each 1H, PCH_2), 2.31 (s, 6H, *p*-$CH_3^{MesA,B}$), 2.12 (br s, 6H, *o*-CH_3^{MesB}), 2.04 (br s, 6H, *o*-CH_3^{MesA}), 1.83/0.95 (each br m, each 1H, H-5), 1.81/1.50 (each br m, each 1H, H-7), 1.69/0.56 (each br m, each 1H, H-6), 1.13/0.95 (each br m, each 1H, BCH_2), 0.82 (br m, 2H, BCH_2CH_3), 0.45 (t, $^{3}J_{HH}$ = 7.5 Hz, 3H, BCH_2CH_3). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 157.9 (=CH), 144.1, 144.0 (each d, each $^{4}J_{PC}$ = 2.9 Hz, *p*-Mes^{A,B}), 142.1 (d, $^{2}J_{PC}$ = 9.4 Hz, *o*-Mes^{A}), 141.9 (br d, $^{2}J_{PC}$ = 9.3 Hz, *o*-Mes^{B}), 132.4 (d, $^{3}J_{PC}$ = 11.1 Hz, *m*-Mes^{A,B}), 131.2 (d, $^{1}J_{PC}$ = 71.3 Hz, =CP), 120.3 (d, $^{1}J_{PC}$ = 80.2 Hz, *i*-Mes^{A}), 119.6 (d, $^{1}J_{PC}$ = 81.5 Hz, *i*-Mes^{B}), 49.0 (d, $^{3}J_{PC}$ = 4.5 Hz, C-7), 48.1 (d, $^{2}J_{PC}$ = 7.8 Hz, C-1), 44.7 (d, $^{3}J_{PC}$ = 12.8 Hz, C-4), 28.7 (d, $^{1}J_{PC}$ = 39.5 Hz, PCH_2), 25.9 (C-6), 25.6 (d,

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$^3J_{PC}$ = 3.4 Hz, C-5), 23.8 (d, $^3J_{PC}$ = 4.5 Hz, 3H, *o*-CH_3^{MesA}), 23.6 (d, $^3J_{PC}$ = 4.2 Hz, 3H, *o*-CH_3^{MesB}), 21.11, 21.09 (each d, each $^5J_{PC}$ = 1.4 Hz, *p*-$CH_3^{MesA,B}$), 17.3 (br, BCH_2), 14.3 (br, BCH_2CH_3), 11.0 (BCH_2CH_3). [C_6F_5 not listed.] $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 299 K): δ = −10.4 ($\nu_{1/2} \approx$ 80 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ = 17.0 ($\nu_{1/2} \approx$ 50 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (m, 4F, *o*-C_6F_5), −164.77, −164.81 (each t, each $^3J_{FF}$ = 20.8 Hz, *p*-C_6F_5), −167.0 (m, 4F, *m*-C_6F_5). HRMS: calcd for $C_{41}H_{40}PBF_{10}Na$ $[M + Na - H]^+$: 787.27002. Found: 787.27022. IR (KBr): ν/cm^{-1} = 2941 (s), 2362 (w), 2343 (w), 1636 (w), 1606 (w), 1559 (w), 1507 (s), 1449 (vs). X-ray crystal structure analysis of compound **14**: formula $C_{41}H_{40}BF_{10}P$, M = 764.51, colorless crystal, 0.23 × 0.13 × 0.05 mm, a = 17.5033(6), b = 11.6428(5), c = 19.5772(13) Å, β = 111.969(3)°, V = 3699.9(3) Å^3, ρ_{calc} = 1.372 g cm^{-3}, μ = 1.364 mm^{-1}, empirical absorption correction (0.744 ≤ T ≤ 0.934), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 31943 reflections collected (±h, ± k, ± l), [(sinθ)/λ] = 0.60 Å^{-1}, 6398 independent (R_{int} = 0.069) and 4845 observed reflections [$I > 2\sigma(I)$], 485 refined parameters, R = 0.058, wR^2 = 0.150, max. (min.) residual electron density 0.30 (−0.30) e Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Solid State NMR Spectroscopy. The ^{11}B MAS NMR spectra were acquired at 11.74 and 7.05 T with a rotor-synchronized Hahn echo sequence (90°-τ-180°-τ-acq.) in case of **4** and single-pulse spectra (45 degree excitation pulses) in case of **8** using spinning frequencies of 14.0−15.0 kHz. 90° excitation pulses of 1.6−3.0 μs length and relaxation delays of 5−20 s were used. Proton decoupling was achieved during data acquisition using the TPPM-15[44] decoupling scheme (a ^1H pulse length of approximately 7.5 μs length corresponding to a 10/12 π pulse was applied). $^{31}P\{^1H\}$ CPMAS NMR experiments were conducted at 7.05 T with a rotation frequency of 10.0 kHz using the following acquisition parameters: ^1H 90° pulse length 7.5 μs, contact time 5 ms, relaxation delay 5 s. $\{^1H\}\rightarrow^{11}B\{^{31}P\}$ CP-REDOR and $\{^1H\}\rightarrow^{31}P\{^{11}B\}$ CP-REAPDOR experiments were conducted at 7.05 T using radio frequency power levels corresponding to 180° pulses of 7 μs length for ^{11}B and 9 μs length for ^{31}P. Spinning speeds of 12.0 kHz were used in both cases. For creating a reproducible magnetization in each experiment, a presaturation comb consisting of 60 90° pulses was applied. ^1H decoupling was achieved by using the TPPM-15 decoupling scheme during the evolution and data acquisition period with rf fields corresponding to a ^1H nutation frequency of 59 kHz. In case of the REAPDOR experiments the ^{11}B resonance was excited for one-third of the rotor period during the dipolar evolution time. All line shape simulations were performed using the DMFIT software (version 2011).[45] For details of the DFT-calculated NMR parameters see the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the syntheses and characterization of all new compounds, and crystal structure data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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