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Electronic control in frustrated Lewis pair chemistry: adduct formation of intramolecular FLP systems with $-P(C_6F_5)_2$ Lewis base components†

Annika Stute, Gerald Kehr, Constantin G. Daniliuc,‡ Roland Fröhlich‡ and Gerhard Erker*

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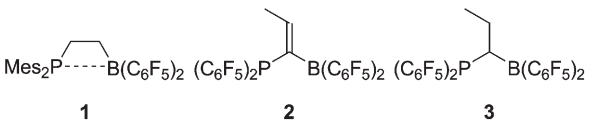
2-Propenylbis(pentafluorophenyl)phosphane adds Piers' borane [$HB(C_6F_5)_2$] with anti-Markovnikov orientation to yield the intramolecular vicinal frustrated P/B Lewis pair **10**. The FLP **10** adds pyridine, acetonitrile or alkyl isocyanides to form simple boron Lewis acid adducts **11–14**, all of which were characterized by X-ray diffraction. The FLP **10** reacts with *trans*-cinnamic aldehyde to give a boron carbonyl adduct **15** that was characterized by an X-ray crystal structure analysis. In contrast, the geminal FLP $(C_6F_5)_2P–CHEt–B(C_6F_5)_2$ (**3**) undergoes 1,2-carbonyl addition reactions with benzaldehyde or *trans*-cinnamic aldehyde to yield the respective five-membered heterocyclic products (**7**, **8**, both characterized by X-ray diffraction). The FLP **10** undergoes 1,2-P/B addition to *p*-tolylacetylene and to 2-methylbutenyne, respectively, to yield the corresponding six-membered heterocyclic products **17** and **18**, respectively (both were characterized by X-ray diffraction).

Introduction

Intramolecular frustrated Lewis pairs (FLPs) have significantly contributed to the development of FLP chemistry.[1,2] Usually, they contain combinations of the $-B(C_6F_5)_2$ Lewis acid functionality with phosphane or amine Lewis bases featuring very bulky substituents, so that both the inter- as well as intramolecular neutralizing Lewis acid/Lewis base adduct formation is precluded or at least substantially hindered (Scheme 1).[3] Intramolecular vicinal FLPs such as **1** have been shown to activate dihydrogen under mild conditions[4,5] and also to bind a variety of small molecules (*e.g.* CO_2, alkenes, alkynes, SO_2 and even NO).[6–9]

In **1** the bulky substituents at boron and phosphorus hinder the internal LA/LB adduct formation by steric repulsion. Compound **1** is a weakly interacting FLP.[3,4] It is known that FLP formation can also be controlled by electronic factors. Compounds **2** and **3** are intramolecular geminal FLP examples without any appreciable P–B interaction. They contain the strongly electron withdrawing $-C_6F_5$ substituents at both boron and phosphorus.[10,11] Both these electronically modified P/B FLPs were not reactive enough to split dihydrogen. However, they underwent a few other typically frustrated Lewis pair reactions, which indicated that frustrated Lewis pair formation can become electronically controlled in addition to the ubiquitous steric control exerted by the presence of sets of suitable very bulky substituents.[10,11]



Scheme 1

We recently described a regiochemical variant of the geminal FLP system **3**, namely the vicinal isomer **10** (see below).[10] In this account we will describe and compare a variety of addition reactions to electronically controlled FLPs **3** (geminal) and **10** (vicinal).

Results and discussion

Reactions of the geminal frustrated Lewis pair $(C_6F_5)_2P–CH(Et)–B(C_6F_5)_2$ (3)

We recently described the synthesis of **3** by $HB(C_6F_5)_2$ hydroboration[12] of the alkenylphosphane **4**. We also presented first examples of typical FLP reactions of **3**, namely its addition to a 1-alkyne, to ethylene, to an isocyanate and to mesityl azide.[10]

Organisch-Chemisches Institut, Corrensstr. 40, 48149 Münster, Germany. E-mail: erker@uni-muenster.de; Fax: +492518336503

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‡X-ray structure analysis.

Table 1 Selected NMR data of the FLP compounds **3** and **5–8**[a]

Compound	**3**	**5**	**6**	**7**[c]	**8**
^{31}P	−40.8	−51.3	25.2	27.9/20.4	23.5
^{11}B	70.9	−0.1	−8.2	1.9/1.9	2.6
C1H ^{1}H	4.40	4.00	3.40	3.25/3.70	3.57
^{13}C	34.1	24.7	39.5	34.2/n.l.	34.4
C4H ^{1}H	—	—	9.08[b]	6.36/6.17	5.88
^{13}C	—	—	183.6[b]	85.8/n.l.	83.3

[a] Chemical shifts in ppm, δ-scale. [b] =C(5)H. [c] Major/minor isomer. n.l. not located.

We here studied a few additional addition reactions of **3**. Especially those with aldehydes turned out to be important in a comparison with the carbonyl addition reactions of the related electron deficient vicinal FLP system (see below).

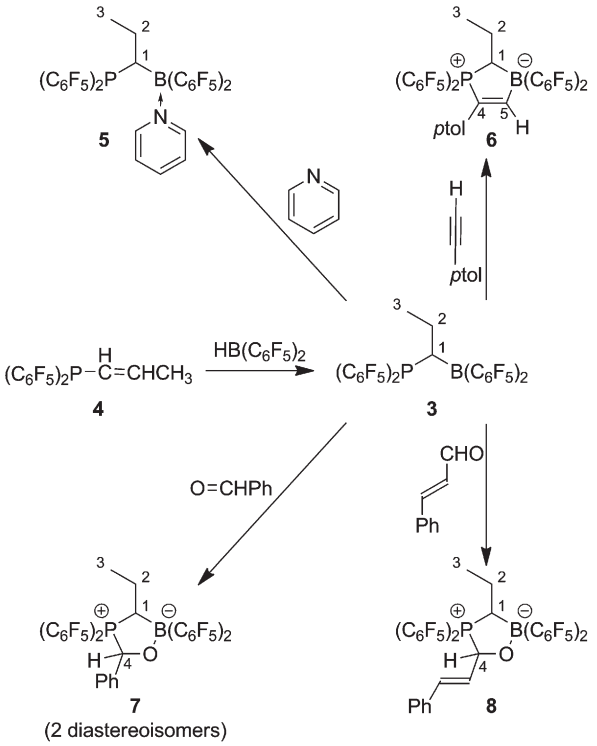
The hydroboration product **3** is characterized by a ^{31}P NMR signal at δ −40.8 and an ^{11}B NMR signal at δ 70.9, which is typical for the presence of a planar-tricoordinate boron center.[13,14] Consequently, we monitored a single set of $-C_6F_5$ ^{19}F NMR signals for the $-B(C_6F_5)_2$ group. In contrast the $-P(C_6F_5)_2$ substituent exhibits the ^{19}F NMR resonances of a pair of diastereotopic C_6F_5 groups.

The FLP **3** was treated with pyridine in pentane at ambient temperature to give the adduct **5** which was isolated in 56% yield as a white solid.[15] The NMR signals of the $(C_6F_5)_2P$ unit of **5** are similar to those of **3**, whereas the ^{11}B NMR signal now indicates the presence of a four-coordinated boron center in compound **5** (see Table 1). This is supported by the observation of the ^{19}F NMR signals of pairs of diastereotopic C_6F_5 substituents at boron and at phosphorus (see Scheme 2).

Compound **3** cleanly undergoes a 1,2-P/B-addition reaction to *p*-tolylacetylene to regioselectively yield the unsaturated five-membered heterocyclic product **6** (70% isolated). The adduct shows typical ^{13}C NMR signals of the former acetylene building block [δC4: 125.5, $^{1}J_{PC}$ = 84.1 Hz and δC5: 183.6 (br)]. The =C(5)H– ^{1}H NMR resonance shows a typical rather large $^{3}J_{PH}$ = 64.3 Hz coupling constant. Again we monitored the typical set of ^{19}F NMR signals of two diastereotopic pairs of C_6F_5-substituents at boron and phosphorus.

We reacted the geminal FLP **3** with benzaldehyde and with *trans*-cinnamic aldehyde and isolated the corresponding 1,2-carbonyl addition products **7** and **8** in 45% and 35% yield, respectively. The isolated benzaldehyde addition product contained two isomers in a 1 : 0.4 molecular ratio. We assume that they are the respective *trans*- and *cis*-diastereoisomers of **7**. Both were characterized spectroscopically from the mixture (see Table 1). We obtained single crystals of *trans*-**7** suitable for characterization by X-ray diffraction (see Fig. 1 and Table 2). The structure shows a five-membered heterocyclic core[11,16] that was formed by 1,2-addition of the FLP **3** to the carbonyl group of benzaldehyde, forming a new B–O and P–C bond. We note that the phosphorus–carbon bond in compound *trans*-**7** is very long (see Fig. 1).

The isolated material (**8**) of the FLP addition of **3** to *trans*-cinnamic aldehyde contains only a single diastereoisomer.



Scheme 2

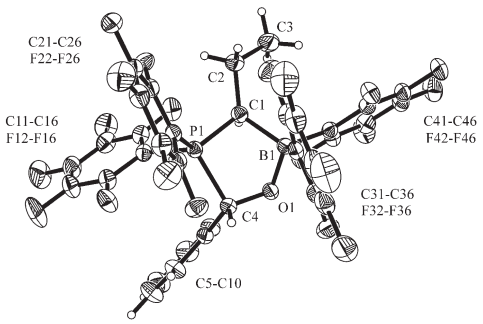


Fig. 1 A view of the molecular structure of the *trans*-**7** isomer (thermal ellipsoids are shown with 30% probability).

Table 2 Selected structural parameters of the compounds *trans*-**7** and *trans*-**8**[a]

Compound	*trans*-**7**	*trans*-**8**
P1–C1	1.781(3)	1.799(2)
C1–B1	1.709(4)	1.717(2)
B1–O1	1.486(3)	1.490(2)
C4–O1	1.388(3)	1.390(2)
P1–C4	1.929(3)	1.867(2)
P1–C1–B1	98.0(2)	99.7(1)
C1–P1–C4	95.7(1)	95.5(1)
B1–O1–C4	113.8(2)	115.9(1)
P1–C4–O1	102.7(2)	95.3(1)
C1–P1–C4–C5	−118.3(2)	166.1(1)
C1–B1–O1–C4	−57.1(3)	35.4(2)
B1–O1–C4–C5	151.9(2)	−177.2(1)

[a] Bond lengths in Å, angles in °.

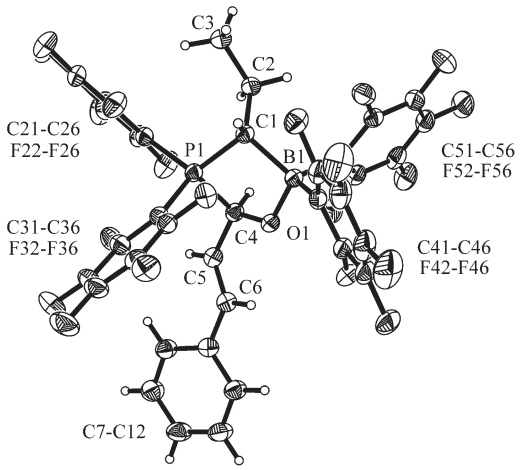


Fig. 2 Molecular structure of the FLP-addition product *trans*-**8** (thermal ellipsoids are shown with 30% probability).

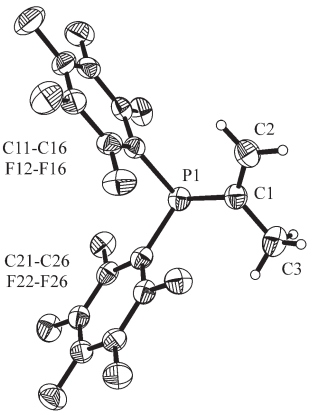


Fig. 3 Molecular structure of the phosphane **9** (thermal ellipsoids are shown with 30% probability).

In situ NMR experiments showed no indication of the formation of a second isomer (see the ESI†). Compound **8** retained the *trans*- –CH═CH– double bond. The X-ray crystal structure analysis of the product (see Fig. 2) shows a *trans*-attachment of the $-C_2H_5$ and –CH═CHPh substituents at the five-membered heterocyclic core (*trans*-**8**). Again, we note that the P1–C4 bond is rather long, although not as extreme as observed in *trans*-**7** (see above).

Formation and reactions of the vicinal FLP 10

We noticed that the outcome of the hydroboration of phosphanyl-substituted alkenes and alkynes with the reactive Piers' borane [$HB(C_6F_5)_2$] reagent was quite sensitive to the substitution pattern of these substrates.[10] It was possible to control the regiochemistry of the $HB(C_6F_5)_2$ addition reaction by attaching alkyl or aryl substituents at specific positions. For this study we prepared compound **10** as we had recently communicated[10] by regioselective $HB(C_6F_5)_2$ hydroboration of the (2-propenyl)-bis(pentafluorophenyl)phosphane **9**. Compound **9** was prepared by treatment of $(C_6F_5)_2PCl$[17] with 2-propenylmagnesium bromide. It was isolated in 64% yield after chromatographic workup. In solution it features ^{1}H NMR signals of the 2-propenyl substituent at δ 5.72 ($^3J_{PH}$ = 39.1 Hz) and 5.53 ($^3J_{PH}$ = 16.7 Hz) of the C═CH_2 unit and a methyl signal at δ 2.04 ($^3J_{PH}$ = 8.4 Hz). The ^{31}P NMR resonance of **9** occurs at δ −42.8 and the compound shows a single set of ^{19}F NMR resonances at δ −130.3 (*o*), −150.9 (*p*) and −161.4 (*m* of C_6F_5). Compound **9** was also characterized by X-ray diffraction (single crystals were obtained from pentane) (see Fig. 3). It shows a trigonal pyramidal coordination geometry at phosphorus (sum of C–P–C bond angles 309.4°). The C1–C2 bond length of the 2-propenyl substituent was found at 1.320(5) Å.

For the experiments carried out in this study the FLP **10** was always generated *in situ* and then used for the respective trapping experiments. For its spectroscopic characterization compound **10** was generated directly by treatment of the alkenylphosphane **9** with the $HB(C_6F_5)_2$ reagent in C_6D_6. The NMR spectra (see Table 3) indicated that 1,2-addition with anti-Markovnikov orientation had taken place yielding the vicinal FLP **10**. We monitored the typical ^{1}H and ^{13}C NMR signals of the central [P]–$CH(CH_3)$–CH_2–[B] unit. Due to the formation of the chiral center (C1, see Scheme 3) the hydrogen atoms at the adjacent CH_2 group are diastereotopic (see Table 3) as are the C_6F_5 substituents at phosphorus [e.g. δ −147.5/−148.5 (*p*-F of C_6F_5)]. The observed ^{11}B chemical shift is typical for a strongly Lewis acidic trigonally planar boron center. Consequently, we observed only a single set of ^{19}F NMR resonances of the pair of C_6F_5 substituents at boron in compound **10** [δ −130.5 (4F, *o*-), −145.8 (2F, *p*-), −160.4 (4F, *m*-F of C_6F_5)].

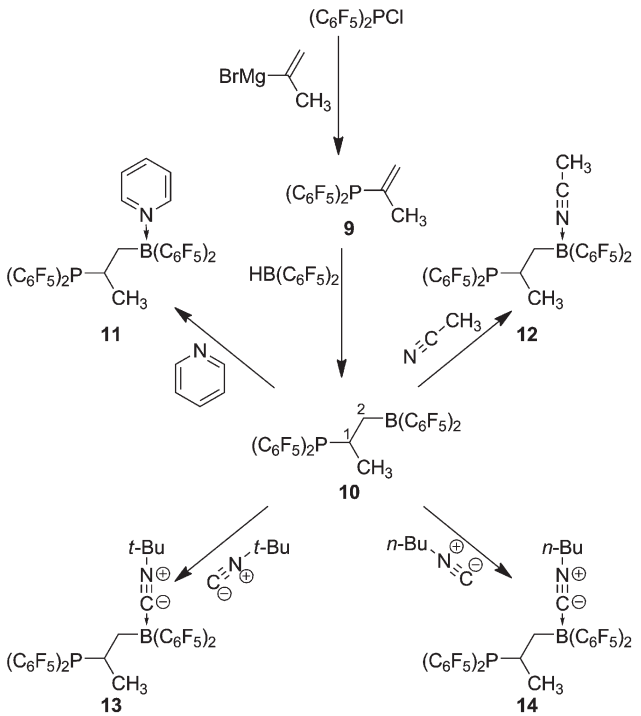
Table 3 Selected NMR data of FLP **10** and its adducts **11–14**[a]

Compound	**10**	**11**	**12**	**13**	**14**
^{31}P	−34.3	−36.3	−36.3	−37.3	−36.9
^{11}B	66.0	−1.5	−6.8	−19.3	−19.1
^{P}CH: ^{1}H	3.63	3.10	3.26	3.10	3.25
^{13}C	27.4	26.2	25.7	26.2	26.8
$^{B}CH_2$: ^{1}H	2.22	2.10	1.54	1.29	1.68
	1.67	1.00	1.54	1.29	1.60
^{13}C	35.8	26.4	25.5	22.9	23.9

[a] Chemical shifts in ppm, δ-scale.

The FLP **10** forms adducts with a variety of nucleophiles that selectively add to the boron Lewis acid. Treatment with pyridine (45 min, rt, pentane) gave the respective pyridine adduct **11** that was isolated in 74% yield. The NMR spectra showed that the $-P(C_6F_5)_2$ moiety was not affected. The system shows the ^{19}F NMR signals of pairs of diastereotopic C_6F_5 substituents at both phosphorus and boron. The X-ray crystal structure analysis of **11** reveals a close to *anti*-periplanar conformational arrangement of the central core of the molecule [*e.g.* θ C1–C2–B1–N1 171.1(2)°, B1–N1: 1.638(3) Å] (see Fig. 4 and Table 4)].

The open vicinal FLP **10** equally facile forms an adduct with acetonitrile. The product **12** was isolated in 73% yield. It



Scheme 3

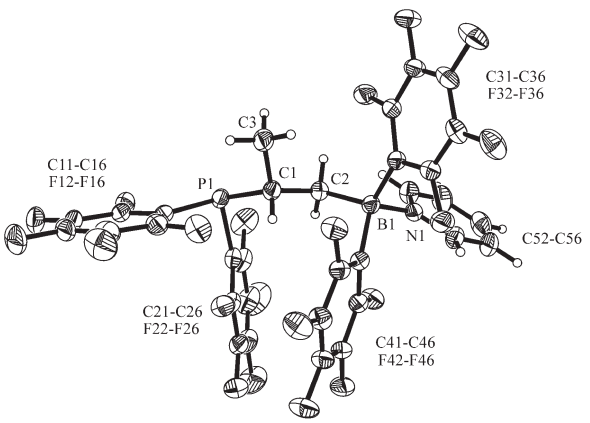


Fig. 4 A view of the molecular structure of the FLP–pyridine adduct **11** (thermal ellipsoids are shown with 30% probability).

Table 4 Selected structural data of the FLP adducts **11–14**[a]

Compound	11	12	13	14
P1–C1	1.855(2)	1.854(2)	1.853(3)	1.848(2)
C1–C2	1.549(3)	1.545(2)	1.541(4)	1.545(3)
C2–B1	1.636(3)	1.616(3)	1.630(4)	1.631(4)
ΣC–P1–C	307.0	308.2	308.5	306.0
C2–B1–N1 or C4	109.3(2)	107.7(2)	105.7(2)	108.7(4)
P1–C1–C2–B1	−158.6(2)	−167.4(1)	−167.0(2)	173.0(2)

[a] Bond lengths in Å, angles in °.

shows the NMR features of the [B]-coordinated acetonitrile ligand at δ 114.9/δ −0.5 (^{13}C) and δ 0.57 (^{1}H), respectively, and an IR(C≡N) band at 2363 cm^{-1} [free N≡C–CH$_3$: $\tilde{\nu}$ = 2292 cm^{-1}

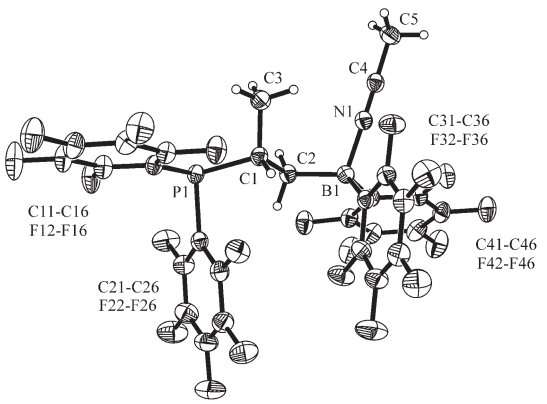


Fig. 5 A projection of the molecular structure of the FLP–acetonitrile adduct **12** (thermal ellipsoids are shown with 30% probability).

(CH$_3$–C≡N combination), 2253 cm^{-1} (C≡N stretch)]. The here observed IR effect is similar to that previously observed for the "parent" (C$_6$F$_5$)$_3$B–N≡C–CH$_3$ adduct [IR: $\tilde{\nu}$(C≡N) = 2367 cm^{-1}].[18–20]

The X-ray crystal structure analysis of the FLP–acetonitrile adduct shows a linear [B]–N≡C–CH$_3$ unit (see Fig. 5 and Table 4) with pertinent bonding parameters of B1–N1 1.597(3) Å and bond angles B1–N1–C4 173.5(2)° and N1–C4–C5 179.5(2)°. Coordination of the nitrile to the boron Lewis acid has resulted in a small shortening of the carbon–nitrogen triple bond [N1–C4: 1.134(2) Å] relative to the free acetonitrile reference [acetonitrile α-phase, 208 K, C≡N: 1.141(2) Å].[19] A similar structural effect had been observed for the acetonitrile ligand in the B(C$_6$F$_5$)$_3$–acetonitrile adduct [d(C≡N): 1.124(3) Å, d(B–N): 1.616(3) Å].[18] In the FLP–acetonitrile adduct **12** we find not only a close to *anti*-periplanar conformational arrangement of the [P]C$_2$[B] core of the molecule in the crystal [dihedral angle P1–C1–C2–B1 −167.4°], but also a close to *gauche* arrangement of the attached N≡C–CH$_3$ unit [θ C1–C2–B1–N1 −73.9(2)°].

The FLP **10** also rapidly adds *tert*-butyl isocyanide to its boron Lewis acid functionality. We isolated the respective adduct **13** as a white solid in 77% yield. The adduct shows typical NMR features (see Table 3). Compound **13** was characterized by X-ray diffraction (see Fig. 6 and Table 4). It shows that the *tert*-butyl isocyanide donor was added to the boron Lewis acid[16] (B1–C4 1.623(4) Å) to give a linear B–L arrangement [B1–C4–N1 176.8(3)°, C4–N1–C5 172.0(3)°, C4–N1 1.137(3) Å]. While the [P]–C1–C2–[B] unit shows an *anti*-periplanar conformation (see Table 4). The C≡N–^{t}Bu donor group is attached in close to *gauche* orientation (dihedral angle C1–C2–B1–C4 51.7(3)°).

We also prepared the **10**–*n*-butyl isocyanide adduct **14**. It shows similar NMR data (for details see Tables 3 and 4 and the ESI†).

We reacted the vicinal FLP **10** with *trans*-cinnamic aldehyde and with benzaldehyde, respectively. In both cases a reaction was observed to give 1 : 1 addition products. However, in detail the outcome of these reactions was markedly different from

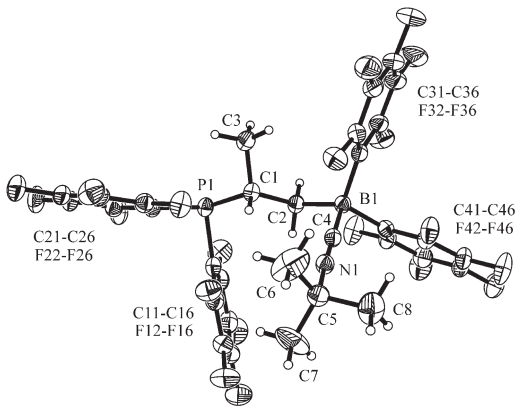


Fig. 6 Molecular structure of the *tert*-butyl isonitrile–FLP adduct **13** (thermal ellipsoids are shown with 30% probability).

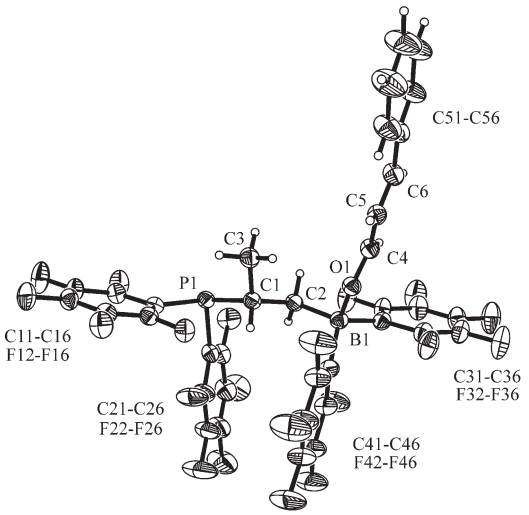
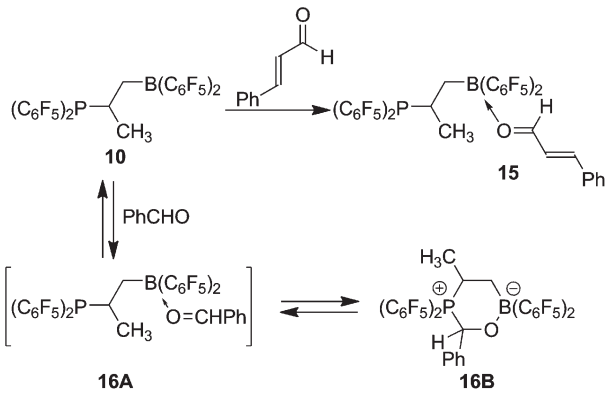


Fig. 7 Molecular structure of the FLP–*trans*-cinnamic aldehyde adduct **15** (thermal ellipsoids are shown with 30% probability).

respective carbonyl addition reactions with the geminal FLP **3** that we have described above.

From the reaction mixture of **10** with *trans*-cinnamic aldehyde (pentane, rt) a white precipitate was formed. The product (**15**) was isolated in 48% yield (see Scheme 4). We obtained crystals suited for the X-ray crystal structure analysis from dichloromethane/pentane by the diffusion method (see Fig. 7). In the crystal, compound **15** is to be described as a simple carbonyl adduct to the boron Lewis acid component of the vicinal frustrated P/B Lewis pair **10**. It features a [P]–CHMe–CH_2–[B] framework with a dihedral angle of −160.1(2)°. The aldehyde oxygen atom is found bonded to boron [B1–O1 1.584(4) Å, angle C2–B1–O1 107.4(2)°, dihedral angle C1–C2–B1–O1 −61.7(3)°]. The bonding parameters of the coordinated *trans*-cinnamic aldehyde are: O1–C4 1.252(3) Å, C4–C5 1.402(4) Å, B1–O1–C4 123.2(2)°. The remote phosphane Lewis base is found untouched by the FLP–*trans*-cinnamic aldehyde adduct formation (sum of the C–P–C bond angles at P1: 309.1°).

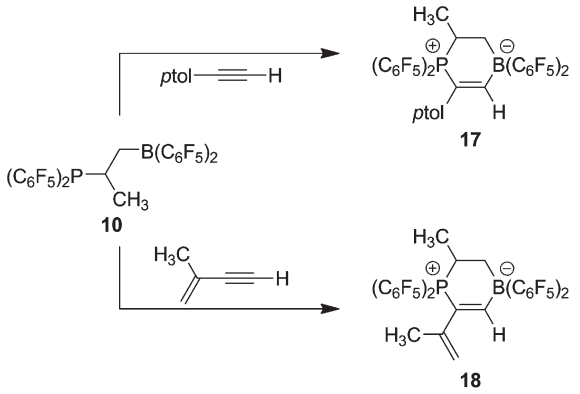
In solution (CD_2Cl_2, 299 K) the adduct **15** features the typical ^{31}P NMR signal of an unperturbed $(C_6F_5)_2P$– substituent[21] (δ −34.8, quin, $^3J_{PF}$ = 28.5 Hz) and an ^{11}B NMR signal at δ 8.3 typical for tetracoordinated boron. The C_6F_5 groups at the boron atom are found diastereotopic (^{19}F NMR below *ca.* 290 K, see ESI†) due to the carbon chirality center (C1) in the bridge. The ^{1}H/^{13}C NMR features of the coordinated O═CH-aldehyde functionality in the adduct **15** were located at δ 8.20/δ 193.8. The NMR spectra of **15** are not temperature invariant. Lowering of the temperature leads to a shifting of *e.g.* the aldehyde O═C*H*– ^{1}H NMR signal and of the ^{31}P NMR features. However, we were only able to monitor a beginning of decoalescence of the latter at very low temperature (*e.g.* below 208 K), giving not enough spectral information for a sound chemical interpretation (the temperature dependent NMR spectra of compound **15** are depicted in the ESI†).



Scheme 4

The reaction of the vicinal FLP **10** with benzaldehyde gave the 1 : 1 adduct **16**, which was isolated in 74% yield (see Scheme 4). Single crystals were obtained. The X-ray crystal structure analysis indicated a six-membered heterocyclic 1,2-addition product (**16B**) being present in the crystal. However, the structure solution was insufficient to describe the bonding parameters in detail (see the ESI†).

In solution compound **16** shows strongly temperature dependent NMR spectra. This shall be illustrated by the behavior of the ^{31}P NMR spectra. At 299 K we observed a slightly broadened single ^{31}P NMR resonance of **16** at *ca.* δ −5.9 (CD_2Cl_2). This is a chemical shift which is lying somewhere in the middle between expected values of a simple [B]–O═CHPh adduct **16A** and a 1,2-P/B addition product **16B**. This signal probably indicates a coalesced mean ^{31}P NMR resonance of an equilibrating system of adduct isomers. This interpretation is supported by the changes monitored of the ^{31}P NMR spectrum with decreasing temperature. Upon lowering the temperature the ^{31}P NMR resonance is rapidly shifted to positive shift values. The signal gets much broader and finally decoalesces at *ca.* 228 K into a major resonance at δ +20.5 and a minor signal at *ca.* δ +5.7 (the spectra are depicted in the ESI†). The former is very typical of a heterocyclic six-membered FLP adduct to the aldehyde (see above, *e.g.* Table 1); the minor intensity signal could indicate the presence of a second isomer or conformer, although a clear identification seems not



Scheme 5

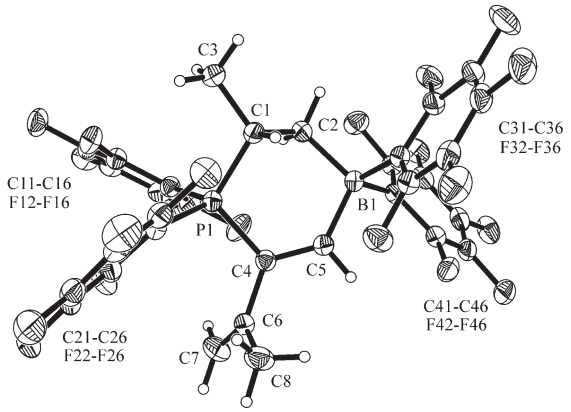


Fig. 8 Molecular structure of compound **18** (thermal ellipsoids are shown with 30% probability).

possible at this time. However, these data indicate that there might be an equilibrium between the cyclic adduct **16B** (possibly two stereoisomers) and an open isomer **16A** which is markedly temperature dependent.

The FLP **10** also undergoes 1,2-addition to acetylenes. We reacted **10** with *p*-tolylacetylene and isolated the 1,2-addition product **17** in 52% yield (see Scheme 5). Compound **17** features a typical ^{31}P NMR signal at δ 10.2 and an ^{11}B NMR resonance at δ −14.6. The ^{1}H NMR signal of the endocyclic =CH–[B] proton occurs at δ 8.92 with a coupling constant of $^{3}J_{PH}$ = 64.1 Hz.

Compound **10** reacts similarly with 2-methylbutenyne to give the 1,2-P/B FLP addition product **18** to the acetylenic moiety.[22] Compound **18** was isolated admixed with a minor component (whose structure is described in the ESI†) in 52% yield [^{31}P NMR δ 8.8, ^{11}B NMR: δ −14.8, ^{1}H NMR: δ 8.66 (=CH[B])].

Compound **18** was characterized by X-ray diffraction (see Fig. 8). In the crystal, compound **18** shows a distorted half-chair heterocyclohexene conformation with characteristic bond lengths of P1–C1 1.804(2) Å, P1–C4 1.783(2) Å, C1–C2 1.547(3) Å, C4–C5 1.340(3) Å, C2–B1 1.644(4) Å and B1–C5 1.618(4) Å. It contains the unperturbed 2-propenyl substituent bonded at C4 (C4–C6 1.493(3) Å, C6–C7 1.332(4) Å).

Conclusions

Lewis acids and bases can very effectively be hindered from undergoing neutralizing adduct formation by steric as well as electronic means. The introduction of the strongly electron-withdrawing C_6F_5-substituents at phosphorus appears to be an effective tool for lowering the Lewis basicity beyond a critical threshold for FLP formation. At the same time the hydroboration reaction of Piers' borane [$HB(C_6F_5)_2$] with alkenylbis(pentafluorophenyl)phosphanes responds very critically to the alkyl (and aryl) substitution pattern at the alkenyl group. In the here described cases the hydroboration reaction of the 1-propenyl derivative resulted in the formation of a geminal FLP (**3**) whereas the (2-propenyl)P(C_6F_5)$_2$ substrate gave the vicinal FLP **10** upon hydroboration. Both the FLPs **3** and **10** are not reactive enough to split dihydrogen, but they undergo a series of other typical FLP addition reactions, *e.g.* to alkynes or to aldehydes. The latter reaction is special in the way that the geminal FLP (**3**) cleanly undergoes a 1,2-addition reaction whereas the vicinal FLP (**10**) seems to feature a competing situation between 1,2-addition and simple carbonyl Lewis acid adduct formation. This indicates that the reduced phosphane nucleophilicity brings FLP chemistry in such electronically controlled systems to its limits. Nevertheless, a variety of FLP reactions seem to still be possible for these electronically determined FLPs so that they may be regarded as useful additions to the manifold of intramolecular frustrated Lewis pair compounds.

Experimental

General comments

All experiments were carried out under a dry argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{31}P NMR spectra were recorded on a Varian 500 MHz INOVA or a Varian 600 MHz UNITY plus NMR spectrometer at ambient temperature unless otherwise stated. Chemical shifts are given in ppm relative to solvents (^{1}H and ^{13}C) or an external standard [$\delta(BF_3{\cdot}OEt_2)$ = 0 for ^{11}B NMR, δ ($CFCl_3$) = 0 for ^{19}F NMR and δ(85% H_3PO_4) = 0 for ^{31}P NMR]. Coupling constants are in Hz. Elemental analysis data were recorded on Foss-Heraeus CHNO-Rapid. HRMS was recorded on GTC Waters Micromass (Manchester, UK). X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN;[23] absorption correction, Denzo;[24] structure solution SHELXS-97;[25] structure refinement SHELXL-97[26] 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. *Exceptions and special features*: For compound *trans*-**8** an unidentified disordered

solvent molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE[27] was therefore used to remove mathematically the effect of the solvent. The half disordered dichloromethane molecule in compound **11** and the disordered pentane molecule in compound **12**, which could not be refined satisfactorily, were removed using the program SQUEEZE. The chemical formula and the molecular mass do not include the squeezed part of the solvent molecules. For compound **13** one half molecule of pentane was found in the asymmetric unit and is disordered across an inversion centre. Several restraints (SADI, SIMU, SAME and ISOR) were used in order to improve refinement stability. For compound **14** the *n*-butyl isocyanide group was found disordered over two positions. Several restraints (SADI, SIMU, ISOR and SAME) were used in order to improve refinement stability. For compound **16b** one disordered half molecule of benzene, which could not be refined satisfactorily, was removed using the program SQUEEZE. $B(C_6F_5)_3$ (caution: the intermediate involved is explosive),[12a–c] $HB(C_6F_5)_2$,[12d,e] $(C_6F_5)_2PCl$,[17] **3**[10] and **10**[10] were prepared according to procedures reported in the literature.

Preparations

Preparation of compound 5. Bis(pentafluorophenyl)-1-propenylphosphane (**4**) (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170 mg, 0.49 mmol) were dissolved in *n*-pentane (30 mL) and stirred for two min. Pyridine (38.9 mg, 0.49 mmol) was added and a white solid precipitated immediately. The solid was isolated *via* filter cannula, washed with *n*-pentane (2 × 20 mL) and dried *in vacuo* to give the product as a white powder (228 mg, 0.275 mmol, 56%). IR (KBr): $\tilde{\nu}$ = 3136 (w), 2973 (w), 2943 (w), 2602 (w), 2363 (w), 1642 (s), 1518 (s), 1460 (s), 1377 (s), 1284 (s), 1165 (w), 1091 (s), 984 (s), 867 (w), 770 (s), 745 (s), 704 (s). Elemental analysis: calcd for $C_{32}H_{11}BF_{20}NP$: C 46.24, H 1.33, N 1.69; found: C 46.66, H 1.21, N 1.47. Mp (DSC): 161 °C. ^{1}H NMR (500 MHz, 298 K, C_7D_8): δ = 8.61 (br, 2H, *o*-py), 6.80 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-py), 6.49 (m, 2H, *m*-py), 4.00 (m, 1H, $^PCH^B$), 1.26/0.46 (each m, each 1H, CH_2), 0.49 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_7D_8): δ = 146.5 (d, J_{PC} = 16.2 Hz, *o*-py), 141.9 (*p*-py), 124.3 (*m*-py), 24.7 (br, $^PCH^B$), 23.4 (br d, $^2J_{PC}$ = 3.9 Hz, CH_2), 13.6 (d, $^3J_{PC}$ = 7.9 Hz, CH_3); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_7D_8): δ = −0.1 ($\nu_{1/2}$ ∼ 200 Hz). ^{19}F NMR (470 MHz, 248 K, C_7D_8): δ = −125.8 (s, 2F, *o*-P^A), −126.9 (s, 1F, *o*-B^A), −128.2 (s, 2F, *o*-B^B), −129.4 (s, 2F, *o*-P^B), −133.1 (s, 1F, *o*′-B^A), −148.0 (s, 1F, *p*-P^A), −149.8 (t, $^3J_{FF}$ = 2.8 Hz, 1F, *p*-P^B), −154.8 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*-B^A), −156.3 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-B^B), −160.4 (m, 2F, *m*-P^B), −160.5 (br, 1F, *m*′-B^A), −161.1 (m, 2F, *m*-P^A), −162.6 (br, 1F, *m*-B^A), −162.9 (m, 2F, *m*-B^B); [$\Delta\delta^{19}F_{p,m}$: 5.7, 7.8 (B^A), 6.6 (B^B), 13.1 (P^A), 10.6 (P^B)]. $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, C_7D_8): δ = −51.3 (m, $\nu_{1/2}$ ∼ 120 Hz).

Preparation of compound 6. Bis(pentafluorophenyl)-1-propenylphosphane (**4**) (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (169.5 mg, 0.49 mmol) were dissolved in *n*-pentane (10 mL) and stirred for one hour at rt. *p*-Tolylacetylene (56.9 mg, 0.49 mmol) was added to the reaction mixture which turned red-orange. After stirring for one hour at rt the solvent was removed *in vacuo* to give a brown residue. The crude product was suspended in *n*-pentane again and the solvent was removed *via* filter cannula. The remaining product was then dried *in vacuo* to give a white solid (299 mg, 0.34 mmol, 70%). IR (KBr): $\tilde{\nu}$ = 3442 (w), 3029 (w), 2970 (w), 2934 (w), 2879 (w), 1644 (s), 1523 (s), 1488 (s), 1462 (s), 1106 (s), 984 (s), 816 (m). Elemental analysis: calcd for $C_{36}H_{14}BF_{20}P$: C 49.80, H 1.63; found: C 49.54, H 1.23. Mp: 170 °C (DSC). ^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 9.08 (d, $^3J_{PH}$ = 64.3 Hz, 1H, =CH), 7.05 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *o*-tol), 6.80 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-tol), 3.40 (m, 1H, $^PCH^B$), 1.90 (s, 3H, *p*-CH_3^{tol}), 1.79 (dm, $^3J_{PH}$ = 29.1 Hz, 1H, CH_2), 1.66 (m, 1H, CH_2), 0.75 (t, $^3J_{HH}$ = 7.3 Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_6D_6): δ = 183.6 (br, =CH), 139.2 (*p*-tol), 130.8 (d, $^2J_{PC}$ = 16.6 Hz, i-tol), 129.9 (*m*-tol), 126.6 (d, $^3J_{PC}$ = 5.9 Hz, *o*-tol), 125.5 (d, $^1J_{PC}$ = 84.1 Hz, =C^{tol}), 39.5 (br, $^PCH^B$), 21.6 (CH_2), 20.8 (*p*-CH_3^{tol}), 16.2 (d, $^3J_{PC}$ = 9.0 Hz, CH_3); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6): δ = −8.2 ($\nu_{1/2}$ ∼ 50 Hz). ^{19}F NMR (470 MHz, 298 K, C_6D_6): δ = −127.3 (m, 2F, *o*-P^A), −127.6 (m, 2F, *o*-P^B), −131.7 (m, 2F, *o*-B^A), −132.0 (m, 2F, *o*-B^B), −138.1 (tm, $^3J_{FF}$ = 22.0 Hz, 1F, *p*-P^B), −139.4 (tm, $^3J_{FF}$ = 22.3 Hz, 1F, *p*-P^A), −156.4 (m, 2F, *m*-P^B), −157.0 (m, 2F, *m*-P^A), −157.6 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-B^A), −158.2 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-B^B), −163.5 (m, 2F, *m*-B^A), −163.7 (m, 2F, *m*-B^B); [$\Delta\delta^{19}F_{p,m}$: 5.9 (B^A), 5.5 (B^B), 17.6 (P^A), 18.3 (P^B)]. $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, C_6D_6): δ = 25.2 ($\nu_{1/2}$ ∼ 50 Hz).

Preparation of compound 7. Bis(pentafluorophenyl)-1-propenylphosphane (**4**) (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170.3 mg, 0.49 mmol) were dissolved in *n*-pentane (10 mL) and stirred for 5 min at rt. Benzaldehyde (52.3 mg, 0.49 mmol) was added and a white solid precipitated. The suspension was stirred for 30 min at rt before the solid was isolated on a Schlenk-frit and washed with *n*-pentane (10 mL). Drying *in vacuo* gave the product (190 mg, 0.22 mmol, 45%). According to $^{31}P\{^{19}F\}$ and ^{1}H NMR spectra two isomers in a ratio of 1 : 0.4 are present in CD_2Cl_2 solution at 258 K. Single crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of compound **7** in dichloromethane at −30 °C. IR (KBr): $\tilde{\nu}$ = 2991 (w), 2940 (w), 2885 (w), 1644 (s), 1598 (w), 1519 (s), 1483 (s), 1459 (s), 1381 (m), 1287 (m), 1224 (w), 1185 (w), 1103 (s), 1027 (w), 973 (s), 919 (m), 872 (w), 836 (w), 784 (m), 751 (m), 726 (w), 710 (m), 626 (w), 588 (w), 540 (w), 521 (w). Elemental analysis: calcd for $C_{34}H_{12}BF_{20}P$: C 47.58, H 1.41; found: C 47.01, H 0.95. Mp: 159 °C (DSC); Dp: 210 °C (DSC). Major isomer: ^{1}H NMR (500 MHz, 258 K, CD_2Cl_2): δ = 7.30 (br, 3H, *o*,*p*-Ph), 7.25 (m, 2H, *m*-Ph), 6.36 (d, $^2J_{PH}$ = 15.3 Hz, 1H, ^OCH), 3.25 (br d, $^2J_{PH}$ = 21.8 Hz, 1H, $^PCH^B$), 1.96/1.71 (each br, each 1H, CH_2), 0.91 (br, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 258 K, CD_2Cl_2): δ = 133.9 (i-Ph), 130.1 (d, J = 4.5 Hz, *p*-Ph)^t, 128.7 (*m*-Ph), 126.9 (br, *o*-Ph)^t, 85.8 (d, $^1J_{PC}$ = 30.8 Hz, ^OCH), 34.2 (br, $^PCH^B$), 19.5 (m, CH_2), 16.6 (m, CH_3); [C_6F_5 not listed, ^{t} tentatively assigned]. $^{11}B\{^1H\}$ NMR (160 MHz, 258 K, CD_2Cl_2): δ = 1.9 ($\nu_{1/2}$ ∼ 120 Hz). ^{19}F NMR (470 MHz, 258 K, CD_2Cl_2): δ = −124.1 (br, 2F, *o*-P^A), −132.3 (m, 2F, *o*-B^A), n.o. (*o*-P^B), −134.5 (m, 2F, *o*-B^B), −138.7

(m, 1F, *p*-P^{A}), −140.0 (m, 1F, *p*-P^{B}), −155.4 (m, 2F, *m*-P^{A}), −157.3 (br, 2F, *m*-P^{B}), −157.9 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-B^{A}), −159.6 (t, $^{3}J_{FF}$ = 19.9 Hz, 1F, *p*-B^{B}), −164.0 (m, 2F, *m*-B^{A}), −164.7 (m, 2F, *m*-B^{B}); [$\Delta\delta^{19}F_{p,m}$: 6.1 (B^{A}), 5.1 (B^{B}), 16.7 (P^{A}), 17.3 (P^{B})]. $^{31}P\{^{19}F\}$ NMR (202 MHz, 258 K, CD_2Cl_2): δ = 27.9 ($\nu_{1/2}$ ~ 85 Hz). (Minor isomer: see the ESI†.)

X-ray crystal structure analysis of compound *trans*-7. Formula $C_{34}H_{12}BF_{20}OP$, M = 858.22, colourless crystals, 0.27 × 0.05 × 0.02 mm, a = 8.8560(4), b = 12.7840(6), c = 14.4856(12) Å, α = 95.877(4), β = 96.842(6), γ = 92.121(3)°, V = 1617.74(17) Å^3, ρ_{calc} = 1.762 g cm^{-3}, μ = 2.133 mm^{-1}, empirical absorption correction (0.596 ≤ T ≤ 0.958), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 24 788 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 5522 independent (R_{int} = 0.052) and 4263 observed reflections [$I > 2\sigma(I)$], 515 refined parameters, R = 0.044, wR^2 = 0.107, max. (min.) residual electron density 0.20 (−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound 8. Bis(pentafluorophenyl)-1-propenylphosphane (**4**) (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170 mg, 0.49 mmol) were dissolved in *n*-pentane (15 mL) and stirred at rt for five min before *trans*-cinnamic aldehyde (64.8 mg, 0.49 mmol) was added. The solution turned yellow and was stirred at rt for one hour. The reaction mixture was concentrated *in vacuo* until a white solid precipitated, which was isolated *via* filter cannula and then dried *in vacuo* to give the product as a white solid (151 mg, 0.171 mmol, 35%). Single crystals suitable for X-ray crystal structure analysis were obtained from a solution of **8** in C_6D_6. IR (KBr): $\tilde{\nu}$ = 2964 (w), 2935 (w), 2877 (w), 1644 (m), 1522 (s), 1486 (s), 1464 (s), 1389 (w), 1305 (m), 1293 (m), 1105 (s), 981 (s), 752 (m), 694 (w), 639 (w), 526 (w). Elemental analysis: calcd for $C_{36}H_{14}BF_{20}OP$: C 48.90, H 1.60; found: C 48.71, H 1.77. Mp: 90 °C (DSC); Dp: 131 °C (DSC). ^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 7.30 (m, 5H, Ph), 6.97 (dd, $^{3}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.4 Hz, 1H, =CH^{CH}), 6.33 (d, $^{3}J_{HH}$ = 15.2 Hz, 1H, =CH^{Ph}), 5.88 (br d, $^{3}J_{HH}$ = 7.4 Hz, 1H, ^{O}CH), 3.57 (dm, $^{2}J_{PH}$ = 16.8 Hz, 1H, ^{P}CH^{B}), 1.91/1.65 (each br m, each 1H, CH_2), 0.93 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, CD_2Cl_2): δ = 136.1 (d, $^{2}J_{PC}$ = 13.6 Hz, =CH^{CH}), 135.6 (d, $^{4}J_{PC}$ = 4.6 Hz, i-Ph), 129.2 (*p*-Ph), 129.1, 127.0 (each Ph), 120.1 (d, $^{3}J_{PC}$ = 5.6 Hz, =CH^{Ph}), 83.3 (d, $^{1}J_{PC}$ = 38.1 Hz, ^{O}CH), 34.4 (br, ^{P}CH^{B}), 21.5 (CH_2), 16.4 (d, $^{3}J_{PC}$ = 6.4 Hz, CH_3); [C_6F_5 not listed]. $^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, CD_2Cl_2): δ = 2.6 ($\nu_{1/2}$ ~ 70 Hz). ^{19}F NMR (470 MHz, 298 K, CD_2Cl_2): δ = −124.5 (br, 2F, *o*-P^{A}), −125.8 (br, 2F, *o*-P^{B}), −133.7 (m, 4F, *o*-B^{A,B}), −138.8 (m, 1F, *p*-P^{A}), −139.4 (m, 1F, *p*-P^{B}), −155.8 (br, 2F, *m*-P^{A}), −156.7 (br, 2F, *m*-P^{B}), −159.0 (br, 1F, *p*-B^{A}), −159.8 (br, 1F, *p*-B^{B}), −164.6 (br, 2F, *m*-B^{A}), −165.2 (br, 2F, *m*-B^{B}); [$\Delta\delta^{19}F_{p,m}$: 5.6 (B^{A}), 5.4 (B^{B}), 17.0 (P^{A}), 17.3 (P^{B})]. $^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, CD_2Cl_2): δ = 23.5 ($\nu_{1/2}$ ~ 60 Hz).

X-ray crystal structure analysis of compound *trans*-8. Formula $C_{36}H_{14}BF_{20}OP{\cdot}1.5\ C_6H_6$, M = 1001.41, colourless crystals, 0.25 × 0.20 × 0.20 mm, a = 13.5250(20), b = 13.9090 (30), c = 14.5825(11) Å, α = 111.609(7), β = 113.015(11), γ = 94.428(12)°, V = 2267.7(6) Å^3, ρ_{calc} = 1.467 g cm^{-3}, μ = 1.609 mm^{-1}, empirical absorption correction (0.689 ≤ T ≤ 0.739), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 33 792 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 7795 independent (R_{int} = 0.039) and 6896 observed reflections [$I > 2\sigma(I)$], 614 refined parameters, R = 0.041, wR^2 = 0.122, max. (min.) residual electron density 0.20 (−0.20) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of phosphane 9.[10] Chlorobis(pentafluorophenyl)phosphane (7.20 g, 18.0 mmol) was dissolved in thf (150 mL) and cooled down to −78 °C. 2-Propenylmagnesium bromide (0.5 M in thf, 36.0 mL, 18.0 mmol) was added dropwise to the reaction mixture, which turned brown after addition. The reaction mixture was stirred at rt for two hours before the solvent was removed *in vacuo*. The residue was suspended in *n*-pentane (100 mL) and filtered in a Schlenk-frit over Celite. The filter pad was washed with *n*-pentane (2 × 80 mL). The filtrate was dried *in vacuo*. Purification by column chromatography (SiO_2 : cyclohexane, R_f = 0.66) gave the product (4.69 g, 11.5 mmol, 64%). [Comment: the product should be kept in the fridge otherwise it slowly decomposes to $(C_6F_5)_2P{-}P(C_6F_5)_2$.] Crystals suitable for crystal structure analysis were obtained by slow evaporation of an *n*-pentane solution at rt.

X-ray crystal structure analysis of compound 9. Formula $C_{15}H_5F_{10}P$, M = 406.16, colourless crystals, 0.20 × 0.13 × 0.05 mm, a = 10.0879(2), b = 14.1955(5), c = 11.6037(3) Å, β = 113.101(2)°, V = 1528.44(7) Å^3, ρ_{calc} = 1.765 g cm^{-3}, μ = 2.672 mm^{-1}, empirical absorption correction (0.617 ≤ T ≤ 0.878), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 15 206 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 2642 independent (R_{int} = 0.042) and 2233 observed reflections [$I > 2\sigma(I)$], 236 refined parameters, R = 0.050, wR^2 = 0.142, max. (min.) residual electron density 0.68 (−0.22) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound 11. Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (150 mg, 0.369 mmol) and bis(pentafluorophenyl)borane (127.8 mg, 0.369 mmol) were dissolved in *n*-pentane (10 mL) and stirred for 10 min at rt to give a white suspension. Pyridine (29.2 mg, 0.369 mmol) was added and a white solid precipitated. After stirring for 45 min at rt all volatiles were removed *in vacuo*, the residue was washed with *n*-pentane (3 × 2 mL) and dried *in vacuo* to give the product as a white solid (226 mg, 0.272 mmol, 74%). Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **11** in dichloromethane at −30 °C. Exact mass: calcd for $C_{32}H_{11}BF_{20}NP + H^+$: 832.04811 m/z; found: 832.04798 m/z. IR (KBr): $\tilde{\nu}$ = 3433 (br), 2973 (w), 2936 (w), 1642 (s), 1518 (s), 1469 (s), 1380 (s), 1284 (s), 1224 (m), 1190 (w), 1088 (s), 976 (s), 841 (m), 809 (m), 693 (s), 626 (m), 577 (w), 506 (w). Elemental analysis: calcd for $C_{32}H_{11}BF_{20}NP$: C 46.24, H 1.33, N 1.69; found: C 46.43, H 1.29, N 1.77. Mp: 200 °C (DSC). ^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 8.08 (m, 2H, *o*-py), 6.46 (m, 1H, *p*-py), 6.18 (m, 2H, *m*-py), 3.10 (m, 1H, ^{P}CH), 2.10 (m, 1H, ^{B}CH$_2$), 1.29 (dd, $^{3}J_{PH}$ = 21.5 Hz,

$^3J_{HH}$ = 6.7 Hz, 3H, CH_3), 1.00 (m, 1H, $^BCH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, C_6D_6): δ = 144.7 (*o*-py), 140.9 (*p*-py), 125.6 (*m*-py), 120.2 (br, i-$C_6F_5^B$), 108.9 (m, i-$C_6F_5^P$), 26.4 (br, $^BCH_2$), 26.2 (m, ^PCH), 17.5 (d, $^2J_{PC}$ = 25.2 Hz, CH_3); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (64 MHz, 300 K, C_6D_6): δ = −1.5 ($\nu_{1/2}$ ~ 430 Hz). ^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = −129.6 (m, 2F, *o*-P^A), −130.25 (m, 2F, *o*-P^B), −130.33 (m, 2F, *o*-B^A), −132.1 (m, 2F, *o*-B^B), −148.9 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^A), −149.9 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^B), −155.9 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-B^A), −156.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-B^B), −160.1 (m, 2F, *m*-P^B), −160.5 (m, 2F, *m*-P^A), −162.8 (m, 4F, *m*-$B^{A,B}$); [$\Delta\delta^{19}F_{p,m}$: 6.9 (B^A), 6.3 (B^B), 11.6 (P^A), 10.2 (P^B)]. $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, C_6D_6): δ = −36.3 (quin, $^3J_{FF}$ = 31.1 Hz).

X-ray crystal structure analysis of compound 11. Formula $C_{32}H_{11}BF_{20}NP$, M = 831.20, colourless crystals, 0.33 × 0.10 × 0.08 mm, a = 9.4074(2), b = 15.6502(6), c = 22.7817(10) Å, β = 96.343(2)°, V = 3333.6(2) Å^3, ρ_{calc} = 1.656 g cm^{-3}, μ = 2.032 mm^{-1}, empirical absorption correction (0.553 ≤ T ≤ 0.854), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 19 676 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 5697 independent (R_{int} = 0.041) and 4614 observed reflections [$I > 2\sigma(I)$], 497 refined parameters, R = 0.042, wR^2 = 0.113, max. (min.) residual electron density 0.18 (−0.27) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound 12. Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (100 mg, 0.246 mmol) and bis(pentafluorophenyl)borane (85.3 mg, 0.246 mmol) were dissolved in *n*-pentane (5 mL) and after stirring for five min the reaction mixture turned cloudy. Acetonitrile (22.8 mg, 0.246 mmol) was added to the reaction mixture and a white solid precipitated instantly. After stirring the suspension for one hour at rt the solid was isolated *via* filter cannula. The product (144 mg, 0.180 mmol, 73%) was washed with *n*-pentane (5 mL) and dried *in vacuo*. Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **12** in dichloromethane. IR (KBr): $\tilde{\nu}$ = 2941 (w), 2363 (m), 1647 (m), 1519 (s), 1469 (s), 1381 (m), 1287 (m), 1092 (s), 977 (s), 888 (w), 855 (w), 819 (w), 768 (w), 744 (w), 675 (w), 511 (w), 426 (w). Elemental analysis: calcd for $C_{29}H_9BF_{20}NP$: C 43.92, H 1.14, N 1.77; found: C 43.96, H 1.16, N 1.60. Mp: 76 °C (DSC). ^1H NMR (600 MHz, 299 K, C_6D_6): δ = 3.26 (br m, 1H, ^PCH), 1.54 (m, 2H, $^BCH_2$), 0.99 (dd, $^3J_{PH}$ = 20.9 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 0.57 (s, 3H, $^{NC}CH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, C_6D_6): δ = 114.9 (^NC), 25.7 (br, ^PCH), 25.5 (br, $^BCH_2$), 18.7 (d, $^2J_{PC}$ = 24.2 Hz, CH_3), −0.5 ($^{NC}CH_3$); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6): δ = −6.8 ($\nu_{1/2}$ ~ 450 Hz). ^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = −130.1 (m, 4F, *o*-$P^{A,B}$), −134.5 (br, 4F, *o*-B), −148.9 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^A), −149.4 (t, $^3J_{FF}$ = 21.3 Hz, 1F, *p*-P^B), −156.2 (t, $^3J_{FF}$ = 21.0 Hz, 2F, *p*-B), −160.2 (m, 2F, *m*-P^B), −160.3 (m, 2F, *m*-P^A), −163.0 (m, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 6.8 (B), 11.4 (P^A), 10.8 (P^B)]. $^{31}P\{^1H\}$ NMR (243 MHz, 299 K, C_6D_6): δ = −36.3 (quin, $^3J_{PF}$ = 29.7 Hz).

X-ray crystal structure analysis of compound 12. Formula $C_{29}H_9BF_{20}NP$, M = 793.15, colourless crystals, 0.37 × 0.21 × 0.21 mm, a = 10.7188(3), b = 12.7599(6), c = 13.1819(5) Å, α = 78.178(4), β = 78.512(3), γ = 80.597(3)°, V = 1715.13(11) Å^3, ρ_{calc} = 1.536 g cm^{-3}, μ = 1.944 mm^{-1}, empirical absorption correction (0.533 ≤ T ≤ 0.685), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 24 911 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 5920 independent (R_{int} = 0.043) and 5299 observed reflections [$I > 2\sigma(I)$], 471 refined parameters, R = 0.040, wR^2 = 0.111, max. (min.) residual electron density 0.19 (−0.24) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound 13. (*Caution: many isonitriles are toxic and must be handled with due care.*) Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (100 mg, 0.246 mmol) and bis(pentafluorophenyl)borane (85.3 mg, 0.246 mmol) were dissolved in *n*-pentane (5 mL) and stirred for two hours at rt to give a cloudy solution. *t*-Butylisonitrile (20.5 mg, 0.246 mmol) was added to give a clear reaction mixture. After stirring at rt for 10 min the reaction mixture was cooled to −78 °C and stirred for 30 min at that temperature while a white solid crushed out. The solvent was removed by filter cannula and the residue was dried *in vacuo* to give a white solid (158 mg, 0.189 mmol, 77%) (small impurities are visible in the NMR spectra). Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **13** in dichloromethane at −30 °C. IR (KBr): $\tilde{\nu}$ = 3433 (br), 2996 (w), 2930 (w), 2874 (w), 2291 (m), 1643 (m), 1517 (s), 1474 (s), 1379 (m), 1240 (s), 1186 (m), 1140 (m), 1092 (s), 978 (s), 908 (w), 838 (w), 810 (w), 777 (w), 753 (w), 733 (w), 662 (w), 637 (w), 536 (w), 514 (w). ^1H NMR (500 MHz, 299 K, $CDCl_3$): δ = 3.10 (m, 1H, ^PCH), 1.66 (s, 9H, $C(CH_3)_3$), 1.29 (m, 2H, $^BCH_2$), 1.05 (dd, $^3J_{PH}$ = 21.4 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, $CDCl_3$): δ = 126.9 (br, ^NC), 116.9 (i-$C_6F_5^B$), 108.6 (m, i-$C_6F_5^P$), 60.6 ($C(CH_3)_3$), 28.9 ($C(CH_3)_3$), 26.2 (m, ^PCH), 22.9 (br, $^BCH_2$), 18.2 (d, $^2J_{PC}$ = 25.5 Hz, CH_3); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, $CDCl_3$): δ = −19.3 ($\nu_{1/2}$ ~ 200 Hz). ^{19}F NMR (470 MHz, 299 K, $CDCl_3$): δ = −129.4, −129.6 (each m, each 2F, *o*-$P^{A,B}$), −132.6, −133.2 (each m, each 2F, *o*-$B^{A,B}$), −149.3 (tm, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-P^A), −149.9 (tm, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-P^B), −156.9 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-B^A), −157.1 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-B^B), −160.2 (m, 4F, *m*-$P^{A,B}$), −163.0 (m, 4F, *m*-$B^{A,B}$); [$\Delta\delta^{19}F_{p,m}$: 6.1 (B^A), 5.9 (B^B), 10.9 (P^A), 10.3 (P^B)]. $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, $CDCl_3$): δ = −37.3 (quin, $^3J_{PF}$ = 30.0 Hz).

X-ray crystal structure analysis of compound 13. Formula $C_{32}H_{15}BF_{20}NP{\cdot}1/2\ C_5H_{12}$, M = 871.30, colourless crystals, 0.27 × 0.10 × 0.10 mm, a = 27.4280(7), b = 20.0877(8), c = 15.7738(4) Å, β = 124.926(2)°, V = 7125.5(4) Å^3, ρ_{calc} = 1.624 g cm^{-3}, μ = 1.928 mm^{-1}, empirical absorption correction (0.624 ≤ T ≤ 0.830), Z = 8, monoclinic, space group $C2/c$ (no. 15), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 17 145 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5948 independent (R_{int} = 0.038) and 4883 observed reflections [$I > 2\sigma(I)$], 547 refined parameters, R = 0.050, wR^2 = 0.135, max. (min.) residual electron density 0.30 (−0.24) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound 14. (*Caution: many isonitriles are toxic and must be handled with due care.*) Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (100 mg, 0.246 mmol) and bis(pentafluorophenyl)borane (85.3 mg, 0.246 mmol) were dissolved in *n*-pentane (10 mL) and stirred for two hours at rt to give a clear solution. *n*-Butylisonitrile (20.5 mg, 0.246 mmol) was added and the reaction mixture was cooled to −78 °C and stirred for one hour at that temperature while a white solid precipitated. The solvent was removed by filter cannula and the residue was dried *in vacuo* to give a white solid (128 mg, 0.153 mmol, 62%) (small amounts of impurities of HB$(C_6F_5)_2{\cdot}CN^nBu$ are visible in the NMR spectra ($\delta^{11}B\{^1H\}$: −30.7). Single crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of an *n*-pentane solution of **14** at rt. ^1H NMR (500 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 3.25 (m, 1H, ^{P}CH), 2.49 (td, $^3J_{HH}$ = 6.7 Hz, J = 1.4 Hz, 2H, $^{N}CH_2$), 1.68/1.60 (each br m, each 1H, $^{B}CH_2$), 1.07 (dd, $^3J_{PH}$ = 20.7 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, $^{CH}CH_3$), 0.97 (m, 2H, $^{CH2}CH_2{}^{CH2}$), 0.85 (m, 2H, $^{CH3}CH_2$), 0.54 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $^{CH2}CH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 128.7 (br, ^{N}C), 117.1 (br, i-$C_6F_5{}^{B}$), 108.8 (br, i-$C_6F_5{}^{P}$), 43.6 ($^{N}CH_2$), 29.2 ($^{CH2}CH_2{}^{CH2}$), 26.8 (m, ^{P}CH), 23.9 (br, $^{B}CH_2$), 19.3 ($^{CH3}CH_2$), 18.6 (d, $^2J_{PC}$ = 25.1 Hz, $^{CH}CH_3$), 12.6 ($^{CH2}CH_3$); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −19.1 ($\nu_{1/2}$ ∼ 250 Hz). ^{19}F NMR (470 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −130.1 (m, 4F, *o*-$P^{A,B}$), −132.6 (m, 2F, *o*-B^{A}), −133.4 (m, 2F, *o*-B^{B}), −148.8 (tm, $^3J_{FF}$ = 20.9 Hz, 1F, *p*-P^{A}), −149.5 (tm, $^3J_{FF}$ = 20.9 Hz, 1F, *p*-P^{B}), −156.2 (tm, $^3J_{FF}$ = 20.0 Hz, 2F, *p*-$B^{A,B}$), −160.3 (m, 4F, *m*-$P^{A,B}$), −162.7 (m, 4F, *m*-$B^{A,B}$); [$\Delta\delta^{19}F_{p,m}$: 6.5 (B), 11.5 (P^{A}), 10.8 (P^{B})]. $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −36.9 (quin, $^3J_{PF}$ = 30.5 Hz).

X-ray crystal structure analysis of compound 14. Formula $C_{32}H_{15}BF_{20}NP$, M = 835.23, colourless crystals, 0.42 × 0.36 × 0.12 mm, a = 9.1649(2), b = 11.6030(2), c = 16.2616(4) Å, α = 75.183(1), β = 75.375(1), γ = 85.283(2)°, V = 1617.31(6) Å^3, ρ_{calc} = 1.715 g cm^{-3}, μ = 0.228 mm^{-1}, empirical absorption correction (0.910 ≤ T ≤ 0.973), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 15 281 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.59 Å^{-1}, 5516 independent (R_{int} = 0.037) and 4873 observed reflections [$I > 2\sigma(I)$], 552 refined parameters, R = 0.048, wR^2 = 0.120, max. (min.) residual electron density 0.33 (−0.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound 15. Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (150 mg, 0.375 mmol) and bis(pentafluorophenyl)borane (130 mg, 0.375 mmol) were dissolved in *n*-pentane (5 mL) and after stirring for five min the reaction mixture turned cloudy. *trans*-Cinnamic aldehyde (50.0 mg, 0.375 mmol) was added to the reaction mixture which turned green-yellow and a white solid precipitated. The solid was isolated *via* filter cannula, washed with *n*-pentane (15 mL) and dried *in vacuo* (158 mg, 0.179 mmol, 48%). Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **15** in dichloromethane. IR (KBr): $\tilde{\nu}$ = 3434 (br), 2966 (w), 2917 (w), 1643 (m), 1611 (s), 1586 (s), 1518 (s), 1461 (s), 1386 (m), 1330 (w), 1288 (m), 1267 (w), 1223 (w), 1197 (m), 1090 (s), 975 (s), 896 (w), 861 (w), 812 (m), 755 (w), 713 (w), 682 (w), 634 (w), 564 (w). Elemental analysis: calcd for $C_{36}H_{14}BF_{20}OP$: C 48.90, H 1.60; found: C 48.21, H 1.84. Mp: 165 °C (DSC). ^1H NMR (600 MHz, 299 K, C_6D_6) : δ = 8.20 (d, $^3J_{HH}$ = 8.6 Hz, 1H, CHO), 6.96 (m, 1H, *p*-Ph), 6.82 (m, 2H, *m*-Ph), 6.76 (m, 2H, *o*-Ph), 6.72 (d, $^3J_{HH}$ = 15.5 Hz, 1H, ^{Ph}CH), 6.56 (dd, $^3J_{HH}$ = 15.5 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, ^{CHO}CH), 3.54 (m, 1H, ^{P}CH), 1.73/1.60 (each m, each 1H, $^{B}CH_2$), 1.28 (dd, $^3J_{PH}$ = 21.2 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, C_6D_6): δ = 193.8 (CHO), 166.7 (br, ^{Ph}CH), 135.2 (*p*-Ph), 132.6 (i-Ph), 131.2 (*o*-Ph), 129.4 (*m*-Ph), 123.3 (^{CHO}CH), 28.6 (br, $^{B}CH_2$), 25.9 (^{P}CH), 19.5 (d, $^2J_{PC}$ = 23.8 Hz, CH_3); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6): δ = 8.3 ($\nu_{1/2}$ ∼ 700 Hz). ^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = −129.3 (m, 2F, *o*-P^{A}), −129.8 (m, 2F, *o*-P^{B}), −133.2 (br, 4F, *o*-B), −148.6 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-P^{A}), −149.6 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^{B}), −155.7 (br, 2F, *p*-B), −160.2 (m, 4F, *m*-$P^{A,B}$), −162.6 (br, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 6.9 (B), 11.6 (P^{A}), 10.6 (P^{B})]. ^{19}F NMR (564 MHz, 248 K, CD_2Cl_2): δ = −129.0, −129.3 (each br, each 2F, *o*-P), −132.7, −135.3 (each m, each 2F, *o*-B), −148.7, −149.6 (each br, each 1F, *p*-P), −157.2 (t, $^3J_{FF}$ = 20.4 Hz, 1H, *p*-B), −158.9 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-B), −160.6 (br m, 4F, *m*-P), −163.7, −164.6 (each m, 2F, *m*-B). $^{31}P\{^1H\}$ NMR (243 MHz, 299 K, C_6D_6): δ = −34.8 (quin, $^3J_{PF}$ = 28.5 Hz).

X-ray crystal structure analysis of compound 15. Formula $C_{36}H_{14}BF_{20}OP$, M = 884.25, colourless crystals, 0.15 × 0.13 × 0.04 mm, a = 10.7451(3), b = 24.4031(8), c = 14.3508(6) Å, β = 110.583(2)°, V = 3522.8(2) Å^3, ρ_{calc} = 1.667 g cm^{-3}, μ = 1.979 mm^{-1}, empirical absorption correction (0.755 ≤ T ≤ 0.925), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 30 969 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 6115 independent (R_{int} = 0.049) and 4880 observed reflections [$I > 2\sigma(I)$], 534 refined parameters, R = 0.053, wR^2 = 0.144, max. (min.) residual electron density 0.33 (−0.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound 16. Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (250 mg, 0.62 mmol) and bis(pentafluorophenyl)borane (212.9 mg, 0.62 mmol) were dissolved in *n*-pentane (10 mL) and stirred for ten min before benzaldehyde (65.3 mg, 0.62 mmol) was added. A white solid precipitated. After stirring overnight the precipitate was isolated *via* filter cannula and the residue was dried *in vacuo* to give the product (392 mg, 0.457 mmol, 74%). Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **16** in dichloromethane at −30 °C. Exact mass: calcd for $C_{34}H_{12}BF_{20}OP + Na^+$: 881.03085 m/z; found: 881.03027 m/z. IR (KBr): $\tilde{\nu}$ = 3437 (br), 2981 (w), 2935 (w), 1644 (s), 1598 (m), 1576 (m), 1524 (s), 1483 (s), 1463 (s), 1394 (m), 1307 (m), 1279 (m), 1230 (w), 1178 (w), 1103 (s), 1010 (m), 984 (s), 921 (m), 849 (w), 792 (m), 766 (w), 728 (w), 701 (m), 680 (m), 643 (w), 568 (w), 511 (w). Elemental analysis: calcd for $C_{34}H_{12}BF_{20}OP$: C 47.58, H 1.41; found: C 47.38, H 1.04. Mp: 149 °C (DSC); Dp: 220 °C (DSC). ^1H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.82 (br s, 1H, ^{O}CH), 7.68 (m, 2H, *o*-Ph), 7.64 (m, 1H, *p*-Ph), 7.48 (m, 2H, *m*-Ph), 3.50 (m, 1H, ^{P}CH), 1.66

(ddd, $^3J_{PH}$ = 30.5 Hz, J_{HH} = 15.5 Hz, J_{HH} = 7.4 Hz), 1.43 (m) (each 1H, $^{B}CH_2$), 1.24 (dd, $^3J_{PH}$ = 22.1 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2): δ = n.o. (^{O}CH), 135.4 (br, *p*-Ph), 133.3 (i-Ph), 130.3 (br, *o*-Ph), 129.9 (*m*-Ph), 120.5 (br, i-$C_6F_5^{B}$), 101.1, 100.8 (each br, i-$C_6F_5^{P}$), 28.6 (br d, $^1J_{PC}$ = 13.3 Hz, ^{P}CH), 25.3 (br, $^{B}CH_2$), 19.1 (d, $^2J_{PC}$ = 7.1 Hz, CH_3); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ = 4.6 ($\nu_{1/2}$ ~ 350 Hz). ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −125.7 (m, 2F, *o*-P^A), −126.9 (m, 2F, *o*-P^B), −134.6 (br, 4F, *o*-B), −143.9 (br, 1F, *p*-P^A), −144.1 (br, 1F, *p*-P^B), −158.0 (m, 2F, *m*-P^A), −158.7 (m, 2F, *m*-P^B), −159.4 (br, 2F, *p*-B), −164.9 (br, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 5.5 (B), 14.1 (P^A), 14.3 (P^B)]. $^{31}P\{^1H\}$ NMR (243 MHz, 299 K, CD_2Cl_2): δ = −5.9 ($\nu_{1/2}$ ~ 70 Hz) [for NMR data at lower temperature see the ESI†].

Preparation of compound 17. Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (100 mg, 0.246 mmol) and bis(pentafluorophenyl)borane (85.3 mg, 0.246 mmol) were dissolved in *n*-pentane (5 mL) and after stirring for five min the reaction mixture turned cloudy. *p*-Tolylacetylene (28.6 mg, 0.246 mmol) was added to the solution which turned orange immediately and after one hour a white solid precipitated. The white solid was isolated *via* filter cannula, washed with *n*-pentane (5 mL) and dried *in vacuo* (114 mg, 0.13 mmol, 52%). Exact mass: calcd for $C_{36}H_{14}BF_{20}P + Na^+$: 891.05052 *m*/*z*; found: 891.05089 *m*/*z*. IR (KBr): $\tilde{\nu}$ = 2960 (w), 1936 (w), 1644 (m), 1525 (s), 1484 (s), 1460 (s), 1395 (m), 1306 (m), 1267 (m), 1111 (s), 1083 (s), 985 (s), 966 (s), 891 (w), 862 (w), 816 (m), 779 (w), 738 (w), 694 (m), 674 (w), 636 (w), 593 (w), 571 (w), 526 (w). Elemental analysis: calcd for $C_{36}H_{14}BF_{20}P$: C 49.80, H 1.63; found: C 49.40, H 1.48. Mp: 216 °C (DSC). ^1H NMR (500 MHz, 299 K, C_6D_6): δ = 8.92 (d, $^3J_{PH}$ = 64.1 Hz, 1H, =CH), 6.84 (m, 2H, *o*-tol), 6.69 (m, 2H, *m*-tol), 3.47 (m, 1H, ^{P}CH), 1.99 (dd, $^3J_{PH}$ = 43.9 Hz, $^3J_{HH}$ = 15.6 Hz, 1H, $^{B}CH_2$), 1.84 (s, 3H, *p*-CH_3^{tol}), 1.57 (m, 1H, $^{B}CH_2$), 0.93 (dd, $^3J_{PH}$ = 22.8 Hz, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, C_6D_6): δ = 187.9 (br, =CH), 139.2 (d, $^5J_{PC}$ = 2.1 Hz, *p*-tol), 134.9 (d, $^2J_{PC}$ = 13.7 Hz, i-tol), 129.7 (d, $^4J_{PC}$ = 1.1 Hz, *m*-tol), 127.8 (*o*-tol), 116.9 (d, $^1J_{PC}$ = 71.0 Hz, $=C^{tol}$), 31.7 (d, $^1J_{PC}$ = 39.1 Hz, ^{P}CH), 23.8 (br, $^{B}CH_2$), 20.8 (*p*-CH_3^{tol}), 18.1 (br, CH_3). $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6): δ = −14.6 ($\nu_{1/2}$ ~ 50 Hz). ^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = −126.1, −127.1 (each br, each 2F, *o*-P), −132.8 (m, 2F, *o*-B^A), −133.9 (m, 2F, *o*-B^B), −135.2, −138.3 (each m, each 1F, *p*-P), −155.8, −156.1 (each m, each 2F, *m*-P), −159.2 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-B^A), −159.9 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-B^B), −163.8 (m, 2F, *m*-B^A), −164.4 (m, 2F, *m*-B^B); [$\Delta\delta^{19}F_{p,m}$: 4.6 (B^A), 4.5 (B^B), 17.5–20.9 (P)]. $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, C_6D_6): δ = 10.2 ($\nu_{1/2}$ ~ 35 Hz).

Preparation of compound 18. Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (120 mg, 0.295 mmol) and bis(pentafluorophenyl)borane (102.2 mg, 0.295 mmol) were dissolved in *n*-pentane (5 mL) and stirred for 15 min at rt to give a cloudy solution. 2-Methylbut-1-en-3-yne (19.5 mg, 0.295 mmol) was added and the reaction mixture was stirred for 90 min at rt. The white precipitate was isolated from the yellow solution by filter cannula. The residue was washed with *n*-pentane (2 × 10 mL) and then dried *in vacuo* to give a white solid (127 mg, 0.154 mmol, 52%). Crystals of **18** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product mixture in dichloromethane at −30 °C. ^1H NMR (600 MHz, 299 K, C_7D_8): δ = 8.66 (d, $^3J_{PH}$ = 65.9 Hz, 1H, $=CH^B$), 4.55 (m, 1H, $=CH_2$), 4.35 (m, 1H, $=CH_2$), 3.26 (m, 1H, ^{P}CH), 1.76 (dd, $^3J_{PH}$ = 42.6 Hz, $^3J_{HH}$ = 15.5 Hz, 1H, $^{B}CH_2$), 1.53 (s, 3H, $=CH_3$), 1.24 (br m, 1H, $^{B}CH_2$), 0.93 (dm, $^3J_{PH}$ = 22.8 Hz, $^{CH}CH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, C_7D_8): δ = 185.0 (br, $=CH^B$), 142.5 (d, $^2J_{PC}$ = 12.5 Hz, $^{CH3}C=$), 117.9 (d, $^1J_{PC}$ = 71.0 Hz, $^{P}C=$), 114.5 (d, $^3J_{PC}$ = 5.8 Hz, $=CH_2$), 31.7 (d, $^1J_{PC}$ = 41.1 Hz, ^{P}CH), 23.6 (br, $^{B}CH_2$), 22.8 (d, $^3J_{PC}$ = 4.2 Hz, $=CH_3$), 18.2 ($^{CH}CH_3$); [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_7D_8): δ = −14.8 ($\nu_{1/2}$ ~ 50 Hz). ^{19}F NMR (564 MHz, 299 K, C_7D_8): δ = −125.8 (br, 2F, *o*-P^A), −127.2 (br, 2F, *o*-P^B), −133.2 (m, 2F, *o*-B^A), −133.9 (m, 2F, *o*-B^B), −136.4 (m, 1F, *p*-P^A), −138.7 (m, 1F, *p*-P^B), −156.1 (m, 2F, *m*-P^B), −156.3 (m, 2F, *m*-P^A), −160.0 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-B^A), −160.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-B^B), −164.3 (m, 2F, *m*-B^A), −164.8 (m, 2F, *m*-B^B); [$\Delta\delta^{19}F_{p,m}$: 4.3 (B^A), 4.3 (B^B), 20.0 (P^A), 17.4 (P^B)]. $^{31}P\{^1H\}$ NMR (243 MHz, 299 K, C_7D_8): δ = 8.8 ($\nu_{1/2}$ ~ 40 Hz).

X-ray crystal structure analysis of compound 18. Formula $C_{32}H_{12}BF_{20}P$, M = 818.20, colourless crystals, 0.20 × 0.05 × 0.04 mm, a = 12.6350(4), b = 18.8200(7), c = 12.7955(4) Å, β = 99.880(3)°, V = 2997.53(17) Å^3, ρ_{calc} = 1.813 g cm^{-3}, μ = 2.237 mm^{-1}, empirical absorption correction (0.663 ≤ T ≤ 0.915), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 25 276 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 5175 independent (R_{int} = 0.043) and 4252 observed reflections [$I > 2\sigma(I)$], 497 refined parameters, R = 0.041, wR^2 = 0.105, max. (min.) residual electron density 0.21 (−0.26) e Å^{-3}, the hydrogen atoms at C7 were refined freely, others were calculated and refined as riding atoms.

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