

Addition reactions to the intramolecular mesityl₂P–CH₂–CH₂–B(C₆F₅)₂ frustrated Lewis pair†

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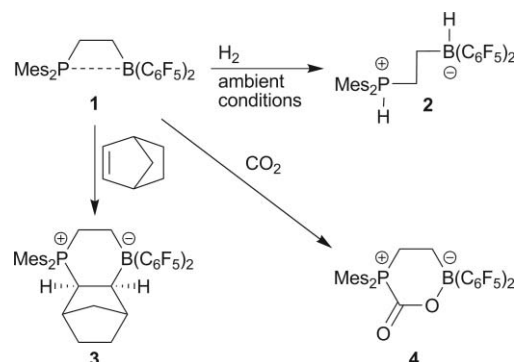
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Hydroboration of dimesitylvinyphosphine with Piers' borane [HB(C₆F₅)₂] gives the ethylene-bridged intramolecular frustrated P/B Lewis pair **1**. It adds pyridine, *tert*-butyl isocyanide or pivalonitrile to the strongly electrophilic boron center to yield the respective adducts **5–7**. Compound **1** undergoes a 1,1-phosphine/borane addition to the terminal nitrogen center of phenyl azide to yield the five-membered heterocycle **8**, featuring a pendant –N=N–Ph. This can be regarded as a boron-stabilized intermediate of a Staudinger reaction. Benzaldehyde and phenyl isocyanate undergo 1,2-P/B additions of **1** to their reactive carbonyl groups to yield the corresponding six-membered heterocycles **9** and **10**, respectively. The P/B Lewis pair reacts with nitrosobenzene by 1,2-addition to the –N=O unit under P–N and O–B bond formation to give the six-membered heterocycle **11**. The compounds **5–11** were characterized by X-ray crystal structure analyses.

Introduction

Lewis acids and Lewis bases usually quench each other when brought together in solution. However, in cases of sufficient steric bulk this neutralization reaction may become completely or at least sufficiently hindered that the typical chemical features of both components prevail in the same solution. Such frustrated Lewis pairs^{1,2} may exhibit separately the typical Lewis acid and Lewis base reactivities of their "antagonistic"³ components.^{4,5} However, they may in some cases also work together and *e.g.* activate or add to various small molecules in concert and/or cooperatively. Typical examples include the heterolytic dihydrogen splitting activity of a variety of bulky phosphine/B(C₆F₅)₃^{1,2,6–9} or bulky amine¹⁰ or carbene/B(C₆F₅)₃ Lewis pairs.^{11,12} We have recently described the ethylene-linked P/B system **1**.¹³ It was characterized as a weakly interacting frustrated Lewis pair. According to a characterization including an advanced DFT calculation it features a four-membered heterocyclic global minimum structure. The activation barrier of reversible P...B dissociation was determined for a series of suitably substituted derivatives as Δ*G*[‡](280 K) ≈ 12 kcal mol^{–1}.¹⁴ The system reacts with a variety of small molecules probably from a *gauche* like open local minimum intermediate.⁹ It is currently one of the most active systems of its kind for heterolytic H₂-activation (to give **2**) and subsequently for the metal-free catalytic hydrogenation of enamines and of bulky imines.^{15,16} It adds (probably concertedly) to olefins, to conjugated enynes and alkynes¹⁷ and even to carbon dioxide¹⁸ (see Scheme 1).

We here wish to report about addition reactions of a variety of organic substrates to the Lewis pair **1** which serve to further characterize the reactivity and the favoured reaction patterns of this



Scheme 1 Activation of H₂, CO₂ and norbornene by the Lewis pair **1**.

unique system. This study includes reactions with monofunctional donors that preferentially attach to the electrophilic boron center and bifunctional reagents that have a choice to also undergo the cooperative P/B addition.

Results and discussion

Preferred addition reactions to the boron center

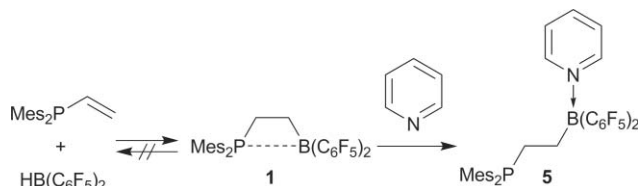
The intramolecular P/B Lewis pair **1** was prepared by treatment of dimesitylvinyphosphine with "Piers' borane" [HB(C₆F₅)₂].¹⁹ At ambient temperature a clean regioselective hydroboration reaction²⁰ was observed to give **1**. We were concerned that the system **1** might possibly undergo retrohydroboration when treated with additional reagents. Therefore, this was checked by treatment of **1** with pyridine, a reagent that would have indicated any reversibly of the formation of **1** by trapping of the HB(C₆F₅)₂ component by pyridine–[HB(C₆F₅)₂] adduct formation.²¹ However, this was not observed. Treatment of **1** with pyridine in a 1:1 molar ratio in pentane at room temperature overnight resulted in a colourless precipitate of the **1**–pyridine adduct (**5**) that was eventually isolated as a solid in 65% yield (see Scheme 2). The compound was characterized by elemental analysis, spectroscopically (NMR spectra in d₆-benzene, Table 1) and by X-ray

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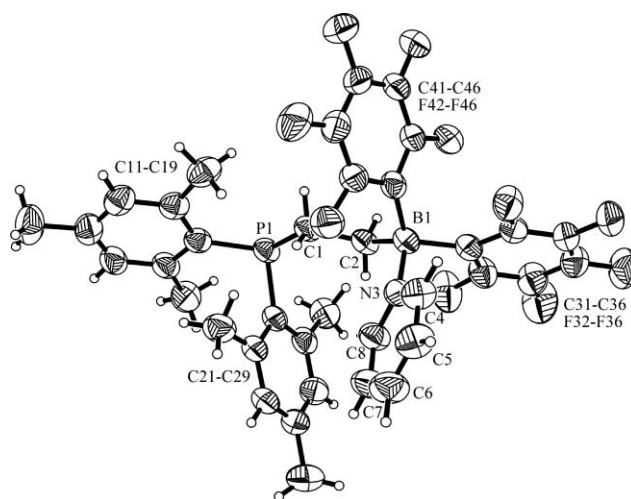
Table 1 Selected NMR features (δ) of compound **1** and its adducts **5–11**

Compound	^{31}P	^{13}C		^{11}B	^{19}F		
		PCH_2	BCH_2		<i>o</i>	<i>p</i>	<i>m</i>
1	+20.6	29.4	18.2	+8.8	−128.4	−157.0	−163.6
5	−16.1	24.4	20.0	−0.2	−131.9	−157.4	−163.1
6	−16.7	26.7	17.9	−18	−133.0	−157.5	−163.3
7	−16.4	25.1	19.6	−1.2	−134.7	−157.6	−163.5
8	+50	31.2	18.2	−5.4	−132.7	−162.1	−166.3
9	+19.6	28.9	13.8	−0.3	−134.7	−162.5	−166.4
					−134.7	−161.4	−165.6
10	+5.1	26.6	14.4	+0.7	−134.2	−159.2	−164.2
11	+46.9	28.1	15.4	+0.4	−133.1	−161.9	−165.5

**Scheme 2** Formation of the pyridine adduct **5**.

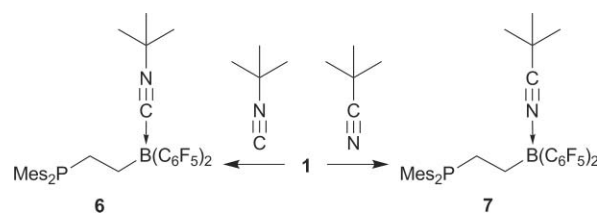
diffraction. Single crystals for the X-ray crystal structure analysis were obtained by slow diffusion of heptane vapor into a solution of compound **5** in benzene. The structure shows that the pyridine has added to the boron center (see Fig. 1 and Table 2). Compound **5** consequently contains a tetracoordinated boron and a non-planar tricoordinated phosphorus atom (sum of C–P–C bonding angles 312.5°). In the crystal the group of aromatic rings around boron adopts a propeller-like geometry. The P–CH₂–CH₂–B unit shows a slight distortion from an *anti*-periplanar arrangement.

The ^1H NMR spectrum of compound **5** shows the typical resonances of the pair of symmetry-equivalent mesityl groups at phosphorus [δ 6.67 (d, $^4J_{\text{PH}} = 2.1$ Hz *m*-CH), δ 2.37 (*o*-CH₃), 2.07 (*p*-CH₃); ^{31}P resonance at δ −16.1] and the typical ^1H NMR signals of the ethylene linker [δ 2.35 (PCH₂), δ 1.62 (BCH₂)]. The ^{11}B NMR resonance of **5** is found at δ −0.2, which is typical of a four-coordinate boron center with such substituents. This is supported by the observed small $\Delta m,p$ difference (5.7 ppm) of the ^{19}F NMR C₆F₅ resonances.²² The $^1\text{H}/^{13}\text{C}$ NMR signals of the coordinated

**Fig. 1** Molecular structure of the pyridine adduct **5**.

pyridine moiety were monitored at δ 7.99 (*o*), 6.56 (*p*), 6.26 (*m*) (^1H)/ δ 145.3 (*o*), 140.6 (*p*), and 125.3 (*m*) (^{13}C).

Compound **1** formed an adduct (**6**) with *tert*-butyl isocyanide as expected (see Scheme 3). The addition product of the isonitrile nucleophile to the electrophilic borane subunit of **1** was isolated as a colourless solid in >70% yield from the reaction mixture. It features a ^{13}C NMR signal of the coordinated isonitrile carbon center at δ 127.8 and a strong IR (C≡N−) band at $\tilde{\nu} = 2287\text{ cm}^{-1}$. The X-ray crystal structure analysis of compound **6** (see Fig. 2, Table 2) features a linear [B]–C≡N–*t*-Bu moiety with typical bonding parameters of B1–C3: 1.622(4) Å, C3–N4: 1.138(3) Å,

**Scheme 3** Formation of the isonitrile and nitrile adducts **6** and **7**.**Table 2** Selected structural data of the adducts **5–11**

Compound	5	6	7	8	9	10	11
Bond lengths (Å)							
P–CH ₂	1.862(2)	1.861(3)	1.861(3)	1.821(2)	1.833(3)	1.815(3)	1.821(4)
CH ₂ –CH ₂	1.539(3)	1.541(3)	1.526(5)	1.545(3)	1.543(3)	1.539(4)	1.534(5)
CH ₂ –B	1.627(3)	1.630(4)	1.619(5)	1.648(3)	1.624(4)	1.609(4)	1.623(6)
B–X	1.645(3)	1.622(4)	1.588(5)	1.590(2)	1.497(3)	1.527(3)	1.509(5)
P–Y	—	—	—	1.662(2)	1.919(2)	1.855(3)	1.656(3)
Bond angles (°)							
P–CH ₂ –CH ₂	109.9(2)	110.7(2)	108.7(2)	108.6(1)	110.7(2)	106.7(2)	115.9(3)
CH ₂ –CH ₂ –B	114.6(2)	112.2(2)	116.8(3)	113.2(2)	113.6(2)	110.9(2)	114.0(3)
CH ₂ –B–X	110.9(2)	104.9(2)	102.3(3)	102.1(2)	108.3(2)	110.2(2)	109.0(3)
CH ₂ –P–Y	—	—	—	96.5(1)	97.3(1)	102.9(1)	100.7(2)
Dihedral angles (°)							
P–CH ₂ –CH ₂ –B	−162.7(2)	−154.0(2)	169.8(2)	−10.0(2)	60.3(2)	−71.9(3)	45.8(4)
CH ₂ –CH ₂ –B–X	73.7(2)	−50.7(3)	−66.5(4)	7.6(2)	−58.9(3)	58.9(3)	−17.5(5)
CH ₂ –CH ₂ –P–Y	—	—	—	7.6(1)	−52.1(2)	47.1(2)	−12.1(3)

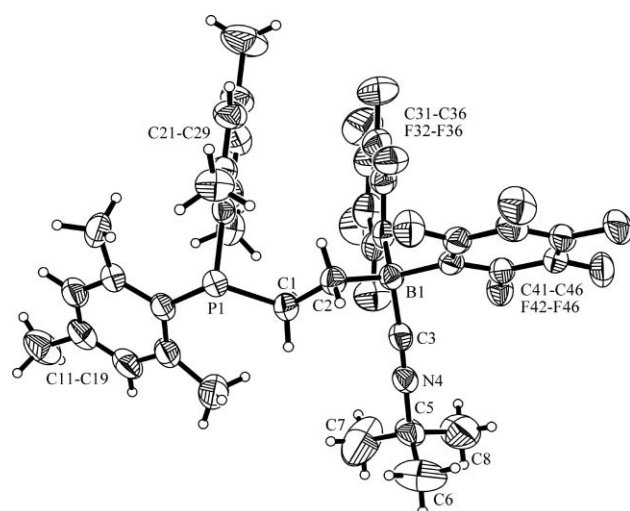


Fig. 2 A view of the molecular structure of the isonitrile adduct 6.

N4–C5: 1.468(3) Å, angles B1–C3–N4: 174.8(3)° and C3–N4–C5: 175.3(3)°.

The reaction of **1** with pivalonitrile could principally have had a remote chance to lead to 1,2-addition of the P/B pair across the $\text{C}\equiv\text{N}$ triple bond. However, we only observed nitrile coordination to the boron atom as expected. The adduct **7** (see Scheme 3) was isolated in *ca.* 60% yield from the reaction mixture (pentane, r.t., overnight). The product **7** was characterized spectroscopically [^{13}C NMR: δ 121.1 ([B]– $\text{N}\equiv\text{C}$ – (for additional data, see Table 1)]. The IR band of the coordinated nitrile [**7**: $\tilde{\nu}$ = 2329 cm^{-1} , *cf.* free $\text{t-Bu-C}\equiv\text{N}$: $\tilde{\nu}$ = 2235 cm^{-1}] is shifted to higher wavenumbers as it is typically observed for strong Lewis-acid adducts.²³

The X-ray crystal structure analysis of **7** shows an open almost *anti*-periplanar [P]– CH_2 – CH_2 –[B] framework (see Table 2 and Fig. 3) with a typical non-planar tricoordinate phosphorus atom and tetracoordinated boron atom. The [B]– $\text{N}\equiv\text{C}$ – t-Bu unit is linear [B1–N1: 1.588(5) Å, angles B1–N1–C3: 173.7(3)°, N1–C3–C4: 178.7(4)°]. The N1–C3 bond is short at 1.136(4) Å.

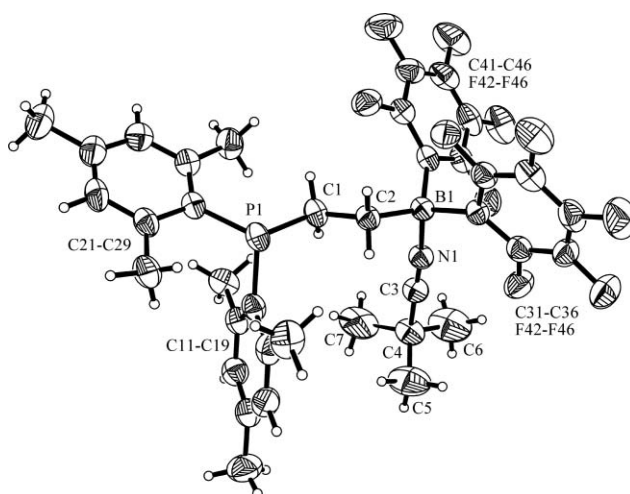
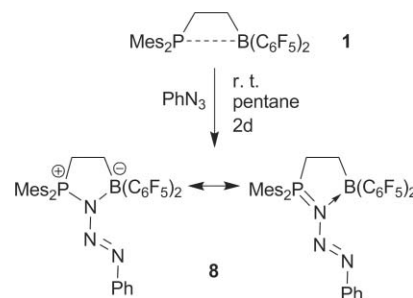


Fig. 3 A view of the molecular structure of the nitrile adduct 7.

Addition to both the P and B components of the Lewis pair

The P/B Lewis pair **1** reacts with phenyl azide to give the five-membered heterocyclic product **8** (see Scheme 4), which was isolated in 77% yield from the respective reaction mixture. The X-ray crystal structure analysis (single crystals were obtained from benzene–heptane by the diffusion method) shows that both the phosphorus and the boron atom have become bonded to the terminal nitrogen atom of the azide reagent (see Fig. 4). The resulting P1–N3 bond length amounts to 1.662(2) Å, the adjacent B1–N3 bond length was found at 1.590(2) Å (angle P1–N3–B1 118.7(1)°). The N3–N4 bond length is 1.374(2) Å; the adjacent N4–N5 bond is much shorter (1.254(2) Å), being in the $\text{N}=\text{N}$ double bond range. The $\text{N}=\text{N}$ unit is *trans*-configured (angles N3–N4–N5: 112.4(1)°, N4–N5–C51: 111.8(2)°).



Scheme 4 Reaction of the Lewis pair **1** with phenyl azide.

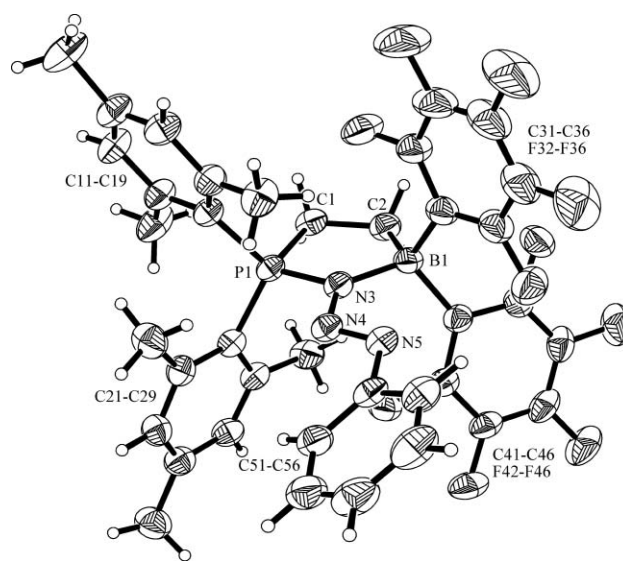
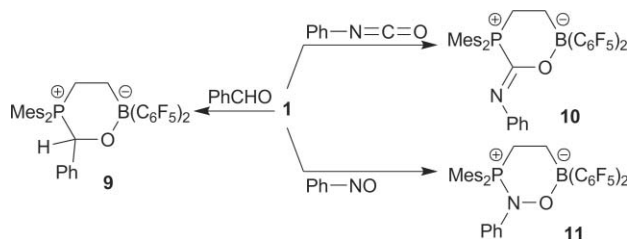


Fig. 4 Molecular structure of compound **8**.

The structure of the phenyl azide addition product **8** can be regarded as an internally boron stabilized intermediate of the Staudinger reaction.^{24–26} It actually may be due to the N–B coordination that the usual course toward the formation of the [P]=NPh phosphine-imine product is not completed in this case. In solution the system **8** shows dynamic ^{31}P NMR spectra. A broad resonance [δ = +50 ($\nu_{1/2}$ ~ 1600 Hz)] observed at ambient temperature decoalesces upon cooling to eventually split into an 1 : 2.3 intensity pair of resonances at δ +37.0 and +58.8 (223 K).

(for details see ESI†). The structure of the two isomers observed in solution still have to be resolved.²⁶

We next reacted the P/B Lewis pair **1** with benzaldehyde. The reaction in pentane rapidly goes to completion at ambient temperature. The product **9** (see Scheme 5) precipitated from the reaction mixture. It was isolated as a white solid in *ca.* 85% yield. Single crystals of **9** suited for the X-ray crystal structure analysis were obtained from benzene/heptane by the diffusion method. The structure (see Fig. 5) shows that the phosphorus atom of **1** has added to the carbonyl carbon atom of the benzaldehyde reagent (P1–C3: 1.919(2) Å, angle P1–C3–O1: 111.3(2)°) and the former carbonyl oxygen was bonded to the boron atom (B1–O1: 1.497(3) Å, angle B1–O1–C3: 117.3(2)°). The resulting six-membered heterocycle shows a distorted chair-like conformation¹⁷ (dihedral angles P1–C3–O1–B1: –66.8(2)°, C1–P1–C3–O1: 55.0(2)°, C2–B1–O1–C3: 64.4(3)°). The phenyl substituent at the ring carbon atom C3 is found in a pseudo-equatorial position.



Scheme 5 Treatment of the Lewis pair **1** with PhCHO, PhNCO and PhNO.

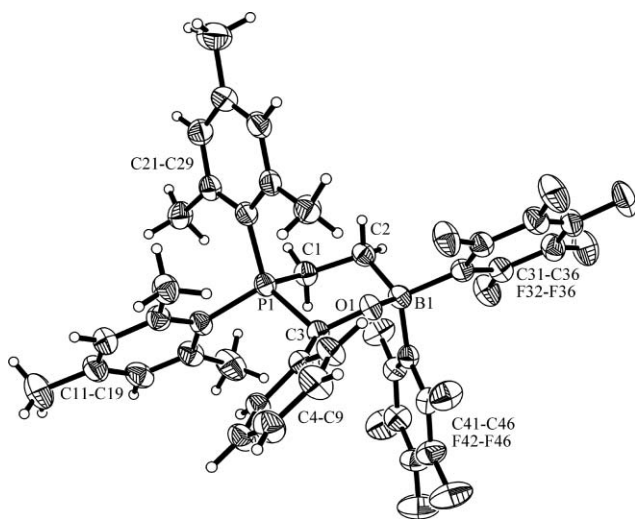


Fig. 5 A Projection of the molecular structure of compound **9**.

Due to the presence of the newly formed chiral center (C3) inside the six-membered heterocycle we observe a total of four separate ¹H NMR resonances of the bridging –CH₂–CH₂– moiety [PCH₂: δ 3.30, 3.15; BCH₂: δ 1.70, 1.09].

As expected, the phosphorus atom bears a pair of diastereotopic mesityl substituents and the boron atom a pair of diastereotopic C₆F₅ substituents (see Table 1 for details). The ³¹P NMR chemical shift of **9** is found in the typical phosphonium range (δ +19.6) and the ¹¹B NMR shift is of a borate type (δ –0.3). The former

benzaldehyde –CH(Ph) unit gives rise to ¹H/¹³C NMR signals at δ 6.23 (1H, d, ²J_{PH} = 15.3 Hz) and δ 85.5 (d, ¹J_{PC} = 29.6 Hz), respectively. The reaction of **1** with phenyl isocyanate takes a similar course.²⁷ The P/B Lewis pair undergoes a regioselective 1,2-addition to the reactive carbonyl group of the heterocumulene reagent to yield **10** (78% isolated, see Scheme 5).

The ¹⁹F NMR spectrum of **10** shows a single set of C₆F₅ resonances (see Table 1) and the ¹H/¹³C NMR spectra feature single sets of signals of the symmetry-equivalent mesityl substituents at phosphorus. The C=NPh imino ¹³C NMR signal of **10** is found at δ 149.1 (d, ¹J_{PC} = 127 Hz).

Single crystals of compound **10** were obtained from dichloromethane. The X-ray crystal structure analysis of **10** shows that 1,2-P/B addition to the isocyanate C=O functionality has resulted in the formation of a six-membered heterocycle (see Fig. 6). It features a C(sp²)–O single bond (C3–O1: 1.313(3) Å, angle C3–O1–B1: 128.8(2)°). The exocyclic imino-functionality (C3–N1: 1.271(3) Å, angles P1–C3–N1: 112.7(2)°, P1–C3–O1: 121.1(2)°, O1–C3–N1: 126.3(2)°) is *E*-configured (dihedral angles P1–C3–N1–C4: 180.0(2)°, O1–C3–N1–C4: 0.7(4)°). The six-membered ring framework of compound **10** features a distorted half-chair like conformation.

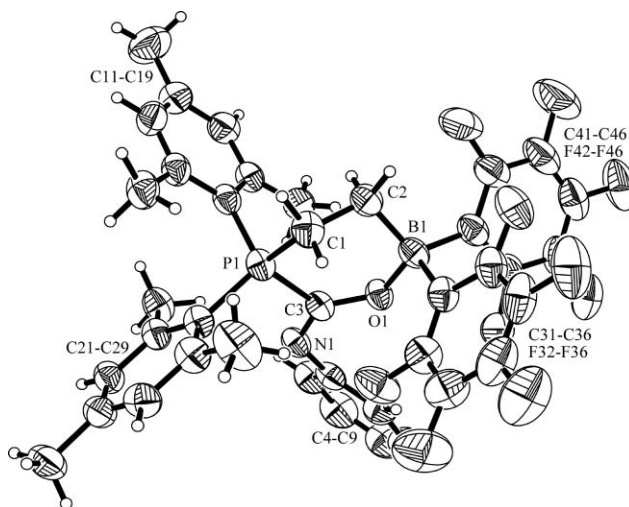


Fig. 6 A view of the molecular structure of compound **10**.

Eventually, we treated the P/B Lewis pair with nitrosobenzene. The reaction proceeds as a 1,2-addition between the phosphine/borane Lewis base/Lewis acid pair with the –N=O π-bond of the reagent to give the six-membered heterocyclic product (**11**). The new compound was isolated in *ca.* 50% yield from the reaction mixture in pentane. Single crystals for the X-ray crystal structure analysis were obtained by diffusion of pentane vapor into a solution of **11** in dichloromethane. The structure determination (see Fig. 7) revealed that P–N and B–O bond formation had taken place (P1–N4: 1.656(3) Å, O3–B1: 1.509(5) Å, angles P1–N4–O3: 106.6(2)°, N4–O3–B1: 110.9(3)°). The coordination geometry at the ring-nitrogen atom N4 is slightly deviating from trigonal planarity (sum of bond angles at N4: 352.7°).

The ³¹P NMR spectrum of **11** shows a signal at δ 46.9; the ¹¹B NMR feature occurs at δ 0.4.

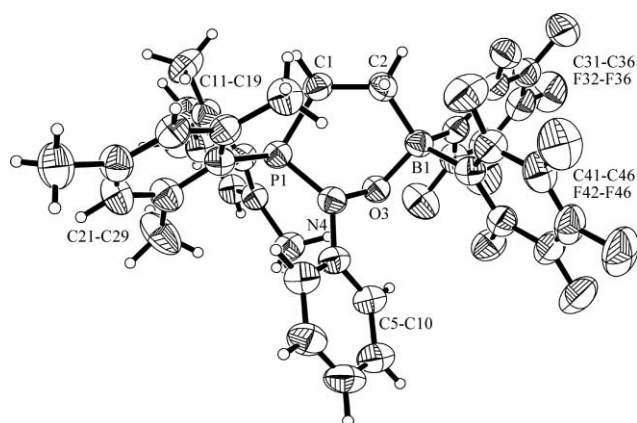
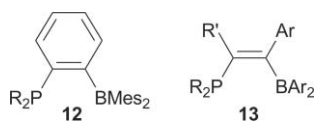


Fig. 7 Molecular structure of the addition product **11** of the Lewis pair **1** to nitrosobenzene.

Conclusions

An increasing amount of addition reactions to frustrated Lewis pairs is currently appearing from the literature.²⁸ Among them the addition reactions to unsaturated substrates may gain an increasing importance, since in some cases this might eventually lead to the discovery of novel activation pathways for such substrates. Previously there have been reports of *e.g.* isocyanate, carbonyl or azide addition reactions to P/B-Lewis pairs such as *e.g.* **12** or **13** (and derivatives thereof).^{4,5,26,27,29} Although the addition modes were similar to the previously reported systems containing configurationally fixed phosphine/borane pairs (see Scheme 6), our new system (**1**) is special in two ways: it contains a very strongly Lewis acidic $-\text{B}(\text{C}_6\text{F}_5)_2$ moiety and it probably reacts from a conformationally non-restricted reactive open intermediate. Nevertheless, the addition reactions of **1** to a large variety of π -substrates seem to be unproblematic and occur readily. This lets us hope that extensions of this work will eventually result in synthetically useful variants of such easily performed addition chemistry of frustrated Lewis pairs.



Scheme 6 Related phosphine/borane linked systems.

Experimental

General considerations

All manipulations were performed under argon using Schlenk-type glassware or in a glove-box. Solvents were dried according to the procedure by Grubbs³⁰ or were distilled from appropriate drying agents and stored under an argon atmosphere.

Melting points were obtained with a DSC Q20 (TA Instruments). IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series). Elemental analyses were performed on a Elementar Vario El III. NMR spectra were recorded on a Bruker AC 200 P (¹H: 64.0 MHz, ³¹P NMR: 81.0 MHz), Bruker ARX 300 (¹⁹F: 282.4 MHz); Varian Inova 500 (¹H: 499.9 MHz, ¹³C: 125.7 MHz, ¹⁹F: 470.3 MHz, ¹¹B: 160.4 MHz, ³¹P: 202.3 MHz)

and on a Varian UnityPlus 600 (¹H: 599.9 MHz, ¹³C: 150.8 MHz, ¹⁹F: 564.4 MHz, ¹¹B: 192.4 MHz, ³¹P: 242.7 MHz). ¹H NMR and ¹³C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ¹⁹F NMR: chemical shifts δ are given relative to CFCl_3 (external reference), ¹¹B NMR: chemical shifts δ are given relative to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (external reference), ³¹P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in H_2O) (external reference). NMR assignments were supported by additional 2D NMR experiments.

X-Ray structure analyses. Data sets were collected with Nonius KappaCCD diffractometers, in case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection: COLLECT,³¹ data reduction: Denzo-SMN,³² absorption correction: Denzo,³³ structure solution: SHELXS-97,³⁴ structure refinement: SHELXL-97,³⁵ graphics: XP (BrukerAXS, 2000). Thermal ellipsoids are shown on the 50% probability level.

Compound 5. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (8 mL) and stirred for 15 min. Upon addition of pyridine (27 μL , 0.34 mmol) the solution became immediately colourless, and within 2 h a white precipitate was formed. After stirring the reaction mixture overnight, the precipitate was isolated *via* cannula filtration. Then the residue was washed with pentane ($3 \times 3 \text{ mL}$) and all volatiles were removed *in vacuo* to yield **5** (159 mg, 65%) as a white powder. Crystals suitable for the X-ray crystal structure analysis were obtained by gas diffusion of heptane into a benzene solution of **5**. Found: C, 61.36; H, 4.49; N, 1.90. Calc. for $\text{C}_{37}\text{H}_{31}\text{BF}_{10}\text{NP}$: C, 61.60; H, 4.33; N, 1.94%. ¹H NMR (600 MHz, 298 K, benzene- d_6) δ 7.99 (2H, m, *o*-Py), 6.67 (4H, d, ⁴ J_{PH} = 2.1 Hz, *m*-Mes), 6.56 (1H, m, *p*-Py), 6.26 (2H, m, *m*-Py), 2.37 (12H, s, *o*-CH₃^{Mes}), 2.35 (2H, m, PCH₂), 2.07 (6H, s, *p*-CH₃^{Mes}), 1.62 (2H, m, BCH₂). ¹³C{¹H} NMR (151 MHz, 298 K, benzene- d_6) δ 148.3 (dm, ¹ J_{FC} = 238 Hz, C₆F₅), 145.3 (*o*-Py), 142.2 (d, ² J_{PC} = 12.8 Hz, *o*-Mes), 140.6 (*p*-Py), 139.8 (dm, ¹ J_{FC} = 247 Hz, C₆F₅), 137.4 (dm, ¹ J_{FC} = 248 Hz, C₆F₅), 137.4 (*p*-Mes), 134.4 (d, ¹ J_{PC} = 24.6 Hz, *i*-Mes), 130.3 (d, ³ J_{PC} = 2.6 Hz, *m*-Mes), 125.3 (*m*-Py), 24.4 (d, ¹ J_{PC} = 15.8 Hz, PCH₂), 121.9 (br, *i*-C₆F₅), 23.2 (d, ³ J_{PC} = 13.2 Hz, *o*-CH₃^{Mes}), 20.7 (*p*-CH₃^{Mes}), 20.0 (br, BCH₂). ¹¹B{¹H} NMR (64 MHz, 298 K, benzene- d_6) δ -0.2 ($\nu_{1/2}$ = 450 Hz). ³¹P{¹H} NMR (81 MHz, 298 K, benzene- d_6) δ -16.1 ($\nu_{1/2}$ = 6 Hz). ¹⁹F{¹H} NMR (282 MHz, 298 K, benzene- d_6) δ -131.9 (2F, *o*-C₆F₅), -157.4 (1F, *p*-C₆F₅), -163.1 (2F, *m*-C₆F₅).

Crystal data for $\text{C}_{37}\text{H}_{31}\text{BF}_{10}\text{NP}$ (**5**), $M = 721.41$, monoclinic, space group $P2_1/n$ (no. 14), $a = 16.1539(6)$, $b = 12.4332(4)$, $c = 17.1214(7)$ Å, $\beta = 95.333(2)^\circ$, $V = 3423.9(2)$ Å³, $D_c = 1.400 \text{ g cm}^{-3}$, $\mu = 1.451 \text{ mm}^{-1}$, $Z = 4$, $\lambda = 1.54178$ Å, $T = 223(2)$ K, 26661 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin \theta)/\lambda] = 0.60 \text{ Å}^{-1}$, 6016 independent ($R_{\text{int}} = 0.055$), and 4855 observed reflections [$I \geq 2\sigma(I)$], 457 refined parameters, $R = 0.047$, $wR^2 = 0.153$.

Compound 6. To a solution of dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) in pentane (5 mL) *tert*-butyl isocyanide (42 μL , 0.36 mmol) was added. The solution was immediately decolourized. It was then stirred for 2 days. Removal of all volatiles *in vacuo* yielded **6** (178 mg, 74%) as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained from a heptane solution at -36°C . $\tilde{\nu}(\text{KBr})/\text{cm}^{-1} = 2287$ (s, CN). Found: C, 60.96;

H, 4.79; N, 1.87. Calc. for $C_{37}H_{35}BF_{10}NP$: C, 61.26; H, 4.86; N, 1.93%. 1H NMR (600 MHz, 298 K, benzene- d_6) δ 6.68 (4H, d, $^4J_{PH} = 2.0$ Hz, *m*-Mes), 2.54 (2H, m, PCH_2), 2.41 (12H, s, *o*- CH_3^{Mes}), 2.08 (6H, s, *p*- CH_3^{Mes}), 1.62 (2H, br m, BCH_2), 0.75 (9H, s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (151 MHz, 298 K, benzene- d_6) δ 148.2 (dm, $^1J_{FC} = 246$ Hz, *o*- C_6F_5), 142.0 (d, $^2J_{PC} = 13$ Hz, *o*-Mes), 140.0 (dm, $^1J_{FC} = 250$ Hz, *p*- C_6F_5), 137.5 (dm, $^1J_{FC} = 250$ Hz, *m*- C_6F_5), 137.5 (*p*-Mes), 134.4 (d, $^1J_{PC} = 24.1$ Hz, *i*-Mes), 130.4 (*m*-Mes), 127.8 ($C\equiv N$), 117.4 (*i*- C_6F_5), 59.6 ($C(CH_3)_3$), 28.2 ($C(CH_3)_3$), 26.7 (d, $^1J_{PC} = 17.0$ Hz, PCH_2), 23.4 (d, $^3J_{PC} = 13.0$ Hz, *o*- CH_3^{Mes}), 20.8 (*p*- CH_3^{Mes}), 17.9 (br, BCH_2). $^{11}B\{^1H\}$ NMR (192 MHz, 298 K, benzene- d_6) δ -18 ($\nu_{1/2} = 230$ Hz). $^{31}P\{^1H\}$ NMR (121 MHz, 298 K, benzene- d_6) δ -16.7 ($\nu_{1/2} = 7$ Hz). $^{19}F\{^1H\}$ NMR (564 MHz, 298 K, benzene- d_6) δ -133.0 (2F, *o*- C_6F_5), -157.5 (1F, *p*- C_6F_5), -163.3 (2F, *m*- C_6F_5).

Crystal data for $C_{37}H_{35}BF_{10}NP$ (**6**), $M = 725.44$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.4592(4)$, $b = 13.2592(5)$, $c = 14.5233(7)$ Å, $\alpha = 99.281(2)$, $\beta = 99.394(2)$, $\gamma = 110.205(3)^\circ$, $V = 1812.55(13)$ Å³, $D_c = 1.329$ g cm⁻³, $\mu = 1.371$ mm⁻¹, $Z = 2$, $\lambda = 1.54178$ Å, $T = 223(2)$ K, 21458 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.60$ Å⁻¹, 6332 independent ($R_{int} = 0.047$), and 5367 observed reflections [$I \geq 2\sigma(I)$], 460 refined parameters, $R = 0.056$, $wR^2 = 0.164$.

Compound 7. Dimesitylvinylphosphine (80 mg, 0.27 mmol) and bis(pentafluorophenyl)borane (94 mg, 0.27 mmol) were dissolved in pentane (6 mL) and stirred for 15 min. Upon addition of pivalonitrile (28 μ L, 0.27 mmol) at room temperature the solution became immediately colourless. After stirring the reaction mixture for 3 h, a white powder started to precipitate. The reaction mixture was stirred overnight, then the precipitate was isolated *via* cannula filtration and washed with pentane (3 \times 2.5 mL). All volatiles were removed *in vacuo* to yield a white powder (118 mg, 60%). Crystals suitable for the X-ray crystal structure analysis were grown by slow diffusion of heptane into a benzene solution of **7**. $\tilde{\nu}(KBr)/cm^{-1} = 2329$ (s, CN). Found: C, 60.95; H, 4.83; N, 2.05. Calc. for $C_{37}H_{35}BF_{10}NP$: C, 61.26; H, 4.86; N, 1.93%. 1H NMR (600 MHz, 298 K, benzene- d_6) δ 6.69 (4H, d, $^4J_{PH} = 2.1$ Hz, *m*-Mes), 2.56 (2H, m, PCH_2), 2.42 (12H, s, *o*- CH_3^{Mes}), 2.08 (6H, s, *p*- CH_3^{Mes}), 1.56 (2H, m, BCH_2), 0.63 (9H, s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (151 MHz, 298 K, benzene- d_6) δ 148.1 (dm, $^1J_{FC} = 242$ Hz, C_6F_5), 142.0 (d, $^2J_{PC} = 12.8$ Hz, *o*-Mes), 139.8 (dm, $^1J_{FC} = 246$ Hz, C_6F_5), 137.5 (dm, $^1J_{FC} = 248$ Hz, C_6F_5), 137.4 (*p*-Mes), 134.4 (d, $^1J_{PC} = 24$ Hz, *i*-Mes), 130.3 (*m*-Mes), 121.0 ($C\equiv N$), 118.3 (br, *i*- C_6F_5), 28.6 (br, $C(CH_3)_3$), 25.9 (br, $C(CH_3)_3$), 25.1 (d, $^1J_{PC} = 16.0$ Hz, PCH_2), 23.3 (d, $^3J_{PC} = 12.9$ Hz, *o*- CH_3^{Mes}), 20.7 (*p*- CH_3^{Mes}), 19.6 (br, BCH_2). $^{11}B\{^1H\}$ NMR (192 MHz, 298 K, benzene- d_6) δ -1.2. $^{31}P\{^1H\}$ NMR (243 MHz, 298 K, benzene- d_6) δ -16.4 ($\nu_{1/2} = 50$ Hz). $^{19}F\{^1H\}$ NMR (564 MHz, 298 K, benzene- d_6) δ -134.7 (2F, *o*- C_6F_5), -157.6 (1F, *p*- C_6F_5), -163.5 (2F, *m*- C_6F_5).

Crystal data for $C_{37}H_{35}BF_{10}NP$ (**7**), $M = 725.44$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.5576(1)$, $b = 22.3280(3)$, $c = 16.9958(4)$ Å, $\beta = 104.650(1)^\circ$, $V = 3509.02(10)$ Å³, $D_c = 1.373$ g cm⁻³, $\mu = 0.159$ mm⁻¹, $Z = 4$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 20451 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.62$ Å⁻¹, 6989 independent ($R_{int} = 0.051$), and 5030 observed reflections [$I \geq 2\sigma(I)$], 491 refined parameters, $R = 0.074$, $wR^2 = 0.179$.

Compound 8. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (8 mL) and stirred for 15 min. After addition of phenyl azide (40 mg, 0.34 mmol) the reaction mixture became immediately cloudy. The reaction mixture was stirred for 2 days, then the precipitate was collected *via* cannula filtration and washed with pentane (3 \times 3 mL). All volatiles were removed *in vacuo* to yield **8** (201 mg, 77%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of heptane into a benzene solution of **8**. Found: C, 59.50; H, 4.10; N, 5.13. Calc. for $C_{38}H_{31}BF_{10}N_3P$: C, 59.94; H, 4.10; N, 5.52%. 1H NMR (500 MHz, 298 K, dichloromethane- d_2) δ 7.28 (2H, m, *m*-Ph), 7.26 (2H, m, *o*-Ph), 7.23 (1H, m, *p*-Ph), 6.95 (4H, d, $^4J_{PH} = 4.6$ Hz, *m*-Mes), 3.28 (2H, m, PCH_2), 2.31 (6H, s, *p*- CH_3^{Mes}), 2.15 (12H, s, *o*- CH_3^{Mes}), 1.78 (2H, m, BCH_2). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, dichloromethane- d_2) δ 149.2 (*i*-Ph), 148.0 (dm, $^1J_{FC} = 240$ Hz, C_6F_5), 143.8 (*p*-Mes), 142.2 (d, $^2J_{PC} = 11.0$ Hz, *o*-Mes), 139.0 (dm, $^1J_{FC} = 240$ Hz, C_6F_5), 137.2 (dm, $^1J_{FC} = 241$ Hz, C_6F_5), 132.2 (d, $^3J_{PC} = 11.8$ Hz, *m*-Mes), 131.4 (br, *i*- C_6F_5), 129.3 (*m*-Ph), 128.6 (*p*-Ph), 124.5 (d, $^1J_{PC} = 87.5$ Hz, *i*-Mes), 121.5 (*o*-Ph), 31.2 (d, $^1J_{PC} = 66.2$ Hz, PCH_2), 22.9 (d, $^3J_{PC} = 5.2$ Hz, *o*- CH_3^{Mes}), 21.1 (d, $^5J_{PC} = 1.5$ Hz, *p*- CH_3^{Mes}), 18.2 (br, BCH_2). $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, dichloromethane- d_2) δ -5.4 ($\nu_{1/2} = 210$ Hz). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, dichloromethane- d_2) δ +50 ($\nu_{1/2} \sim 1600$ Hz). ^{19}F NMR (470 MHz, 298 K, dichloromethane- d_2) [all resonances are broad] δ -132.7 (2F, *o*- C_6F_5), -162.1 (1F, *p*- C_6F_5), -166.3 (2F, *m*- C_6F_5).

Crystal data for $C_{38}H_{31}BF_{10}N_3P \cdot 2C_6H_6$ (**8**), $M = 917.65$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.8351(4)$, $b = 13.8395(4)$, $c = 21.6049(7)$ Å, $\beta = 109.595(1)^\circ$, $V = 4460.5(2)$ Å³, $D_c = 1.366$ g cm⁻³, $\mu = 1.250$ mm⁻¹, $Z = 4$, $\lambda = 1.54178$ Å, $T = 223(2)$ K, 43759 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda] = 0.60$ Å⁻¹, 7883 independent ($R_{int} = 0.053$), and 6856 observed reflections [$I \geq 2\sigma(I)$], 592 refined parameters, $R = 0.046$, $wR^2 = 0.132$.

Compound 9. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (8 mL) and stirred for 15 min. Upon addition of benzaldehyde (34 μ L, 0.34 mmol) the solution turned to colourless and after 1 h a white precipitate had formed. The precipitate was isolated *via* cannula filtration after 5 h, washed with pentane (2 \times 2 mL) and dried *in vacuo* to afford **9** (218 mg, 86%). Crystals suitable for X-ray diffraction were grown by slow diffusion of heptane into a benzene solution of **6**. Found: C, 62.29; H, 3.86. Calc. for $C_{39}H_{32}BF_{10}OP$: C, 62.59; H, 4.31%. 1H NMR (500 MHz, 298 K, dichloromethane- d_2) δ 7.22 (1H, m, *p*-Ph), 7.11 (2H, m, *m*-Ph), 7.06 (2H, m, *o*-Ph), 6.91, 6.85 (each 2H, each br, *m*-Mes), 6.23 (1H, d, $^2J_{PH} = 15.3$ Hz, CH), 3.30, 3.15 (each 1H, each m, PCH_2), 2.32, 2.24 (each 3H, each s, *p*- CH_3^{Mes}), 2.27, 1.97 (each 6H, each br, *o*- CH_3^{Mes}), 1.70, 1.09 (each 1H, each m, BCH_2). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, dichloromethane- d_2) δ 148.6 (dm, $^1J_{FC} = 240$ Hz, C_6F_5), 148.2 (dm, $^1J_{FC} = 243$ Hz, C_6F_5), 144.2, 143.4 (*p*-Mes), 142.7, 142.6 (each br, *o*-Mes), 139.0 (dm, $^1J_{FC} = 251$ Hz, $2 \times C_6F_5$), 137.2 (dm, $^1J_{FC} = 248$ Hz, $2 \times C_6F_5$), 137.1 (*i*-Ph), 132.5, 131.4 (each br d, each $^3J_{PC} = 10.2$ Hz, *m*-Mes), 128.8 (d, $^5J_{PC} = 3.8$ Hz, *p*-Ph), 127.9 (d, $^4J_{PC} = 4.7$ Hz, *m*-Ph), 127.7 (d, $^3J_{PC} = 3.2$ Hz, *o*-Ph), 123.1, 124.2 (each br, *i*- C_6F_5), 123.4 (d, $^1J_{PC} = 55.5$ Hz, *i*-Mes), 121.0 (d, $^1J_{PC} = 56.8$ Hz, *i*-Mes), 85.5 (d, $^1J_{PC} = 29.6$ Hz, CH), 28.9 (d, $^1J_{PC} = 42.5$ Hz, PCH_2), 24.3, 24.0

(br, *o*-CH₃^{Mes}), 21.1, 21.0 (br, *p*-CH₃^{Mes}), 13.8 (br, BCH₂). ¹H{¹H} NMR (192 MHz, 298 K, dichloromethane-d₂) δ -0.3 (ν_{1/2} = 140 Hz). ³¹P{¹H} NMR (243 MHz, 298 K, dichloromethane-d₂) δ 19.6 (ν_{1/2} = 70 Hz). ¹⁹F NMR (564 MHz, 298 K, dichloromethane-d₂) δ -134.7 (2F, *o*), -162.5 (1F, *p*), -166.4 (2F, *m*) (C₆F₅^A), -134.7 (2F, *o*), -161.4 (1F, *p*), -165.6 (2F, *m*) (C₆F₅^B).

Crystal data for C₃₉H₃₁BF₁₀OP (**9**), *M* = 748.43, orthorhombic, space group *P*2₁2₁2₁ (no. 19), *a* = 11.4602(3), *b* = 13.8298(4), *c* = 21.8599(7) Å, *V* = 3464.63(17) Å³, *D*_c = 1.435 g cm⁻³, μ = 1.470 mm⁻¹, *Z* = 4, λ = 1.54178 Å, *T* = 223(2) K, 13725 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å⁻¹, 5824 independent (*R*_{int} = 0.035), and 5536 observed reflections [*I* ≥ 2σ(*I*)], 475 refined parameters, *R* = 0.039, w*R*² = 0.102, Flack 0.00(2).

Compound 10. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (6 mL) and stirred for 15 min. Upon addition of phenyl isocyanate (185 μL, 1.70 mmol) at room temperature a white solid began to precipitate. After the reaction mixture had been stirred for 3 h, the solid was isolated *via* cannula filtration and washed with pentane (2 × 2 mL). Removal of all volatiles *in vacuo* yielded **10** (202 mg, 78%). Crystals suitable for the X-ray crystal structure analysis were grown by slow evaporation of a dichloromethane solution at -36 °C. Found: C, 61.23; H, 4.22; N, 1.88. Calc. for C₃₉H₃₁BF₁₀NOP: C, 61.52; H, 4.10; N, 1.84%. ¹H NMR (600 MHz, 298 K, benzene-d₆) δ 7.82 (2H, m, *o*-Ph), 7.20 (2H, m, *m*-Ph), 6.91 (1H, m, *p*-Ph), 6.41 (4H, d, ⁴*J*_{PH} = 4.2 Hz, *m*-Mes), 2.69 (2H, m, PCH₂), 2.05 (12 H, s, *o*-CH₃^{Mes}), 1.86 (6H, s, *p*-CH₃^{Mes}), 1.70 (2H, dm, ³*J*_{PH} = 26.3 Hz, BCH₂). ¹³C{¹H} NMR (151 MHz, 298 K, benzene-d₆) δ 149.1 (d, ¹*J*_{PC} = 127.1 Hz, C^N), 148.3 (dm, ¹*J*_{FC} = 239 Hz, C₆F₅), 145.9 (d, ³*J*_{PC} = 22.7 Hz, *i*-Ph), 143.6 (d, ⁴*J*_{PC} = 2.9 Hz, *p*-Mes), 142.9 (d, ²*J*_{PC} = 9.1 Hz, *o*-Mes), 139.7 (dm, ¹*J*_{FC} = 252 Hz, C₆F₅), 137.6 (dm, ¹*J*_{FC} = 252 Hz, C₆F₅), 132.1 (d, ³*J*_{PC} = 11.5 Hz, *m*-Mes), 128.8 (*m*-Ph), 126.6 (*p*-Ph), 125.8 (*o*-Ph), 123.0 (br, *i*-C₆F₅), 120.0 (d, ¹*J*_{PC} = 78.9 Hz, *i*-Mes), 26.6 (d, ¹*J*_{PC} = 39.9 Hz, PCH₂), 23.2 (d, ³*J*_{PC} = 4.4 Hz, *o*-CH₃^{Mes}), 20.7 (*p*-CH₃^{Mes}), 14.4 (br, BCH₂). ¹¹B{¹H} NMR (192 MHz, 298 K, benzene-d₆) δ 0.7. ³¹P{¹H} NMR (243 MHz, 298 K, benzene-d₆) δ 5.1 (ν_{1/2} = 3 Hz). ¹⁹F{¹H} NMR (564 MHz, 298 K, benzene-d₆) δ -134.2 (2F, *o*-C₆F₅), -159.2 (1F, *p*-C₆F₅), -164.2 (2F, *m*-C₆F₅).

Crystal data for C₃₉H₃₁BF₁₀NOP·CH₂Cl₂·½C₅H₁₂ (**10**), *M* = 882.43, monoclinic, space group *C*2/*c* (no. 15), *a* = 29.5440(6), *b* = 14.3430(4), *c* = 22.6139(7) Å, β = 122.078(1)°, *V* = 8119.6(4) Å³, *D*_c = 1.444 g cm⁻³, μ = 2.533 mm⁻¹, *Z* = 8, λ = 1.54178 Å, *T* = 223(2) K, 57011 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å⁻¹, 7244 independent (*R*_{int} = 0.054), and 6260 observed reflections [*I* ≥ 2σ(*I*)], 556 refined parameters, *R* = 0.062, w*R*² = 0.182.

Compound 11. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) were dissolved in pentane (6 mL) and stirred for 15 min. After addition of nitrosobenzene (36 mg, 0.34 mmol) the reaction mixture was stirred overnight, whereupon a brownish powder precipitated. The precipitate was collected *via* cannula filtration and washed with pentane (2 × 2.5 mL). All volatiles were removed *in vacuo* to yield **11** (128 mg, 50%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **11** at -36 °C. Found: C,

60.94; H, 4.29; N, 2.03. Calc. for C₃₈H₃₁BF₁₀NOP: C, 60.90; H, 4.17; N, 1.87%. ¹H NMR (600 MHz, 298 K, benzene-d₆) δ 6.95 (2H, m, *o*-Ph), 6.67 (2H, m, *m*-Ph), 6.54 (1H, m, *p*-Ph), 6.39 (4H, d, ⁴*J*_{PH} = 4.0 Hz, *m*-Mes), 2.67 (2H, m, PCH₂), 2.12 (12 H, br, *o*-CH₃^{Mes}), 2.09 (2H, m, BCH₂), 1.82 (6H, s, *p*-CH₃^{Mes}). ¹³C NMR (126 MHz, 298 K, benzene-d₆) δ 148.5 (dm, ¹*J*_{FC} = 240 Hz, C₆F₅), 143.6 (d, ⁴*J*_{PC} = 2.8 Hz, *p*-Mes), 142.9 (d, ²*J*_{PC} = 5.4 Hz, *i*-Ph), 142.2 (d, ²*J*_{PC} = 10.8 Hz, *o*-Mes), 139.1 (dm, ¹*J*_{FC} = 245 Hz, C₆F₅), 137.2 (dm, ¹*J*_{FC} = 247 Hz, C₆F₅), 131.9 (d, ³*J*_{PC} = 11.5 Hz, *m*-Mes), 128.2 (*m*-Ph), 125.2 (d, ³*J*_{PC} = 1.1 Hz, *p*-Ph), 124.8 (d, ¹*J*_{PC} = 76.6 Hz, *i*-Mes), n.o. (*i*-C₆F₅), 121.3 (d, ³*J*_{PC} = 1.5 Hz, *o*-Ph), 28.1 (d, ¹*J*_{PC} = 70.1 Hz, PCH₂), 22.6 (d, ³*J*_{PC} = 4.0 Hz, *o*-CH₃^{Mes}), 20.6 (d, ⁵*J*_{PC} = 1.4 Hz, *p*-CH₃^{Mes}), 15.4 (br, BCH₂). ¹¹B{¹H} NMR (192 MHz, 298 K, benzene-d₆) δ 0.4 (br). ³¹P{¹H} NMR (242 MHz, 298 K, benzene-d₆) δ 46.9 (ν_{1/2} = 3 Hz). ¹⁹F{¹H} NMR (564 MHz, 298 K, benzene-d₆) δ -133.1 (2F, *o*-C₆F₅), -161.9 (1F, *p*-C₆F₅), -165.5 (2F, *m*-C₆F₅).

Crystal data for C₃₈H₃₁BF₁₀NOP·CH₂Cl₂ (**11**), *M* = 834.34, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 13.0829(6), *b* = 15.0592(7), *c* = 19.0565(9) Å, β = 99.870(2)°, *V* = 3698.9(3) Å³, *D*_c = 1.498 g cm⁻³, μ = 2.745 mm⁻¹, *Z* = 4, λ = 1.54178 Å, *T* = 223(2) K, 27107 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å⁻¹, 6490 independent (*R*_{int} = 0.072), and 4687 observed reflections [*I* ≥ 2σ(*I*)], 502 refined parameters, *R* = 0.069, w*R*² = 0.197.

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