



# Borane Adducts of Aromatic Phosphorus Heterocycles: Synthesis, Crystallographic Characterization and Reactivity of a Phosphinine-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Lewis Pair

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In memory of Professor Paul C. J. Kamer.

**Abstract:** A phosphinine-borane adduct of a Me<sub>3</sub>Si-functionalized phosphinine and the Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> has been synthesized and characterized crystallographically for the first time. The reaction strongly depends on the nature of the substituents in the  $\alpha$ -position of the phosphorus heterocycle. In contrast, the reaction of B<sub>2</sub>H<sub>6</sub> with various substituted phosphinines leads to an equilibrium between the starting materials and the phosphinine-borane adducts that is determined by the Lewis basicity of the phosphinine. The

novel phosphinine borane adduct (**6**-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) shows rapid and facile insertion and [4+2] cycloaddition reactivity towards phenylacetylene. A hitherto unknown dihydro-1-phosphabarrelene is formed with styrene. The reaction with an ester provides a new, facile and selective route to 1-R-phosphinium salts. These salts then undergo a [4+2] cycloaddition in the presence of Me<sub>3</sub>Si-C $\equiv$ CH and styrene to cleanly form unprecedented derivatives of 1-R-phosphabarrelenium salts.

## Introduction

Tertiary phosphines (PR<sub>3</sub>) readily react with various electrophilic species. For instance, they can be protonated and also form phosphine-borane adducts upon reaction with boranes (BR<sub>3</sub>).<sup>[1]</sup> Boranes are particularly important as protecting groups for phosphines, especially for the synthesis of P-stereogenic compounds, as they can easily be removed afterwards by reaction with amines or more basic phosphines.<sup>[2]</sup> In recent years, the interaction of phosphines with boranes has been widely explored in the context of "frustrated Lewis pairs" (FLPs).<sup>3</sup> The reactivity of phosphines towards boranes is typically

related to the pronounced basicity and nucleophilicity of phosphines, but steric factors on both the donor and the acceptor site also play a significant role.<sup>[3,4]</sup>

In contrast to classical phosphines,  $\lambda^3$ -phosphinines (phosphabenzenes) are extremely weak bases and very poor nucleophiles. This can be attributed to the rather high 3 s character of the phosphorus lone pair in C<sub>5</sub>H<sub>5</sub>P, which is much higher than the value found for the nitrogen lone pair in pyridine C<sub>5</sub>H<sub>5</sub>N (64% 3 s vs. 29% 2 s character).<sup>[5]</sup> Nevertheless, phosphinines are very good  $\pi$ -acceptors due to an energetically low-lying LUMO.<sup>[6]</sup> Thus, they readily form coordination compounds particularly with late transition metals in low oxidation states.<sup>[5,7]</sup> On the other hand, little is known about the reactivity of phosphinines towards main group-based Lewis acids. Reed and co-worker succeeded in protonating the phosphorus atom in 2,4,6-tris-*t*Bu- $\lambda^3$ -phosphinine with the in situ generated, non-oxidizing superacid H[CHB<sub>11</sub>Me<sub>5</sub>Cl<sub>6</sub>] to afford the salt [H(C<sub>5</sub>H<sub>2</sub><sup>*t*</sup>Bu<sub>3</sub>P)][CHB<sub>11</sub>Me<sub>5</sub>Cl<sub>6</sub>] (1-H, Figure 1).<sup>[8]</sup>

Recently we have shown direct methylation of phosphinine **2** by using the strong alkylating reagent [(CH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup>[Al(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> (2-CH<sub>3</sub>).<sup>[9]</sup> According to DFT calculations by Erhardt and Frenking, the bond dissociation energy of a phosphinine-borane adduct is about 70% that of a pyridine-borane adduct (25.8 vs. 35.6 kcal mol<sup>-1</sup>).<sup>[10]</sup> Based on this calculated value, the formation of phosphinine-borane adducts should consequently be possible. As a first indication, Nöth and Deberitz observed a decrease in the vapor pressure upon adding B<sub>2</sub>H<sub>6</sub> to 2,4,6-triphenylphosphinine (**3**) at low temperatures.<sup>[11]</sup> This indicated the formation of the adduct **3**-BH<sub>3</sub> (Figure 1). At room temperature, however, the equilibrium shifted again to the starting materials. Even though this observation was mentioned in a

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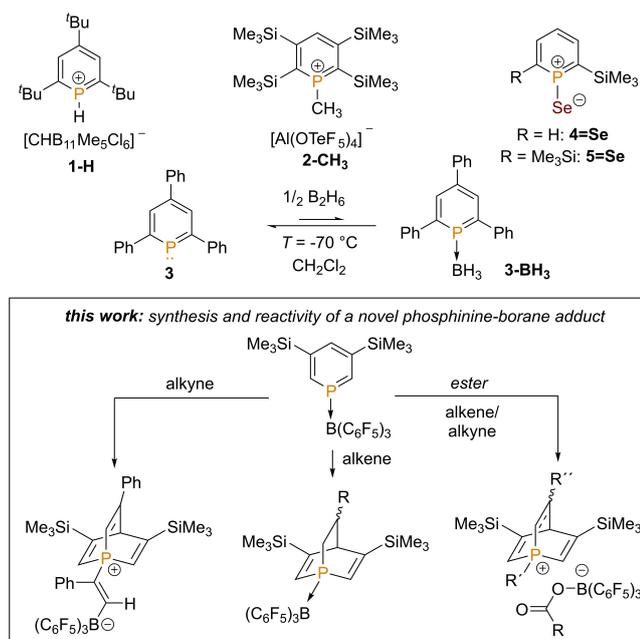
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**Figure 1.** Reactivity of phosphinines towards Lewis acids and selenium, and a brief summary of this work.

footnote almost 50 years ago, no additional reports on adduct formations of phosphinines with boranes, or other main group compounds have been published since, even though borane adducts with five-membered aromatic phosphorus heterocycles are known.<sup>[12]</sup> In this respect, we recently found that the basicity and nucleophilicity of phosphinines can be increased significantly by introducing  $\sigma$ -donating  $\text{Me}_3\text{Si}$  substituents to the aromatic phosphorus heterocycle.<sup>[13]</sup> This allowed for the synthesis and characterization of the first phosphinine selenides ( $4 = \text{Se}$ ,  $5 = \text{Se}$ ).<sup>[14]</sup> These results prompted us to investigate the reaction between phosphinines and boranes in more detail and in this work we report the first preparation, crystallographic characterization and reactivity of a phosphinine-borane adduct.

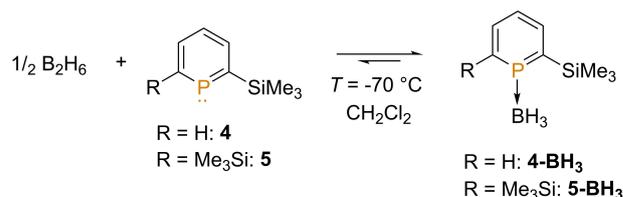
## Results and Discussion

As mentioned above, the presumed existence of a phosphinine-borane adduct ( $3\text{-BH}_3$ ) is based solely on the observed

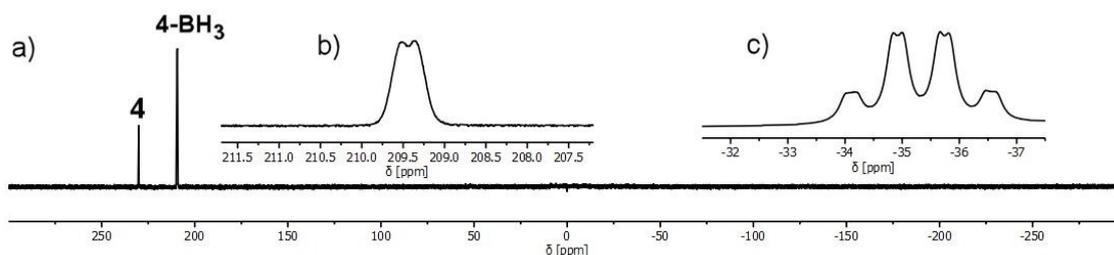
reduction of the vapor pressure when adding  $\text{B}_2\text{H}_6$  to 2,4,6-triphenylphosphinine **3** (Figure 1). In order to obtain more conclusive data and to verify the assumption, we first decided to repeat this experiment. Diborane was condensed into a solution of **3** in dichloromethane at  $T = -70^\circ\text{C}$ . In order to shift the equilibrium more to the side of the product, an excess of diborane was used and the solution was investigated by means of low-temperature NMR spectroscopy. At  $T = -70^\circ\text{C}$ , the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture shows a second, yet rather small, signal at  $\delta = 163.1$  ppm (cf.  $\delta = 179.0$  ppm for **3**). The equilibrium of the reaction is clearly located on the side of the starting materials, even though a large excess of diborane was used. This is also confirmed by the  $^{11}\text{B}$  NMR spectrum of the solution. Even if the experiment corroborates the evidence for the existence of a phosphinine-borane adduct, any subsequent isolation and characterization of the phosphinine-borane adduct remained unsuccessful due to its low concentration (ratio  $3/3\text{-BH}_3 \approx 20:1$ ). We anticipated that the higher basicity and nucleophilicity of  $\text{Me}_3\text{Si}$ -substituted phosphinines could shift the equilibrium in favor of the sought-after products. Therefore, phosphinines **4** and **5** were reacted with a slight excess of diborane (Scheme 1).<sup>[13,15]</sup> Analogous to the reaction of **3** with  $\text{B}_2\text{H}_6$ , the reaction mixture was kept at temperatures below  $T = -70^\circ\text{C}$  and investigated by means of low-temperature NMR spectroscopy. For both reactions a new, broad signal can be observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, which is slightly shifted to higher field when compared to the starting material (**4**:  $\delta = 230.7$  ppm;  $4\text{-BH}_3$ :  $\delta = 209.4$  ppm; **5**:  $\delta = 256.4$  ppm;  $5\text{-BH}_3$ :  $\delta = 226.0$  ppm).

Much to our delight, phosphinine **5** shows the highest conversion ( $5\text{-BH}_3/5 = 98:2$ ), while phosphinine **4** forms considerably less of the phosphinine-borane adduct ( $4\text{-BH}_3/4 = 88:12$ , Figure 2a).

This is perfectly in line with our assumption that the more basic phosphinine **5** should shift the equilibrium more to the



**Scheme 1.** Reaction of phosphinines **4** and **5** with diborane.

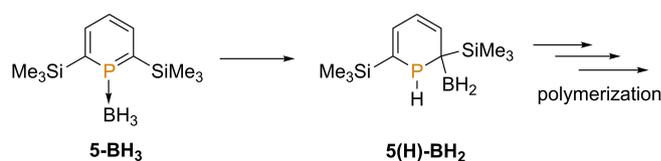


**Figure 2.** a)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction of **4** with  $\text{B}_2\text{H}_6$ . b) Enlargement of the signal of  $4\text{-BH}_3$ . c)  $^{11}\text{B}$  NMR spectrum of  $4\text{-BH}_3$ .

right side of the reaction equation (see above and Scheme 1). We noticed, however, that increasing the temperature to room temperature only had a marginal influence on the position of the equilibrium. In the case of the reaction of **4** with  $B_2H_6$ , a splitting of the new signal in the  $^{31}P\{^1H\}$  NMR spectrum into a doublet ( $^1J_{(P,B)} = 18$  Hz) can be observed (Figure 2b). As  $^{11}B$  has a nuclear spin of  $3/2$ , splitting of the  $^{31}P\{^1H\}$  NMR signal into a quartet is to be expected. Our observation might thus be due to a significant broadening of these signals. In the  $^{11}B$  NMR spectra of the reaction mixtures, a new signal at  $\delta = -34.6$  ( $5-BH_3$ ) or  $-35.3$  ppm ( $4-BH_3$ ) can be observed in addition to the signal for excess diborane. The chemical shifts are in good agreement with values typically found for phosphine-borane adducts. Moreover, the  $^{11}B$  signal for  $4-BH_3$  shows a quartet, caused by the coupling to the three  $^1H$  atoms. This signal is additionally split into a doublet by coupling to the  $^{31}P$  atom with  $^1J_{(B,P)} = 18$  Hz. The same coupling constant is also found in the  $^{31}P\{^1H\}$  NMR spectrum (Figure 2c). This confirms the existence of a phosphine-borane adduct. The  $^1H$  NMR spectra of the reaction mixtures show that the aromatic protons are somewhat more strongly shielded than in the free phosphinines. The signals of the borane protons can be found at  $\delta = 1.5$  ppm.

As  $B_2H_6$  is highly reactive, we also attempted to use the commercially available  $BH_3 \cdot SMe_2$  adduct as a borane source for the reaction with **4**. In this case, we could also observe the formation of  $4-BH_3$ , however, the equilibrium of the reaction was clearly located on the side of the starting material, even when using a large excess of  $BH_3 \cdot SMe_2$ . This can most likely be attributed to a competition between dimethylsulfide and the phosphinine to form an adduct with the Lewis acidic borane. Once again, this clearly shows the low basicity and nucleophilicity of phosphinines compared to classical phosphines.

During the course of our NMR investigations, we noticed that a subsequent reaction took place with the initially formed phosphine-borane adducts  $4-BH_3$  and  $5-BH_3$ , even at  $T = -70^\circ C$ , which made crystallization and further characterization of  $4-BH_3$  and  $5-BH_3$  impossible. While warming the NMR samples up to room temperature, a colorless, viscous oil formed inside the NMR tube and within a few weeks, a slightly yellow solid formed. Additionally, when the adducts were stored at low temperatures, a colorless solid formed over time, which turned into a pale yellow solid as the final product after a few months. In the  $^{11}B$  NMR spectrum only a large number of very broad signals can be detected while the  $^{31}P\{^1H\}$  NMR spectra showed mainly a very broad signal at  $\delta = 21.4$  ppm. Boranes are frequently used in the hydroboration of double bonds and the hydroboration of phospho-alkenes has previously been reported.<sup>[16]</sup> It is therefore reasonable to assume that the subsequent hydroboration of the  $P=C$  double bond in  $4-BH_3$  and  $5-BH_3$  slowly takes place, while insoluble polymers are finally formed (Scheme 2). According to quantum chemical calculations by Ermolaeva and Ionkin as well as experimental work by Yoshifuji et al. on the reaction of phospho-alkenes with  $BH_3$ , we suggest that the regioisomer  $5(H)-BH_2$ , shown in Scheme 2, is initially formed.<sup>[17,18]</sup> The chemical shift of  $\delta = -21.4$  ppm, observed during the further conversion of  $5-BH_3$ , is



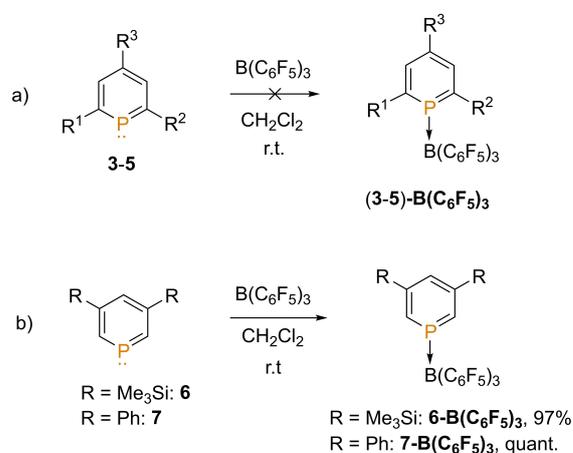
**Scheme 2.** Potential hydroboration of the  $P=C$  double bond in  $5-BH_3$  and subsequent polymerization.

in line with the chemical shift of  $\delta = -6.4$  ppm reported by Yoshifuji et al. for the product of the hydroboration of a phospho-alkene, which subsequently dimerized.<sup>[18]</sup> Moreover, Arbuzov and co-workers reported polymerization reactions with hydroborated phospho-alkenes.<sup>[16]</sup> This finding could explain the formation of the insoluble solid in the reaction mixtures of  $4-BH_3$  and  $5-BH_3$ , which could not be further characterized thus far.

In order to avoid hydroboration of the  $P=C$  double bond, we decided to use the strong Lewis acid  $B(C_6F_5)_3$  in combination with phosphinines **3–5** in  $CH_2Cl_2$  at room temperature. However, no reaction could be observed as judged by  $^{31}P\{^1H\}$  NMR spectroscopy (Scheme 3a).

Apparently, formation of the adduct between phosphinines **3–5** and the sterically demanding  $B(C_6F_5)_3$  is hindered by the bulky phenyl and  $Me_3Si$  substituents at the  $\alpha$ -position of the phosphinine. We therefore considered the reaction of phosphinine **6**, which contains  $Me_3Si$  substituents at the 3,5-positions of the ring, with  $B(C_6F_5)_3$  in  $CH_2Cl_2$  at room temperature. Compound **6** was recently reported by us and its gas phase basicity was calculated to be higher than that of unsubstituted phosphinine  $C_5H_5P$ , but lower than for **5**, which contains  $Me_3Si$  groups at the 2,6-positions.<sup>[14]</sup>

Nevertheless, we were delighted to detect only one signal in the  $^{31}P\{^1H\}$  NMR spectrum of the reaction mixture, which is shifted upfield with respect to the starting material ( $\delta = 176.6$  vs. 206.4 ppm). The  $^1H$ ,  $^{19}F$  and  $^{11}B$  NMR spectra also indicate the successful and quantitative conversion of **6** to the phosphine-borane adduct **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** (Scheme 3b).

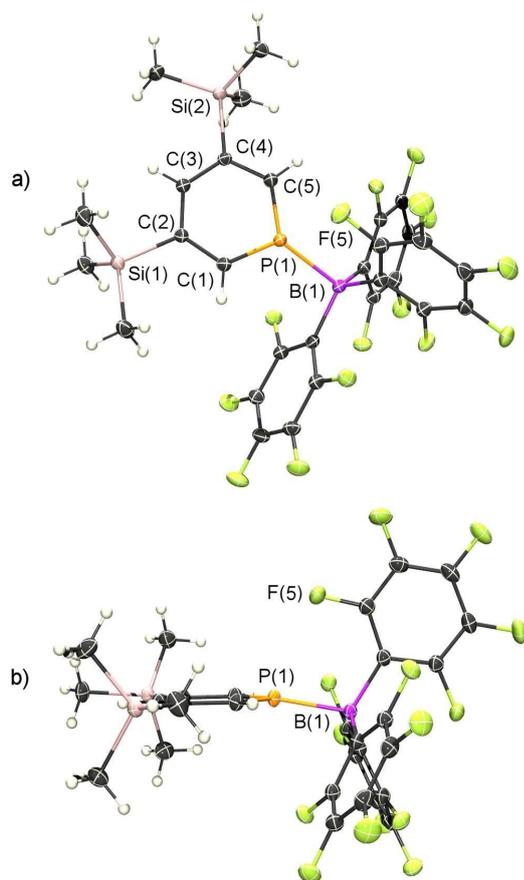


**Scheme 3.** Reaction of phosphinines **3–5** with  $B(C_6F_5)_3$ .

We considered that the high Lewis acidity of  $B(C_6F_5)_3$  might also allow the formation of adducts with less basic phosphinines, such as 3,5-diphenylphosphinine (7). Gratifyingly, the quantitative formation of 7- $B(C_6F_5)_3$  was also observed upon reaction of 7 with  $B(C_6F_5)_3$  in  $CH_2Cl_2$  at room temperature ( $^31P$  { $^1H$ } NMR:  $\delta = 182.7$  ppm). As already anticipated, these results clearly show that steric factors play a significant role in the interaction between phosphinines and boranes with strong Lewis acidic properties.

Crystals of 6- $B(C_6F_5)_3$ , suitable for X-ray diffraction, were obtained by slow evaporation of a solution of the phosphinine–borane adduct in a mixture of dichloromethane and *n*-pentane and the molecular structure of the first crystallographically characterized phosphinine–borane adduct, along with selected bond lengths, angles and distances are depicted in Figure 3.

The P(1)–B(1) distance of 2.042 Å is shorter than in the corresponding triphenylphosphine adduct  $Ph_3P \rightarrow B(C_6F_5)_3$  (2.181 Å).<sup>[19]</sup> Figure 3 clearly shows that sterically demanding substituents in the  $\alpha$ -position of the phosphorus heterocycle, such as  $Me_3Si$  or Ph groups, would indeed prevent any adduct formation. Interestingly, a closer look at the solid-state structure of 6- $B(C_6F_5)_3$  reveals that F(5) is located directly above the

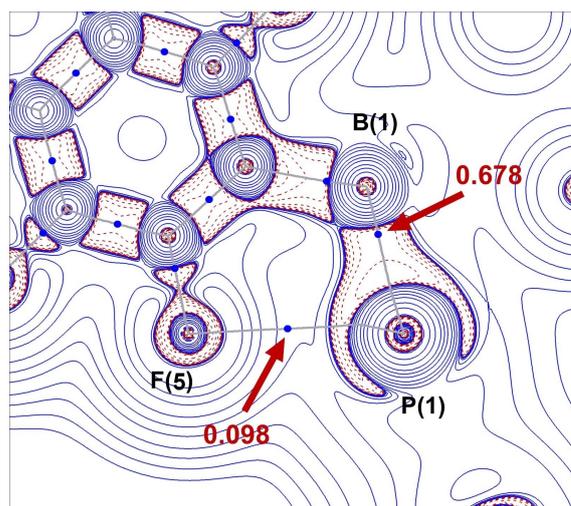


**Figure 3.** a) Top and b) side views of the Molecular structure of 6- $B(C_6F_5)_3$  in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: P(1)–B(1): 2.0415(12); P(1)–C(1): 1.7046(11); P(1)–C(5) 1.1.7082(10); P(1)–F(5) 2.8679(8); C(1)–P(1)–C(5): 106.87(5); B(1)–P(1)–C(3): 168.36(4);  $\Sigma(C-B-C)$ : 338.14(9).

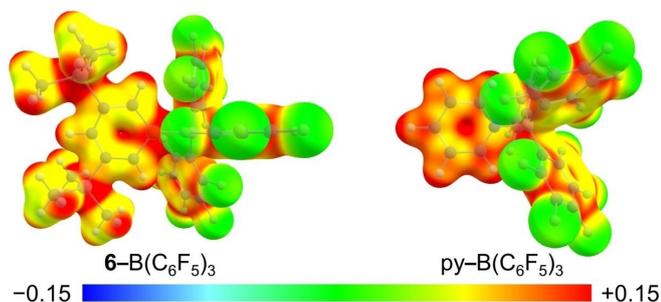
phosphorus atom. One of the electron lone pair of F(5) points directly towards the LUMO of the phosphinine, while the distance between F(5) and P(1) is 2.868 Å, which is shorter than the sum of the van der Waals radii (3.34 Å).<sup>[20]</sup> Additionally, the boron–phosphorus bond is slightly tilted out of the plane of the phosphinine ring (Figure 3b). These observations could indicate a significant fluorine–phosphorus interaction, which might stabilize the adduct further. However, the NMR spectra do not show such an interaction at room temperature nor at  $T = -70^\circ C$ , as all *ortho*-fluorine atoms remain magnetically equivalent.

In order to gain more insight into a possible interaction between P(1) and F(5), the electron density distributions were calculated for 6- $B(C_6F_5)_3$ , and the results are depicted in Figure 4 as Laplacian plots through the atoms P(1), B(1) and F(5). This indicates that a bond-critical point (red arrow) can be detected between P(1) and F(5), however, the value of  $0.098 \text{ e}\text{\AA}^{-3}$  is very low. In comparison, the value for the bond critical point between P(1) and B(1) is  $0.678 \text{ e}\text{\AA}^{-3}$ . We therefore suggest that the presence of a bond-critical point between P(1) and F(5) should not be over interpreted.

Instead, we propose on the basis of the calculations and the charges of the atoms that the fluorine–phosphorus interaction can rather be attributed as an electrostatic effect. This is best visualized in the electrostatic potential plot of 6- $B(C_6F_5)_3$ , in which the green, negatively polarized fluorine atom (F5) is directly positioned above the red, positively polarized phosphorus atom (Figure 5, left). For comparison, the electrostatic potential plot of the pyridine– $B(C_6F_5)_3$  adduct was also calculated (Figure 5 right). In this case, a higher electron density can be observed at the heteroatom of the ring due to the higher electronegativity of nitrogen, compared to phosphorus. Consequently, the fluorine atom is positioned above the C–N



**Figure 4.** 2D contour plot of the Laplacian of the electron density  $\nabla^2\rho(r)$  in the P(1)–B(1)–F(5) plane of 6- $B(C_6F_5)_3$ . Red dashed contours indicate regions of local charge accumulation ( $\nabla^2\rho(r) < 0$ ); Blue contours indicate regions of local charge depletion ( $\nabla^2\rho(r) > 0$ ). Bond paths are shown as gray lines. Bond critical points (BCPs) shown as blue dots. The red arrows indicate the electron density  $\rho(r)$  [e  $\text{\AA}^{-3}$ ] for the BCPs.



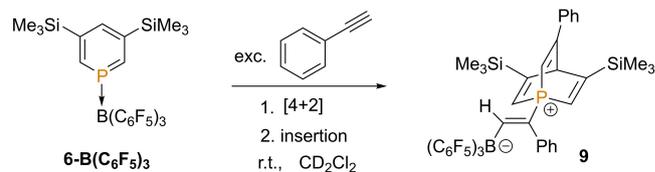
**Figure 5.** Electrostatic potential of **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** (left) and pyridine-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (right) calculated at the B3LYP-D3(BJ)/def2-TZVPP level of theory. The electrostatic potential [a.u.] is mapped onto electron density isosurfaces of 0.02 eau<sup>-3</sup>.

bond. The B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> moiety shows the expected propeller-like geometry with no unusually short N–F contacts.

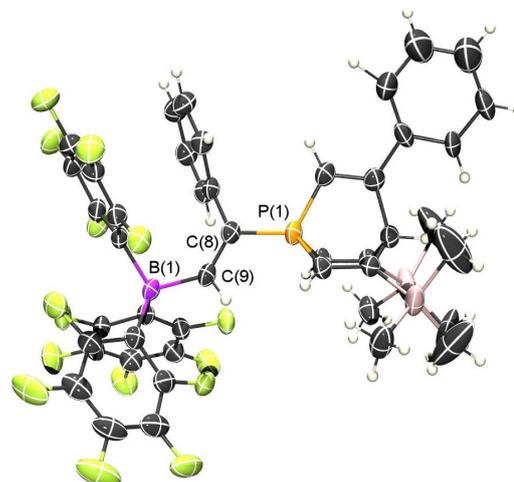
As expected, we found that the phosphorus-boron interaction in such Lewis pairs is rather weak, due to the low basicity and nucleophilicity of the aromatic phosphorus heterocycle (see above). The calculated bond dissociation enthalpy for the reaction  $LB + B(C_6F_5)_3 \rightarrow LB-B(C_6F_5)_3$  (LB = Lewis base) is  $\Delta H^\circ = -54.9 \text{ kJ} \cdot \text{mol}^{-1}$  for **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>**, which is almost half the value obtained for the triphenylphosphine adduct  $Ph_3P-B(C_6F_5)_3$  ( $\Delta H^\circ = -110.2 \text{ kJ} \cdot \text{mol}^{-1}$ ).

Based on our observations and due to the strong polarization of the phosphorus heterocycle caused by the interaction with the Lewis acid, we anticipated that **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** might exhibit a pronounced reactivity particularly towards unsaturated substrates. Previous studies have shown that activated alkynes can react with certain phosphinines, phosphinine–metal complexes, 1-methylphosphinium salts, phosphinine-sulfides and phosphinine-selenides to form 1-phosphabarrelene derivatives.<sup>[14,21–23]</sup> This orbital controlled [4 + 2] cycloaddition reaction proceeds by a 1,4-addition of the dienophile across the phosphorus heterocycle. Again, this process is facilitated by increasing the polarization of the aromatic phosphinine, for example, by P coordination to a metal center or by oxidation to a formal P(V) derivative. In this respect, we first considered the reaction between **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** and the less reactive phenylacetylene. So far, no 1-phosphabarrelene derivatives, generated from this dienophile and the corresponding phosphorus heterocycle, have been reported to date. Much to our delight, upon addition of excess  $PhC\equiv CH$ , we could observe a quantitative and selective reactivity at room temperature to a new compound (**9**) after 100 min. The product shows a single resonance at  $\delta = -18.3 \text{ ppm}$  in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. However, its analysis by high resolution mass spectrometry indicates that **9** is not only a simple borane adduct of a 1-phosphabarrelene. The crystallographic characterization reveals that next to a regioselective cycloaddition of phenylacetylene to the phosphinine ring, a further insertion of  $PhC\equiv CH$  into the P→B bond occurred and the zwitterionic alkenyl-phosphabarrelenium borate salt **9** had been formed (Scheme 4 and Figure 6).

The regioselective activation of terminal alkynes both by frustrated and classical Lewis acid/phosphine pairs has been



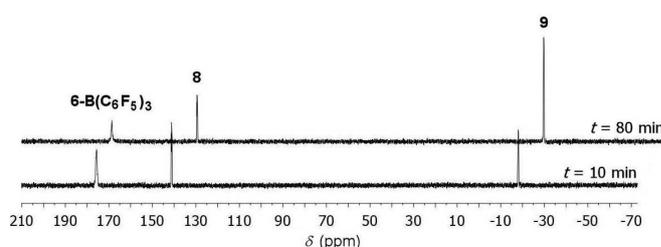
**Scheme 4.** Reaction of **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** with excess phenylacetylene.



**Figure 6.** Molecular structure of **9** in the crystal. Displacement ellipsoids are shown at the 50% probability level for one orientation of the 1-phosphabarrelene moiety. Selected bond lengths [Å]: P(1)–C(8): 1.767(4); C(8)–C(9): 1.344(6); C(9)–B(1): 1.626(6).

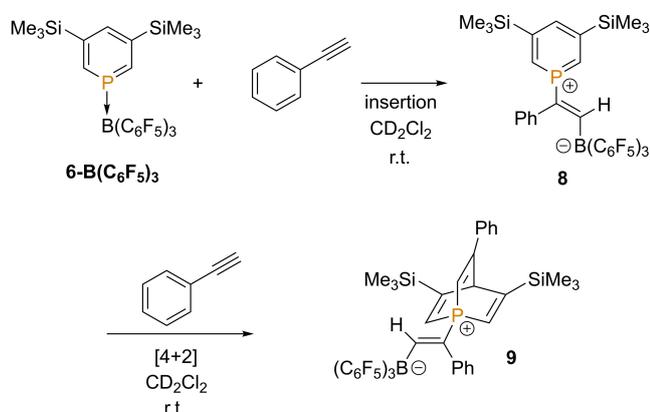
reported in literature before. Nevertheless, the formation of phosphonium alkynyl borate salts ( $R_3PH^+ PhC\equiv C-B(C_6F_5)_3^-$ ) is also observed in this case, resulting from deprotonation of the alkyne by the basic phosphine.<sup>[24]</sup> By performing the reaction of **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** with  $PhC\equiv CH$  in a 1:1 ratio, additional information on the mechanism of the product formation could be obtained. Figure 7 shows the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the reaction mixture at  $t = 10$  and 80 min after addition of the alkyne to the phosphinine–borane adduct.

Interestingly, a transient intermediate (**8**) can be observed during the course of the reaction, which fully converts to **9** when excess phenylacetylene is applied. In the 1:1 reaction, the ratio between the starting material **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>**, **8** and the product

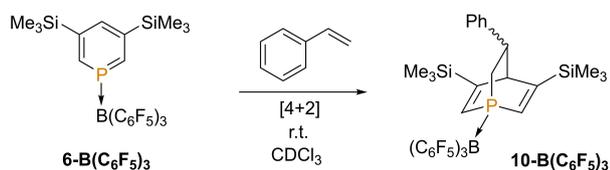


**Figure 7.** <sup>31</sup>P{<sup>1</sup>H} NMR spectra for the reaction of **6-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** with  $PhC\equiv CH$  at a 1:1 ratio.

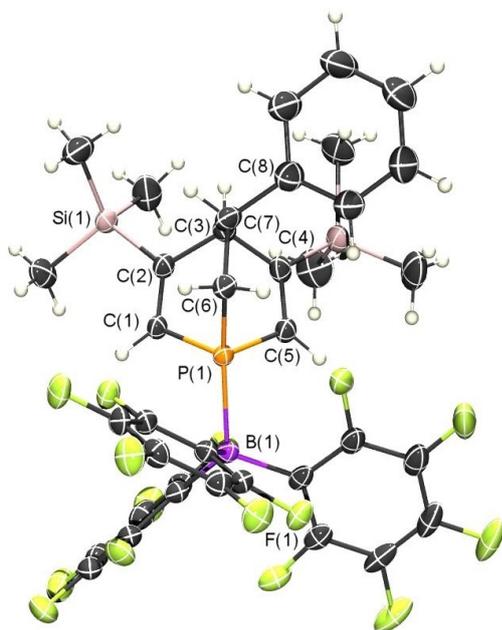
**9** remains constant after  $t=80$  min. The chemical shift of **8** at  $\delta=140.0$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum is characteristic for a phosphinium salt (see below). We therefore anticipate that intermediate **8** is a zwitterionic alkenyl-phosphinium borate



Scheme 5. Reaction of  $6\text{-B}(\text{C}_6\text{F}_5)_3$  with excess phenylacetylene.



Scheme 6. Reaction of  $6\text{-B}(\text{C}_6\text{F}_5)_3$  with styrene.



**Figure 8.** Molecular structure of  $10\text{-B}(\text{C}_6\text{F}_5)_3$  in the crystal. Displacement ellipsoids are shown at the 50% probability level for one enantiomer. Selected bond lengths [Å] and angles [°]: P(1)–B(1): 2.030(3); P(1)–C(1): 1.806(7); P(1)–C(5): 1.793(3); P(1)–C(6): 1.840(3); C(1)–C(2): 1.340(3); C(4)–C(5): 1.341(4); C(6)–C(7): 1.559(4). C(1)–P(1)–C(5): 100.21(12); C(1)–P(1)–C(6): 98.04(12); C(5)–P(1)–C(6): 100.54(12).

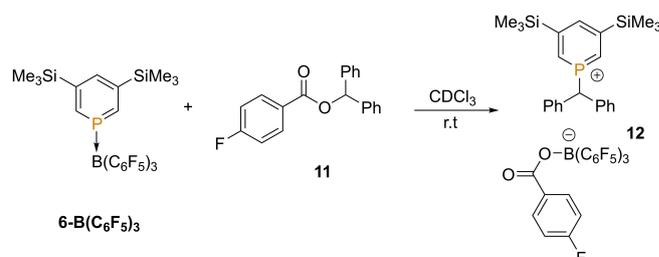
salt, which is first generated by insertion of  $\text{PhC}\equiv\text{CH}$  into the dative  $\text{P}\rightarrow\text{B}$  bond (Scheme 5). Intermediate **8** further reacts rapidly in a  $[4+2]$  cycloaddition reaction with  $\text{PhC}\equiv\text{CH}$  to form the final product **9** (Scheme 5). As a matter of fact, 1-*R*-phosphinium salts readily react with alkynes to 1-*R*-phospha-barrelenium salts even at low temperature.<sup>[22d,25]</sup> Cycloaddition reactions at highly polarized Te/B-heterocycles have also been observed by Stephan et al.<sup>[26]</sup> By means of  $^{31}\text{P}$  NMR spectroscopy we can further rule out that **8** is the 1-*H*-phosphinium salt, which might be generated by deprotonation of phenylacetylene.

As cycloaddition reactions of  $\text{C}=\text{C}$  double bonds to six-membered aromatic phosphorus heterocycles are unprecedented in the literature, we subsequently treated  $6\text{-B}(\text{C}_6\text{F}_5)_3$  with styrene (Scheme 6).

Again, we could observe the rapid, quantitative and selective conversion of  $6\text{-B}(\text{C}_6\text{F}_5)_3$  to a new product, which shows a single resonance at  $\delta=-38.0$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Crystals of the product, suitable for X-ray diffraction were obtained by slow evaporation of the solvent. The result of the X-ray crystal structure analysis is depicted in Figure 8 along with selected bond lengths and angles and unambiguously confirms that a racemic mixture of the cycloaddition product  $10\text{-B}(\text{C}_6\text{F}_5)_3$  had been formed. This compound represents the first example of a dihydro-1-phospha-barrelenium derivative. It is interesting to note that only one regioisomer is formed in the conversion of  $6\text{-B}(\text{C}_6\text{F}_5)_3$  with styrene. In  $10\text{-B}(\text{C}_6\text{F}_5)_3$ , the phenyl group of the former styrene substrate is pointing away from the  $\text{B}(\text{C}_6\text{F}_5)_3$  moiety, most likely due to steric effects during the  $[4+2]$  cycloaddition step, as this reaction is orbital controlled.<sup>[22,23]</sup>

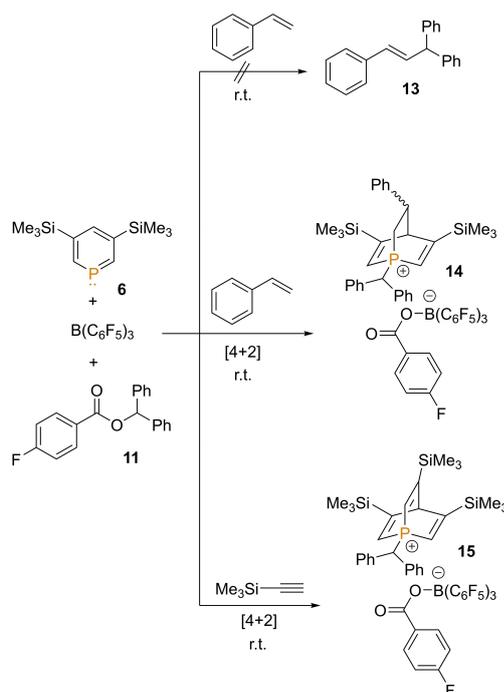
Motivated by these initial results, we attempted to apply  $6\text{-B}(\text{C}_6\text{F}_5)_3$  in typical frustrated Lewis-pair reactions.<sup>[27]</sup> As styrene derivatives react with diaryl-substituted esters in the presence of the FLP system  $\text{R}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$  to form substituted olefins, we decided to treat  $6\text{-B}(\text{C}_6\text{F}_5)_3$  first with ester **11** (Scheme 7).<sup>[28]</sup>

Much to our surprise, the reaction of  $6\text{-B}(\text{C}_6\text{F}_5)_3$  with **11** in  $\text{CDCl}_3$  proceeds instantaneously. The NMR spectroscopic analysis of the reaction mixture reveals again the selective and quantitative formation of a single, new species. This compound shows a resonance at  $\delta=156.8$  ppm in the  $^{31}\text{P}$  NMR spectrum, which is corroborated in the corresponding  $^1\text{H}$  NMR spectrum with a coupling constant of  $^2J_{\text{P-H}}=27.0$  Hz to the alkyl CH. This is in line with the presence of the 1-*R*-phosphinium salt **12**, as the  $^{31}\text{P}\{^1\text{H}\}$  NMR signal of the related 1-methyl-phosphinium cation can be observed at  $\delta=160.2$  ppm.<sup>[9,21]</sup> Most intriguingly,



Scheme 7. Study of the reactivity of  $6\text{-B}(\text{C}_6\text{F}_5)_3$  towards ester **11**.

phosphonium salts can currently only be prepared in a multistep synthesis, or alternatively, with the very strong methylation reagent  $[(\text{CH}_3)_2\text{Cl}]^+[\text{Al}(\text{OTeF}_5)_4]^-$  due to the low nucleophilicity of the phosphorus atom (see above, Figure 1).<sup>[9,21,29]</sup> Our first results, depicted in Scheme 8, thus impressively show that various novel phosphonium salts might be easily formed by making use of phosphine–borane adducts in combination with aromatic alkyl esters. To this end, 1-*R*-phosphonium salts can be generated and further explored,



Scheme 8. Reaction of **6** with  $\text{B}(\text{C}_6\text{F}_5)_3$ , ester **11**, styrene and TMS-acetylene.

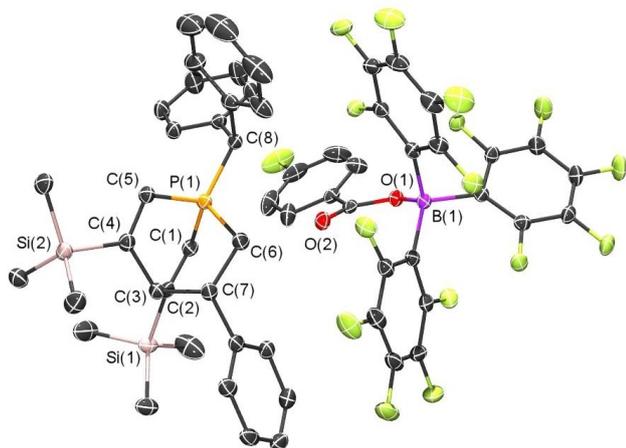


Figure 9. Molecular structure of **14** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and co-crystallized THF are omitted for clarity. Selected bond lengths [Å]: P(1)–C(1): 1.783(2); P(1)–C(8): 1.8199(19); P(1)–C(5): 1.779(2); P(1)–C(6): 1.821(2); C(1)–C(2): 1.347(3); C(2)–C(3): 1.525(3); C(3)–C(4): 1.533(3); C(4)–C(5): 1.341(3); B(1)–O(1): 1.514(2).

which are otherwise synthetically inaccessible. However, at this point, we do not have any insight into the reaction mechanism of this surprisingly fast quaternization reaction, which can occur either through a single-electron (radical) or a two-electron transfer mechanism during the C–O bond scission reaction.<sup>[28]</sup>

Subsequently, we added styrene to **11** and observed again the spontaneous formation of a single species, which shows a signal at  $\delta = -6.4$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The same immediate reactions occurs, when **6** was mixed with  $\text{B}(\text{C}_6\text{F}_5)_3$ , **11** and styrene in an equimolar ratio with  $\text{CHCl}_3$  as solvent. However, we could not detect any signals of the substituted olefin **13** by means of  $^1\text{H}$  NMR spectroscopy (Scheme 8).

Crystals, suitable for X-ray diffraction were obtained of the reaction product **14** by slow evaporation of the solvent. The result of the X-ray crystal structure analysis is depicted in Figure 9 along with selected bond lengths and angles.

Interestingly, crystallographic characterization of **14** (Figure 9) reveals the first example of a dihydro-1-*R*-phosphabarrelenium salt. The compound forms by a fast and regioselective [4+2] cycloaddition of styrene to the aromatic 1-*R*-phosphonium heterocycle. It should be mentioned that the reaction of a related 1-methyl-1-phospha-7-bora-norbornadiene with phenylacetylene has recently been described by us.<sup>[30]</sup>

Finally, we also converted rapidly, quantitatively and selectively a mixture of **6**, ester **11** and  $\text{Me}_3\text{Si}-\text{C}\equiv\text{CH}$  towards the corresponding 1-*R*-phosphabarrelenium salt **15** (Scheme 8), which we could also characterize crystallographically (Figure 10).

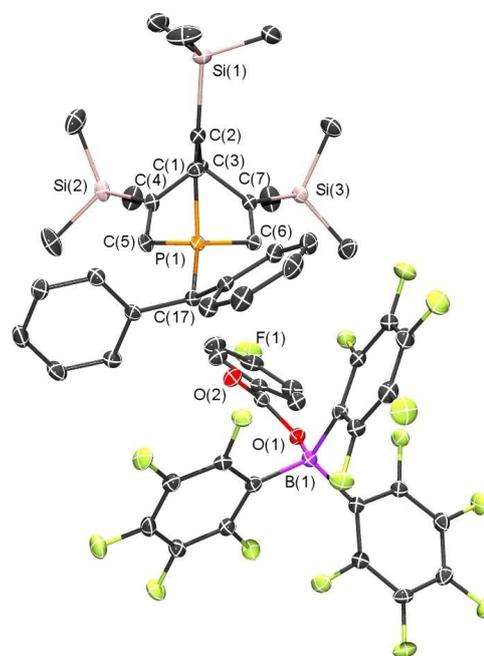


Figure 10. Molecular structure of **15** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–C(17): 1.8235(19); P(1)–C(1): 1.7951(19); P(1)–C(5): 1.7873(19); P(1)–C(6): 1.792(2); C(1)–C(2): 1.342(3); C(2)–C(3): 1.558(3); C(4)–C(5): 1.339(3); C(6)–C(7): 1.338(3); B(1)–O(1): 1.510(2). C(5)–P(1)–C(6): 100.35(9); C(5)–P(1)–C(1): 99.68(9); C(1)–P(1)–C(6): 101.00(9).

## Conclusion

In conclusion, we could demonstrate that the equilibrium of the reaction between 2,4,6-triphenylphosphinine and  $B_2H_6$  is almost exclusively located on the side of the starting materials, even at low temperature. In contrast, more basic  $Me_3Si$ -substituted phosphinines lead to a shift of the equilibrium towards the products, although complete conversion to phosphinine–borane adducts is still not achieved. This demonstrates that  $Me_3Si$ -substituted phosphinines are still rather weak Lewis bases. Moreover, hydroboration of the  $P=C$  double bond is observed with  $B_2H_6$ , which presumably leads to the formation of polymeric species. The use of the much stronger, yet more sterically demanding, Lewis acid  $B(C_6F_5)_3$  reveals a strong influence of the  $\alpha$  substituents of the aromatic phosphorus heterocycle on the formation of a discrete adduct. Phosphinines with Ph or  $Me_3Si$  substituents in the *ortho* position of the phosphinine prevent any reaction with  $B(C_6F_5)_3$ , whereas 3,5-bis(trimethylsilyl)phosphinine as well as 3,5-diphenylphosphinine undergo complete conversion to the phosphinine–borane adduct. In the case of 3,5-bis(trimethylsilyl)phosphinine, the product could be characterized crystallographically. The solid-state structure reveals an interaction between the phosphorus atom and one of the fluorine atoms of the Lewis acid; this is supported by theoretical calculations. We could further highlight that the novel phosphinine–borane adduct shows distinct insertion and subsequent  $[4+2]$  cycloaddition reactivity towards phenylacetylene. This results in a zwitterionic alkenyl-phosphabarrelenium borate salt that is formed selectively and quantitatively. With styrene, the borane adduct of a dihydrophosphabarrelene is formed. In the presence of an ester, the Lewis pair forms 1-*R*-phosphininium salts. This route significantly improves upon the previous multistep synthesis, as this procedure is performed at room temperature in a fast, facile, and selective manner. The cationic heterocycle was then shown to readily undergo a  $[4+2]$  cycloaddition reaction with styrene ultimately forming the first example of a dihydro-1-*R*-phosphabarrelenium salt. The  $[4+2]$  cycloaddition of the 1-*R*-phosphininium salt generated *in situ* with TMS-acetylene quantitatively affords the corresponding 1-*R*-phosphabarrelenium salt. The results presented herein highlight how the phosphinine–borane adduct  $6-B(C_6F_5)_3$  apparently mimics frustrated Lewis-pair reactivity. Our results provide fascinating new perspectives for the future, particularly with respect to the activation of small molecules and the synthesis of adducts of phosphinines with other main group elements and compounds. Experiments in this direction are currently being pursued in our laboratories.

## Experimental Section

Experimental details are given in the Supporting Information.

Deposition Numbers 2067304 (for  $6-B(C_6F_5)_3$ ), 2121299 (for **9**), 2067303 (for **13**) and 2121300 (for **14**) contain the supplementary crystallographic data for this paper. These data are provided free of

charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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