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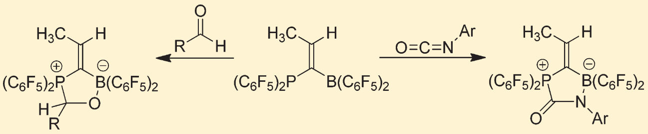
Electronic Control of Frustrated Lewis Pair Behavior: Chemistry of a Geminal Alkylidene-Bridged Per-pentafluorophenylated P/B Pair

Christoph Rosorius, Gerald Kehr, Roland Fröhlich, Stefan Grimme, and Gerhard Erker*

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany

Supporting Information



ABSTRACT: "Markovnikov" hydroboration of bis(pentafluorophenyl)(propynyl)phosphine (**12**) with Piers' borane [HB(C_6F_5)$_2$] gives the frustrated Lewis pair (FLP) (C_6F_5)$_2$P−(μ-C=CHCH$_3$)−B(C_6F_5)$_2$ (**13**) as the major product in good yield. FLP **13** adds cleanly to 1-alkynes to form the five-membered heterocyclic products **15** (two examples). It adds to the C=N double bond of arylisocyanates to yield the five-membered heterocycles **16** (two examples), and it regioselectively adds to aldehydes to yield the B−O/P−C bonded heterocycles **17** (from benzaldehyde) and **18** (from *trans*-cinnamic aldehyde), respectively. Dynamic ^{19}F NMR spectroscopy indicates a rapidly occurring reversible P−C bond dissociation process taking place in **17** and **18** [**17**: $\Delta G^{\ddagger}_{diss}$(328 K) = 14.7 ± 0.3 kcal/mol; **18**: $\Delta G^{\ddagger}_{diss}$(368 K) = 11.9 ± 0.2 kcal/mol]. The products **15a**, **15b**, **17**, and **18** were characterized by X-ray diffraction. This chemistry indicates that frustrated Lewis pair behavior can be induced electronically by the choice of suitable substituents at the Lewis base.

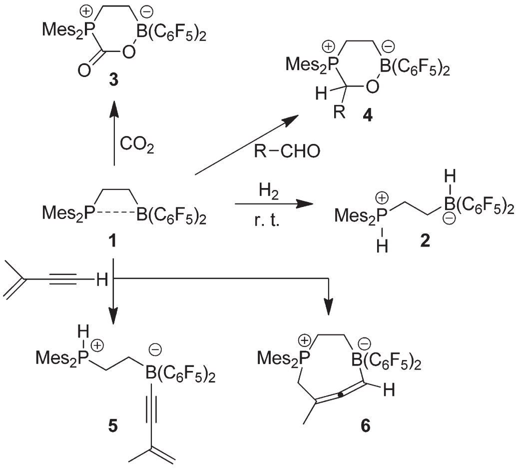
INTRODUCTION

Lewis acids and bases usually quench each other by strong adduct formation when brought together in solution.[1] The adducts may have interesting properties in themselves,[2] but they usually do not exhibit any of the typical chemical features of their individual components. The adduct formation may be hindered or even be made impossible by introducing sterically bulky substituents at either of the components.[3] The resulting coexisting Lewis acid/Lewis base pairs can show the individual properties of their respective antagonists,[4] but, more importantly, they may exhibit cooperative behavior toward a variety of substrates. With the introduction of R−B(C_6F_5)$_2$-type Lewis acids this rather new field of frustrated Lewis pair chemistry[5] has taken up an enormous development.[6,7] Frustrated Lewis pairs (FLPs) have shown to activate dihydrogen and to add to alkenes or alkynes and even to CO$_2$ or N$_2$O.[8,9]

With the intramolecular ethylene-bridged P/B system **1** we have early on contributed an intramolecular FLP whose characteristic features were to a large extent determined by sterics.[10] It is a weakly interacting Lewis pair.[11] Compound **1** currently is one of the most active metal-free activators of dihydrogen. It has served as an active hydrogenation catalyst toward selective unsaturated substrates.[12] It adds to carbon dioxide[8] and to a variety of carbonyl compounds.[13] It competitively reacts with terminal alkynes by either proton abstraction or addition (see Chart 1).[13b,14]

The increasing number of reports about the chemistry of sterically determined FLPs posed the question whether it would be possible to design and generate frustrated Lewis pairs whose properties would be governed by electronic effects rather than the ubiquitous steric control. We found a first successful leading answer in the following system: hydroboration of the very electron poor alkenylphosphine **7** with Piers' borane [HB(C_6F_5)$_2$][15] took an unusual course.[16] We isolated the "Markovnikov" 1,2 addition product (**8**) featuring a geminal pair of a strongly electrophilic −B(C_6F_5)$_2$ group and a weakly basic −P(C_6F_5)$_2$ moiety (Chart 2). The system **8** so far was not active in the H$_2$ activation, but it showed a number of typical FLP reactions with a variety of unsaturated organic substrates. We have now found a second example of such an electronically controlled frustrated Lewis pair system that shows that this new approach to generate Lewis acid/Lewis base pairs that feature typical frustrated Lewis pair behavior might be rather general. This recent development in FLP

Chart 1



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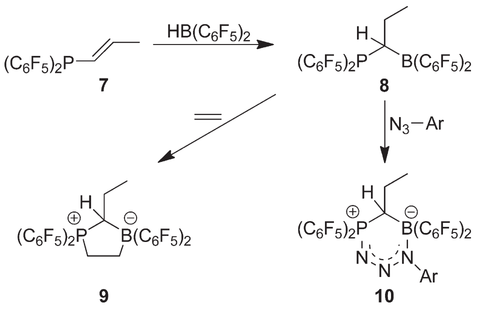
chemistry will be illustrated in this article with this new example of an electronically controlled P/B Lewis pair.

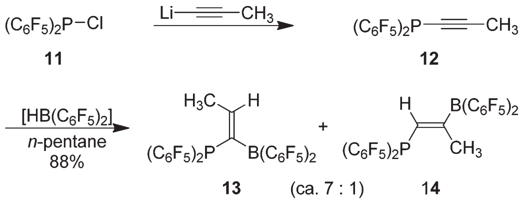
■ RESULTS AND DISCUSSION

Generation of the New Frustrated Lewis Pair. For generating the new FLP (**13**) we first reacted bis(pentafluorophenyl) chlorophosphine (**11**)[17] with propynyllithium to yield the reagent **12** (Scheme 1). Its treatment with Piers' borane [$HB(C_6F_5)_2$][15] at room temperature gave a ca. 7:1 mixture of the two regioisomeric products **13** and **14** isolated in a combined yield of close to 90%. The major product is the "Markovnikov" addition product **13**. It features a very typical set of ^{1}H NMR spectral data of the $=CHCH_3$ moiety [methyl: doublet at δ 1.58 ($^3J_{H,H}$ = 6.9 Hz) and doublet of quartets with $^3J_{P,H} \approx 24$ Hz at δ 6.73 (see Figure 1)]. The minor product (**14**) in contrast features a broad methyl signal at δ 2.00 and a broad $=CH$ resonance at δ 7.50. The major product (**13**) features a ^{31}P NMR signal at δ −62.8 and a broad ^{11}B NMR resonance at δ 60, which is typical for tricoordinated boron in a $RB(C_6F_5)_2$-type system. Consequently, we observe a set of the $-B(C_6F_5)_2$-derived ^{19}F NMR signals at δ −128.9 (*o*), −146.2 (*p*), and −160.2 (*m*) with the typical large $\Delta\delta_{m,p}$ separation[18] of 14.0 ppm. The corresponding ^{19}F NMR signals of the $P(C_6F_5)_2$ moiety occur at δ^{19}F −128.1 (*o*), −148.0 (*p*), and −159.7, respectively.

Chart 2



Scheme 1



We used this mixture, containing the geminal FLP **13** as the dominating major product, for the addition reactions that are subsequently described in this article. The presence of the minor product (**14**) did not pose any problem. It was removed from the respective addition products during the typical workup procedures of the reaction mixtures.

Reactions with 1-Alkynes. We first reacted the FLP **13** with 1-pentyne. The reaction was carried out in pentane solution at ambient temperature. After 12 h stirring a white precipitate had formed, which was collected by filtration and was shown to be the pure 1-pentyne addition product (**15a**) to the FLP **13**. Product **15a** was isolated in a yield of 62%. It was characterized by C, H elemental analysis, by spectroscopy, and by X-ray crystal structure analysis (single crystals were obtained from a solution in d_6-benzene by slow evaporation of the solvent).

The structure determination of **15a** has confirmed that the major hydroboration product (see Scheme 1) was indeed the "Markovnikov" addition product **13**. This part of the structure of **15a** features a trisubstituted olefin with a *Z*-orientation of the methyl group at C2 and phosphorus at C3. Boron is found geminal to phosphorus. The P/B pair has been 1,2-added to the alkyne with a "Markovnikov"-like orientation. The central five-membered heterocycle is close to planar with a sum of endocyclic bond angles of 539.2° (molecule A) [crystallographically independent molecule B: 539.4°]. The $B-C(sp^2)$ bond lengths around B1 are in a range between 1.599(8) and 1.660(8) Å (see Table 1). At phosphorus the pair of endocyclic $P1-C(sp^2)$ bonds is slightly shorter than the adjacent $P1-C_6F_5$ σ-bonds (see Table 1).

The product **15a** features a ^{31}P NMR resonance at δ 0.9, which shows a complex pattern due to the partially relaxed $^3J_{P,B}$ coupling. The ^{11}B NMR signal appears as a doublet at δ −9.8 ($^3J_{P,B} \approx 40$ Hz), a typical chemical shift of tetracoordinated boron (^{19}F NMR: $\Delta\delta_{p,m}$ [of $B(C_6F_5)_2$] = 5.1). The ^{1}H NMR

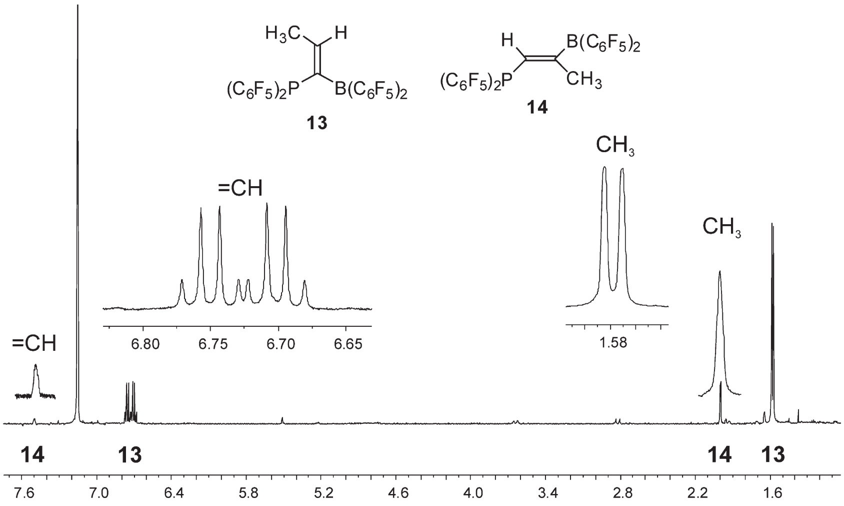


Figure 1. ^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of the **13**/**14** mixture (7:1) obtained by $HB(C_6F_5)_2$ hydroboration of $(C_6F_5)_2P-C{\equiv}C-CH_3$.

Table 1. Selected Structural Data of the FLP/Alkyne Adducts 15a and 15b[a]

	15a[b]		15b
C2−C3	1.327(7)	1.329(7)	1.330(4)
P1−C3	1.774(5)	1.766(5)	1.785(3)
P1−C4	1.792(5)	1.789(5)	1.785(3)
P1−C11	1.821(5)	1.819(5)	1.813(3)
P1−C21	1.824(5)	1.821(5)	1.817(3)
C4−C5	1.314(7)	1.322(8)	1.341(4)
B1−C3	1.651(7)	1.642(7)	1.657(4)
B1−C5	1.599(8)	1.611(8)	1.617(4)
B1−C31	1.651(8)	1.646(7)	1.631(5)
B1−C41	1.660(8)	1.652(8)	1.653(4)
P1−C3−B1	106.5(3)	107.1(3)	104.6(2)
C3−P1−C4	99.9(2)	100.0(3)	98.5(1)
C3−B1−C5	103.0(4)	102.8(4)	102.0(2)
P1−C4−C5	107.5(4)	107.6(4)	108.5(2)
B1−C5−C4	122.3(4)	121.9(5)	119.6(3)

[a] Bond length in Å, angles in deg. [b] Two independent molecules in the unit cell.

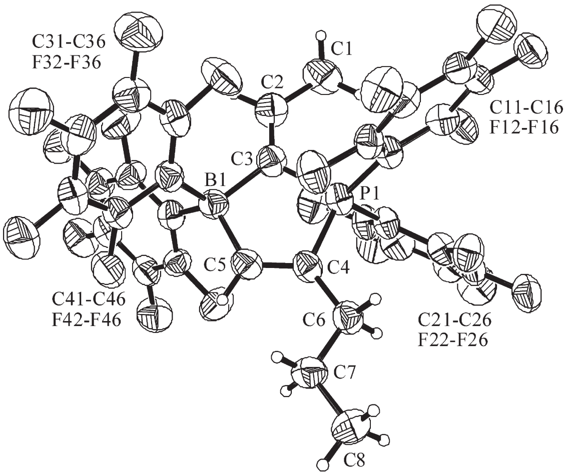
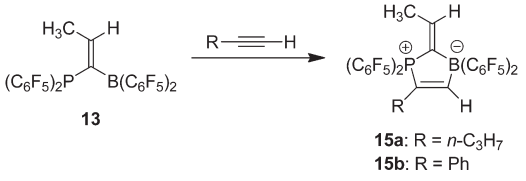


Figure 2. Molecular structure of the heterocycle **15a**.

Scheme 2



olefin 2-H resonance occurs at δ 7.02 with a typical large $^3J_{P,H}$ = 62.3 Hz, while the corresponding 5-H signal is at δ 8.27 ($^3J_{P,H}$ = 61.5 Hz).

The reaction of the FLP **13** with phenylacetylene was carried out analogously, and we isolated the addition product **15b** in 64% yield. The compound was also characterized by X-ray diffraction (see Figure 3 and Table 1). The overall structural features of the close to planar five-membered P/B-containing heterocycle (the sum of internal bonding angles is 533.2°) are similar to those of its congener **15a**.

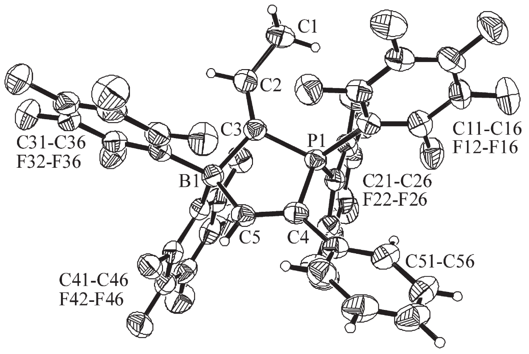
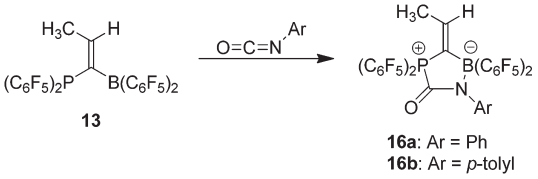


Figure 3. Molecular structure of compound **15b**.

Scheme 3



Compound **15b** features NMR resonances at δ ^{11}B: −10.1 (d, $^3J_{P,B}$ ≈ 39 Hz) and δ ^{31}P: −2.8 (partially relaxed 1:1:1:1 q, $^3J_{P,B}$ ≈ 39 Hz). It shows ^{1}H NMR signals of the olefinic 5-H at δ 8.73 (with $^3J_{P,H}$ = 57.3 Hz) and 2-H at δ 6.86 (with $^3J_{P,H}$ = 63.6 Hz). Its adjacent methyl group gives rise to a ^{1}H NMR dd at δ 1.93 (with $^3J_{H,H}$ = 7.1 Hz and $^4J_{P,H}$ = 3.5 Hz).

Reactions with Carbonyl Compounds. Frustrated Lewis pairs react with a variety of carbonyl compounds. Even less reactive FLPs are known to add to very reactive organic carbonyl substrates, such as alkyl- or arylisocyanates.[13,19] Therefore, we first treated the new electronically modified FLP **13** with phenylisocyanate and *p*-tolylisocyanate, respectively. The reaction of **13** with Ph−N=C=O in pentane at room temperature produced compound **16a** as a white solid, which was isolated in 65% yield. The product showed a ^{13}C NMR carbonyl carbon resonance at δ 159.1 (with a $^1J_{P,C}$ coupling of ca. 119 Hz). It exhibits a corresponding intensive ν(C=O) stretching band in the IR spectrum at 1699 cm^{-1}. The system features NMR signals of the heteroatoms at δ ^{31}P: −30.1 (with a $^3J_{P,H}$ coupling constant of ca. 61 Hz to the olefinic 2-H proton of the backbone) and δ ^{11}B: −4.7. These data indicate that we have encountered a rare example of a FLP addition to the C=N moiety of the isocyanate reagent and not to the mostly preferred O=C group of the heterocumulene, analogously to that observed by us upon treatment of the related geminal FLP **8** with an arylisocyanate.[16,20] The reaction of **13** with *p*-tolylisocyanate took a similar course to yield **16b** [65% isolated; δ ^{11}B: −4.5; δ ^{31}P: −32.0; δ ^{13}C (C=O): 158.7 (d, $^1J_{P,C}$ = 115.4 Hz); ν(C=O) = 1699 cm^{-1}].

We eventually reacted the FLP **13** with aldehydes. This revealed the same interesting new features in the addition reaction of frustrated Lewis pairs. Treatment of **13** with benzaldehyde at room temperature in pentane resulted in a precipitate

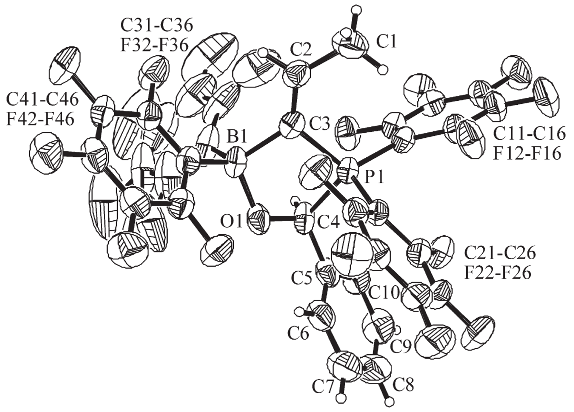


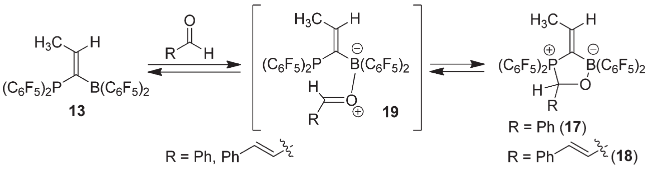
Figure 4. View of the molecular structure of the FLP/benzaldehyde addition product **17**.

Table 2. Selected Structural Data of the Aldehyde/FLP Addition Products 17 and 18[a]

	17	18
C2−C3	1.313(8)	1.336(4)
P1−C3	1.773(5)	1.777(2)
P1−C4	1.886(6)	1.910(2)
P1−C11	1.807(5)	1.818(2)
P1−C21	1.803(5)	1.823(3)
B1−C3	1.670(8)	1.650(4)
B1−O1	1.498(8)	1.501(3)
B1−C31	1.643(9)	1.643(4)
B1−C41	1.627(8)	1.654(4)
O1−C4	1.398(6)	1.387(3)
P1−C3−B1	104.1(4)	104.4(2)
C3−P1−C4	94.6(2)	95.4(1)
P1−C4−O1	96.6(3)	99.0(2)
C4−O1−B1	111.1(5)	111.7(2)
O1−B1−C3	102.6(4)	103.6(2)

[a] Bond length in Å, angles in deg.

Scheme 4



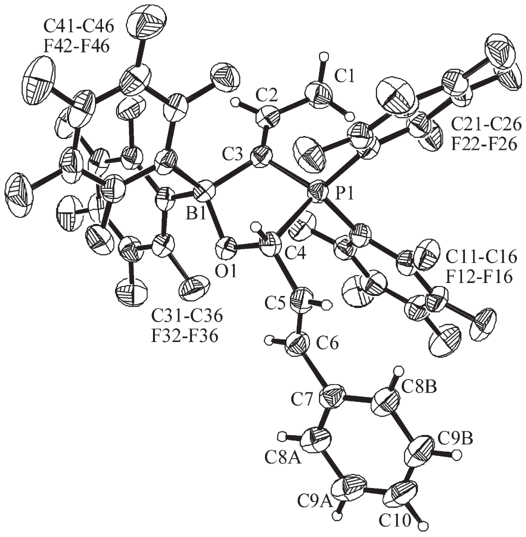


Figure 5. Molecular structure of compound **18**.

of the addition product **17**, which was isolated as a white solid in 65% yield. Single crystals of **17** suited for X-ray crystal structure analysis were obtained from d_2-dichloromethane by slow evaporation of the solvent at −34 °C. The structure (see Figure 4) of compound **17** shows that the P/B pair has added to the C=O functionality of benzaldehyde, forming a new boron-to-oxygen and phosphorus-to-carbon bond. The five-membered heterocycle attains a twist-like conformation that deviates from planarity (sum of internal bond angles inside the five-membered ring: 509.0°). We note that the P−C4 bond is markedly elongated, as judged by comparison with the adjacent three P−C bonds inside compound **17** (see Table 2).

In solution compound **17** exhibits chemical shifts of the NMR-active heteroatoms at δ ^{11}B: 0.7 and δ ^{31}P: −5.5. It shows the typical ^{1}H NMR features of the exocyclic =CHCH$_3$ unit at δ 7.28 [dq, $^3J_{\mathrm{P,H}}$ = 61.5 Hz, $^3J_{\mathrm{H,H}}$ = 7.0 Hz (1H)] and δ 1.95 [dd, $^3J_{\mathrm{H,H}}$ = 7.0 Hz, $^4J_{\mathrm{P,H}}$ = 3.5 Hz (3H)].

Compound **17** contains a newly formed chirality center at C4. Therefore, both the C_6F_5 groups at phosphorus and the C_6F_5 groups at boron are pairwise diastereotopic. At 298 K we observe four sets of three broad ^{19}F NMR resonances, two *ortho*-, two *para*-, and two *meta*-signals for the P(C_6F_5)$_2$ substituent, like the six resonances for the B(C_6F_5)$_2$ unit. Heating the sample to 363 K resulted in a pairwise coalescence of the ^{19}F NMR resonances of the diastereotopic C_6F_5 groups at phosphorus and boron. This observation indicates the loss of chirality, probably by the reversible cleavage of the C4−P1 bond to get the aldehyde adduct **19** as a reactive intermediate. From the dynamic ^{19}F NMR spectra we estimated a Gibbs activation energy of $\Delta G^{\ddagger}_{\mathrm{diss}}$ (328 K) = 14.7 ± 0.3 kcal/mol (based on the p-$C_6F_5^{\,B}$ resonance) for the P−C bond cleavage process in **17**. In a crossover experiment we could show that the formation of the aldehyde addition product **17** was reversible (for details see the Experimental Section and the Supporting Information).

Treatment of the FLP **13** with *trans*-cinnamic aldehyde in pentane rapidly resulted in the formation of a white precipitate of the product **18**, which was isolated as a solid in 74% yield. The X-ray crystal structure analysis (see Figure 5 and Table 2) confirmed that the FLP **13** had 1,2-added to the carbonyl function of the reagent to give a five-membered heterocyclic structure with a pendant Ph−CH=CH functional group. The ring is slightly twisted (sum of internal bond angles: 514.1°). In compound **18** the P1−C4 bond to the former aldehyde carbon atom is even longer than in **17**. In fact, at P1−C4 = 1.910(2) Å it is by more than 0.13 Å longer than the adjacent P1−C3 bond and by ca. 0.09 Å longer than the P1−C_6F_5 linkages.

Compound **18** also contains a newly formed chirality center inside the five-membered heterocycle at C4. Therefore, there should be two pairs of diastereotopic C_6F_5 groups, one at phosphorus and one at boron. At 233 K in d_2-dichloromethane we monitored in the ^{19}F NMR spectra of compound **18** the *o*-fluorine signals of two different C_6F_5 groups at P and the *o*-fluorine NMR signals of two different C_6F_5 groups at B. However, on raising the monitoring temperature of the NMR experiment, we observed that the signals of all the respective diastereotopic pairs coalesce and eventually give rise to the observation of a single set of $P(C_6F_5)_2$ and another one of the $B(C_6F_5)_2$ moiety (see Figure 6). We assume the analogous dynamic process to that for **17**: a rapid and reversible cleavage of the P1−C4 bond resulting in the reversible formation of the intermediate **19**. The easy formation of this carbonyl adduct by P−C bond dissociation might be indicated by the uniquely long phosphorus carbon linkage, as observed in the solid-state structure of compound **18**. From the dynamic ^{19}F NMR spectra we calculated a Gibbs activation energy of $\Delta G^{\ddagger}_{\mathrm{diss}}(268\ \mathrm{K}) = 11.9 \pm 0.2$ kcal/mol (based on the p-$C_6F_5^{B}$ resonance) for the P−C bond cleavage process in **18** (for details see the Supporting Information).

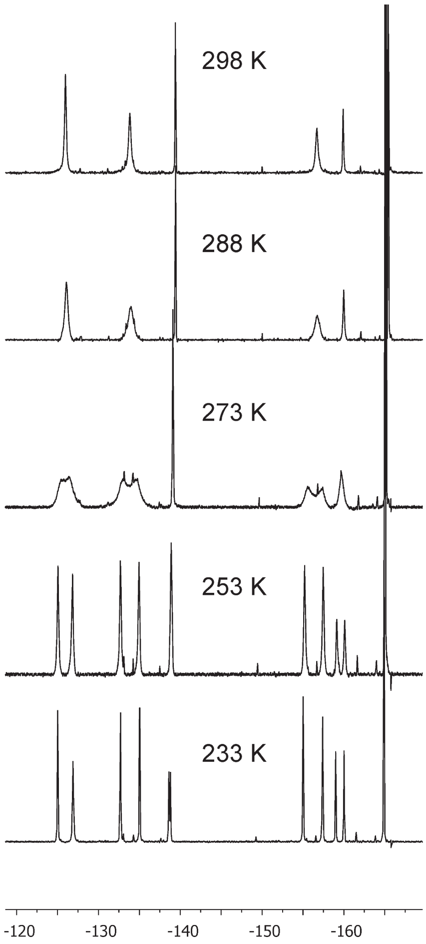
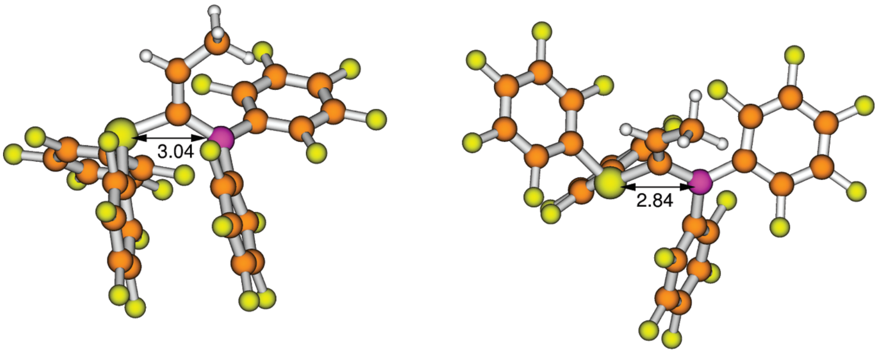


Figure 6. Temperature-dependent ^{19}F NMR spectra of compound **18** (in d_2-dichloromethane, 470 MHz).

Quantum Chemical Calculation. Quantum-chemical calculations were performed at the dispersion-corrected meta-GGA level employing large triple-ζ type basis sets (abbreviated here as TPSS-D3/def2-TZVP[21]), as outlined in detail in the Supporting Information. Inclusion of bulk solvation effects by continuum solvation models (COSMO[22]) has been considered in test calculations, but the energetic effects in the relatively nonpolar solvents used in the experiments are generally small (except for one case, see below) and thus not considered in most of the treatments.

We first performed a conformational search for the new FLP **13**. Four conformers within an energy window of 4 kcal/mol have been found. From these, only the lowest two with an energy difference of 0.9 kcal/mol are relevant under ambient conditions. The structures are shown in Figure 7.

Both conformers have a P−B distance (2.84 and 3.04 Å) that is larger by more than 0.5 Å compared to that in more common FLPs, for which these distances have been computed (e.g., **1**, for which r(P−B) is 2.24 Å at the same theoretical level). They can be interconverted by rotation around the P−C(B) bond vector. In the energetically more favored one (**13A**, left in Figure 7) the lone pair on the phosphorus atom is pointing "away" from the boron atom and is probably not reactive in addition reactions. This situation, however, is reversed in **13B**, which should be thermally accessible under the experimental conditions. According to population analysis, electronic communication between the B and P atoms in both conformers takes place mainly "through-bond" (i.e., via the C_1 bridge), but is weak, as indicated by small covalent P−B (Wiberg) bond orders of 0.13 and 0.06 for **13A** and **13B**, respectively (the corresponding value for **1** is 0.72). **13A** is significantly stabilized by noncovalent stacking interactions between two C_6F_5 rings located on the P and B atoms, respectively (shortest C···C contact of about 3.2 Å). According to very accurate *ab initio* estimated CCSD(T)/CBS



13A **13B**

Figure 7. Optimized structures (TPSS-D3/def2-TZVP) of the two energetically lowest conformers **13A** and **13B** of FLP **13** (the left one (A) is favored energetically by 0.9 kcal/mol). The B−P distances are given in Å.

results, the hexafluorobenzene dimer interaction provides about 5.7 kcal/mol stabilization (for comparison the corresponding TPSS-D3/def2-TZVP value is 5.6 kcal/mol).

The reactions of Ph−N=C=O, Ph−CH=O, and Ph−CH=CH−CH=O with FLP **13** were also investigated theoretically. The optimized structures of the corresponding products **16a**, **17**, and **18** in general agree very well with the X-ray data (computed structures are given in the Supporting Information). For example, the relatively long, newly formed P1−C4 bond in **17** and **18** (exptl: 1.89 and 1.91 Å) is reproduced by the calculations (theory: 1.922 and 1.949 Å). The reaction energies for the experimentally observed carbonyl substrates are given in Table 3 in comparison to the corresponding value for dihydrogen addition.

As can be seen in Table 3, the reactions of **13** with all carbonyl compounds are strongly exothermic, with large absolute values for the two aldehydes and a significantly smaller (but still large) value of −16 kcal/mol for Ph−N=C=O. The reaction with dihydrogen is much less exothermic (−7.3 kcal/mol), but only slightly less favorable than the corresponding reaction for the four-membered-ring FLP **1** (−8.3 kcal/mol). Although this qualitatively agrees with the observed inability of **13** to activate H_2 under the applied typical reaction conditions, the $\Delta\Delta E$ of only 1 kcal/mol is small, and kinetic reasons may be also responsible. In this case, inclusion of bulk solvation effects by COSMO for a dielectric constant of 10 increases the exothermicity of H_2 addition to −10.8 kcal/mol for **13** but to −13.9 kcal/mol for **1**; that is, the difference between FLPs **13** and **1** increases to 3 kcal/mol, which better explains the observations. The clear reason for this is the larger separation of the formal charges in the zwitterionic product from **1** (1,4-distance) compared to **13** (1,3-distance). In any case, our theoretical results for **13** indicate that it behaves electronically and thermodynamically very similar to other FLPs despite its larger P−B distance and the electron-accepting aryl substituents on phosphorus.

Table 3. Energies for Reaction of FLP (13) with Various Substrates (TPSS-D3/def2-TZVP)[a]

	E (kcal/mol)
H_2	−7.3
H_2 (**1**)	−8.3
Ph−N=C=O	−16.1
Ph−CH=O	−25.6
Ph−CH=CH−CH=O	−24.8

[a] For comparison, the value for reaction of **13** and the conventional FLP (**1**) with dihydrogen are also given.

Finally, we have investigated the origin of the observed dynamical behavior of **17**. Besides the experimentally observed closed form of the addition product, we could locate a second minimum by rotation around the B−O bond vector. As can be seen in Figure 8, in this open isomer the P−C bond is completely broken. At the TPSS-D3/def2-TZVP level, this form is higher in energy by only 13.7 kcal/mol. This value has been checked by single-point calculations with the more accurate PWPB95 double-hybrid functional,[23] which yields an almost identical isomerization energy of 13.5 kcal/mol. This value is in excellent agreement with the barrier of ca. 14 kcal/mol, as estimated from temperature-dependent NMR experiments (see above).

CONCLUSIONS

Our study shows that FLP behavior not only can be induced by the introduction of steric bulk, as it is usually done, but can also be achieved by suitable electronic means. Attaching the strongly electron-withdrawing pair of C_6F_5 substituents at the phosphorus Lewis base component results in a drastic reduction of the basicity and the nucleophilicity of the phosphorus atom. Consequently, we see no Lewis acid/Lewis base quenching in the Lewis pair **13**, although the P and the B centers are spacially close together. Nevertheless, the typical spectroscopic features of a free tricoordinated strongly electrophilic boron Lewis acid are observed for **13**, and the DFT calculation confirms that.

Although the $(C_6F_5)_2P$ Lewis base is weak—it does for instance not deprotonate the 1-alkynes, in contrast to many other FLPs—the P/B pair in **13** shows typical frustrated Lewis pair behavior. It adds to unsaturated organic substrates to form the respective heterocyclic five-membered-ring adducts. Some of the reactivities and selectivities of these addition reactions are reversible. From the dynamic NMR behavior of an example it has become apparent that the P−C bond formation of the aldehyde addition is reversible. At the same time preferred C=N addition over O=C addition to the isocyanates is rather uncommon. Both features may be explained by respective stabilized carbocation-like borane adducts as reactive intermediates.

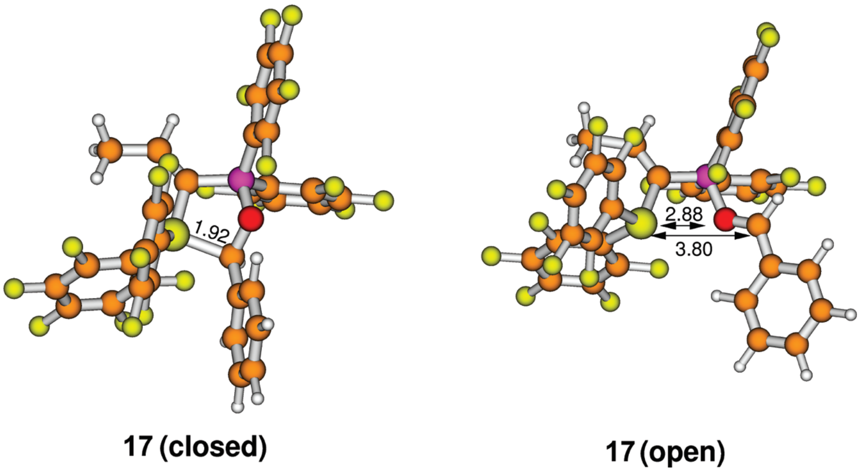


Figure 8. Optimized structures (TPSS-D3/def2-TZVP) of the two isomers of Ph−CH=O adduct **17**. Distances are given in Å.

The fact that the introduction of the strongly electron-withdrawing C_6F_5 substituents at phosphorus still leads to a pronounced frustrated Lewis pair behavior in the P/B pair **13** indicates that electronic steering of FLP properties might become a viable alternative to the usually determining steric features. We think that this observation will further increase the scope of frustrated Lewis pair formation and utilization of their specific chemical properties.

■ EXPERIMENTAL SECTION

General Information. All reactions were carried out under argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHNO-Rapid. Mass spectrometry: Orbitrap LTQ XL (Thermoscientific) for ESI measurements. NMR: Bruker AV 300 (^{1}H: 300 MHz, ^{13}C: 76 MHz, ^{31}P: 122 MHz, ^{19}F: 282 MHz, ^{11}B: 96 MHz), Bruker AV 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz, ^{13}C, 126 MHz, ^{31}P: 162 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz, ^{13}C, 151 MHz, ^{31}P: 243 MHz, ^{19}F: 564 MHz, ^{11}B: 193 MHz). Assignments of the resonances are supported by 2D experiments. Melting points/decomposition temperature: DSC 2010 (TA-Instruments) apparatus, determined by the baseline method. Infrared spectroscopy: Varian 3100 FT-infrared spectroscopy (ExcaliburSeries) spectrometer. 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 (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228−234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112−122), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997). *R*-values are given for the observed reflections, wR_2-values for all independent ones. All figures are drawn with 50% probability.

Materials. The compounds propynyllithium,[24] bis(pentafluorophenyl) chlorophosphine (**11**),[17] and bis(pentafluorophenyl)borane [$HB(C_6F_5)_2$][15] were prepared according to modified literature procedures.

Preparation of Bis(pentafluorophenyl)propynylphosphine (12). A solution of bis(pentafluorophenyl)chlorophosphine (**11**) (9.81 g, 24.5 mmol, 1 equiv) in *n*-pentane (4 mL) was added to a suspension of propynyllithium (1.13 g, 24.5 mmol, 1 equiv) in dry THF (80 mL) at −78 °C. The resulting slightly yellow suspension was warmed to room temperature and stirred for two hours. The solvent of the resulting yellow solution was removed *in vacuo*, and the orange-red residue was dissolved in *n*-pentane before being filtrated over Celite to remove the formed lithium chloride. The solvent of the filtrate was removed *in vacuo*, and the resulting residue was purified by distillation (p = 0.11 mbar, 97 °C) to get **12** as a colorless oil (4.04 g, 10 mmol, 41%). Anal. Calcd for $C_{15}H_3F_{10}P$ (404.1 g/mol): C 44.58, H 0.75. Found: C 44.19, H 0.69. IR $\tilde{\nu}$ (KBr)/cm^{-1}: 2197 [st, ν(C≡C)] w. ^{1}H NMR (400 MHz, [D_6]-benzene, 296 K): δ 1.45 (d, $^4J_{P,H}$ = 2.8 Hz, 1H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, [D_6]-benzene, 296 K): δ 4.8 (d, $^3J_{P,C}$ = 1.2 Hz, CH_3), 67.6 (m, ^{P}C≡)^t, 107.7 (m br, *i*-C_6F_5), 109.2 (d, $^2J_{P,C}$ = 14.3 Hz, ≡C)^t, 137.6 (dm, $^1J_{F,C}$ ≈ 255 Hz, *o*-C_6F_5), 142.8 (dm, $^1J_{F,C}$ ≈ 257 Hz, *p*-C_6F_5), 147.6 (dm, $^1J_{F,C}$ ≈ 251 Hz, *m*-C_6F_5), [^{t} tentative assignment].

Preparation of Compounds 13 and 14. A solution of bis(pentafluorophenyl)propynylphosphine (**12**) and *n*-pentane (10 mL) was added to a suspension of bis(pentafluorophenyl)borane (3.14 g, 9.11 mmol, 1 equiv) in *n*-pentane (150 mL) at −78 °C. Upon warming to room temperature and stirring for two hours, the color turned from colorless to slightly yellow. The solvent was removed *in vacuo*, and a mixture of the Markovnikov and the anti-Markovnikov product (**13**:**14** = 7:1; from the ^{1}H NMR experiment) was obtained as a yellow, viscous foam (5.97 g, 7.96 mmol, 88%). Mp: 88 °C. Anal. Calcd for $C_{27}H_4BF_{20}P$ (750.1 g/mol): C 43.23, H 0.54. Found: C 43.20, H not detected. IR $\tilde{\nu}$ (KBr)/cm^{-1}: 2922 w, 1647 s, 1520 s, 1477 s, 1316 s, 1289 m, 1208 m, 1151 m, 1090 s, 979 s, 873 w, 829 w, 782 w, 694 w, 640 w, 507 w, 420 w.

Major compound **13**. ^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ 1.58 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, CH_3), 6.73 (dq, $^3J_{P,H}$ = 24.4 Hz, $^3J_{H,H}$ = 6.9 Hz, 1H, CH). ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 298 K): δ 19.7 (d, $^3J_{P,C}$ = 22.6 Hz, CH_3), 108.0 (m, *i*-PC_6F_5), 113.2 (m, *i*-BC_6F_5), 137.6 (dm, $^1J_{F,C}$ ≈ 254 Hz, *o*-C_6F_5), 137.7 (dm, $^1J_{F,C}$ ≈ 256 Hz, *o*-C_6F_5), 142.2 (br, $^BC^P$), 142.9 (dm, $^1J_{F,C}$ ≈ 258 Hz, *p*-C_6F_5), 143.7 (dm, $^1J_{F,C}$ ≈ 255 Hz, *p*-C_6F_5), 147.1 (dm, $^1J_{F,C}$ ≈ 247 Hz, *m*-C_6F_5), 147.7 (dm, $^1J_{F,C}$ ≈ 253 Hz, *m*-C_6F_5), 163.8 (d, $^2J_{P,C}$ = 22.2 Hz, CH). ^{11}B{^{1}H} NMR (160 MHz, [D_6]-benzene, 298 K): δ 60.2 ($\nu_{1/2}$ ≈ 1400 Hz). ^{19}F NMR (470 MHz, [D_6]-benzene, 298 K): δ −160.2 (2F, *m*), −146.2 (1F, *p*), −128.9 (2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 14.0], −159.7 (2F, *m*), −148.0 (1F, *p*), −128.1 (2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 11.7], [assignment supported by ^{19}F{^{31}P} NMR experiment]. ^{31}P{^{1}H} NMR (202 MHz, [D_6]-benzene, 298 K): δ −62.8 (m).

Minor compound **14**. ^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ 2.00 (s, 3H, CH_3), 7.50 (s, 1H, CH). ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 298 K): δ 18.3 (d, $^3J_{P,C}$ = 28.0 Hz, CH_3), 143.1 (d, $^2J_{P,C}$ = 22.2 Hz, CH)^a, 161.4 ($^PC^B$)^b [^{a} from the ghsqc NMR experiment, ^{b} from the ghmbc NMR experiment]. ^{19}F NMR (564 MHz, [D_6]-benzene, 298 K): δ −160.2 (2F, *m*), −144.5 (1F, *p*), −128.9 (2F, *o*) (BC_6F_5), −159.8 (2F, *m*), −148.4 (1F, *p*), −130.4 (2F, *o*) (PC_6F_5) [assignment supported by ^{19}F{^{31}P} NMR experiment]. ^{31}P{^{1}H} NMR (202 MHz, [D_6]-benzene, 298 K): δ −66.6 (quint, $^3J_{P,F}$ = 26.4 Hz).

Reactions of 13 with Small Molecules. *General Procedures.* The mixture **13**/**14** (1 equiv) was dissolved in *n*-pentane (5 mL) and then treated with a solution of the respective substrate (1 equiv) in *n*-pentane (1−2 mL) at room temperature. Upon stirring the reaction mixture for 12 h at room temperature, the resulting precipitate was collected and washed with *n*-pentane (3 × 5−10 mL). Subsequently the obtained solid was dried *in vacuo* to get the respective product.

Preparation of Compound ***15a***. Mixture **13**/**14** (200 mg, 0.27 mmol, 1 equiv) reacted with 1-pentyne (18.0 mg, 0.27 mmol, 1 equiv) to give **15a** as a white solid (135 mg, 0.165 mmol, 62%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of **15a** in [D_6]-benzene. Anal. Calcd for $C_{32}H_{12}BF_{20}P$ (818.2 g/mol): C 46.97, H 1.48. Found: C 46.56, H 1.60. Mp: 225 °C. ^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ 0.73 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, $^{CH2}CH_3$), 1.36 (m, 2H, $CH_2{}^{CH3}$), 1.45 (dd, $^3J_{H,H}$ = 7.1 Hz, $^4J_{P,H}$ = 3.6 Hz, 3H, CH_3), 1.94 (q, $^3J_{P,H}$ = $^3J_{H,H}$ = 7.8 Hz, 2H, CH_2), 7.02 (dq, $^3J_{P,H}$ = 62.3 Hz, $^3J_{H,H}$ = 7.1 Hz, 1H, =CH), 8.27 (d, $^3J_{P,H}$ = 61.5 Hz, 1H, =CH^B). ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 298 K): δ 13.7 ($^{CH2}CH_3$), 20.8 (d, $^3J_{P,C}$ = 7.8 Hz, $CH_2{}^{CH3}$), 21.9 (d, $^3J_{P,C}$ = 17.2 Hz, CH_3), 31.2 (d, $^2J_{P,C}$ = 16.7 Hz, CH_2), 124.6 (d, $^1J_{P,C}$ = 89.1 Hz, =C^P), 132.9 (br, $^PC^B$), 155.9 (br, =CH), 180.6 (br, =CH^B) [C_6F_5 not listed]. ^{11}B{^{1}H} NMR (160 MHz, [D_6]-benzene, 298 K): δ −9.8 (br d, $^3J_{P,B}$ ≈ 40 Hz). ^{19}F NMR (470 MHz, [D_6]-benzene, 298 K): δ −164.2 (m, 2F, *m*), −159.1 (m, 1F, *p*), −132.7 (m, 2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 5.1], −156.7 (m, 2F, *m*), −138.6 (m, 1F, *p*), −130.0 (m, 2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 18.1]. ^{31}P{^{1}H} NMR (202 MHz, [D_6]-benzene, 298 K): δ 0.9 (m, patially relaxed $^3J_{P,B}$).

X-ray Crystal Structure Analysis of ***15a***: formula $C_{32}H_{12}BF_{20}P$, M = 818.20, colorless crystal 0.25 × 0.12 × 0.07 mm, a = 11.1848(4) Å, b = 15.8115(6) Å, c = 18.1557(10) Å, β = 103.037(3)°, V = 3128.0(2) Å^3, ρ_{calc} = 1.737 g cm^{-3}, μ = 2.144 mm^{-1}, empirical absorption correction (0.616 ≤ T ≤ 0.864), Z = 4, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, T = 223 K, ω and φ scans, 28 344 reflections collected (±h, −k, −l), [(sin θ)/λ] = 0.60 Å^{-1}, 9090 independent (R_{int} = 0.059) and 7709 observed reflections [$I \geq 2\sigma(I)$], 977 refined parameters, R = 0.049, wR^2 = 0.125, Flack parameter 0.04(3), max. residual electron density 0.36 (−0.24) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

*Preparation of Compound **15b**.* Mixture **13**/**14** (200 mg, 0.27 mmol, 1 equiv) reacted with phenylacetylene (28 mg, 0.27 mmol, 1 equiv) to get **15b** as a white solid (146 mg, 0.17 mmol, 64%). Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of **15b** in [D$_2$]-dichloromethane at −34 °C. Anal. Calcd for $C_{35}H_{10}BF_{20}P$ (852.2 g/mol): C 49.33, H 1.18. Found: C 48.71, H 0.79. MS-ESI-EM: calcd. for ($C_{35}H_{10}BF_{20}P$)H 853.0378, found 853.03749. Mp: 111 °C. ^{1}H NMR (400 MHz, [D$_2$]-dichloromethane, 296 K): δ 1.93 (dd, $^{3}J_{H,H}$ = 7.1 Hz, $^{4}J_{P,H}$ = 3.5 Hz, 3H, CH$_3$), 6.86 (dm, $^{3}J_{P,H}$ = 63.6 Hz, 1H, =CH), 7.20 (m, 2H, *o*-Ph), 7.31 (m, 3H, *m*-, *p*-Ph), 8.73 (dm, $^{3}J_{P,H}$ = 57.3 Hz, 1H, =CH^{B}). ^{13}C{^{1}H} NMR (101 MHz, [D$_2$]-dichloromethane, 296 K): δ 21.7 (br d, $^{3}J_{P,C}$ = 18.2 Hz, CH$_3$), 126.5 (d, $^{2}J_{P,C}$ = 94.8 Hz, ^{P}C=), 127.2 (d, $^{3}J_{P,C}$ = 5.6 Hz, *o*-Ph), 129.2 (d, *J* = 1.1 Hz, *p*-Ph), 129.3 (*m*-Ph), 132.7 (br, ^{P}C^{B})^{b}, 133.9 (dm, $^{2}J_{P,C}$ = 18.3 Hz, *i*-Ph), 154.3 (=CH), 184.3 (br, =CH^{B}) [C$_6$F$_5$ not listed, ^{b} from the ghmbc NMR experiment]. ^{11}B{^{1}H} NMR (160 MHz, [D$_2$]-dichloromethane, 298 K): δ −10.1 (d, $^{3}J_{P,B}$ ≈ 39 Hz). ^{19}F NMR (470 MHz, [D$_2$]-dichloromethane, 298 K): δ −165.3 (2F, *m*), −160.6 (t, $^{3}J_{F,F}$ = 20 Hz, 1F, *p*), −133.2 (2F, *o*) (BC$_6$F$_5$) [Δδ^{19}F$_{mp}$ = 4.7], −157.0 (2F, *m*), −140.6 (1F, *p*), −127.9 (2F, *o*) (PC$_6$F$_5$) [Δδ^{19}F$_{mp}$ = 16.4]. ^{31}P{^{1}H} NMR (202 MHz, [D$_2$]-dichloromethane, 298 K): δ −2.8 (1:1:1:1 q, $^{3}J_{P,B}$ ≈ 39 Hz).

*X-ray Crystal Structure Analysis of **15b**:* formula $C_{35}H_{10}BF_{20}P\cdot{}^{1}/_{2}\,CH_2Cl_2$, *M* = 894.67, colorless crystal 0.35 × 0.20 × 0.10 mm, *a* = 33.3804(8) Å, *b* = 40.8995(9) Å, *c* = 9.9755(4) Å, *V* = 13619.0(7) Å^3, ρ_{calc} = 1.745 g cm^{-3}, μ = 2.740 mm^{-1}, empirical absorption correction (0.447 ≤ *T* ≤ 0.771), *Z* = 16, orthorhombic, space group *Fdd*2 (No. 43), λ = 1.54178 Å, *T* = 223 K, ω and φ scans, 14 647 reflections collected (±*h*, −*k*, −*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 5675 independent (R_{int} = 0.041) and 5458 observed reflections [$I \geq 2\sigma(I)$], 543 refined parameters, *R* = 0.037, wR_2 = 0.094, Flack parameter 0.47(2), max. residual electron density 0.44 (−0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

*Preparation of Compound **16a**.* Mixture **13**/**14** (200 mg, 0.27 mmol, 1 equiv) reacted with phenylisocyanate (28.0 mg, 0.27 mmol, 1 equiv) to yield the product **16a** as a white solid (148 mg, 0.17 mmol, 65%). Anal. Calcd for $C_{32}H_{12}BF_{20}P$ (869.2 g/mol): C 46.98, H 1.04, N 1.61. Found: C 46.87, H 1.22, N 1.54. Decomp.: 174 °C. ^{1}H NMR (500 MHz, [D$_2$]-dichloromethane, 298 K): δ 2.01 (dd, $^{3}J_{H,H}$ = 7.0 Hz, $^{4}J_{P,H}$ = 3.6 Hz, 3H, CH$_3$), 7.11 (m, 2H, *o*-Ph), 7.12 (m, 1H, *p*-Ph), 7.16 (dq, $^{3}J_{P,H}$ = 61.3 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 1H, =CH), 7.21 (m, 2H, *m*-Ph). ^{13}C{^{1}H} NMR (126 MHz, [D$_2$]-dichloromethane, 298 K): δ 22.7 (br d, $^{4}J_{P,H}$ = 17.9 Hz, CH$_3$), 125.1 (*o*-Ph), 125.3 (br, =C^{B}), 127.1 (*p*-Ph), 128.9 (*m*-Ph), 140.9 (d, $^{3}J_{P,H}$ = 11.4 Hz, *i*-Ph), 157.3 (=CH), 159.1 (d, $^{1}J_{P,C}$ = 118.8 Hz, C=O) [C$_6$F$_5$ not listed]. ^{11}B{^{1}H} NMR (192 MHz, [D$_2$]-dichloromethane, 298 K): δ −4.7 ($\nu_{1/2}$ ≈ 80 Hz). ^{19}F NMR (564 MHz, [D$_2$]-dichloromethane, 298 K): δ −164.7 (m, 2F, *m*), −158.1 (m, 1F, *p*), −132.8 (br, 2F, *o*) (BC$_6$F$_5$) [Δδ^{19}F$_{mp}$ = 6.6], −155.7 (m, 2F, *m*), −137.4 (m, 1F, *p*), −125.9 (br, 2F, *o*) (PC$_6$F$_5$) [Δδ^{19}F$_{mp}$ = 8.3]. ^{31}P NMR (243 MHz, [D$_2$]-dichloromethane, 298 K): δ −30.1 (dm, $^{3}J_{P,H}$ ≈ 61 Hz). ^{31}P{^{1}H} NMR (243 MHz, [D$_2$]-dichloromethane, 298 K): δ −30.1 (m, $\nu_{1/2}$ ≈ 35 Hz).

*Preparation of Compound **16b**.* Mixture **13**/**14** (200 mg, 0.27 mmol, 1 equiv) reacted with *para*-tolyl-isocyanate (35.0 mg, 0.27 mmol, 1 equiv) to yield the product **16b** as a white solid (148 mg, 0.17 mmol, 65%). Anal. Calcd for $C_{35}H_{11}BF_{20}OP$ (883.2 g/mol): C 47.60, H 1.26, N 1.59. Found: C 47.48, H 0.61, N 1.79. MS-ESI-EM: calcd for ($C_{35}H_{11}BF_{20}OP$)H 884.0436, found 884.04350. Decomp.: 184 °C. ^{1}H NMR (500 MHz, [D$_6$]-benzene, 298 K): δ 1.39 (dd, $^{3}J_{H,H}$ = 6.9, Hz, $^{4}J_{P,H}$ = 3.6 Hz, 3H, CH$_3$), 1.83 (s, 3H, CH$_3$^{Tol}), 6.83 (m, 2H, *m*-Tol), 6.87 (dq, $^{3}J_{P,H}$ = 60.6 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 1H, =CH), 7.37 (m, 2H, *o*-Tol). ^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 298 K): δ 20.7 (CH$_3$^{Tol}), 21.9 (br d, $^{4}J_{P,C}$ = 17.5 Hz, CH$_3$), 125.1 (*o*-Tol), 126.3 (br, ^{P}C^{B})^{b}, 129.6 (*m*-Tol), 137.2 (*p*-Tol), 138.5 (d, $^{3}J_{P,C}$ = 12.0, Hz, *i*-Tol), 156.4 (m, =CH), 158.7 (d, $^{1}J_{P,C}$ = 115.4 Hz, C=O) [C$_6$F$_5$ not listed, ^{b} from the ghmbc NMR experiment]. ^{11}B{^{1}H} NMR (160 MHz, [D$_6$]-benzene, 298 K): δ −4.5 ($\nu_{1/2}$ ≈ 100 Hz). ^{19}F NMR (470 MHz, [D$_6$]-benzene, 298 K): δ −163.7 (m, 2F, *m*), −156.6 (m, 1F, *p*), −132.2 (br, 2F, *o*) (BC$_6$F$_5$) [Δδ^{19}F$_{mp}$ = 7.1], −155.6 (m, 2F, *m*), −136.2 (m, 1F, *p*), −127.0 (br, 2F, *o*) (PC$_6$F$_5$) [Δδ^{19}F$_{mp}$ = 19.4]. ^{31}P{^{1}H} NMR (202 MHz, [D$_6$]-benzene, 298 K): δ −32.0 ($\nu_{1/2}$ ≈ 30 Hz).

*Preparation of Compound **17**.* Mixture **13**/**14** (200 mg, 0.27 mmol, 1 equiv) reacted with benzaldehyde (28.0 mg, 0.27 mmol, 1 equiv) to form a slightly yellow reaction solution. After 12 h the product **17** was obtained as a white solid (148 mg, 0.172 mmol, 65%). Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of **17** in [D$_2$]-dichloromethane at −34 °C. Anal. Calcd for $C_{35}H_{10}BF_{20}P$ (856.2 g/mol): C 47.70, H 1.18. Found: C 47.98, H 1.39. Mp: 95 °C. ^{1}H NMR (500 MHz, [D$_2$]-dichloromethane, 298 K): δ 1.95 (dd, $^{3}J_{H,H}$ = 7.0 Hz, $^{4}J_{P,H}$ = 3.5 Hz, 3H, CH$_3$), 6.34 (d, $^{2}J_{P,H}$ = 15.3 Hz, 1H, CH), 7.23 (m, 2H, *o*-Ph), 7.27 (m, 2H, *m*-Ph), 7.28 (dq, $^{3}J_{P,H}$ = 61.5 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 1H, =CH), 7.36 (m, 1H, *p*-Ph). ^{13}C{^{1}H} NMR (151 MHz, [D$_2$]-dichloromethane, 298 K): δ 22.9 (br d, $^{3}J_{P,C}$ = 15.0 Hz, CH$_3$), 85.5 (br d, $^{1}J_{P,C}$ = 40.9 Hz, CH), 126.7 (d, $^{3}J_{P,C}$ = 5.7 Hz, *o*-Ph), 129.0 (d, *J* = 4.0 Hz, *m*-Ph), 130.4 (d, *J* = 4.8 Hz, *p*-Ph), 133.6 (d, $^{2}J_{P,C}$ = 3.6 Hz, *i*-Ph), 133.8 (br, ^{P}C^{B})^{b}, 158.0 (br, =CH) [C$_6$F$_5$ not listed, ^{b} from the ghmbc NMR experiment]. ^{11}B{^{1}H} NMR (160 MHz, [D$_2$]-dichloromethane, 298 K): δ 0.7 ($\nu_{1/2}$ ≈ 80 Hz). ^{19}F NMR (470 MHz, [D$_2$]-dichloromethane, 298 K): δ −165.4 (m, 2F, *m*), −160.4 (m, 1F, *p*), −135.1 (m, 2F, *o*) (BC$_6$F$_5$^{A}) [Δδ^{19}F$_{mp}$ = 5.0], −165.4 (m, 2F, *m*), −159.4 (m, 1F, *p*), −132.5 (m, 2F, *o*) (BC$_6$F$_5$^{B}) [Δδ^{19}F$_{mp}$ = 6.0], −158.2 (m, 2F, *m*), −139.6 (m, 1F, *p*), −126.6 (m, 2F, *o*), (PC$_6$F$_5$^{A}) [Δδ^{19}F$_{mp}$ = 18.6], −155.4 (m, 2F, *m*), −139.4 (m, 1F, *p*), −124.6 (m, 2F, *o*) (PC$_6$F$_5$^{A}) [Δδ^{19}F$_{mp}$ = 16.0]. ^{31}P NMR (202 MHz, [D$_2$]-dichloromethane, 298 K): δ −5.5 (dm, $^{3}J_{P,H}$ ≈ 62 Hz). ^{31}P{^{1}H} NMR (202 MHz, [D$_2$]-dichloromethane, 298 K): δ −5.5 ($\nu_{1/2}$ ≈ 60 Hz).

*X-ray crystal structure analysis of **17**:* formula $C_{34}H_{10}BF_{20}OP$, *M* = 856.20, colorless crystal, 0.25 × 0.15 × 0.05 mm, *a* = 10.6020(3) Å, *b* = 17.5414(6) Å, *c* = 18.9734(6) Å, β = 90.290(2)°, *V* = 3528.5(2) Å^3, ρ_{calc} = 1.612 g cm^{-3}, μ = 1.955 mm^{-1}, empirical absorption correction (0.641 ≤ *T* ≤ 0.909), *Z* = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, *T* = 223 K, ω and φ scans, 19 821 reflections collected (±*h*, −*k*, −*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 5790 independent (R_{int} = 0.068) and 4198 observed reflections [$I \geq 2\sigma(I)$], 515 refined parameters, *R* = 0.085, wR_2 = 0.259, solvent molecules could not be identified; therefore the SQUEEZE routine was used, group C31−C36 refined with thermal restraints (ISOR), max. residual electron density 0.85 (−0.72) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

*Preparation of Compound **18**.* Mixture **13**/**14** (100 mg, 0.13 mmol, 1 equiv) reacted with cinnamic aldehyde (17.5 mg, 0.13 mmol, 1 equiv) to form a bright yellow reaction solution. The product **18** was obtained as a white solid (85 mg, 0.098 mmol, 74%). Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of **18** in [D$_2$]-dichloromethane at −34 °C. Anal. Calcd for $C_{36}H_{12}BF_{20}OP$ (864.2 g/mol): C 49.01, H 1.37. Found: C 49.17, H 1.49. Decomp.: 140 °C. ^{1}H NMR (400 MHz, [D$_2$]-dichloromethane, 295 K): δ 1.96 (dd, $^{3}J_{H,H}$ = 7.0 Hz, $^{4}J_{P,H}$ = 3.5 Hz, 3H, CH$_3$), 5.91 (br d, $^{3}J_{H,H}$ = 7.1 Hz, CH), 6.29 (br d, $^{3}J_{H,H}$ = 15.8 Hz, 1H, =CH^{Ph}), 6.91 (dd, $^{3}J_{H,H}$ = 15.8 Hz, $^{3}J_{H,H}$ = 7.5 Hz, 1H, =CH^{CH}), 7.26 (dq, $^{3}J_{P,H}$ = 63.3 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 1H, =CH), 7.30 (m, 2H, *m*-Ph), 7.32 (m, 3H, *o*-, *p*-Ph). ^{13}C{^{1}H} NMR (101 MHz, [D$_2$]-dichloromethane, 295 K): δ 23.1 (br d, $^{3}J_{P,C}$ = 15.7 Hz, CH$_3$), 84.0 (br d, $^{1}J_{P,C}$ = 43.5 Hz, CH), 120.2 (m, =CH^{Ph}), 127.0 (br, *m*-Ph), 129.15 (*o*-Ph), 129.24 (*p*-Ph), 133.7 (br, $^{P}C^{B}$)^{b}, 135.5 (m, *i*-Ph), 136.1 (m, $=CH^{CH}$)^{a}, 158.1 ($=$CH) [C_6F_5 not listed, ^{a} from the ghsqc NMR experiment, ^{b} from the ghmbc NMR experiment]. ^{11}B NMR (96 MHz, [D_2]-dichloromethane, 296 K): δ 0.9 (s, $\nu_{1/2} \approx 100$ Hz). ^{19}F NMR (470 MHz, [D_2]-dichloromethane, 298 K): δ −165.3 (m, 2F, *m*), −159.8 (br, 1F, *p*), −133.8 (br, 2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp} = 5.5$], −156.6 (br, 2F, *m*), −139.3 (br, 1F, *p*), −125.9 (br, 2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp} = 17.3$]. ^{19}F NMR (470 MHz, [D_2]-dichloromethane, 233 K): δ −164.9 (m, 2F, *m*), −160.0 (m, 1F, *p*), −135.1 (m, 2F, *o*) ($BC_6F_5{}^{A}$) [$\Delta\delta^{19}F_{mp} = 5.5$], −164.9 (m, 2F, *m*)−159.0 (m, 1F, *p*), −132.7 (m, 2F, *o*) ($BC_6F_5{}^{B}$) [$\Delta\delta^{19}F_{mp} = 5.9$], −157.4 (m, 2F, *m*), −138.8 (m, 1F, *p*), −126.9 (m, 2F, *o*) ($PC_6F_5{}^{A}$) [$\Delta\delta^{19}F_{mp} = 18.6$], −155.4 (m, 2F, *m*), −138.6 (m, 1F, *p*), −125.0 (m, 2F, *o*) ($PC_6F_5{}^{B}$) [$\Delta\delta^{19}F_{mp} = 16.6$]. $^{31}P\{^{1}H\}$ NMR (243 MHz, [D_2]-dichloromethane, 296 K): δ −6.9 (br, $\nu_{1/2} \approx 70$ Hz).

X-ray crystal structure analysis of ***18****:* formula $C_{36}H_{12}BF_{20}OP \cdot 2\,CH_2Cl_2$, $M = 1052.09$, colorless crystal, 0.23 × 0.20 × 0.14 mm, $a = 10.9273(4)$ Å, $b = 11.9928(4)$ Å, $c = 16.7507(8)$ Å, $\alpha = 70.979(5)°$, $\beta = 89.996(4)°$, $\gamma = 73.451(5)°$, $V = 1978.89(14)$ Å^3, $\rho_{calc} = 1.766$ g cm^{-3}, $\mu = 4.303$ mm^{-1}, empirical absorption correction ($0.438 \le T \le 0.584$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223$ K, ω and φ scans, 26 239 reflections collected ($\pm h, -k, -l$), [$(\sin\theta)/\lambda$] = 0.60 Å^{-1}, 6850 independent ($R_{int} = 0.049$) and 5901 observed reflections [$I \ge 2\sigma(I)$], 587 refined parameters, $R = 0.044$, $wR_2 = 0.113$, max. residual electron density 0.33 (−0.41) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Additional experimental and spectroscopic details. CIF files for compounds **15a**, **15b**, **17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: erker@uni-muenster.de.

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