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Reactions of an Intramolecular Frustrated Lewis Pair with Unsaturated Substrates: Evidence for a Concerted Olefin Addition Reaction

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Abstract: The intramolecular frustrated Lewis pair $(mesityl)_2P-CH_2-CH_2-B(C_6F_5)_2$ was generated in situ by $HB(C_6F_5)_2$ hydroboration of dimesitylvinylphosphine. The compound reacts with 1-pentyne by C−H bond cleavage. It undergoes a 1,2-addition to the carbonyl group of *trans*-cinnamic aldehyde to yield a zwitterionic six-membered heterocycle by B−O and P−C bond formation. The Lewis pair regioselectively adds to the electron-rich C═C double bond of ethyl vinyl ether, and it selectively undergoes an *exo-cis*-2,3-addition to norbornene. A combined experimental/theoretical study suggests that this reaction takes place in an asynchronous concerted fashion with the B−C bond being formed in slight preference to the P−C bond. The addition products were characterized by X-ray crystal structure analyses.

Introduction

Lewis acids and Lewis bases usually undergo a neutralization reaction when brought together. It requires special measures to prevent this ubiquitous quenching reaction from taking place. Attaching sufficiently bulky substituents at the respective central atoms is a way of preserving the typical properties of a Lewis acid in the presence of a complementary Lewis base and vice versa. Such "antagonistic"[1,2] (or "frustrated")[3−5] Lewis pairs can exhibit rather special chemical reactivities that result from a probably cooperative interaction of the non-self-quenched pair. The heterolytic splitting and activation of dihydrogen is an important feature of a variety of P/B or N/B pairs of this type, of which an increasing number of examples is presently emerging in the literature.[6−9]

The addition to C═C multiple bonds is another example. This was probably first realized by the Wittig group in Heidelberg. They observed that 1,2-didehydrobenzene (**2**) formed the zwitterionic product **3** in the presence of a mixture of, e.g., PPh_3 and BPh_3.[1] In the same context, Tochtermann had observed that the usual anionic butadiene polymerization reaction did not take place when the conjugated diene was exposed to the trityl anion initiator in the presence of the BPh_3 Lewis acid; the trapping product **6** was formed instead (see Scheme 1).[2] Wittig and Tochtermann realized the special nature of these combinations of bulky Lewis acids and Lewis bases. Tochtermann coined the term "antagonistisches Paar" for such Lewis pairs.[2,10]

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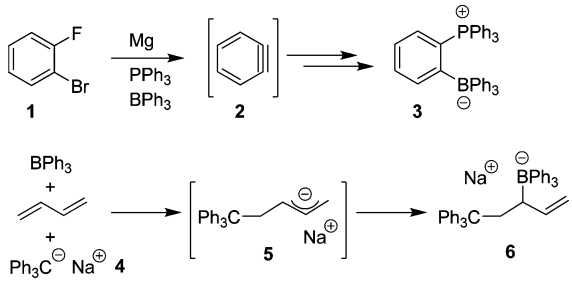
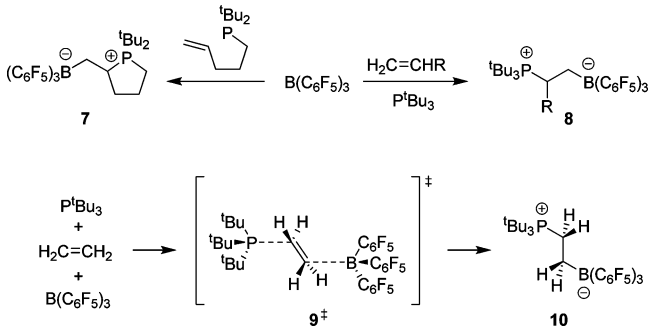
(10) Remarkably, this expression was only used in the German version of Tochtermann's *Angewandte Chemie* paper; he refrained from using the equivalent expression, "antagonistic pair", in the English version of the paper.

10.1021/ja903511s CCC: $40.75

Scheme 1



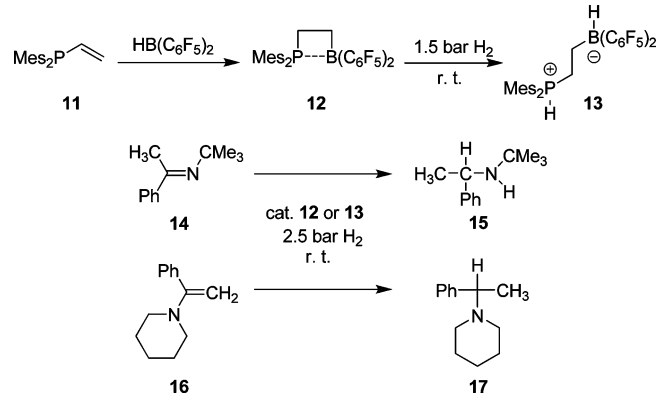
Scheme 2



Stephan et al. explored the chemistry of "frustrated" Lewis pairs consisting of very bulky phosphines and the strong Lewis acid $B(C_6F_5)_3$.[3−6] They found that some systems underwent clean olefin addition reactions (see Scheme 2).[11,12] Pápai et al. analyzed the parent reaction by quantum chemical calculations and concluded it was an antiperiplanar asynchronous concerted addition with the B−C bond formation slightly preceding the P−C bond formation.[13]

We recently described the system **12**,[14,15] which was characterized as an intramolecular "antagonistic/frustrated" Lewis pair.[14−17] It is one of the most active "metal-free" systems for heterolytic H_2 splitting. It catalyzes the hydrogenation of bulky imines (e.g., **14**) and of enamines (e.g., **16**) very effectively under mild reaction conditions (see Scheme 3).[18a] We have now

Scheme 3



found that the ethylene-bridged P/B Lewis pair **12** rapidly adds to a variety of unsaturated organic substrates, probably in a cooperative manner to some. In this article we describe some typical reactions and attempt a mechanistic description of this unique addition mode based on a combination of experiment and theory using a selected example.

Results and Discussion

Experimental Investigations: Reactions with Alkenes and Alkynes. Stephan et al. had shown that intermolecular frustrated Lewis pairs can undergo 1,2-addition reactions to alkynes, yielding alkenes of type **18**. However, sometimes (sp)C−H deprotonation competes with formation of the addition product (**19**, see Scheme 4).[18b] We have now reacted the intramolecular frustrated Lewis pair **12**, generated in situ by treatment of

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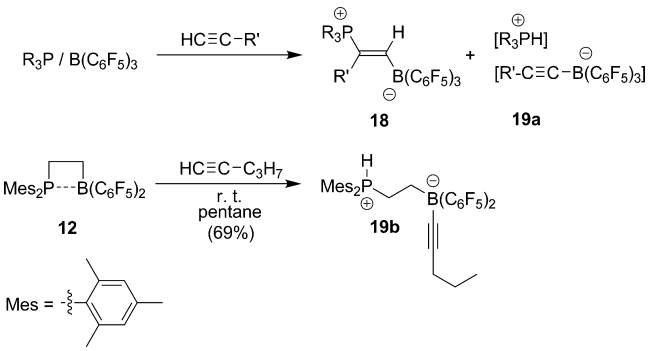
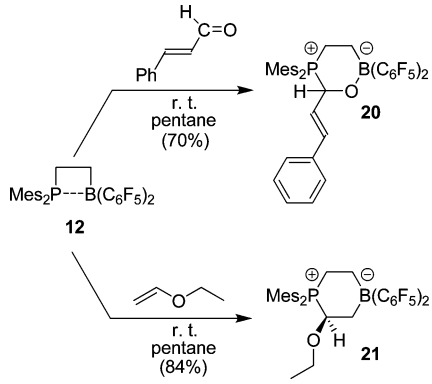
Scheme 4



Scheme 5



$Mes_2P{-}CH{=}CH_2$ (**11**) with 1 equiv of $HB(C_6F_5)_2$,[19] with 1-pentyne, observing only the C−H cleavage pathway in this case to yield **19b**. The product was characterized spectroscopically, by C,H elemental analysis, and by X-ray diffraction (for details see the Experimental Section and the Supporting Information).

We chose *trans*-cinnamic aldehyde as an example of a strongly electron deficient alkene substrate for the reaction with **12**. This reaction has a selectivity choice: the P/B addition can take place in a 1,2-fashion using either the C=C or the C=O functional group, or it can employ both and add in the 1,4-position (Scheme 5). The reaction between **12** and cinnamic aldehyde in pentane solution at ambient temperature gave a single reaction product, which was isolated in 70% yield. The obtained compound (**20**) was identified as the product of 1,2-addition of the bifunctional antagonistic Lewis pair to the aldehyde moiety.

The selective formation of **20** is evidenced by the disappearance of the typical aldehyde NMR and IR features in favor of [P]−CH−O[B] NMR signals at δ 5.74 (1H) and δ 81.3 [$^1J_{PC}$ = 35.1 Hz, (^{13}C)], and we monitor the ^{13}C NMR signals of the remaining C=C double bond at δ 123.6 and δ 133.8 ($^3J_{PC}$ = 12.1 Hz). The zwitterionic six-membered heterocyclic ring

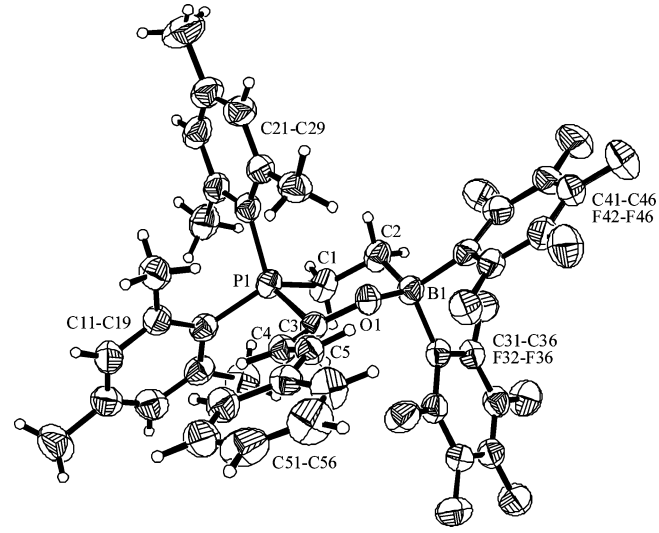


Figure 1. Projection of the molecular geometry of compound **20**. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): P1−C1 1.819(3), P1−C3 1.891(3), C1−C2 1.541(4), C2−B1 1.625(4), B1−O1 1.493(3), O1−C3 1.374(3), C3−C4 1.498(3), C4−C5 1.324(3); C1−P1−C3 95.4(1), C11−P1−C21 108.5(1), C2−B1−O1 108.9(2), C31−B1−C41 105.7(2), C3−C4−C5 122.1(2); P1−C1−C2−B1 66.3(3), B1−O1−C3−P1 −60.0(3), B1−O1−C3−C4 163.4(2).

system of compound **20** contains a newly formed chirality center. Therefore, we observe sets of ^{1}H/^{13}C NMR signals of a diastereotopic pair of mesityl groups at phosphorus and ^{19}F NMR signals of a pair of diastereotopic C_6F_5 substituents at tetracoordinated boron.[20,21] The ^{11}B NMR resonance of **20** is found at δ −0.5, and the ^{31}P NMR signal is at δ 16.1.

Compound **20** was characterized by an X-ray crystal structure analysis (single crystals were obtained from benzene plus heptane by the diffusion method). The molecule exhibits a distorted chair conformation of the central zwitterionic six-membered heterocycle. The former carbonyl oxygen atom is found bonded to boron, and the former aldehyde carbonyl carbon center is now attached to the phosphorus atom. Ring formation has resulted in a differentiation of the individual aryl rings of both the C_6F_5 pair at boron and the mesityl pair at P (*cis* or *trans* to the *trans*-Ph−CH=CH− functionality at C3). The remaining C4−C5 C=C double bond is found in a *trans*-configuration (see Figure 1).

Ethyl vinyl ether was used as an electron-rich olefinic substrate for the P/B addition reaction of the antagonistic pair **12**. $Mes_2P{-}CH_2{-}CH_2{-}B(C_6F_5)_2$ indeed adds rather rapidly to this substrate at ambient temperature in pentane. The reaction is highly regioselective. We isolated the zwitterionic six-membered heterocyclic product **21** in >80% yield (Scheme 5). The regioselective formation of the six-membered ring product was confirmed by an X-ray crystal structure analysis (see below); it also followed clearly from the spectroscopic features of the isolated product. Compound **21** shows the NMR signals of a pair of diastereotopic mesityl substituents at phosphorus (^{31}P: δ +23.4) and a pair of diastereotopic C_6F_5 groups at boron (^{11}B: δ −13.3). This is due to the formation of a chirality center

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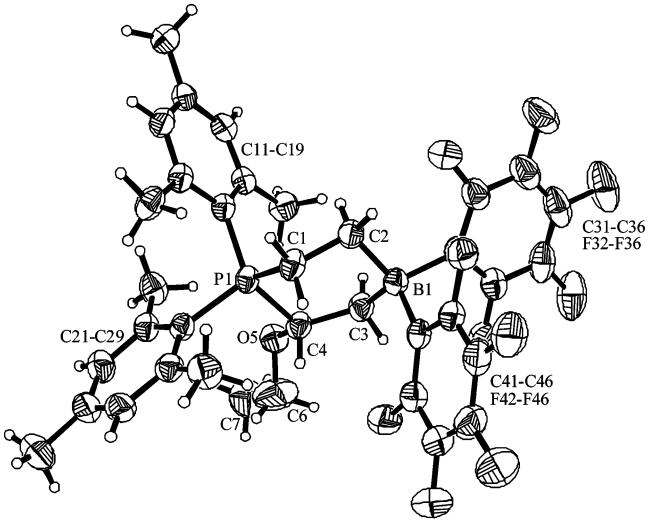


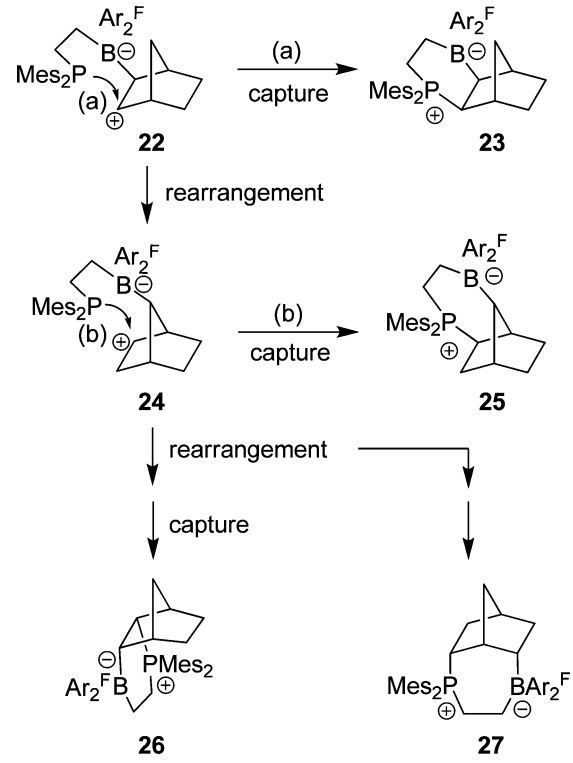
Figure 2. View of the molecular geometry of compound **21**. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): P1−C1 1.817(2), P1−C4 1.862(2), C1−C2 1.540(3), C2−B1 1.633(3), B1−C3 1.649(3), C3−C4 1.520(3), C6−C7 1.493(5); C1−P1−C4 99.1(1), C11−P1−C21 108.0(1), C2−B1−C3 107.5(2), C31−B1−C41 104.8(2); P1−C1−C2−B1 −76.5(2), B1−C3−C4−P1 42.0(3), B1−C3−C4−O5 172.8(2).

adjacent to P; the [P]−*CH*(−OR)CH_2[B] unit shows a ^{1}H NMR resonance at δ 5.03 and a ^{13}C NMR signal at δ 85.1 with $^1J_{PC}$ = 55.4 Hz. The ^{1}H NMR features of the adjacent −CH_2−[B] hydrogens are very characteristic for a pair of diastereotopic methylene H atoms positioned β to phosphorus in this overall situation.[14,15] They give rise to resonances at δ 1.65 and δ 2.92, the latter of which shows typical large $^3J_{PH}$ coupling constant of ca. 45 Hz.

Compound **21** was characterized by an X-ray crystal structure analysis (single crystals were obtained from a dichloromethane solution at −36 °C). Compound **21** exhibits a distorted chairlike six-membered heterocyclic core with typical bond lengths at the heteroatoms. The corresponding endocyclic bond angles at the formally charged heteroatoms amount to 99.1(1)° (C1−P1−C4) and 107.5(2)° (C2−B1−C3), respectively. The −OCH_2CH_3 substituent at the ring carbon atom C4 is found in a pseudoequatorial orientation (see Figure 2). One mesityl group at P1 is oriented *cis* to the −OR substituent and thus axially (C11−C19), whereas the other is oriented *trans* and hence equatorially (C21−C29). There is a similar differentiation of the C_6F_5 groups at the distal boron atom (C31−C36, *cis*, equatorial; C41−C46, *trans*, axial orientation).

Reaction with Norbornene: The Mechanistic Quest. Before we describe the experimental outcome of the reaction of the antagonistic Lewis pair with norbornene, let us briefly consider what could happen. Let us assume the reaction would proceed

Scheme 6



in a stepwise manner; then, the addition of the boron Lewis acid part of **12** could lead to the reactive zwitterionic intermediate **22** (see Scheme 6).[22] Sextet rearrangements in the norbornyl cation system are known to be fast.[23−26] Consequently, there would be a competition between internal capture (to form **23**) and Wagner−Meerwein rearrangement to a new zwitterion (**24**). This again would face competition between internal nucleophilic capture (to form **25**) and further rearrangement. In this way, by using the complete repertoire of sextet rearrangement combinations of the norbornyl cation system [i.e., Wagner−Meerwein rearrangement in combination with *endo*-2,6-H shift and *exo*-2,3-H shift (Nametkin rearrangement)], it is in principle possible to formulate the potential formation of any of the four products depicted in Scheme 6 (and Figure 3). The isomeric zwitterionic addition products feature the added P/B pair in the *exo*-2,3- (**23**), 2,7- (**25**), *endo*-2,3- (**26**), or *endo*-2,6-positions (**27**) (a complete rearrangement scheme is provided in the Supporting Information).

We first needed to determine the relative energy of the potential adduct isomers **23**, **25**−**27** in order to later see whether an addition reaction of the antagonistic P/B Lewis pair **12** to

(22) Direct attack from the *exo* face is usually prevailing in norbornene addition reactions. See, e.g.: (a) Stille, J. K.; Hughes, R. D. *J. Org. Chem.* **1971**, *36*, 340–344. (b) Brown, H. C.; Kawakami, J. H.; Liu, K.-T. *J. Am. Chem. Soc.* **1970**, *92*, 5536–5538. (c) Jefford, C. W.; Hill, D. T. *Tetrahedron Lett.* **1969**, *10*, 1957–1960. (d) Bond, F. T. *J. Am. Chem. Soc.* **1968**, *90*, 5326–5328. (e) Huisgen, R.; Knupfer, H.; Sustmann, R.; Wallbillich, G.; Weberndoerfer, V. *Chem. Ber.* **1967**, *100*, 1580–1592. (f) Cristol, S. J.; Morrill, T. C.; Sanchez, R. A. *J. Org. Chem.* **1966**, *31*, 2719–2725. (g) Huisgen, R.; Seidel, M.; Wallbillich, G.; Knupfer, H. *Tetrahedron* **1962**, *17*, 3–29. (h) Rondestvedt, C. S., Jr.; Ver Nooy, C. D. *J. Am. Chem. Soc.* **1955**, *77*, 4878–4883. (i) Ver Nooy, C. D.; Rondestvedt, C. S., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 3583–3586. (j) van Tamelen, E. E.; Shamma, M. *J. Am. Chem. Soc.* **1954**, *76*, 2315–2317.

(23) (a) Meerwein, H.; Van Emster, K. *Chem. Ber.* **1920**, *53*, 1815–1829. (b) Meerwein, H.; Van Emster, K. *Chem Ber.* **1922**, *55*, 2500–2528.

(24) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1949**, *71*, 2953–2953.

(25) (a) von Ragué Schleyer, P.; Watts, W. E.; Fort, R. C., Jr.; Comisarow, M. B.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5679–5680. (b) Saunders, M.; von Ragué Schleyer, P.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5680–5681. (c) Goering, H. L.; Schewene, C. B. *J. Am. Chem. Soc.* **1965**, *87*, 3516–3518. (d) Funke, B.; Winstein, S. *Tetrahedron Lett.* **1971**, *19*, 1477–1480. (e) Collins, C. J.; Harding, C. E. *Liebigs Ann. Chem.* **1971**, *745*, 124–134. (f) Wenke, G.; Lenoir, D. *Tetrahedron* **1979**, *35*, 489–498.

(26) Reviews: (a) Berson, J. A. In *Molecular Rearrangements*; Mayo, P., Ed.; Interscience: New York, 1963; Vol. 1, pp 111−231. (b) Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152–160. (c) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41–52. (d) Brown, H. C. In *The Nonclassical Ion Problem*; Plenum Press: New York, 1977.

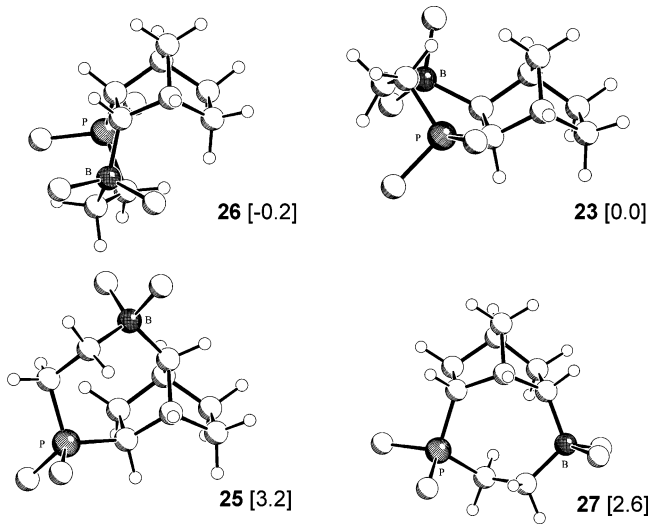


Figure 3. DFT-calculated structures and relative energies [in kcal mol^{-1}] (B2PLYP-D/QZVP(-g,-f)//B97-D/def2-TZVP level) of the adducts **23**, **25**−**27** (for clarity, the major parts of the Mes and C_6F_5 substituents are not shown).

the norbornene C═C double bond would have taken place in a regime of thermodynamic or kinetic control. That was done by a state-of-the-art DFT calculation (full optimization with dispersion-corrected B97-D functional[27] and the large def2-TZVP AO basis set;[28] single-point energies for these structures using the very accurate B2PLYP-D[29] double-hybrid density functional with the huge QZVP(-g,-f) basis set;[30] in all calculations we used TURBOMOLE;[31] for technical details, see the Supporting Information). This calculation on the fully substituted systems **23**, **25**−**27**, i.e., with the large mesityl and C_6F_5 substituents attached at their backbones, gave us the structures of the four isomers, as they are depicted in Figure 3, and their relative energies.

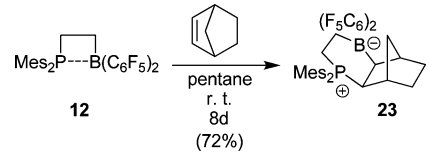
According to these calculations, the *endo*-2,3-adduct (**26**) is nearly isoenergetic with the *exo*-2,3-adduct isomer (**23**). The remaining pair of isomers (**25**, **27**) is markedly higher in energy (see Figure 3). Formation of a mixture of the *exo*-2,3- (**23**) and *endo*-2,3-products (**26**) would be expected upon reaction of **12** with norbornene under thermodynamic control.

This is not observed experimentally. The reaction of the intramolecular antagonistic Lewis pair **12** with norbornene at room temperature in pentane gave a single product (isolated in >70% yield), which was identified as the *exo*-2,3-adduct **23** (see Scheme 7 and Figures 4 and 5). The compound was characterized by C,H elemental analysis, by an X-ray crystal structure analysis, and spectroscopically.

The X-ray crystal structure analysis shows that the bifunctional [P]−CH_2−CH_2−[B] reagent has been added from the *exo* side to give the *exo*-2,3-adduct isomer **23**. The anellated heterocyclic six-membered ring adopts a distorted half-chair conformation.

The NMR spectra of compound **23** show the typical signals of the unsymmetrically *exo*-2,3-disubstituted norbornene framework [e.g., C2, δ 37.6 (^{1}H δ 3.29); C1, δ 44.0 ($^1J_{PC}$ = 32.9 Hz) (^{1}H δ 3.20)]. A ^{11}B NMR signal appears at δ −11.8 and a ^{31}P NMR resonance at δ 31.2. There are ^{19}F NMR signals for a pair of diastereotopic C_6F_5 substituents at boron (*p*-C_6F_5, δ −162.8/−163.8). Compound **23** shows sets of ^{1}H/^{13}C NMR signals for a pair of diastereotopic mesityl groups at phosphorus (e.g., ^{1}H of *p*-CH_3 at δ 2.02/1.94). The system is so sterically congested that rotation of the mesityl groups around the P−C(sp^2) bonds is hindered on the NMR time scale at ambient temperature. Consequently, we observe a total of four *ortho*-mesityl-CH_3 ^{1}H NMR signals at δ 2.57/1.60 and δ 2.41/1.70 (600 MHz, 298 K). The protons of the [P]−CH_2−CH_2−[B] section of the zwitterionic six-membered heterocyclic subunit of compound **23** are pairwise diastereotopic, as expected [^{1}H, δ 2.89/2.63 ([P]−CH_2)]. One of the distal CH_2 hydrogens shows the rather large $^3J_{PH}$ coupling constant that is typical for this arrangement [^{1}H, δ 2.21 ($^3J_{PH}$ = 35.5 Hz)/0.36 (CH_2−[B])].

Scheme 7



These results indicate that the product formation observed in the reaction of **12** with norbornene to give **23** is taking place

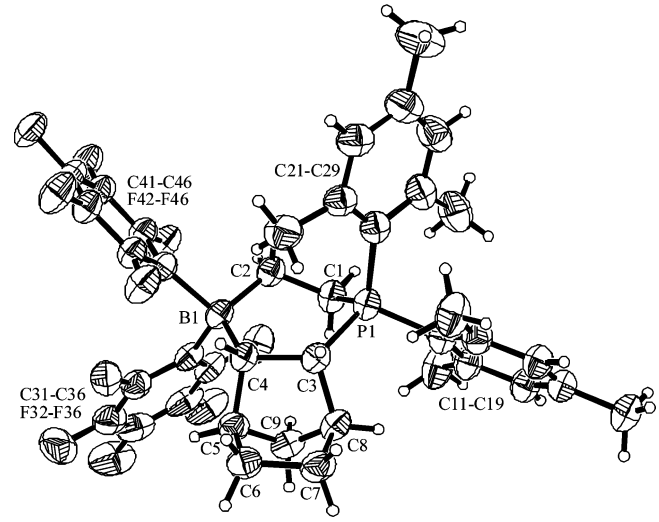


Figure 4. View of the molecular geometry of compound **23**. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): P1−C1 1.802(2), P1−C3 1.830(2), C1−C2 1.538(3), C2−B1 1.648(3), B1−C4 1.695(3), C3−C4 1.601(2), C4−C5 1.551(3), C3−C8 1.567(3); C1−P1−C3 102.9(1), C11−P1−C21 105.2(1), C2−B1−C4 112.0(2), C31−B1−C41 102.4(1); P1−C1−C2−B1 −72.3(2), P1−C3−C4−B1 8.7(2), P1−C3−C4−C5 136.7(1), C8−C3−C4−B1 −116.0(2).

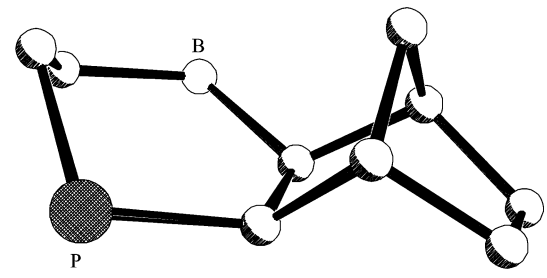


Figure 5. Projection of the molecular structure of the core atoms of the *exo*-2,3-adduct **23**.

(27) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
(28) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829–5835.
(29) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.
(30) Weigend, F.; Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *119*, 12753–12762.
(31) (a) Ahlrichs, R.; Bär, M.; Här, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169. (b) Ahlrichs, R.; et al. *TURBOMOLE*, version 6.0; Universität Karlsruhe, 2009; http://www.turbomole.com.

Scheme 8

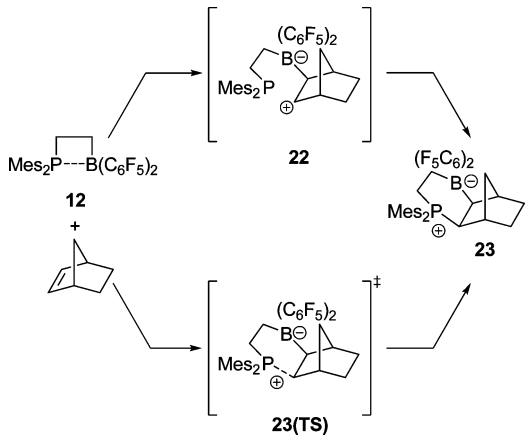


Table 1. Calculated Relative Energies and Reaction Energies of **12**/**12B** with Norbornene (N) for Products **23**, **25**−**27**, Transition States (TS), and the Corresponding Model Compounds without the Substituents on Boron and Phosphorous (Denoted by Suffix B)[a]

reaction	B97-D[a]	B2PLYP-D[b]
No Substituents on B,P		
12B + N → *exo* complex	−11.3	−6.4
12B + N → *endo* complex	−5.7	0.5
12B + N → **23B** (*exo*)	−13.8(0.0)	−13.5 (0.0)
12B + N → **26B** (*endo*)	−12.5 (1.3)	−11.6 (1.9)
12B + N → **23B(TS)**	4.1	11.4
12B + N → **26B(TS)**	8.7	16.9
"Real" Systems		
12 + N → **23** (*exo*)	−16.0 (0.0)	−19.4 (0.0)
12 + N → **26** (*endo*)	−16.3 (−0.3[c])	−19.6 (−0.2[c])
12 + N → **25**	−12.8 (3.2)	−16.2(3.2)
12 + N → **27**	−13.3 (3.0)	−16.8(2.6)
12 + N → **23(TS)**	8.8	12.3
12 + N → **26(TS)**	15.3	19.4

[a] def2-TZVP AO basis. [b] def2-QZVP(-g,-f) AO basis using B97-D/def2-TZVP optimized structures. [c] The correction to H_{298} for the relative energy is 0.5 kcal/mol. The COSMO correction ($\epsilon = 2$) is −0.1 kcal/mol (favoring **26**). [a] Values in parentheses are relative energies of the isomers.

under kinetic control—the specific outcome is, therefore, mechanistically relevant. The by far predominant formation of **23** under our reaction conditions can be explained either by a stepwise reaction pathway through a reactive intermediate (**22**) that undergoes internal trapping of the incipient carbenium ion by the neighboring phosphine nucleophile (to form **23**) faster than rearrangement, or by a concerted mechanism (Scheme 8). Although this distinction is probably not synthetically important, it is relevant for a principal mechanistic understanding of this general reaction type. We have therefore carried out a detailed theoretical analysis of the reaction pathway.

Theoretical Studies. First we want to discuss basic energetic aspects of the reactants and products (see Table 1) and the computed transition states (TS), and then analyze the reaction mechanism. In addition to the "real" system with the bulky C_6F_5/mesityl substituents, we also considered smaller model structures in which these large aryl substituents were replaced by hydrogen atoms (dubbed **12B**, **23B**−**27B** in the following), which simplified the quantum chemical computations considerably. However, comparison of the results for these two systems also provides insight into the effect of the substituents, which seems to be not entirely clear also in the related hydrogen activation reactions by such frustrated Lewis pairs. This is briefly discussed

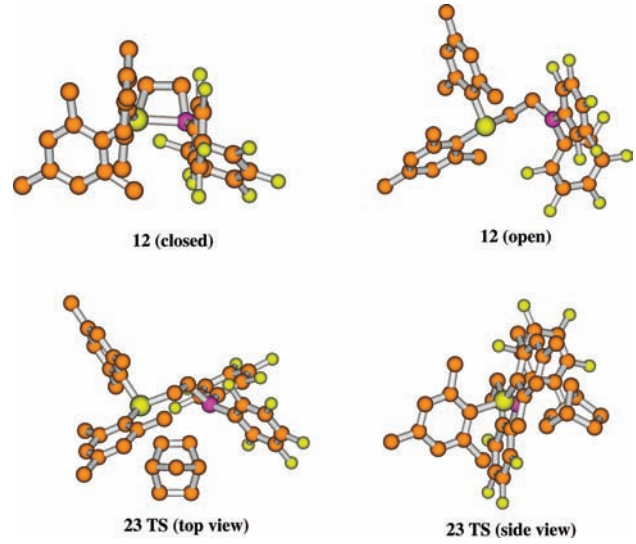


Figure 6. Optimized structures of the open (gauche) and quenched conformations of **12** and of the *exo* transition state **23(TS)** at the B97-D/def2-TZVP level.

at the end of this section. Because the two different density functional methods applied (B97-D and B2PLYP) provide very similar results, only the higher level B2PLYP-D data are considered here; for more details, the reader is referred to Table 1 and the Supporting Information.

The open (gauche) form of **12** is found to be less stable than a "quenched" four-membered ring (see Figure 6) by 13.0 kcal/mol. This dissociation step is required to initiate the reaction. We also found precomplexes of the borane fragment with norbornene but will not discuss these further because they are likely influenced significantly by solvation effects that are mostly absent in our theoretical treatment. The computed reactions of **12** (closed form) with norbornene are strongly exothermic in a range of 16−19 kcal/mol. The *endo* addition product (**26**) is slightly (0.2 kcal/mol) lower in energy than **23**(*exo*), while **25**−**27** are higher by about 2.6−3.2 kcal/mol (see Figure 3 above). The correction to enthalpy at 298 K by B97-D/SV(P) computations of harmonic vibrational frequencies stabilizes **23** in favor of **26** by 0.5 kcal/mol. Solvent effects have been estimated using the COSMO continuum solvation model[32] employing a dielectric constant of 2 for a nonpolar alkane-type solvent. The computed contribution is about 0.1 kcal/mol and therefore negligible. We conclude from the results of the very reliable B2PLYP-D method (estimated error for the relative energy of less than ±0.5 kcal/mol) that, under equilibrium conditions, both isomers **23** and **26** should be experimentally observable (computed equilibrium fractions between 40 and 80% at 298 K for each when considering computational error bars).

The computed reaction barrier for the *exo* attack is about 7 kcal/mol lower than for the corresponding *endo* reaction.[22] The structures of both TS look qualitatively similar except for a slightly higher asymmetry regarding B−C and P−C bond formation (see below) in the *endo* case. The B2PLYP-D *exo* forward barrier is computed to be 12.3 kcal/mol, which seems to be a reasonable value for a fast chemical process that occurs at ambient temperature. From benchmark studies of B2PLYP

(32) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 799–805.

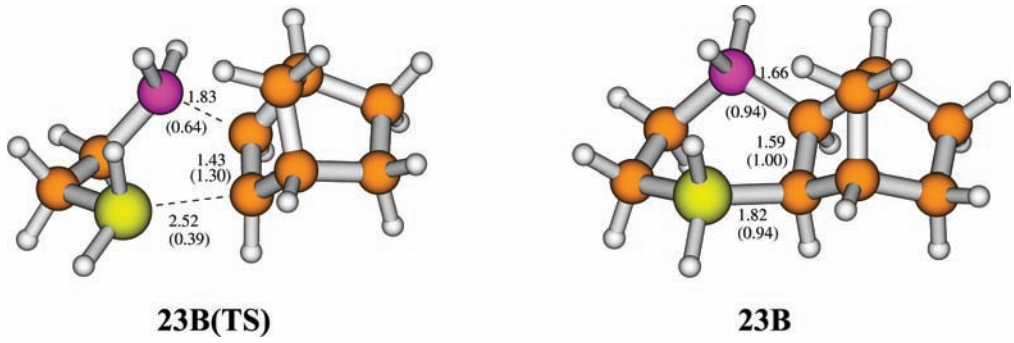


Figure 7. Optimized structures of the *exo* transition state **23B(TS)** and of the product **23B** at the B97-D/def2-TZVP level with interatomic distances in Å (Wiberg bond order in brackets).

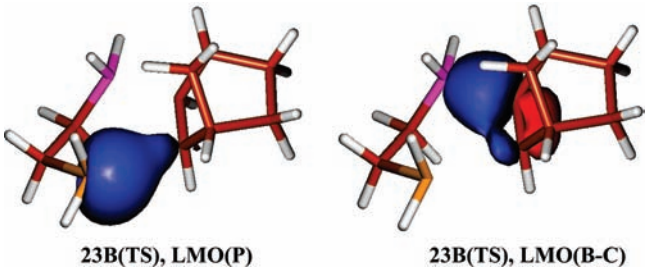


Figure 8. View of the localized Kohn−Sham MOs (LMO) at the transition-state structure **23B(TS)** corresponding to the P(lone-pair)−C(π*) (left) and the B(p)−C(π) (right) interactions.

and related functionals,[33] it is known that such barriers should be accurate to ±1−2 kcal/mol.

Analysis of the electronic structure of the transition state has been performed in detail for the model compounds only. The localized (frontier) Kohn−Sham molecular orbitals formed by B(p)−π and P(lone pair)−π* interactions are shown in Figure 8. It is clearly seen that the two bonds are formed in a synchronous but asymmetric manner. As also indicated by the bond orders (and bond lengths), the B−C bond is slightly ahead of the P−C bond. The corresponding bond orders for **23(TS)** are reduced to 0.37 and 0.21, respectively, for B−C and P−C, i.e., to about 50−60% of the values for **23B(TS)**.

For the substituent effects, a rather mixed picture emerges. In contrast to **12**, the open (gauche) form of **12B** is found to be almost as stable as the quenched conformer (energy difference of 0.6 kcal/mol at the B97-D/def2-TZVP level). On the other hand, the overall reaction energies for **12** and **12B** are not very different, indicating a rather small substituent effect. The same holds for the relative energies of **23(B)**, **25**−**27(B)** and also the barriers. For the transition-state structures (see Figures 6 and 7) we note only an elongation of the forming B−C and P−C bonds in **23(TS)** compared to **23B(TS)** (by about 0.36 and 0.23 Å, respectively), probably due to steric reasons. The increase of the former C═C bond length to about 1.40 Å in **23(TS)** is almost identical with and without substituents (1.43 Å in **23B(TS)**), indicating similar progress along the reaction coordinate. The complexation energies of the borane group at the double bond are also given in Table 1 for the model system (for the substituted systems, the corresponding complexes, due to steric reasons, are more of van der Waals type and therefore not discussed here). Similarly to the TS, the *exo* complex is more stable than the *endo* form (by a similar amount of about 6−7 kcal/mol), which reflects its "early" character as expected for an exothermic reaction. We also tried to find zwitterionic species like **22** (see Schemes 6 and 8). For the model compound, we initially stabilized **22B** by rotation around the PC−CB bond to a *trans* conformation in order to avoid self-quenching of the formal zwitterion pair. However, in the unconstrained geometry optimization, such an assumed intermediate **22B** was converted to the already described borane-group-double-bond complex. Whether this result is due to neglect of the solvent or points to a nonexistence of species **22** is beyond the capabilities of the present quantum chemical procedures.

In summary, according to the theoretical results, the addition of **12** to the double bond of norbornene occurs via an initial P−B "bond" dissociation followed by a concerted but slightly asynchronous bimolecular reaction induced by B(p)−π and P(lone pair)−π* frontier orbital interactions. The reaction is strongly exergonic (about −19 kcal/mol), with an energy barrier of 12.3 kcal/mol and a corresponding rather "early" transition state. The bulky Mes/C_6F_5 substituents do not interfere sterically with the norbornene (also not in the TS) but rather stabilize the product side by several kcal/mol due to noncovalent interactions.[34] Of the four possible stereoisomers of the product, the *exo*-2,3 and *endo*-2,3 forms are most stable (by about 3 kcal/mol). When including corrections to H_{298}, the *exo* form **23** becomes lower in enthalpy than the *endo* isomer by 0.3 kcal/mol. Considering the error in the computations, however, the two isomers (**23**, **26**) should be regarded as isoenthalpic and therefore should both be detectable under experimental *equilibrium* conditions (which is not observed). Thus, in agreement with the results of computations of the *endo* and *exo* transition states, we conclude that the reaction occurs under kinetic control in the experiment.

Conclusions

The bifunctional frustrated $Mes_2P-CH_2-CH_2-B(C_6F_5)_2$ Lewis pair **12** undergoes 1,2-addition reactions with a variety of unsaturated organic substrates. These reactions feature distinct

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(34) (a) El-azizi, Y.; Schmitzer, A.; Collins, S. K. *Angew. Chem.* **2006**, *118*, 982−987; *Angew. Chem., Int. Ed.* **2006**, *45*, 968−973 and references cited therein. (b) Cockroft, S. L.; Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 8594–8595. (c) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593–598. See also: (d) Martin, E.; Spendley, C.; Mountford, A. J.; Coles, S. J.; Horton, P. N.; Hughes, D. L.; Hursthouse, M. B.; Lancaster, S. J. *Organometallics* **2008**, *27*, 1436–1446. (e) Blackwell, J. M.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 1400–1407. (f) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369–1377.

chemo- and regioselectivities. Compound **12** adds to the aldehyde C═O functionality of *trans*-cinnamic aldehyde and leaves the C═C bond untouched. The 1,2-addition to the −CH═O functional group takes place regioselectively with B−O and P−C bond formation. Also the 1,2-addition of **12** to the polar enol ether C═C double bond is regioselective. The boron atom adds to the $=CH_2$ terminus. The observed regioselective reactions of **12** with both the carbonyl C═O group and the enol ether RO−CH═CH_2 moiety are as would be expected for a stepwise reaction pathway involving the respective stabilized internal ion pairs. This regioselective outcome would, however, probably also be expected from a concerted addition pathway with the weakly interaction P/B system of **12** acting as a cooperative pair.[35]

We have obtained evidence from our combined experimental and theoretical study that the 1,2-addition of **12** to the norbornene C═C double bond is a concerted reaction, although it is probably markedly asynchronous, with the B−C bond formed to a larger extent in the transition state (**23(TS)**) than the P−C bond. The *cis* addition mode, of course, is enforced in our example by the short $-CH_2-CH_2-$ bridge connecting the antagonistic P/B Lewis pair in the compound **12**.

Is this actually a new type of a concerted reaction? A simple topological analysis reveals that each of the reactive centers in the antagonistic Lewis pair **12** is involved with one specific orbital, namely the empty p-orbital at boron and the orbital containing the electron pair at phosphorus. Therefore, our 1,2-addition reaction of the antagonistic P/B Lewis pair of **12** to norbornene bears some resemblance to the class of "cheletropic" reactions in Woodward−Hoffmann chemistry,[36] except that the pair of doubly occupied/empty orbitals in the typical cheletropic examples[37] is located at the same single atom. Therefore, one might term examples such as the concerted 1,2-addition of an antagonistic Lewis pair, where these two essential orbitals are located at *different* atoms, as "two-site cheletropic reactions". Analysis of further examples of these and topologically related reactions that are beginning to increasingly appear in the literature will show how important and how widely spread this new reaction type might be.

Experimental Section

General Procedures. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glovebox) under an atmosphere of argon. Solvents were dried according to Grubbs[38] or were distilled from appropriate drying agents and stored under an argon atmosphere. The following NMR instruments were used for physical characterization of the compounds: Bruker ARX 300 spectrometer (^{19}F, 282.4 MHz; ^{11}B, 96.3 MHz; ^{31}P, 121.5 MHz), Varian Inova 500 (^{1}H, 499.9 MHz; ^{13}C, 125.7 MHz; ^{19}F, 470.3 MHz; ^{11}B, 160.4 MHz; ^{31}P, 202.3 MHz), and Varian UnityPlus 600 (^{1}H, 599.9 MHz; ^{13}C, 150.8 MHz; ^{19}F, 564.4 MHz; ^{11}B, 192.4 MHz; ^{31}P, 242.7 MHz). ^{1}H NMR and ^{13}C NMR, chemical shift δ is given relative to TMS and referenced to the solvent signal; ^{19}F NMR, chemical shift δ is given relative to $CFCl_3$ (external reference); ^{11}B NMR, chemical shift δ is given relative to $BF_3 \cdot Et_2O$ (external reference); ^{31}P NMR, chemical shift δ is given relative to H_3PO_4 (85% in D_2O) (external reference). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a Elementar Vario El III instrument. IR spectra were recorded on a Varian 3100 FT-IR spectrometer (Excalibur Series).

X-ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction, Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326); absorption correction, Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228−234); structure solution, SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473); structure refinement, SHELXL-97 (Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122); graphics, XP (BrukerAXS, 2000).

Materials. Dimesitylvinylphosphine[14] and bis(pentafluorophenyl)borane[19] were prepared according to literature procedures. Norbornene was used without further purification; cinnamaldehyde was distilled under reduced pressure prior to use. 1-Pentyne was distilled using vacuum transfer. Ethyl vinyl ether was distilled from sodium using vacuum transfer.

Synthesis of Compound 19. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and $HB(C_6F_5)_2$ (117 mg, 0.34 mmol) were dissolved in pentane (6 mL) and stirred for 15 min. 1-Pentyne (37 μL, 0.37 mmol) was added at room temperature, and after 1 h a white-yellow solid began to precipitate. After the reaction mixture had been stirred for 4 days, the solid was isolated via cannula filtration and washed twice with pentane (2.5 mL). Removal of all volatiles in vacuo yielded **19** (167 mg, 69%) as a white powder. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **19** in benzene. Anal. Calcd for $C_{37}H_{34}BF_{10}P$: C, 62.55; H, 4.82. Found: C, 62.10; H, 4.40. ^{1}H NMR (600 MHz, 298 K, C_6D_6): δ = 6.49 (1H, dt, $^{1}J_{PH}$ = 475 Hz, $^{3}J_{HH}$ = 7.7 Hz, P−H), 6.35 (4H, d, $^{4}J_{PH}$ = 4.0 Hz, *m*-Mes), 2.93 (2H, m, $^{P}CH_2$), 2.34 (2H, t, $^{3}J_{HH}$ = 7.1 Hz, $\equiv CH_2$), 1.91 (12 H, s, *o*-CH_3^{Mes}), 1.83 (6H, s, *p*-CH_3^{Mes}), 1.64 (2H, sext, $^{3}J_{HH}$ = 7.1 Hz, CH_2), 1.52 (2H, br, CH_2^{B}), 1.10 (3H, t, $^{3}J_{HH}$ = 7.1 Hz, CH_3). ^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6): δ = 148.9 (dm, $^{1}J_{FC}$ = 238 Hz, C_6F_5), 145.0 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-Mes), 142.8 (d, $^{2}J_{PC}$ = 9.5 Hz, *o*-Mes), 138.7 (dm, $^{1}J_{FC}$ = 246 Hz, C_6F_5), 137.4 (dm, $^{1}J_{FC}$ = 249 Hz, C_6F_5), 131.5 (d, $^{3}J_{PC}$ = 10.8 Hz, *m*-Mes), 129.0 (br, *i*-C_6F_5), 113.6 (d, $^{1}J_{PC}$ = 75.9 Hz, *i*-Mes), 98.0 (br, $^{B}C\equiv$), 94.8 (br, $\equiv C$), 25.3 (d, $^{1}J_{PC}$ = 35.4 Hz, $^{P}CH_2$), 23.9 (CH_2), 23.1 ($\equiv CH_2$), 21.6 (d, $^{3}J_{PC}$ = 6.6 Hz, *o*-CH_3^{Mes}), 20.8 (*p*-CH_3^{Mes}), 20.5 (CH_2^{B}), 13.9 (CH_3). ^{11}B{^{1}H} NMR (192 MHz, 298 K, C_6D_6): δ = −17.4 ($\nu_{1/2}$ = 60 Hz). ^{31}P NMR (243 MHz, 298 K, C_6D_6): δ = −5.3 ($^{1}J_{PH}$ = 475 Hz). ^{31}P{^{1}H} NMR (243 MHz, 298 K, C_6D_6): δ = −5.3 ($\nu_{1/2}$ = 48 Hz). ^{19}F{^{1}H} NMR (564 MHz, 298 K, C_6D_6): δ = −132.1 (4F, *o*-C_6F_5), −162.7 (2F, *p*-C_6F_5), −165.8 (4F, *m*-C_6F_5). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2359 (w), 2341 (w).

X-ray Crystal Structure Analysis of 19. Formula $C_{37}H_{34}BF_{10}P \cdot 1.5C_6H_6$, M = 827.58, colorless crystal 0.25 × 0.10 × 0.10 mm, a = 17.2244(4), b = 12.5179(4), and c = 21.0243(7) Å, β = 110.039(1)°, V = 4258.7(2) Å^3, ρ_{calc} = 1.291 g cm^{-3}, μ = 1.227

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mm^{-1}, empirical absorption correction ($0.749 \le T \le 0.887$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 31 506 reflections collected (h,k,l), [(sin θ)/λ] = 0.60 $Å^{-1}$, 7483 independent ($R_{int} = 0.055$) and 5991 observed reflections [$I \ge 2\sigma(I)$], 541 refined parameters, $R = 0.056$, $wR^2 = 0.154$, max. (min.) residual electron density 0.32 (−0.32) e $Å^{-3}$, disorder in the group C5−C7 refined with split positions, hydrogen atom at phosphorus from difference Fourier map, others calculated and refined as riding atoms.

Synthesis of Compound 20. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and $HB(C_6F_5)_2$ (117 mg, 0.34 mmol) were dissolved in pentane (10 mL) and stirred for 15 min. Upon addition of cinnamaldehyde (42 μL, 0.34 mmol) at room temperature, a white precipitate formed immediately. After the reaction mixture was stirred overnight, the precipitate was isolated via cannula filtration. The residue was then washed twice with pentane (2 mL), and all volatiles were removed in vacuo to yield **20** (184 mg, 70%). Crystals suitable for X-ray crystal structure analysis were obtained by gas diffusion of heptane into a solution of **20** in benzene at room temperature. Anal. Calcd for $C_{41}H_{34}BF_{10}OP$: C, 63.58; H, 4.42. Found: C, 63.12; H, 4.54. ^{1}H NMR (600 MHz, 298 K, CD_2Cl_2): δ = 7.29 (2H, m, *m*-Ph), 7.23 (3H, m, *p*-, *o*-Ph), 6.98 (2H, br s, *m*-Mes^A), 6.94 (2H, br s, *m*-Mes^B), 6.93 (1H, ddd, $^3J_{HH} = 15.5$ Hz, $^4J_{PH} = 6.2$ Hz, $^4J_{HH} = 1.9$ Hz, $=CH^{Ph}$), 6.11 (1H, dt, $^3J_{HH} = 15.5$ Hz, $^3J_{PH} \approx {}^3J_{HH} = 4.3$ Hz, =CH), 5.74 (1H, ddd, $^2J_{PH} = 6.2$ Hz, $^4J_{HH} = 1.9$ Hz, $^3J_{HH} = 4.3$ Hz, HCO), 3.31, 3.04 (each 1H, each br m, $^PCH_2$), 2.36 (6H, s, *o*-CH_3^{MesB}), 2.32 (3H, s, *p*-CH_3^{MesA}), 2.28 (3H, s, *p*-CH_3^{MesB}), 2.23 (6H, s, *o*-CH_3^{MesA}), 1.67, 1.02 (each 1H, each br m, $^BCH_2$). ^{13}C{^{1}H} NMR (151 MHz, 298 K, CD_2Cl_2): δ = 144.3 (*p*-Mes^A), 143.7 (*p*-Mes^B), 142.8 (*o*-Mes^B), 142.5 (*o*-Mes^A), 136.7 (d, $^4J_{PC} = 3.8$ Hz, *i*-Ph), 133.8 (d, $^3J_{PC} = 12.1$ Hz, $=CH^{Ph}$), 132.7 (br d, $^3J_{PC} = 7.7$ Hz, *m*-Mes^A), 131.5 (br d, $^3J_{PC} = 7.7$ Hz, *m*-Mes^B), 129.0 (*m*-Ph), 128.3 (*p*-Ph), 126.9 (*o*-Ph), 123.6 (=CH), 122.8 (d, $^1J_{PC} = 60.5$ Hz, *i*-Mes^B), 119.6 (d, $^1J_{PC} = 60.5$ Hz, *i*-Mes^A), 81.3 (d, $^1J_{PC} = 35.1$ Hz, HCO), 28.4 (d, $^1J_{PC} = 42.1$ Hz, $^PCH_2$), 24.5 (*o*-CH_3^{MesA}), 23.6 (*o*-CH_3^{MesB}), 21.1 (*p*-$CH_3^{MesA,B}$), 13.9 (br, $^BCH_2$), n.o. (C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, 298 K, CD_2Cl_2): $\delta = -0.5$ ($\nu_{1/2} = 150$ Hz). ^{31}P{^{1}H} NMR (243 MHz, 298 K, CD_2Cl_2): $\delta = 16.1$ ($\nu_{1/2} = 12$ Hz). ^{19}F{^{1}H} NMR (564 MHz, 298 K, CD_2Cl_2): $\delta = -134.6$ (2F, *o*-), −162.5 (1F, *p*-), −166.4 (2F, *m*-) ($C_6F_5^A$), −134.8 (2F, *o*-), −161.4 (1F, *p*-), −165.6 (2F, *m*-) ($C_6F_5^B$).

X-ray Crystal Structure Analysis of 20. Formula $C_{41}H_{34}BF_{10}OP$, $M = 774.46$, colorless crystal 0.20 × 0.15 × 0.10 mm, $a = 9.4496(3)$, $b = 30.8893(11)$, and $c = 12.4289(4)$ Å, $\beta = 98.642(2)°$, $V = 3586.7(2)$ $Å^3$, $\rho_{calc} = 1.434$ g cm^{-3}, $\mu = 1.440$ mm^{-1}, empirical absorption correction ($0.762 \le T \le 0.869$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 29 245 reflections collected (h,k,l), [(sin θ)/λ] = 0.60 $Å^{-1}$, 6310 independent ($R_{int} = 0.061$) and 4839 observed reflections [$I \ge 2\sigma(I)$], 493 refined parameters, $R = 0.050$, $wR^2 = 0.127$, max. (min.) residual electron density 0.20 (−0.25) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Preparation of Compound 21. Dimesitylvinylphosphine (100 mg, 0.34 mmol) and $HB(C_6F_5)_2$ (117 mg, 0.34 mmol) were dissolved in pentane (6 mL) and stirred for 15 min. Upon addition of ethyl vinyl ether (36 μL, 0.37 mmol) at room temperature, a white solid began to precipitate. After the reaction mixture was stirred for 24 h, the solid was isolated via cannula filtration and washed twice with pentane (2 mL). Removal of all volatiles in vacuo yielded **21** (204 mg, 84%). Crystals suitable for X-ray crystal structure analysis were grown by slow concentration of a solution of **21** in dichloromethane at −36 °C. Anal. Calcd for $C_{36}H_{34}BF_{10}P$: C, 60.52; H, 4.80. Found: C, 60.23; H, 4.71. ^{1}H NMR (500 MHz, 298 K, C_6D_6): $\delta = 6.46$ (2H, d, $^4J_{PH} = 4.0$ Hz, *m*-Mes^B), 6.39 (2H, d, $^4J_{PH} = 3.7$ Hz, *m*-Mes^A), 5.03 (1H, dt, $^3J_{HH} = 12.4$ Hz, $^2J_{PH} \approx {}^3J_{HH} = 4.4$ Hz, CH), 3.52, 2.74 (each 1H, each dq, $^4J_{PH} = 9.0$ Hz, $^3J_{HH} = 7.1$ Hz, CH_2^{Et}), 2.92 (1H, ddd, $^3J_{PH} = 44.6$ Hz, $^2J_{HH} = 13.5$ Hz, $^3J_{HH} = 4.4$ Hz, $^OCH_2^B$), 2.47, 2.34 (each 1H, each m, $^PCH_2$), 2.15 (6H, s, *o*-CH_3^{MesB}), 1.88 (6H, s, *o*-CH_3^{MesA}), 1.88 (2 × 3H, s, *p*-$CH_3^{MesA,B}$), 1.96 (dm, $^3J_{PH} = 39.9$ Hz), 1.27 (m) (each 1H, $^BCH_2$), 1.65 (1H, ddd, $^2J_{HH} = 13.5$ Hz, $^3J_{HH} = 12.4$ Hz, $^3J_{PH} = 8.7$ Hz, $^OCH_2^B$), 0.68 (3H, t, $^3J_{HH} = 7.1$ Hz, CH_3). ^{13}C{^{1}H} NMR (125 MHz, 298 K, C_6D_6): δ = 149.3, 148.9 (each dm, each $^1J_{FC} = 237$ Hz, each 2 × C_6F_5), 143.1, 142.9 (each d, $^4J_{PC} = 3.0$ Hz, *p*-$Mes^{A,B}$), 142.2 (d, $^2J_{PC} = 8.8$ Hz, *o*-Mes^B), 141.9 (d, $^2J_{PC} = 8.8$ Hz, *o*-Mes^A), 138.7 (dm, $^1J_{FC} = 246$ Hz, 2 × C_6F_5), 137.6 (dm, $^1J_{FC} = 248$ Hz, 4 × C_6F_5), 132.2 (d, $^3J_{PC} = 10.9$ Hz, *m*-Mes^A), 131.6 (d, $^3J_{PC} = 10.9$ Hz, *m*-Mes^B), 129.0 (br, *i*-C_6F_5), 122.3 (d, $^1J_{PC} = 69.9$ Hz, *i*-Mes^B), 121.8 (d, $^1J_{PC} = 69.9$ Hz, *i*-Mes^A), 85.1 (d, $^1J_{PC} = 55.4$ Hz, CH), 66.3 (d, $^3J_{PC} = 11.0$ Hz, CH_2^{Et}), 28.3 (d, $^1J_{PC} = 39.0$ Hz, $^PCH_2$), 27.6 (br, $^OCH_2^B$), 23.9 (d, $^3J_{PC} = 4.2$ Hz, *o*-CH_3^{MesB}), 23.8 (d, $^3J_{PC} = 3.2$ Hz, *o*-CH_3^{MesA}), 20.7, 20.6 (each d, $^5J_{PC} = 1.5$ Hz, *p*-$CH_3^{MesA,B}$), 16.4 (br, $^BCH_2$), 14.8 (CH_3), ^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6) $\delta = -13.3$ ($\nu_{1/2} = 80$ Hz). ^{31}P{^{1}H} NMR (202 MHz, 298 K, C_6D_6): $\delta = 23.4$ ($\nu_{1/2} = 6$ Hz). ^{19}F{^{1}H} NMR (470 MHz, 298 K, C_6D_6): $\delta = -133.5$ (2F, *o*-), −162.2 (1F, *p*-), −165.1 (2F, *m*-) ($C_6F_5^A$), −133.7 (br, 2F, *o*-), −161.1 (1F, *p*-), −164.5 (2F, *m*-) ($C_6F_5^B$).

X-ray Crystal Structure Analysis of 21. Formula $C_{36}H_{34}BF_{10}OP$, $M = 714.41$, colorless crystal 0.40 × 0.30 × 0.25 mm, $a = 33.6177(10)$, $b = 12.8660(4)$, and $c = 16.5773(5)$ Å, $\beta = 111.635(2)°$, $V = 6665.0(4)$ $Å^3$, $\rho_{calc} = 1.424$ g cm^{-3}, $\mu = 1.496$ mm^{-1}, empirical absorption correction ($0.586 \le T \le 0.706$), $Z = 8$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 22 950 reflections collected (h,k,l), [(sin θ)/λ] = 0.60 $Å^{-1}$, 5877 independent ($R_{int} = 0.042$) and 5364 observed reflections [$I \ge 2\sigma(I)$], 449 refined parameters, $R = 0.048$, $wR^2 = 0.135$, max. (min.) residual electron density 0.36 (−0.30) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Synthesis of Compound 23. To a solution of dimesitylvinylphosphine (100 mg, 0.34 mmol) and $HB(C_6F_5)_2$ (117 mg, 0.34 mmol) in pentane (10 mL) was added norbornene (621 mg, 6.6 mmol). The reaction mixture was stirred for 8 days at room temperature, and during that time a white solid precipitated. The precipitate was isolated via cannula filtration, washed with pentane (10 mL), and dried in vacuo to yield **23** (173 mg, 72%). Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **23** in benzene. Anal. Calcd for $C_{39}H_{36}BF_{10}P$: C, 63.60; H, 4.93. Found: C, 63.91; H, 5.42. ^{1}H NMR (600 MHz, 298 K, C_6D_6/CD_2Cl_2): $\delta = 6.65$ (1H, br, *m*-Mes^A), 6.55 (1H, br, *m*′-Mes^A), 6.55 (1H, br, *m*-Mes^B), 6.48 (1H, br, *m*′-Mes^B), 3.29 (1H, m, 2-H), 3.20 (1H, m, 3-H), 2.89, 2.63 (each 1H, each m, $^PCH_2$), 2.57 (3H, s, *o*-CH_3^{MesB}), 2.41 (3H, s, *o*-CH_3^{MesA}), 2.21 (1H, dm, $^3J_{PH} = 35.5$ Hz, $^BCH_2$), 2.02 (3H, s, *p*-CH_3^{MesA}), 2.00 (1H, br, 1-H), 1.94 (3H, s, *p*-CH_3^{MesB}), 1.79 (1H, dd, $^3J_{HH} = 12.0$ Hz, 3.5 Hz, 4-H), 1.70 (3H, s, *o*′-CH_3^{MesA}), 1.60 (3H, s, *o*′-CH_3^{MesB}), 1.42 (2H, m, 6-H), 1.23, 1.11 (each 1H, each m, 5-H), 1.19, 0.72 (each 1H, each m, 7-H), 0.36 (1H, m, $^BCH_2$). ^{13}C{^{1}H} NMR (151 MHz, 298 K, C_6D_6/CD_2Cl_2): δ = 149.2 (dm, $^1J_{FC} = 238$ Hz, 2 × C_6F_5), 148.5 (dm, $^1J_{FC} = 234$ Hz, 2 × C_6F_5), 143.9 (d, $^2J_{PC} = 8.3$ Hz, *o*-Mes^B), 143.2 (d, $^4J_{PC} = 2.8$ Hz, *p*-Mes^A), 142.9 (d, $^4J_{PC} = 2.8$ Hz, *p*-Mes^B), 142.7 (d, $^2J_{PC} = 8.2$ Hz, *o*-Mes^A), 141.3 (d, $^2J_{PC} = 8.2$ Hz, *o*′-Mes^A), 141.1 (d, $^2J_{PC} = 9.1$ Hz, *o*′-Mes^B), 138.1 (dm, $^1J_{FC} = 263$ Hz, 2 × C_6F_5), 137.2 (dm, $^1J_{FC} = 251$ Hz, 4 × C_6F_5), 132.7 (d, $^3J_{PC} = 10.6$ Hz, *m*′-Mes^B), 132.4 (d, $^3J_{PC} = 10.2$ Hz, *m*′-Mes^A), 132.0 (d, $^3J_{PC} = 10.9$ Hz, *m*-Mes^A), 131.5 (d, $^3J_{PC} = 11.0$ Hz, *m*-Mes^B), 123.0 (d, $^1J_{PC} = 72.2$ Hz, *i*-Mes^A), 122.3 (d, $^1J_{PC} = 75.9$ Hz, *i*-Mes^B), 44.0 (d, $^1J_{PC} = 32.9$ Hz, C3), 43.7 (C1), 42.8 (C4), 38.3 (C7), 37.6 (br, C2), 33.9 (d, $^3J_{PC} = 14.9$ Hz, C5), 32.4 (C6), 25.9 (d, $^1J_{PC} = 41.5$ Hz, $^PCH_2$), 24.8 (*o*-CH_3^{MesB}), 24.6 (d, $^3J_{PC} = 2.4$ Hz, *o*-CH_3^{MesA}), 22.3 (d, $^3J_{PC} = 5.2$ Hz, *o*′-CH_3^{MesA}), 22.2 (d, $^3J_{PC} = 5.1$ Hz, *o*′-CH_3^{MesB}), 20.9 (d, $^5J_{PC} = 1.4$ Hz, *p*-CH_3^{MesA}), 20.6 (d, $^5J_{PC} = 1.3$ Hz, *p*-CH_3^{MesB}), 14.8 (br, $^BCH_2$), n.o. (*i*-C_6F_5). ^{11}B{^{1}H} NMR (96 MHz, 298 K, C_6D_6/CD_2Cl_2): $\delta = -11.8$ ($\nu_{1/2} = 70$ Hz). ^{31}P{^{1}H} NMR (122 MHz, 298 K, C_6D_6/CD_2Cl_2): $\delta = 31.2$ ($\nu_{1/2} = 15$ Hz). ^{19}F{^{1}H} NMR (282 MHz, 298

K, C_6D_6/ CD_2Cl_2): $\delta = -132.1$ (br, 4F, *o*-C_6F_5),−162.8, −163.8 (each 1F, *p*-C_6F_5), −165.9, −166.5 (each 2F, *m*-C_6F_5).

X-ray Crystal Structure Analysis of 23. Formula $C_{39}H_{36}BF_{10}P \cdot 1.5C_6H_6$, $M = 853.62$, colorless crystal 0.30 × 0.20 × 0.10 mm, $a = 12.1477(5)$, $b = 12.2155(5)$, and $c = 15.1806(6)$ Å, $\alpha = 74.541(2)$, $\beta = 72.625(2)$, and $\gamma = 82.110(2)°$, $V = 2068.01(15)$ Å^3, $\rho_{calc} = 1.371$ g cm^{-3}, $\mu = 1.281$ mm^{-1}, empirical absorption correction ($0.700 \leq T \leq 0.883$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 30 905 reflections collected (h,k,l), [(sin θ)/λ] = 0.60 Å^{-1}, 7290 independent ($R_{int} = 0.049$) and 6649 observed reflections [$I \geq 2\sigma(I)$], 547 refined parameters, $R = 0.049$, $wR^2 = 0.133$, max. (min.) residual electron density 0.31 (−0.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

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Supporting Information Available: Experimental details and information about the quantum chemical calculations and the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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