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An Al/P-Based Frustrated Lewis Pair as an Efficient Ambiphilic Ligand: Coordination of Boron Trihalides, Rearrangement, and Formation of HBX_2 Complexes (X = Br, I)

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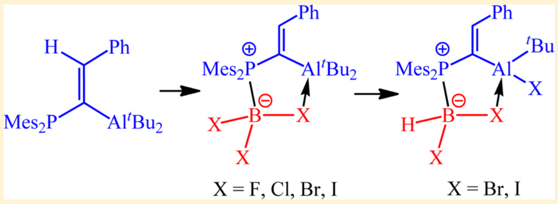
Supporting Information

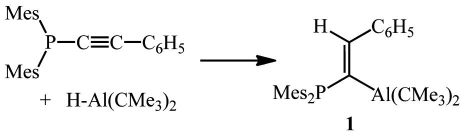
ABSTRACT: The Al/P-based frustrated Lewis pair (FLP) Mes_2P—C(═CH—Ph)—Al(CMe_3)$_2$ (**1**) reacted with boron halides BX_3 (X = F, Cl, Br, I) as an ambiphilic ligand to form complexes (**2**−**5**) in which the boron atoms were coordinated to phosphorus and one of the halogen atoms to aluminum. Nonplanar five-membered heterocycles resulted that had five different ring atoms (AlCPBX). The distance of the bridging halogen atoms to the AlCPB plane increased steadily with the radius of the halogen atoms. Only the BF_3 adduct showed a dynamic behavior in solution at room temperature with equivalent *tert*-butyl or mesityl groups in the NMR spectra, while in other cases, the rigid conformation led to the magnetic inequivalence of the substituents at Al and P with well-resolved signals for each group. The BBr_3 and BI_3 complexes underwent in solution at room temperature a spontaneous stereoselective rearrangement with the concomitant release of isobutene. The obtained products, Mes_2P—(μ-C═CH—Ph)(μ-HBX_2)—AlX(CMe_3) (**6** and **7**) may be viewed as unique adducts of a modified new Al/P-based FLP, Mes_2P—C(═CH—Ph)—AlX(CMe_3) (X = Br, I), with dihalogenboranes, HBX_2. The trapped boranes are either completely unknown (X = I) or unstable in the free form. Quantum−chemical calculations suggest an ionic rearrangement mechanism via the formation of a borenium cation, β-hydride elimination, and hydride transfer. The bromine migration from boron to aluminum corresponds to a formal suprafacial 1,3-sigmatropic rearrangement.



■ INTRODUCTION

Frustrated Lewis pairs (FLPs) have found considerable interest in recent research.[1] They have Lewis acidic and basic centers in single molecules or bimolecular systems and show a unique chemical reactivity as evident from the efficient coordination and activation of diverse substrates such as carbon dioxide or dihydrogen. Only recently Al/P-based FLPs were shown to be powerful alternatives to the usually applied B/P-based systems. Because of the inherently high Lewis acidity of aluminum atoms, these FLPs do not require an activation of the acceptor atoms by electron-withdrawing fluorinated substituents. They are excellent reagents for the coordination and activation of inorganic and organic compounds such as carbon dioxide,[2−4] terminal alkynes,[2,5] alkenes,[6] hydrogen,[7] carbonyl compounds,[8] or isocyanates.[4] They are applicable as ion-pair receptors for the effective coordination of strongly polar alkali metal hydrides,[9] in unprecedented hydride transfer reactions by phase-transfer catalysis,[9] and as efficient main-group-based catalysts for the dehydrogenation of amineboranes.[10] Hydroalumination of alkynylphosphines is a facile method for the generation of such compounds,[2] but steric shielding by bulky groups bonded to phosphorus and aluminum is required to prevent secondary reactions such as dimerization via intermolecular Al−P interactions[11] or the formation of persistent adducts with sterically less shielded dialkylaluminum hydrides or alkynylphosphines.[11] These reactions verify the strong donor−acceptor capability of these Al/P-based FLPs because the $HAlR_2$ adducts were formed in the presence of excess alkyne, while the alkyne adducts were formed despite an excess of the hydride. Most experiments of our group are based on the Al/P-based FLP **1** (Scheme 1) that is easily available in a multigram scale by treatment of dimesityl-phenylethynylphosphine with di(*tert*-butyl)aluminum hydride.[2] The specific bifunctionality of these compounds with donor and acceptor sites in single molecules should allow their application as efficient ligands for the coordination of polar or even ionic compounds as was previously shown with alkali metal hydrides,[9] dialkylaluminum hydrides,[11] or borane, BH_3.[10] In this Article, we report on the reactions of **1** with boron trihalides. In addition to

Scheme 1. Formation of Al/P FLP 1



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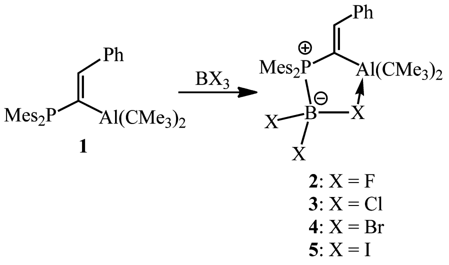
investigations in the coordination mode and the influence of the size of the halogen atoms on the structure and stability of the expected adducts, we were interested in possible secondary reactions that in view of the well-known alkylation capability of alkylaluminum groups could result in halogen−alkyl exchange reactions.

■ RESULTS AND DISCUSSION

Formation of BX_3 Adducts. The adducts **2**−**5** were obtained by treatment of FLP **1** with BF_3·THF or the halides BCl_3, BBr_3, and BI_3 in toluene below room temperature or −20 °C (Scheme 2). Solutions of **2** (X = F) and **3** (X = Cl) were thermally stable and could be stored at room temperature or slightly elevated temperatures without decomposition. The colorless crystalline products were isolated in yields of greater than 87% after recrystallization from mixtures of *n*-hexane and 1,2-difluorobenzene or the pure fluorinated solvent. Compounds **4** (X = Br) and **5** (X = I) in contrast were thermally unstable and decomposed in solution at temperatures greater than 0 °C. At −20 °C, they were formed in high purity. Concentration and storage of the reaction mixtures at low temperature afforded the colorless products in moderate yields of 71% and 30%. Owing to the instability of these adducts, the NMR data were recorded at 0 °C allowing the unambiguous identification of the products despite the formation of some minor impurities.

Scheme 2. Synthesis of BX_3 Adducts 2−5



The molecular structures of compounds **2**−**4** confirmed the formation of adducts between the bifunctional FLP **1** and BX_3 via B−P bonding interactions and B−X−Al bridges (Figures 1 and 2). Five-membered heterocycles were formed that contained five different ring atoms (BPCAlX). The Al−C (204 pm), P−C (182 pm), and B−P distances (205 pm, Table 1) in the heterocycles are similar in all compounds. The B−P bond lengths are relatively long compared to adducts of aryl- or alkylphosphines with boron halides that usually are between 192 and 202 pm.[12] The difference may be caused by ring strain, steric interactions of BX_3 with the bulky mesityl groups, and the bifunctional coordination of the BX_3 molecules via boron and halogen atoms. All other structural parameters in the backbone of the adducts correlate with the size of the halogen atoms. The terminal B−X bond lengths are similar to values observed for BX_3−phosphine adducts,[12] with the B−X distances to the bridging halogen atoms expectedly being lengthened by 13 (X = F) to 9 pm (X = Br). The Al−X distances are in the upper range typically observed for Al−X−Al bridges of dialkyl- or diarylaluminum halides.[13] M−X−B bridges are rare in main-group metal chemistry, possibly as a result of the weak donor capability of boron-bound halogen atoms. Only a few examples are reported in the literature, and those are limited exclusively to the tetrafluorborate anion.[14] A broader structural variety was observed for respective transition metal compounds.[15] Interestingly, the angle P−C−Al of BF_3 adduct **2** with relatively short B−F and Al−F bonds is smaller (114.1(1)°) than that of free FLP **1** (119.0(av)°),[2] while larger values of 121.5(1) and 122.9(av)° were detected for **3** (X = Cl) and **4** (X = Br). The intramolecular P···Al distances increase simultaneously from 322.5 to 339.8 pm (328.7 pm in **1**). The unfavorable fit between the bite of the bifunctional ligand (distance between donor and acceptor centers of the FLP) and the steadily increasing B−X and Al−X bond lengths results in an increasing deviation of the bridging halogen atom from the average plane of the four remaining ring atoms (BPCAl) and larger torsion angles Al−C−P−B that may indicate an increasing steric strain in these molecules. While the fluorine atom is almost in the same plane as these atoms (only 23 pm above the plane), the bromine atom deviates by 64 pm. The increasing displacement of the halogen atoms results in a slight rotation of the $Al(CMe_3)_2$ group in particular in comparison of the Cl and Br

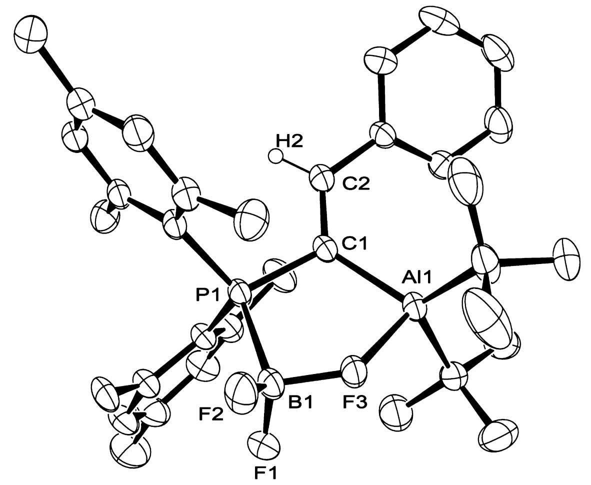


Figure 1. Molecular structure and numbering scheme of **2** (similar scheme for **3**); displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of H2 have been omitted. See Table 1 for important bond lengths and angles.

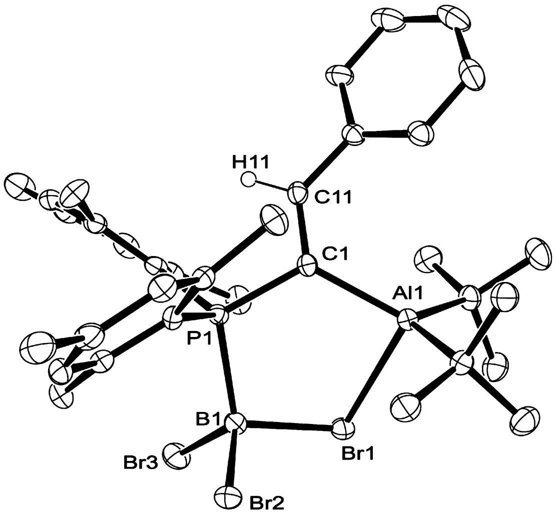


Figure 2. Molecular structure and numbering scheme of **4**; displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of H11 have been omitted. See Table 1 for important bond lengths and angles.

Table 1. Selected Structural Parameters of BX_3 Adducts **2**−**4** and HBI_2 Adduct **7**

	2 (X = F)	**3** (X = Cl)	**4** (X = Br)[b]	**7** (HBI_2)
P−B (pm)	205.3(3)	204.9(3)	205.1	199.3(3)
B−X_t (pm)	135.5 (av)	182.0 (av)	199.2	220.0(3)
B−X_{br} (pm)	148.8(3)	193.2(4)	207.9	229.7(3)
Al−X_{br} (pm)	191.3(2)	240.0(1)	255.8	274.06(9)[c]
P−C−Al (deg)	114.1(1)[a]	121.5(1)	122.9	121.7(1)
B−X−Al (deg)	130.0(2)	107.88(9)	103.1	81.77(8)
B···Al (pm)	308.8	351.3	364.4	331.4
P···Al (pm)	322.5[a]	337.2	339.8	335.4
deviation of X from plane (pm)	23.2	59.4	63.8	152.9
torsion angle Al−C−P−B (deg)	9.3(2)	−11.6(2)	15.7	−27.9(2)
activation barrier	48.3 kJ/mol	61.8 kJ/mol	Dec.	–

[a] For comparison: P−C−Al = 119.0° (av) and P···Al = 328.7 pm (av) in FLP **1**. [b] Average values from three independent molecules. [c] Al−I(terminal) = 256.10(9) pm.

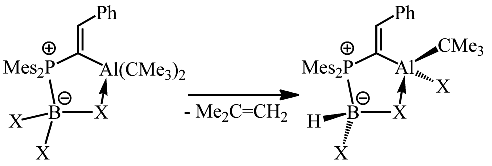
compounds and leads to a relatively short contact between a methyl group of a CMe_3 substituent and the boron atom (B···C distance is 424 pm in **3** and 413 pm in **4**) despite an increasing B···Al distance. These structural details are important for the understanding of the dynamic behavior of these compounds in solution and their reluctance to undergo secondary reactions (see below). Regrettably, the instability of BI_3 adduct **5** in solution prevented the growing of single crystals and the determination of its molecular structure.

Only BF_3 adduct **2** showed the expected simple ^1H NMR spectrum at room temperature with a singlet for both *tert*-butyl groups and a single set of resonances for two chemically equivalent mesityl groups. Cooling to −60 °C resulted in a slight broadening of the *tert*-butyl singlet and a strong broadening of the resonance of the *ortho*-methyl groups, while the signal of the *para*-methyl groups remained unchanged. The fluorine atoms showed a broad singlet in the ^{19}F NMR spectrum at room temperature. A splitting into two resonances with an intensity ratio of 2 to 1 was observed on cooling a toluene solution to −15 °C. The second resonance was assigned to the bridging fluorine atom and consists of a doublet of triplets by coupling to the terminal fluorine atoms and the phosphorus atom. This observation may be interpreted in terms of a fast rotation of the BF_3 group at room temperature with an exchange of the fluorine atoms between terminal and bridging positions. At low temperature, the structure is fixed with the bridging fluorine atom being part of an almost planar heterocycle and consequently equivalent *tert*-butyl and mesityl substituents. In contrast, a splitting of the *tert*-butyl and mesityl resonances was observed for solutions of adducts **3**−**5** at room temperature that indicated a rigid conformation with magnetically inequivalent substituents. Hindered rotation across the P−C(mesityl) bonds resulted in a further splitting of the *ortho*-Me groups into four resonances in the ^1H and ^{13}C NMR spectra. This behavior correlates to the radii of the heavier halogen atoms and the longer B−X and Al−X bonds in the Al−X−B bridges that result in an increasing displacement of the bridging halogen atoms from the plane of the remaining four ring atoms (see molecular structures). With these continuous structural changes, the oscillation of the halogen atoms between both sides of the five-membered rings becomes energetically unfavorable and requires a drastic distortion of the bond parameters in the rings for a planar transition state. The halogen atoms are preferably localized on one side of the ring, and the equilibration of the substituents at aluminum and phosphorus is prevented by a high activation barrier. The alternating coordination of two halogen atoms by rotation of the BX_3 groups about the P−B bonds may offer a reasonable alternative explanation for the observed exchange processes. Equivalent substituents were observed for the BCl_3 adduct only upon heating a solution to about +60 °C. Activation barriers for the rotation of the BX_3 groups were estimated to be 48.3 kJ/mol (X = F) and 61.8 kJ/mol (X = Cl).[16] The latter value should be treated with caution because slow decomposition of **3** was observed at elevated temperature that may influence the exchange process. Similar temperature-dependent NMR experiments failed for BBr_3 and BI_3 adducts **4** and **5** because they readily rearranged in solution above room temperature or even at 0 °C.

Formation of HBX_2 Adducts 6 and 7. Storing solutions of BBr_3 adduct **4** in benzene at 2 °C for 5 days in a sealed NMR tube yielded reproducibly in a selective and unprecedented rearrangement compound **6** with only one *tert*-butyl group bonded to aluminum and a hydridic hydrogen atom attached to boron (Scheme 3). Isobutene was formed as a byproduct and was identified by its characteristic NMR shifts ($\delta(^1H)$ = 4.74 and 1.59). All attempts to repeat this reaction on a preparative scale failed. The reactions did not go to completion, and inseparable mixtures of compounds were obtained. Compound **6** was identified by NMR spectroscopy as the main component. A similar product (**7**) was obtained when FLP **1** was treated with BI_3 at 0 °C. The corresponding adduct **5** could only be identified as an intermediate on the basis of its characteristic NMR data. Compound **7** is insoluble in hydrocarbons and was isolated directly from the reaction mixture as an amorphous solid in 69% yield. Its NMR spectra had to be recorded in CD_2Cl_2 solutions, although slow decomposition was observed in this solvent at temperatures as low as 0 °C.

Only iodine compound **7** was obtained as a crystalline solid and characterized by crystal structure determination (Figure 3). The NMR spectra of **6** and **7** were almost identical, and it is a

Scheme 3. Rearrangement of Adducts **4** and **5**



4: X = Br
5: X = I

6: X = Br
7: X = I

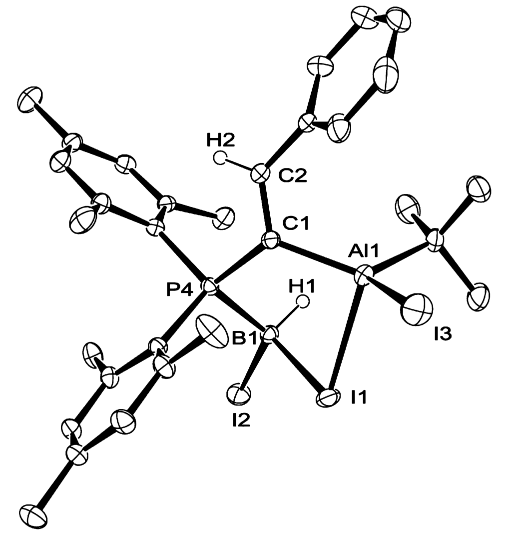


Figure 3. Molecular structure and numbering scheme of **7**; displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of H1 and H2 have been omitted. See Table 1 for important bond lengths and angles.

reasonable assumption that both compounds are isostructural. Compound **7** may be described as an adduct of the unknown halogenoborane HBI_2 with the unique halogen-functionalized FLP $Mes_2P{-}C({=}CH{-}Ph){-}Al(CMe_3)(I)$ in which compared to the FLP **1** a *tert*-butyl group at aluminum has been replaced by an iodine atom. Pure HBX_2 compounds are unstable in the condensed phase and have been obtained only in matrix experiments, in the gas phase, or in equilibrium mixtures with other boron species (with the exception of X = I).[17] In contrast, adducts with carbene, amine, or thioether ligands are stable. They have been characterized by crystal structure determination; some are commercially available and have been used in hydroboration reactions.[18] We did not find any reference on HBI_2. Hence, adduct **7** is a unique compound in which unknown diiodoborane is stabilized by coordination to our bifunctional FLP **1**. Compounds **6** and **7** may be formed by a halogen−*tert*-butyl exchange between boron and aluminum, while the B−H bond is formed by β-hydride elimination. This is the first time that the di(*tert*-butyl)aluminum group of FLP **1** reacted as an effective alkylating reagent to form new and unexpected compounds. Five-membered heterocycles are formed that feature Al−I−B bridges. The relatively long B−I (229.7(3) pm) and Al−I distances (274.06(9) pm, Table 1) to the bridging iodine atom cause its large displacement of 152.9 pm from the BPCAl plane. The angle P−C−Al (121.7(1)°) is similar to that of BBr_3 adduct **4**. The remaining *tert*-butyl group and the hydrogen atom bonded to boron are on the same side of the central heterocycle. Boron and aluminum have both a chiral coordination sphere with four chemically different substituents. The *R*,*S*-configurated molecule (B: *R*; Al: *S*) is depicted in Figure 3 with the enantiomeric form being generated by the crystallographic center of symmetry.

The NMR spectra of both compounds are consistent with the constitution of **7** in the solid state. Resonances of a *tert*-butyl group and two independent mesityl substituents were observed. The vinylic hydrogen atoms gave doublets by coupling to the phosphorus atoms with $^3J_{PH}$ coupling constants of 37.7 and 34.6 Hz that are characteristic of a *cis* arrangement of hydrogen and four-coordinate phosphorus atoms across C═C bonds[2,9−11] and are similar in range to those of adducts **2**−**5**. The terminal B−H hydrogen atoms gave broad resonances at δ = 5.07 and 4.50, and singlets were observed for the phosphorus atoms in the ^{31}P NMR spectra at δ = 6.3 and 5.1. It is interesting to note that even the crude products showed only a single ^{31}P NMR resonance although there are two stereogenic centers in these molecules (Al and B) that should give rise to the formation of diastereomeric molecules. In order to exclude a fast exchange between both possible isomers (*R*,*R* and *R*,*S* plus their enantiomers) by ring opening and fast rotation, we conducted low-temperature NMR experiments as low as −70 °C. No change was observed except the usual chemical shift alterations and a lower half-width associated with the resonances at lower temperature. The results of the NMR spectroscopic characterization confirm a highly stereoselective rearrangement and the formation of only a single stereo isomer (and its enantiomer).

The reaction mechanism was elucidated by density functional theory calculations. Preliminary geometry optimizations for the gas phase were performed at the M062x/6-31G(D) level, and final results were obtained by the M062x/6-311+G(d,p)+GD3 method, which includes the robust M062x functional of Zhao and Truhlar[19] as well as the GD3-dispersion correction as developed by Grimme et al.[20] In order to simulate unspecific solvent effects, solvent reaction field calculations using the CPCM polarizable conductor calculation model (solvent = benzene) at the M062x/6-311+G(d,p)+GD3//M062x/6-311+G(d,p) level were performed. For all calculations, the GAUSSIAN09-D01[21] package of programs was used. In the following, we discuss structural properties and relative energies (kcal/mol) based on the solvent model including zero point corrections (M062x/6-31G(d)). Natural charges (natural bond orbital (NBO) charges) were obtained from NBO calculations[22] as implemented in Gaussian09.

We started our calculations with FLP **1** that is characterized by a relatively long intramolecular nonbonding P−Al distance of 332.5 pm (X-ray structure analysis: 328.7 pm). Positive NBO charges were obtained for the Lewis-acidic Al (+1.998) and the Lewis-basic P atoms (+0.876). Coordination of BBr_3 afforded compound **4** with a five-membered AlCPBBr heterocycle in an exothermic reaction (−31.8 kcal/mol). The direct comparison of the calculated total energies of **4** and **6** indicates that the overall rearrangement reaction is exothermic by −14.5 kcal/mol (−12.7 kcal/mol for the intermediate van der Waals complex of **6** and isobutene, **C**). For the rearrangement of **4** to **6**, we first considered a concerted process that at a first sight seemed to offer an excellent explanation for the experimentally observed high selectivity. However, the approach of *tert*-butyl hydrogen atoms to the boron atom resulted in an almost continuous increase in energy (up to about >68 kcal/mol) and resulted in a high energy local minimum (E_{rel} = 30.5 kcal/mol) that is characterized by a B−H bond, an isolated bromide anion (Al···Br 537.0 pm), and a substantially enlarged Al−C bond (232.5 pm) to the leaving isobutene moiety. This not very reasonable intermediate gives the observed product **6** over a barrier of only a few kilocalories per mole in a strong exothermic reaction. This calculated very endothermic reaction pathway indicates that the negligibly low Lewis acidity of the four-coordinate boron atom in **4** does not support a concerted reaction pathway under the experimentally applied conditions.

In the next step, we resorted to mechanisms that were based on ionic intermediates. BBr_3 adduct **4** may be considered as an internal Lewis acid−base pair (NBO charges: B, −0.250; Al,

+1.887). Cleavage of the endocyclic B−Br bond should result in the formation of an open chain zwitterionic species, BBr_2^+—C(=CH—Ph)—$AlBr(CMe_3)_2^-$ (NBO charges: B, −0.033; Al +1.777), featuring a four-coordinate aluminum atom and a three-coordinate boron atom. This species is only 22.5 kcal/mol higher in energy than adduct **4**. It seemed to be an excellent intermediate to activate a *tert*-butyl group by its Lewis-acidic boron atom. However, ring closure to heterocyclic compound **4** is strongly preferred over rearrangement.

A reasonable low-barrier mechanism was only obtained by electrolytic dissociation and the complete removal of a terminal bromine atom of **4** to yield the ionic species **A** (Figure 4). In solution, this process may be supported by interactions with solvent molecules and the presence of Lewis-acidic species such as BBr_3 or uncoordinated FLP **1** to yield the cation of **A** with a counterion such as BBr_4^- (calculated Br^- affinity of BBr_3 in benzene solution: −29.6 kcal/mol). The reaction energy for the formation of **A** (sum of the cation of **A** and BBr_4^-) from **4** and BBr_3 was calculated to be +36.3 kcal/mol considering the particular treatment of the solvation process by the CPCM approach. In comparison, the dissociation of **4** into the cation of **A** and the Br^- anion requires 65.8 kcal/mol according to the same theoretical procedure. The intermediate formation of cationic **A** is strongly supported by a recently obtained compound in which a BBr_2^+ cation is stabilized by coordination to a Lewis base. It was synthesized by treatment of sterically highly shielding 2,6-dimesitylpyridine with two equivalents of BBr_3.[23] The second equivalent of BBr_3 captured the released Br^- anion to yield the $[BBr_4]^-$ counterion. The cationic species **A** with a three-coordinate boron atom has expectedly a significantly higher Lewis acidity (and hydride affinity; NBO charge at B: +0.065) at boron compared to **4**. Indeed, the calculated reaction pathway for the H···B approach starting from **A** results now in smooth migration of one hydrogen atom from a CMe_3 group to the boron atom with an activation barrier of only 21.6 kcal/mol with respect to **A**. The corresponding transition state **TS1** is characterized by C···H and B···H distances of 141.6 and 131.6 pm and a significant lengthening of the respective C−Al bond (210.0 pm). Relaxation of the transition state results in C−H bond cleavage with the formation of **B** and isobutene that is weakly coordinated to aluminum with strongly differing Al−C distances (Al···$C(H_2)$ 226.2 pm; Al···$C(Me_2)$ 274.1 pm; 13.7 kcal/mol lower in energy than **A**). Al−C distances of 230−264 pm were reported for few structurally characterized Al−alkene complexes.[24] The last step of this reaction sequence is the nucleophilic addition of the bromide ion released from BBr_4^- to yield a van der Waals complex (**C**) with the isobutene molecule placed between one of the two mesityl substituents at phosphorus and the phenyl ring that is 12.7 kcal/mol lower in energy compared to **4**. Finally, experimentally observed compound **6** is formed by the complete removal of isobutene (E_{rel} = −14.5 kcal/mol with respect to **4**). Because of the coordination of the alkene to aluminum in the cation of **B**, the bromide ion is forced to approach selectively from the opposite side of the heterocycle yielding in agreement with the experimental observations exclusively the enantiomeric (*R*,*S*)- or (*S*,*R*)-forms of compound **6**.

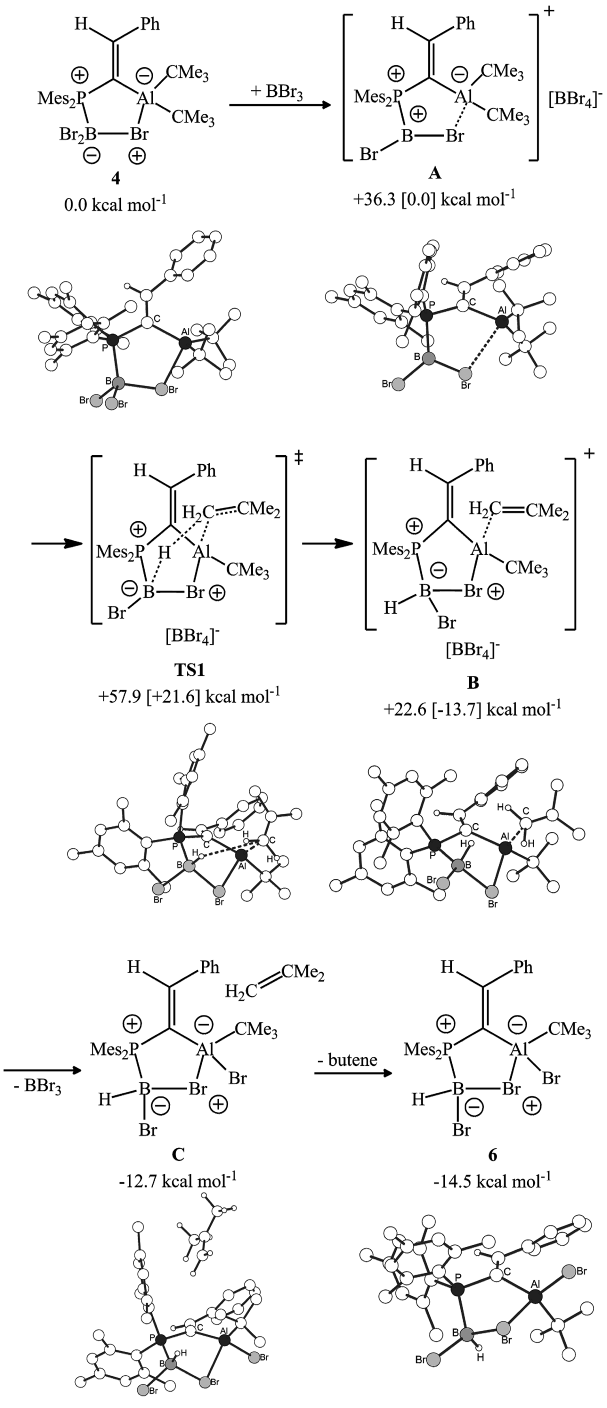


Figure 4. Calculated structures and relative energies (kcal/mol) (M062x/6-311+G(d,p)//M062x/6-311+G(d,p) + GD3+cpcm-(benzene) + zpe (M062x/6-31G(d)) for the stereoselective rearrangement of compound **4** (E_{rel} = 0.0 kcal/mol) to **6**; relative energies in square brackets refer to the sum of the cation of **A** + BBr_4^-. Selected bond lengths and interatomic distances (pm): **4**: P—B 206.1, B—Br_t 200.0 and 200.3, B—Br_{br} 209.6, Al—Br_{br} 261.5; **A**: P—B 196.8, B—Br_t 188.1, B—Br_{br} 191.3, Al···Br_{br} 297,5; **TS1**: P—B 199.8, B—Br_t 195.0, B—Br_{br} 204.1, Al—Br_{br} 254.1, Al—C 210.0, C=C 143.3, C···H 141.6, B···H 131.6; **B**: P—B 200.0, B—Br_t 198.6, B—Br_{br} 212.7, Al—Br_{br} 249.5, Al—C 226.2; **C**: P—B 199.8, B—Br_t 199.9, B—Br_{br} 209.8, Al—Br_{br} 254.9; Al···$C(H_2)$=C 456.9, Al···C=$C(Me_2)$ 543.8; **6**: P—B 200.7, B—Br_t 199.1, B—Br_{br} 211.5, Al—Br_{br} 253.7.

On the basis of these results, the mechanism of the stereoselective formation of BHX_2 adducts **6** and **7** comprises the cleavage of an Al−C bond with the fragmentation of a CMe_3 group into a hydride anion and isobutene, B−H bond formation, and a sigmatropic 1,3-rearrangement of a bromide anion from boron to aluminum. According to the relevant bond lengths, these rearrangement steps are characterized mechanistically by significant pericyclic properties. The suggested route with a cationic intermediate resembles a superfacial 1,3-dyotropic rearrangement observed for an organosilicon compound that has been published only recently and comprises an exchange of a silicon bonded chlorine atom by a *tert*-butyl group.[25] In contrast to the mechanism reported in this article (Figure 4), an intact *tert*-butyl group migrated without *β*-elimination and formation of isobutene. A silyl cation was calculated to be the key intermediate in this unique reaction.

■ CONCLUSION

The bifunctionality of Al/P-based FLP **1** with donor and acceptor sites in a single molecule allows its application as an efficient ligand for the coordination of ambiphilic compounds such as boron trihalides. The boron atoms of the products were coordinated to the basic phosphorus atoms, and one of the halogen atoms occupied a bridging position between Al and B. The properties of these compounds depend considerably on the size of the halogen atoms. The fluorine atom is almost in the plane of the resulting AlCPBX heterocycle, while the bromine atom deviates by 64 pm. The increasing deviation of the halogen atoms from the average plane influences the molecular dynamics and favors secondary rearrangement reactions. The BBr_3 adduct rearranges slowly at ambient temperature, but the corresponding iodine compound is difficult to handle in solution even at temperatures below 0 °C. Rearrangement results in the stereoselective formation of HBX_2 adducts. Interestingly the obvious concerted reaction pathway has a very high activation barrier and can be ruled out by the results of quantum−chemical calculations. They support instead the formation of a cationic intermediate that results from cleavage of a B−Br bond and contains a highly Lewis-acidic borenium cation. This initially formed species activates a *tert*-butyl group bonded to aluminum to give the migrating hydride ion by *β*-hydride elimination. The isobutene leaving group is coordinated to the aluminum atom and favors the selective attack of the bromine atom from the backside of the central heterocycle.

Uncoordinated HBX_2 compounds are unstable, but they can be isolated as adducts with different donor molecules and are applicable in hydroboration reactions. HBI_2 has previously not been reported. In our case, these molecules are stabilized by the specific donor−acceptor capability of the FLP. The unprecedented adducts are promising starting materials for secondary reactions such as functionalization by salt elimination or hydroboration. Reduction may yield low-valent, highly electron deficient boron species that are stabilized by the donor−acceptor functionality of **1**. These investigations are in the focus of our current research activities.

■ EXPERIMENTAL SECTION

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-pentane and *n*-hexane with $LiAlH_4$; toluene with Na/benzophenone and 1,2-difluorobenzene with molecular sieves) using standard Schlenks. NMR spectra were recorded in various deuterated solvents using Bruker Avance I and III spectrometers (^1H, 400; ^{13}C, 100 MHz; ^{11}B, 128 MHz; ^{31}P, 162 MHz; ^{19}F, 377 MHz) and referenced internally to residual solvent resonances (chemical shift data in *δ*). ^{13}C, ^{31}P, and ^{11}B NMR spectra were all proton-decoupled. The assignment of NMR spectra is based on HMBC, H,H-ROESY, HSQC, and DEPT135 data. Elemental analyses were determined by the microanalytic laboratory of the Westfälische Wilhelms-Universität Münster. IR spectra were recorded as Nujol mulls between CsI or KBr plates on a Shimadzu Prestige 21 spectrometer. FLP **1** was obtained according to a literature procedure.[2] The boron trihalides BX_3 were applied as purchased.

Synthesis of the FLP/BF_3 Adduct, 2. A solution of FLP **1** (0.541 g, 1.06 mmol) in 20 mL of toluene was treated with the trifluoroborane−THF complex ($F_3B \leftarrow THF$; 0.12 mL, 1.06 mmol) at room temperature. The mixture was stirred at room temperature for 15 h. The solvent was removed in vacuum. The residue was dissolved in a 1:1 mixture of *n*-hexane and 1,2-difluorobenzene (8 mL). Cooling the solution to −20 °C afforded colorless crystals of **2** (0.582 g, 95%). Anal. calcd (found) for $C_{34}H_{46}AlPBF_3$ (%): C, 70.3 (70.4); H, 8.0 (7.5). mp (argon, sealed capillary): 149 °C (dec.). ^1H NMR (C_6D_6, 400 MHz, 298 K): 1.21 (18 H, s, $Al(CMe_3)_2$), 1.94 (6 H, s, *p*-CH_3), 2.29 (12 H, s, *o*-CH_3), 6.59 (4 H, d, $^4J_{PH}$ = 3.2 Hz, *m*-H_{Mes}), 7.02 (1 H, t, $^3J_{HH}$ = 7.3 Hz, *p*-H_{Ph}), 7.09 (2 H, *pseudo*-t, outer line spacing 14.6 Hz, *m*-H_{Ph}), 7.29 (2 H, d, $^3J_{HH}$ = 7.2 Hz, *o*-H_{Ph}), 7.96 (1 H, d, $^3J_{PH}$ = 37.5 Hz, P—C═C—H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 298 K): 16.9 (s br, $Al(CMe_3)_2$), 20.8 (s, *p*-CH_3), 24.8 (d, $^3J_{PC}$ = 5.6 Hz, *o*-CH_3), 31.5 (s, Al(C*Me*$_3$)$_2$), 122.1 (d, $^1J_{PC}$ = 54.8 Hz, *ipso*-C_{Mes}), 127.7 (s, *o*-C_{Ph}), 129.6 (s, *m*-C_{Ph}), 130.3 (s, *p*-C_{Ph}), 131.6 (d, $^3J_{PC}$ = 9.0 Hz, *m*-C_{Mes}), 140.5 (s br, P—C═C—H), 141.5 (d, $^3J_{PC}$ = 27.2 Hz, *ipso*-C_{Ph}), 141.8 (d, $^4J_{PC}$ = 2.7 Hz, *p*-C_{Mes}), 143.5 (d, $^2J_{PC}$ = 8.5 Hz, *o*-C_{Mes}), 162.7 (d, $^2J_{PC}$ = 9.1 Hz, P—C═C—H). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 298 K): −10.7 (br, not clearly resolved multiplet). $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz, 298 K): 4.3 (d, $^1J_{PB}$ = 160 Hz). ^{19}F NMR (C_6D_6, 377 MHz, 298 K): −127.1 (br). ^{19}F NMR (C_6D_6, 377 MHz, 213 K): −125.0 (2 F, s br, terminal F), −131.9 (1 F, dt br, $^2J_{FF}$ = 78 Hz, $^2J_{PF}$ = 168 Hz, bridging F). IR (paraffin, CsI, cm^{-1}): 1773 (vw), 1736 (vw), 1603 (m), 1585 (w), 1540 (w), 1522 (vw), 1506 (m) *ν*(C═C), phenyl; 1466 (vs), 1377 (vs) (paraffin); 1290 (w), 1269 (m) *δ*CH_3; 1211 (w), 1190 (w), 1173 (w), 1153 (vw), 1099 (w), 1074 (vw), 1059 (vw), 1028 (m), 961 (vw), 932 (m), 893 (w), 868 (m), 852 (m), 797 (s), 746 (s) *ν*CC, *ν*BF; 723 (s, paraffin); 692 (m) *δ*phenyl; 638 (m), 592 (m), 577 (m), 550 (m), 517 (vw), 490 (w), 463 (w), 424 (vw), 405 (w), 395 (w), 361 (m), 332 (vw) *δ*CC, *δ*BF, *ν*PB, *ν*AlC. FT Raman (neat, cm^{-1}): 3058 (w), 3032 (w), 2925 (m), 2871 (w), 2831 (m), 2761 (vw), 2695 (vw) *ν*CH; 1600 (s), 1540 (vs) *ν*C═C, phenyl; 1491 (w), 1461 (w), 1443 (w), 1381 (w), 1339 (vw), 1291 (w), 1214 (m), 1183 (w), 1052 (vw), 1026 (vw), 1002 (w), 964 (vw), 934 (vw), 896 (vw), 871 (vw), 812 (vw), 763 (vw) *ν*CC, *ν*BF; 622 (vw), 572 (w), 553 (w), 531 (vw), 494 (vw), 459 (vw), 426 (vw), 409 (vw), 359 (vw), 317 (vw), 296 (vw), 225 (vw), 197 (vw), 163 (vw), 134 (m), 108 (s), 72 (vs) *δ*CC, *δ*BF, *ν*PB, *ν*AlC. MS (EI, 20 eV, 363 K, *m*/*z*): 512 (6%) $\mathbf{1}^+$, $M^+ - BF_3$; 456 (7%), 455 (22%) $\mathbf{1}^+ - CMe_3$.

Synthesis of the FLP/BCl_3 Adduct, 3. A solution of FLP **1** (0.406 g (0.79 mmol) in 20 mL of toluene was cooled to −20 °C and treated with a solution of BCl_3 in toluene (0.79 mL, 1.0 M, 0.093 g, 0.79 mmol). The mixture was warmed to 0 °C and stirred for 2 h at this temperature. The solvent was removed in vacuum at 0 °C. Residual volatiles were carefully removed in vacuum (10^{-3} Torr). The residue was dissolved in 1,2-difluorobenzene and cooled to −20 °C to yield colorless crystals of **3** (0.432 g, 87%). Anal. calcd (found) for $C_{34}H_{46}AlPBCl_3$ (%): C, 64.8 (65.2); H, 7.4 (7.4). mp (argon, sealed capillary): >118 °C (dec.). ^1H NMR (toluene-d_8, 400 MHz, 280 K): 0.76 and 1.51 (each 9 H, s, $Al(CMe_3)_2$), 1.59, 2.20, 2.58, and 2.83 (each 3 H, s, *o*-CH_3), 1.93 and 1.99 (each 3 H, s, *p*-CH_3), 6.53 and 6.74 (each 1 H, s br, *m*-H_{Mes}), 6.55 (2 H, s, *m*-H_{Mes}), 7.01 (1 H, t, $^3J_{HH}$ = 7.1 Hz, *p*-H_{Ph}), 7.07 (2 H, *pseudo*-t, outer line spacing 14.6 Hz, *m*-H_{Ph}), 7.20 (2 H, d, $^3J_{HH}$ = 7.2 Hz, *o*-H_{Ph}), 7.96 (1 H, d, $^3J_{PH}$ = 36.5 Hz, P—C═C—H); similar shifts were observed at room temperature, but the resonances became broad, and the signals of the *para*-Me groups coincided; coalescence of the *tert*-butyl and *ortho*-Me resonances occurred at about +60 °C, decomposition prevented a detailed assignment of the spectra at elevated temperature in the range of a fast exchange. $^{13}C\{^1H\}$ NMR (toluene-d_8, 100 MHz, 280 K): 17.9 and 18.5 (each s br, $Al(CMe_3)_2$), 20.7 (s, *p*-CH_3), 25.3, 25.4, 27.2, and 30.4 (each s br, *o*-CH_3), 31.6 and 32.8 (each s, Al(C*Me*$_3$)$_2$), 125.2 and 125.3 (each s br, *ipso*-C_{Mes}), 128.0 (s, *o*-C_{Ph}), 130.0 (s, *m*-C_{Ph}), 130.4 (s, *p*-C_{Ph}), 131.5, 131.6, and 132.2 (each s br, *m*-C_{Mes}), 141.0 (s br, P—C═C—H), 141.2 and 141.6 (each s br, *p*-C_{Mes}), 141.4 (d, $^3J_{PC}$ =

27.5 Hz, *ipso*-C$_{Ph}$), 142.8, 143.5, 143.6, and 144.0 (each s br, *o*-C$_{Mes}$), 162.4 (d, $^2J_{PC}$ = 6.5 Hz, P—C═C—H). ^{31}P{^{1}H} NMR (toluene-d_8, 162 MHz, 280 K): 16.5 (poorly resolved quartet, br, outer line spacing about 430 Hz). ^{11}B{^{1}H} NMR (toluene-d_8, 128 MHz, 280 K): 9.9 (d, $^1J_{PB}$ = 165 Hz). IR (paraffin, CsI, cm^{-1}): 1732 (vw), 1603 (m), 1533 (w) νC═C, phenyl; 1456 (vs), 1375 (vs) (paraffin); 1292 (w), 1269 (w), 1246 (w) δCH$_3$; 1209 (w), 1155 (w), 1101 (vw), 1076 (w), 1028 (m), 1005 (w), 961 (vw), 932 (s), 895 (w), 870 (s), 853 (s), 808 (s), 791 (m), 745 (s) νCC, νBCl; 723 (vs) (paraffin); 696 (m) δphenyl; 631 (s), 606 (w), 571 (s), 545 (m), 524 (w), 490 (m), 463 (m), 440 (w), 405 (w), 359 (w), 343 (m) δCC, νPB, νAlC, νBCl. MS (EI, 20 eV, 353 K, *m*/*z*): 512 (10%) **1**$^+$, M$^+$ − BCl$_3$; 456 (14%), 455 (41%) **1**$^+$ − CMe$_3$, 118 (1), 116 (1%) BCl$_3$$^+$.

Synthesis of the FLP/BBr$_3$ Adduct, 4. A cooled (−20 °C) solution of FLP **1** (0.31 g, 0.61 mmol) in toluene (10 mL) was treated with BBr$_3$ (0.06 mL, 0.15 g, 0.61 mmol). The pale yellow mixture was stirred for 1 h at −20 °C, concentrated at 0 °C, and cooled to −45 °C to afford colorless crystals of compound **4** (0.33 g, 71%). Compound **4** is stable as a solid material only at low temperatures (−32 °C); at room temperature, it rearranges slowly in the solid state and in solution to yield HBBr$_2$ adduct **6**. NMR data were recorded at low temperature (275 K); rearrangement occurred already under this condition, but the resonances of **4** could be assigned unambiguously. Anal. calcd (found) for C$_{34}$H$_{46}$AlBBr$_3$P (%): C, 53.5 (53.6); H, 6.1 (6.1). mp (argon, sealed capillary): 75 °C (dec.). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 275 K): 0.81 and 1.58 (each 9 H, s, Al(C*Me*$_3$)$_2$), 1.59, 2.34, 2.62, and 2.94 (each 3 H, s, *o*-CH$_3$), 1.90 and 1.98 (each 3 H, s, *p*-CH$_3$), 6.53 (3 H, s, *m*-H$_{Mes}$), 6.75 (1 H, s, *m*-H$_{Mes}$), 6.98 (1 H, m, *p*-H$_{Ph}$), 7.05 (2 H, *pseudo*-t, outer line spacing 14.8 Hz, *m*-H$_{Ph}$), 7.20 (2 H, d, $^3J_{HH}$ = 7.4 Hz, *o*-H$_{Ph}$), 8.01 (1 H, d, $^3J_{PH}$ = 37.3 Hz, P—C═C—*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100 MHz, 275 K): 18.3 and 18.7 (each s br, Al(CMe$_3$)$_2$), 20.7 (s, *p*-CH$_3$), 25.6 (s, *o*-CH$_3$), 26.9 (s, *o*-CH$_3$), 28.5 (d, $^3J_{PC}$ = 5.2 Hz, *o*-CH$_3$), 31.1 (s br, *o*-CH$_3$), 31.8 and 33.1 (each s, Al(C*Me*$_3$)$_2$), 125.1 (d, $^1J_{PC}$ = 54.0 Hz, *ipso*-C$_{Mes}$), 126.4 (d, $^1J_{PC}$ = 63.0 Hz, *ipso*-C$_{Mes}$), 128.2 (d, $^4J_{PC}$ = 1.0 Hz, *o*-C$_{Ph}$), 129.7 (s, *m*-C$_{Ph}$), 130.4 (s, *p*-C$_{Ph}$), 131.6 (d br, $^3J_{PC}$ = 10.0 Hz, *m*-C$_{Mes}$), 131.6 (s br, *m*-C$_{Mes}$), 131.7 (s br, *m*-C$_{Mes}$), 132.2 (d br, $^3J_{PC}$ = 10.9 Hz, *m*-C$_{Mes}$), 141.3 (d, $^3J_{PC}$ = 28.0 Hz, *ipso*-C$_{Ph}$), 141.7 (s, *p*-C$_{Mes}$), 142.2 (d, $^1J_{PC}$ = 35.0 Hz, PC═CH), 142.6 (d, $^2J_{PC}$ = 8.0 Hz, *o*-C$_{Mes}$), 143.9 (s br, *o*-C$_{Mes}$), 144.4 (d br, $^2J_{PC}$ = 10.0 Hz, *o*-C$_{Mes}$), 162.0 (d, $^2J_{PC}$ = 5.4 Hz, PC═CH). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 275 K): 20.1 (poorly resolved quartet, br, $^1J_{PB}$ = 153 Hz). ^{11}B NMR (C$_6$D$_6$, 128 MHz, 300 K): −5.7 (d, $^1J_{PB}$ = 153 Hz). IR (paraffin, CsI, cm^{-1}): 1601 (m), 1580 (w), 1526 (w) νC═C, phenyl; 1460 (vs), 1377 (vs) (paraffin); 1302 (vw), 1288 (w) δCH$_3$; 1171 (w), 1157 (w), 1026 (m), 932 (m), 872 (m), 853 (m), 809 (m), 783 (m), 748 (s) νCC; 723 (vs) (paraffin); 694 (m), 671 (w) δphenyl; 646 (w), 625 (s), 569 (s), 490 (w), 461 (s) δCC, νAlC, νPC, νBBr. MS (EI, 20 eV, 483 K, *m*/*z*, experimental intensities agree with expected isotopic pattern; only the most intense peak of each fragment is given): 764 (2.3%) and 762 (2.2%) M$^+$, 372 (34%) Mes$_2$P—C(H)═CH—Ph$^+$, 119 (17%) Mes$^+$.

Synthesis of the FLP/BI$_3$ Adduct, 5. A cooled (−20 °C) solution of FLP **1** (0.210 g, 0.41 mmol) in toluene (4 mL) was treated with a solution of BI$_3$ (0.160 g, 0.41 mmol) in 1 mL of the same solvent. The yellow solution was stirred for 1 h at −20 °C. A colorless solid of **5** was obtained without concentration upon storing of the solution at −20 °C (0.11 g, 30%). Adduct **5** is unstable and decomposes slowly at room temperature in the solid state (in particular under vacuum) and rearranges in solution to yield HBI$_2$ adduct **7**. Therefore, we were not able to obtain a correct elemental analysis and to grow single crystals. NMR spectra were recorded at 280 K. mp (argon, sealed capillary): 101 °C (dec.). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 280 K): 0.78 and 1.60 (each 9 H, s, Al−C*Me*$_3$), 1.54, 2.46, 2.63, and 3.03 (each 3 H, s, *o*-CH$_3$), 1.60 (9 H, s, Al−C*Me*$_3$), 1.90 and 1.98 (each 3 H, s, *p*-CH$_3$), 6.53, 6.54, 6.57, and 6.79 (each 1 H, s br, *m*-H$_{Mes}$), 6.98 (1 H, t, $^3J_{HH}$ = 7.4 Hz, *p*-H$_{Ph}$), 7.05 (2 H, *pseudo*-t, outer line spacing 14.8 Hz, *m*-H$_{Ph}$), 7.22 (2 H, d, $^3J_{HH}$ = 7.3 Hz, *o*-H$_{Ph}$), 8.02 (1 H, d, $^3J_{PH}$ = 38.4 Hz, P—C═C—*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100 MHz, 280 K): 18.7 and 19.2 (each s br, Al(CMe$_3$)$_2$), 20.7 (s, *p*-CH$_3$), 26.0 (d, $^3J_{PC}$ = 1.6 Hz, *o*-CH$_3$), 29.3 (d, $^3J_{PC}$ = 3.1 Hz, *o*-CH$_3$), 30.4 (d, $^3J_{PC}$ = 5.0 Hz, *o*-CH$_3$), 31.7 (s, *o*-CH$_3$), 32.4 and 33.6 (each s, Al(C*Me*$_3$)$_2$), 125.6 (d, $^1J_{PC}$ = 53.7 Hz, *ipso*-C$_{Mes}$), 128.4 (d, $^4J_{PC}$ = 2.0 Hz, *o*-C$_{Ph}$), 129.2 (d, $^1J_{PC}$ = 20.1 Hz, *ipso*-C$_{Mes}$), 130.0 (s, *m*-C$_{Ph}$), 130.3 (s, *p*-C$_{Ph}$), 131.5 (d, $^3J_{PC}$ = 8.9 Hz, *m*-C$_{Mes}$), 131.6 (d, $^3J_{PC}$ = 10.8 Hz, *m*-C$_{Mes}$), 131.9 (d, $^3J_{PC}$ = 11.1 Hz, *m*-C$_{Mes}$), 132.4 (d, $^3J_{PC}$ = 10.8 Hz, *m*-C$_{Mes}$), 141.0 (d, $^3J_{PC}$ = 28.7 Hz, *ipso*-C$_{Ph}$), 141.66 (d, $^4J_{PC}$ = 3.0 Hz, *p*-C$_{Mes}$), 141.75 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C$_{Mes}$), 142.0 (d, $^2J_{PC}$ = 6.9 Hz, *o*-C$_{Mes}$), 144.2 (d, $^2J_{PC}$ = 4.0 Hz, *o*-C$_{Mes}$), 144.3 (d, $^2J_{PC}$ = 12.3 Hz, *o*-C$_{Mes}$), 144.9 (d, $^2J_{PC}$ = 9.3 Hz, *o*-C$_{Mes}$), 144.9 (br, $^1J_{PC}$ = 14.0 Hz, PC═CH), 161.2 (d, $^2J_{PC}$ = 4.4 Hz, PC═CH). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 280 K): 20.4 (poorly resolved quartet, br., $^1J_{PB}$ = 123 Hz). ^{11}B NMR (C$_6$D$_6$, 128 MHz, 280 K): −58.7 (d, $^1J_{PB}$ = 123 Hz). IR (paraffin, KBr, cm^{-1}): 1603 (s), 1576 (m), 1553 (s), 1516 (s) νC═C, phenyl; 1466 (vs), 1452 (vs), 1375 (vs) paraffin; 1337 (s), 1314 (s), 1292 (vs), 1265 (s), 1246 (s) δCH$_3$; 1209 (s), 1173 (s), 1157 (m), 1109 (m), 1074 (s), 1026 (m), 1013 (s), 1001 (m), 968 (m), 957 (m), 932 (s), 895 (m), 870 (s), 851 (vs), 808 (vs), 777 (vs), 747 (vs) νCC; 723 (s) paraffin; 696 (s), 629 (s), 565 (vs), 529 (vs), 509 (s), 486 (vs), 461 (m), 430 (vs) δCC, νAlC, νPC. MS (EI, 25 eV, 473 K, *m*/*z*, experimental intensities agree with expected isotopic pattern; only the most intense peak of each fragment is given): 764 (2%) M$^+$ − Al(CMe$_3$)$_2$ + H, 653 (100%) M$^+$ − BI − CMe$_3$ − butene, 525 (29%) M$^+$ − 2CMe$_3$ − BI$_2$, 119 (31%) Mes$^+$.

FLP/HBBr$_2$ Adduct, 6. The selective rearrangement of **4** to **6** was observed only in C$_6$D$_6$ solution in a sealed NMR tube at 275 K over 5 d. We were not able to reproduce this reaction in a preparative scale in different solvents (toluene, benzene) and at different temperatures. In all cases, mixtures of compounds were obtained with **6** as the main component. Separation of the mixtures by recrystallization from different solvents failed. The unambiguous characterization and identification of **6** is based on the results of the NMR experiments and a comparison with data from the corresponding iodine compound **7**. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 300 K): 0.99 (9 H, s, Al−C*Me*$_3$), 1.93 and 1.97 (each 3 H, s, *p*-CH$_3$), 2.19 and 2.55 (each 6 H, s, *o*-CH$_3$), 5.07 (s br, HBBr), 6.57 (2 H, d, $^4J_{PH}$ = 2.8 Hz, *m*-H$_{Mes}$), 6.60 (2 H, d, $^4J_{PH}$ = 3.3 Hz, *m*-H$_{Mes}$), 6.96 (1 H, m, *p*-H$_{Ph}$), 7.07 (2 H, *pseudo*-t, outer line spacing 14.8 Hz, *m*-H$_{Ph}$), 7.56 (2 H, d, $^3J_{HH}$ = 7.4 Hz, *o*-H$_{Ph}$), 7.69 (1 H, d, $^3J_{PH}$ = 37.7 Hz, P—C═C—*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100 MHz, 300 K): 17.7 (s br, AlCMe$_3$), 20.7 (s, *p*-CH$_3$), 24.2 (d, $^3J_{PC}$ = 4.1 Hz, *o*-CH$_3$), 26.9 (d, $^3J_{PC}$ = 2.9 Hz, *o*-CH$_3$), 30.2 (s, AlC*Me*$_3$), 121.8 (d, $^1J_{PC}$ = 62.9 Hz, *ipso*-C$_{Mes}$), 123.8 (d, $^1J_{PC}$ = 54.8 Hz, *ipso*-C$_{Mes}$), 128.6 (s, *o*-C$_{Ph}$), 129.7 (s, *m*-C$_{Ph}$), 130.3 (s, *p*-C$_{Ph}$), 131.7 (d, $^3J_{PC}$ = 10.0 Hz, *m*-C$_{Mes}$), 131.8 (d, $^3J_{PC}$ = 10.0 Hz, *m*-C$_{Mes}$), 137.1 (s, PC═CH), 140.6 (d, $^3J_{PC}$ = 26.7 Hz, *ipso*-C$_{Ph}$), 141.5 (d, $^4J_{PC}$ = 2.8 Hz, *p*-C$_{Mes}$), 142.2 (d, $^4J_{PC}$ = 2.6 Hz, *p*-C$_{Mes}$), 143.0 (d, $^2J_{PC}$ = 6.8 Hz, *o*-C$_{Mes}$), 143.1 (d, $^2J_{PC}$ = 6.9 Hz, *o*-C$_{Mes}$), 161.6 (d, $^2J_{PC}$ = 4.1 Hz, PC═CH). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162 MHz, 300 K): 6.3 (s br). ^{11}B NMR (C$_6$D$_6$, 128 MHz, 300 K): −4.4 (s br).

Synthesis of the FLP/HBI$_2$ Adduct, 7. A cooled (0 °C) solution of FLP **1** (0.14 g, 0.27 mmol) in toluene (6 mL) was treated with a solution of BI$_3$ (0.11 g, 0.28 mmol) in toluene (4 mL). Stirring was continued for 14 h at this temperature. All volatiles were removed in vacuum, and the residue was treated with 1 mL of *n*-pentane. The solvent was removed in vacuum, and the solid residue was washed with 2 mL of 1,2-difluorobenzene. The solvent was removed by a pipet, and the solid was dried in vacuum to yield **7** as a colorless amorphous solid in relatively high purity (0.16 g, 69%). Compound **7** is insoluble in hydrocarbons and only sparingly soluble in 1,2-difluorobenzene. It dissolves in CH$_2$Cl$_2$, but the solutions are unstable at room temperature. The NMR spectra were recorded at 0 °C. Small resonances indicate the formation of impurities even under these mild conditions. Anal. calcd (found) for C$_{30}$H$_{38}$AlBPI$_3$ (%): C, 42.5 (41.9); H, 4.5 (4.5). mp (argon, sealed capillary): >105 °C (dec.). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, 275 K): 0.57 (9 H, s, Al−C*Me*$_3$), 2.24 and 2.48 (each 6 H, s, *o*-CH$_3$), 2.30 and 2.32 (each 3 H, s, *p*-CH$_3$), 4.50 (1 H, s br, BH), 6.94 and 6.98 (each 2 H, d br, $^4J_{PH}$ = 3.0 Hz, *m*-H$_{Mes}$), 7.40 (3 H, m, *p*-H$_{Ph}$ and *m*-H$_{Ph}$), 7.60 (2 H, br, *o*-H$_{Ph}$), 7.74 (1 H, d, $^3J_{PH}$ = 34.6 Hz, P—C═C—*H*). ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz, 275 K): 17.7 (s br, AlCMe$_3$), 21.0 and 21.1 (each s, *p*-CH$_3$), 24.8 and 27.9 (each s br, *o*-CH$_3$), 29.6 (s, AlC*Me*$_3$), 122.7 (d, $^1J_{PC}$ = 37.6 Hz, *ipso*-C$_{Mes}$),

Table 2. Crystal Data and Structure Refinement for Compounds 2−4 and 7

	compd			
	$2{\cdot}C_6H_4F_2$	3	4	$7{\cdot}0.5C_6H_4F_2$
empirical formula	$C_{40}H_{50}AlBF_5P$	$C_{34}H_{46}AlBCl_3P$	$C_{34}H_{46}AlBBr_3P$	$C_{33}H_{40}AlBFI_3P$
fw (M/(g mol^{-1}))	694.56	629.82	763.20	905.11
cryst syst	triclinic	trigonal	monoclinic	monoclinic
space group	*P*-1	*R*-3	$P2_1/c$	$P2_1/n$
a (pm)	940.52(5)	4402.4(6)	974.49(4)	1215.87(7)
b (pm)	1211.37(6)	4402.4(6)	3518.0(2)	1446.69(6)
c (pm)	1754.0(1)	966.5(2)	3051.8(1)	2086.8(1)
α (deg)	92.43(3)	90	90	90
β (deg)	103.07(3)	90	94.685(1)	105.568(5)
γ (deg)	104.46(3)	120	90	90
vol (nm^3)	1.8746(2)	16.22(1)	10.4275(8)	3.5360(3)
Z	2	18	12	4
temp (K)	153(2)	153(2)	153(2)	153(2)
density (Mg m^{-3})	1.230	1.160	1.458	1.700
abs coeff (mm^{-1})	0.149 (Mo Kα)	0.344 (Mo Kα)	3.575 (Mo Kα)	2.748 (Mo Kα)
θ range (deg)	1.75−27.96	1.60−27.97	1.86−28.01	1.73−27.94
reflns collected	14 175	40 506	106 291	44 525
ind reflns	8920 (R_{int} = 0.0415)	8642 (R_{int} = 0.0758)	25043 (R_{int} = 0.0520)	8428 (R_{int} = 0.0716)
parameters	475	374	1117	398
R1[a]	0.0591	0.0480	0.0379	0.0274
wR2 (all data)[b]	0.1645	0.1002	0.0943	0.0618
largest diff. peak and hole (e nm^{-3})	638, −570	386, −387	691, −453	1171, −1025

[a] Observation criterion: $I > 2\sigma(I)$. R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. [b] wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

123.3 (d, $^1J_{PC}$ = 47.0 Hz, *ipso*-C_{Mes}), 129.1 (s br, *o*-C_{Ph}), 129.5 (s, *m*-C_{Ph}), 130.2 (s, *p*-$C_{Ph,}$), 131.7 (d, $^3J_{PC}$ = 10.6 Hz, *m*-C_{Mes}), 131.9 (d, $^3J_{PC}$ = 10.1 Hz, *m*-C_{Mes}), 137.0 (s br, PC=CH), 140.5 (d, $^3J_{PC}$ = 26.5 Hz, *ipso*-C_{Ph}), 141.9 and 142.6 (each d, $^4J_{PC}$ = 2.0 Hz, *p*-C_{Mes}), 142.9 (two resonances coincide, d, $^2J_{PC}$ = 9.0 Hz, *o*-C_{Mes}), 162.1 (s, PC=CH). ^{31}P NMR (CD_2Cl_2, 162 MHz, 275 K): 5.1 (s br). ^{11}B NMR (CD_2Cl_2, 128 MHz, 275 K): −28.9 (br). IR (paraffin, CsI, cm^{-1}): 2033 (w), 1912 (w), 1819 (w), 1736 (w), 1599 (m), 1570 (m), 1547 (w), 1533 (w) νC=C, νBH, phenyl; 1434 (m), 1375 (m) paraffin; 1290 (w), 1267 (w), 1250 (w) δCH_3; 1202 (w), 1172 (w), 1153 (w), 1098 (w), 1074 (w), 1026 (m), 932 (m), 878 (w), 849 (m), 808 (m), 789 (w), 747 (s) νCC; 723 (s) paraffin; 704 (m) δphenyl; 669 (w), 629 (m), 613 (sh), 583 (s), 559 (s), 515 (m), 478 (m), 469 (m), 442 (w), 397 (m), 380 (w), 353 (w), 330 (m) δCC, νAlC, νPC, νBI, νAlI. MS (EI, 25 eV, 473 K, *m*/*z*, experimental intensities agree with expected isotopic distribution; only the most intense peak of each fragment is given): 791 (1%) $M^+ - CMe_3$, 652 (84%) $M^+ - CMe_3 - HBI$, 525 (8%) $M^+ - CMe_3 - HBI_2$, 265 (8%) BI_2^+.

X-ray Crystallography. Crystals suitable for X-ray crystallography were obtained by recrystallization from a mixture of *n*-hexane and 1,2-difluorobenzene (**2**: −20 °C), 1,2-difluorobenzene (**3**: −20 °C; **7**: +5 °C), or the reaction mixture (concentrated at 0 °C) at −32 °C (**4**). Intensity data were collected on Bruker APEX II and QUAZAR diffractometers with monochromated Mo Kα radiation. The collection method involved ω scans. Data reduction was carried out using the program SAINT+.[26] The crystal structures were solved by direct methods using SHELXTL.[27] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using SHELXTL. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Further details are summarized in Table 2. Compound **2** crystallized with a molecule of 1,2-difluorobenzene per formula unit; the solvent molecule was disordered over two positions, and all atoms were refined on split positions (0.66:0.34). The crystals of **3** contained strongly disordered solvent molecules, which could not be localized and refined. We applied the SQUEEZE program[28] in PLATON and found large voids with an electron count corresponding to five 1,2-difluorobenzene molecules per unit cell. Compound **4** had three independent molecules per asymmetric unit. The crystals of **7** contained half a molecule of 1,2-difluorobenzene per formula unit, which was disordered across a crystallographic center of symmetry. Further crystallographic data is summarized in Table 2. CCDC numbers 997863 (**2**), 997864 (**3**), 997865 (**4**), and 997866 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Database Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray structure data (cif) and results of quantum−chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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