

# C–H Activation of Isobutylene Using Frustrated Lewis Pairs: Aluminum and Boron $\sigma$ -Allyl Complexes\*\*

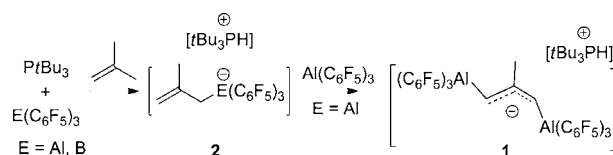
Gabriel Ménard and Douglas W. Stephan\*

Although the activation of small molecules has been the purview of transition-metal chemistry for the past half-century, parallels between the reactivity of transition-metal and main-group compounds have become increasingly prevalent in recent years.<sup>[1]</sup> Among the approaches that involve main-group compounds, frustrated Lewis pairs (FLPs), that is, the combination of Lewis acids and bases that are sterically inhibited from forming classical adducts, have drawn particular attention. While FLPs initially garnered much attention for their ability to heterolytically activate H<sub>2</sub>,<sup>[2]</sup> they have also been shown to activate small molecules such as CO<sub>2</sub>,<sup>[3]</sup> N<sub>2</sub>O,<sup>[4]</sup> NO,<sup>[5]</sup> alkenes, alkynes, among others.<sup>[1c]</sup> The majority of the published work on FLPs exploits boron-based Lewis acids, particularly B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>[1c]</sup> More recently, we<sup>[3b,d,6]</sup> and others,<sup>[3i,7]</sup> have begun to explore the use of aluminum in such chemistry. Whereas boron/phosphine (B/P) and aluminum/phosphine (Al/P) FLPs are capable of CO<sub>2</sub> capture, only the adducts derived from the Al/P FLPs have been shown to undergo further reactions, resulting in CO<sub>2</sub> reduction.<sup>[3b,d]</sup>

Allyl groups are important fragments in organic synthesis;<sup>[8]</sup> however, the installation of such groups using unactivated olefin compounds usually requires the use of harsh bases, such as KOtBu/*n*BuLi.<sup>[9]</sup> In addition, the use of activated olefins,<sup>[10]</sup> such as allyl halides,<sup>[11]</sup> ethylene ketals,<sup>[12]</sup> allyl alkoxides,<sup>[13]</sup> and trimethylsilyl olefin derivatives,<sup>[14]</sup> have been used to install allyl substituents.<sup>[8c,9,15]</sup> While such reagents can be employed for the allylation of carbonyl functionalities,<sup>[11,16]</sup> the allylation of olefins has only been achieved in a limited number of cases.<sup>[10a,17]</sup> To this end, we have explored the reactivity of boron- and aluminum-based FLPs in the C–H activation of isobutylene as a route to  $\sigma$ -allyl anion salts. The nature of these products is established and contrasted herein. Whereas allyl borates form in a reversible reaction, the corresponding allyl aluminate undergoes subsequent ethylene insertion, thus providing a rare example of the allylation of an unactivated olefin.

The addition of 1 atm of isobutylene to a 1:1 solution of *t*Bu<sub>3</sub>P and Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in C<sub>6</sub>D<sub>3</sub>Br, contained in a J-Young NMR

tube at 25°C, led to an exothermic reaction with the generation of a 1:1 mixture of a new product and *t*Bu<sub>3</sub>P, as indicated by the <sup>31</sup>P NMR resonances at 60 and 62 ppm, respectively. Repetition of the reaction with a 1:2 ratio of *t*Bu<sub>3</sub>P/Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> led to the formation of a single product. This species **1** was isolated from a scaled-up reaction by trituration of the reaction mixture with hexanes (Scheme 1). The <sup>31</sup>P{<sup>1</sup>H} and <sup>31</sup>P NMR spectra revealed a resonance at 60 ppm with a strong P–H coupling constant of 426 Hz, which is consistent with the value of a one-bond coupling and thus the formation of the *t*Bu<sub>3</sub>PH<sup>+</sup> ion. The <sup>19</sup>F{<sup>1</sup>H} NMR spectrum exhibited only three resonances, thus suggesting that the Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> fragments exist in equivalent environments. The <sup>1</sup>H NMR spectrum exhibited a broad singlet at 3.91 ppm and a sharp singlet at 2.10 ppm, with a relative integration of four and three, respectively. When the <sup>1</sup>H NMR spectrum was acquired at low temperature (–30°C), the resonance at 3.91 ppm split into two broad singlets.<sup>[18]</sup> Collectively, these data imply the formation of an anionic compound containing a bridging allyl moiety between two equivalent Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> fragments together with the corresponding phosphonium cation and thus the formulation of **1** as [*t*Bu<sub>3</sub>PH][[(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Al]<sub>2</sub>(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)]. The NMR data support an allyl geometry that is likely  $\mu_2$ - $\eta^1$ : $\eta^1$ , although the  $\mu_2$ - $\eta^3$ : $\eta^3$  geometry could not be dismissed (Scheme 1). Single crystal X-ray crystallography confirmed the former binding mode (Figure 1).<sup>[18]</sup> Whereas



Scheme 1. Synthesis of **1** and **2**.

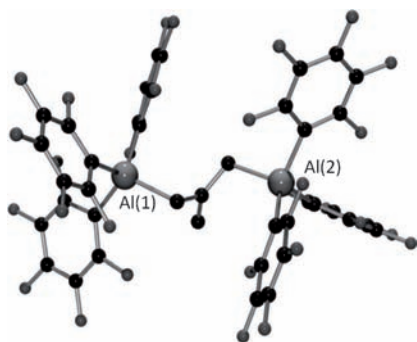
the metric parameters of the cation are unexceptional, those of the anion are rather interesting. The planar allyl fragment is linked to the two aluminum centers through sigma interactions with the methylene units, thus giving rise to Al–C distances of 2.080(4) Å and 2.094(4) Å. The two Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> moieties are oriented in a transoid disposition, which minimizes the steric congestion. The C–C distances between these terminal carbon atoms and the central carbon atom of the allyl fragment are 1.415(6) Å and 1.411(6) Å, with a corresponding C<sub>Al</sub>–C–C<sub>Al</sub> angle of 121.8(4)°.

Whereas a number of recent reports have described early main-group allyl metal compounds,<sup>[9,19]</sup> as well as allyl aluminum compounds,<sup>[11c,20]</sup> the compound described above is, to the best of our knowledge, the first example of an isolable allyl species that is derived from facile C–H

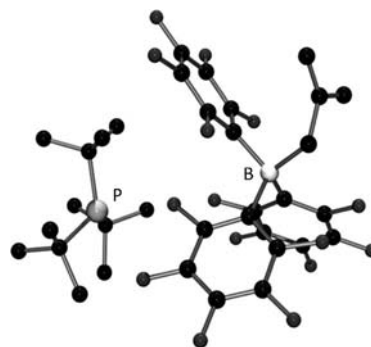
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**Figure 1.** POV-ray depiction of the anion of **1**. H atoms are omitted for clarity.



**Figure 2.** POV-ray depiction of **2**. H atoms are omitted for clarity.

activation. It should be noted that C–H activation of alkynes by FLPs has been previously reported.<sup>[3i,6,21]</sup> Furthermore, compound **1** is the first example of a compound having a bridging allyl moiety between two aluminum centers. It is noteworthy that the formation of **1** appears to be reversible: slow regeneration of the initial FLP mixture with concurrent release of isobutylene was observed upon prolonged heating of **1** at 60 °C under vacuum.

The analogous reaction employing  $B(C_6F_5)_3$  was performed in fluorobenzene solution. Thus, a 1:2 mixture of  $tBu_3P$  and  $B(C_6F_5)_3$  was exposed to an atmosphere of isobutylene for 1 hour. The addition of pentane to the solution resulted in the isolation of product **2** ( $E=B$ ) in modest yield (<50%) by precipitation and then filtration.  $^{31}P\{^1H\}$  NMR analysis of a solution of **2** ( $E=B$ ) in  $CD_2Cl_2$  revealed the formation of the expected  $tBu_3PH^+$  cation. Furthermore, the  $^{11}B\{^1H\}$  NMR spectrum exhibited a sharp singlet at –13 ppm and the  $^{19}F\{^1H\}$  spectrum exhibited resonances at –131.6, –164.3, and –167.2 ppm, all of which are associated with  $C_6F_5$  rings on a four-coordinate boron center. However, the  $^1H$  NMR spectrum exhibited four resonances in addition to the resonances at 5.02 and 1.59 ppm for the phosphonium cation: two mutually coupled doublets each integrating for one proton were found in the olefinic region at 4.01 and 3.83 ppm, and two singlets were found in the aliphatic region at 2.20 and 1.45 ppm, which integrated to two and three protons, respectively. These data were consistent with an asymmetric allyl fragment and suggested the presence of an allyl borate anion. Indeed, X-ray crystallography confirmed the structure of **2** ( $E=B$ ) as being  $[tBu_3PH][B(C_6F_5)_3[CH_2C(CH_3)=CH_2]]$  (Figure 2).<sup>[18]</sup> The geometry of the boron center is tetrahedral with the B–C bond distance for the allyl fragment being 1.665(2) Å. The B–C–C angle was found to be 116.01(8)°. The central carbon atom of the allyl fragment is bonded to a boron-bound methylene, a terminal methylene, and a terminal methyl group with C–C bond distances of 1.507(2) Å, 1.337(2) Å, and 1.501(2) Å, respectively.

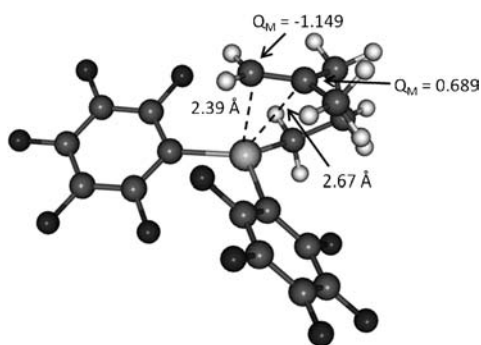
The sensitive species **2** ( $E=B$ ) was synthesized in higher yield (83%) when the stoichiometry of the reagents,  $tBu_3P$  and  $B(C_6F_5)_3$ , was reduced to 1:1. The facile synthesis of **2** ( $E=B$ ) at ambient temperature from commercially available reagents stands in marked contrast to the multistep syntheses that are often used to access known allyl borates.<sup>[11a,b]</sup>

Interestingly, when a solution of **2** ( $E=B$ ) in either  $CD_2Cl_2$  or  $C_6D_5Br$  in a J-Young NMR tube was monitored by NMR spectroscopy, the formation of approximately one equivalent of free  $tBu_3P$  and free isobutylene, as well as significant broadening of the  $^{19}F$ ,  $^{11}B$ , and allylic-based  $^1H$  NMR resonances was observed, thus suggesting that the loss of isobutylene is facile. In the presence of excess borane, an allyl bis(borate) analogue of **1** was not observed spectroscopically. Indeed, all efforts to generate and isolate an allyl bis(borate) species through variation of the stoichiometry were unsuccessful. The apparent preference of boron to form an allyl monoborate anion, which incorporates a terminal olefinic unit, is consistent with the weak interactions of  $B(C_6F_5)_3$  with olefins<sup>[22]</sup> and the weaker Lewis acidity of  $B(C_6F_5)_3$  compared with  $Al(C_6F_5)_3$ .<sup>[23]</sup>

The reaction of **1** and **2** ( $E=B$ ) with ethylene was probed. In the case of **2** ( $E=B$ ), its treatment with ethylene resulted only in the release of isobutylene with concomitant formation of the known ethylene addition product  $tBu_3PCH_2CH_2B(C_6F_5)_3$ .<sup>[24]</sup> The addition of more borane did not lead to the formation of different products. In marked contrast, the treatment of the bridging allyl species **1** with ethylene resulted in a slow reaction at ambient temperature. When the temperature was raised to 60 °C, the reaction was complete in 6 hours. NMR analysis of the reaction mixture revealed the formation of three products, **3**, **4**, and **5** in addition to the generation of a small amount of  $Al(C_6F_5)_3$  (see Scheme 2). Based on the integration of the  $^{19}F\{^1H\}$  NMR spectrum of the reaction mixture, compound **5** and  $Al(C_6F_5)_3$  accounted for approximately 20% of the available aluminum, with the remainder being associated with the major products **3** and **4**. This mixture was separated by careful workup.<sup>[18]</sup> The NMR spectra of **3** indicated the presence of the  $[tBu_3PH]^+$  ion; in addition, the  $^{19}F\{^1H\}$  NMR spectrum exhibited three multiplets at –122.1, –157.4, and –163.5 ppm and the  $^{27}Al$  NMR spectrum exhibited a broad singlet at 116 ppm, thus indicating the presence of a symmetric aluminate species. These data, together with elemental analysis, allowed us to identify compound **3** as being the salt  $[tBu_3PH][Al(C_6F_5)_4]$ .

Detailed 1D and 2D NMR analysis of **4** indicated that it was derived from the incorporation of one equivalent of ethylene into the aluminum allyl moiety of **1**. This species also exhibited  $^{19}F$  NMR resonances at –122.0, –152.1, and –160.8 ppm but no signal was observed in the  $^{27}Al$  NMR

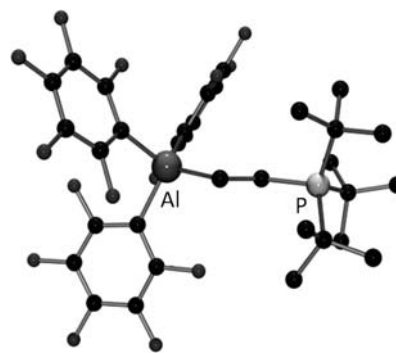
spectrum because of line broadening. These data allow us to propose  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{Al}(\text{C}_6\text{F}_5)_2$  as being the structure of **4**, which is presumably derived from the insertion of ethylene into the aluminum–allyl bond, reminiscent of the insertions into aluminum–alkyl bonds that were first reported by Ziegler.<sup>[25]</sup> Inspection of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum indicated that the fully substituted carbon atom of the olefinic residue resonated at 188.5 ppm, which is significantly downfield of the corresponding resonance of the unbound alkene analogue, 2-methyl-1-pentene (147 ppm). Similarly deshielded carbon nuclei resonances have been observed for vinyl aluminum species.<sup>[26]</sup> The terminal olefinic carbon atom was observed as a quintet at 105.5 ppm; in  $^1\text{H}$ - and  $^{19}\text{F}$ -decoupled  $^{13}\text{C}$  NMR spectra this signal is a singlet, thus implying that the carbon nucleus was coupling to four equivalent fluorine atoms.<sup>[18]</sup> Collectively, these data suggest that the terminal carbon atom is weakly bound to the aluminum center, thus resulting in a significantly polarized olefin double bond. However, attempts to obtain crystals suitable for X-ray diffraction failed, therefore the structure of **4** was probed through DFT computations performed at the M06-2X/6-311++G(d,p) level<sup>[27]</sup> (Figure 3). The computed



**Figure 3.** Computed geometry of **4** showing Al–C distances and Mulliken charges on olefinic carbon atoms.

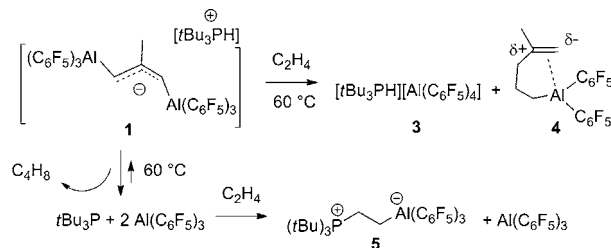
geometry shows a slight pyramidalization of aluminum (the sum of angles being  $352.9^\circ$ ) with the olefinic fragment being oriented near the aluminum center and with Al–C distances of 2.39 Å and 2.67 Å for the terminal and substituted carbon atoms, respectively. Mulliken charges at the terminal and substituted carbon atoms were found to be  $-1.149$  and  $0.689$ , respectively, consistent with a highly polarized olefin. This result is also consistent with  $^{13}\text{C}$  NMR data<sup>[28]</sup> and the analysis of the molecular orbitals, which reveals an interaction of the terminal carbon atom with the aluminum center. Furthermore, interactions of the Lewis acidic center with olefin fragments have been observed in closely related boron and aluminum species.<sup>[22,29]</sup>

The minor product **5** was independently synthesized by the reaction of  $t\text{Bu}_3\text{P}$ ,  $\text{Al}(\text{C}_6\text{F}_5)_3$ , and ethylene at  $25^\circ\text{C}$ , and exhibited a  $^{31}\text{P}$  resonance at 45.1 ppm and a broad singlet at 132 ppm in the  $^{27}\text{Al}$  NMR spectrum. These data, taken together with the  $^{19}\text{F}$  and  $^1\text{H}$  NMR data, were consistent with  $t\text{Bu}_3\text{PCH}_2\text{CH}_2\text{Al}(\text{C}_6\text{F}_5)_3$  as being the structure of **5**, for which a boron analogue is known<sup>[24]</sup>. The structure of **5** was confirmed by X-ray crystallography (Figure 4).<sup>[18]</sup>



**Figure 4.** POV-ray depiction of **5**. H atoms are omitted for clarity.

The formation of **3–5** is consistent with competing reactions involving components from the equilibrium governing the formation of **1** (Scheme 2). Thus, thermal loss of isobutylene from **1** generates free phosphine and alane, which



**Scheme 2.** Reaction pathways of **1** with ethylene affording **3–5**.

can react with ethylene to give **5** with residual  $\text{Al}(\text{C}_6\text{F}_5)_3$ . Alternatively, the direct reaction of ethylene with **1** results in insertion of the olefin moiety into the Al–C bond of the allyl aluminum fragment and subsequent aryl group redistribution to afford the salt **3** and the alane **4**. The separation of the salts **3** and **5** from the alanes **4** and  $\text{Al}(\text{C}_6\text{F}_5)_3$  was readily achieved based on their relative solubilities, and **3** was subsequently separated from **5** by careful precipitation. The separation of **4** from  $\text{Al}(\text{C}_6\text{F}_5)_3$  required an alternative strategy. Based on the integration of the  $^{19}\text{F}$  NMR spectrum, an equimolar amount of  $t\text{Bu}_3\text{P}$ , relative to the  $\text{Al}(\text{C}_6\text{F}_5)_3$ , was added; subsequent exposure of the mixture to ethylene, allowed the reaction of residual  $\text{Al}(\text{C}_6\text{F}_5)_3$  and  $t\text{Bu}_3\text{P}$  to occur to give **5**, thus allowing the extraction of **4** into hexanes.<sup>[18]</sup>

It is interesting to note that P/B FLP combinations have previously shown two divergent pathways in their reaction with alkynes, thus affording either a zwitterionic material derived from P/B FLP addition to the alkyne or deprotonation of the alkyne affording an alkynyl borate salt.<sup>[3e,6]</sup> In contrast, only addition product zwitterions have been reported for the reactions of FLPs with ethylene, propene, hexene,<sup>[24]</sup> and norbornene.<sup>[30]</sup> Presumably in the present cases, the use of the basic phosphine  $t\text{Bu}_3\text{P}$  and the disubstituted olefin, isobutylene, disfavors such addition reactions because of steric hindrance, thus affording boron- and aluminum-based  $\sigma$ -allyl anion salts instead. These species are the first examples of products derived from FLP-based C–H activa-

tion of an unactivated olefin. Whereas the allyl monoborate is generated by a reversible reaction, in which the B/P FLP reacts with ethylene to give an addition product, the allyl bis(aluminate) reacts directly with ethylene through an insertion of the olefin into the Al–C bond, thus affording a new approach to C–C bond formation and olefin elaboration. Further application of this reactivity continues to be the subject of intense study.

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- [18] See the Supporting Information, **1**:  $P\bar{1}$ ,  $a = 12.6080(7)$ ,  $b = 13.8369(8)$ ,  $c = 19.2878(11)$  Å,  $\alpha = 96.396(2)$ ,  $\beta = 97.763(2)$ ,  $\gamma = 101.782(2)^\circ$ ,  $V = 3230.1(3)$  Å<sup>3</sup>,  $Z = 2$ , data ( $>2\sigma$ ) = 15134, variables = 906,  $R(>2\sigma) = 0.0736$ ,  $R(\text{all}) = 0.2289$ , GOF = 1.018. **2**: triclinic,  $P\bar{1}$ ,  $a = 8.6571(3)$ ,  $b = 13.0426(5)$ ,  $c = 15.3468(6)$  Å,  $\alpha = 84.625(2)$ ,  $\beta = 85.379(2)$ ,  $\gamma = 78.860(2)^\circ$ ,  $V = 1689.23(11)$  Å<sup>3</sup>,  $Z = 2$ , data ( $>2\sigma$ ) = 12858, variables = 474,  $R(>2\sigma) = 0.0395$ ,  $R(\text{all}) = 0.1104$ , GOF = 1.036. **5**: monoclinic,  $P2_1/c$ ,  $a = 11.1182(4)$ ,  $b = 18.3639(7)$ ,  $c = 17.0112(6)$  Å,  $\beta = 106.677(2)^\circ$ ,  $V = 3327.1(2)$  Å<sup>3</sup>, data ( $>2\sigma$ ) = 7967, variables = 451,  $R(>2\sigma) = 0.0527$ ,  $R(\text{all}) = 0.1564$ , GOF = 1.032. CCDC 863779 (**1**), 863780 (**2**), and 863781 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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