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Perspective

Comparative study of fluorinated triarylalanes and their borane counterparts

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SUMMARY

The chemistry of Lewis acids, in particular that of triarylboranes, has received unprecedented attention in recent years. Particularly in their role as the Lewis acid component of frustrated Lewis pairs (FLPs), boranes have shown astonishing properties, for example in their ability to bind H_2 reversibly. With the current spotlight on main-group chemistry, the heavier aluminum homologs have not yet received much attention. Herein, we provide an overview of the synthesis, properties, and reactivities of fluorinated triarylalanes [$Al(Ar^F)_3$] in direct comparison to their boron counterparts [$B(Ar^F)_3$]. In part, the scarcity of studies on fluorinated triarylalanes could be attributed to their shock- and thermal-sensitive nature, which has hampered progress in this field. However, because of their enhanced Lewis acidity compared to their boron complements, they have shown promising behavior in the fields of FLPs and, more recently, frustrated radical pairs (FRPs). They are also capable of effectively catalyzing polymerizations and hydroboration reactions and have proven to be useful as aryl nucleophiles in stochiometric reactions.

INTRODUCTION

The organization of the periodic table periodically groups elements that exhibit similar properties and chemical behavior. The group 13 elements boron and aluminum both exhibit similar reactivities, but subtle differences in their properties when moving down the group from boron to aluminum can lead to changes in structure, bonding, and reactivity. This in turn can be exploited in synthesis and catalysis. One example of the differences between boron and aluminum can be observed in their halides of formula EX_3 (E = B, Al; X = F, Cl, Br) existing as an electron sextet. In BX_3, intramolecular p^π-p^π bonding stabilizes the boron center. Aluminum, however, has a lower tendency for π-bonding, and therefore, intermolecular dimerization occurs with bridging halogens between aluminum centers (tetrahedral Al coordination).[1] The property of possessing six valence electrons gives EX_3 compounds the ability to accept further electrons into the vacant p-orbital, rendering them Lewis acidic.[2] The chemistry of EX_3 Lewis acids (e.g., BF_3 or $AlCl_3$) is broad, and their application as reagents and catalysts in organic synthesis is widely studied.[3] To increase the Lewis acidity, and therefore enhance the reactivity of trivalent aluminum and boron compounds, more electron withdrawing fluorinated aryl substituents can be installed, generating $E(Ar^F)_3$ compounds (E = B, Al; Ar^F = fluorinated aryl substituent). In these compounds, the Lewis acidity can be tuned by the number and the position of the fluorine atoms on the aryl groups.[4] While the chemistry of fluorinated triarylborane Lewis acids $B(Ar^F)_3$ is intensively studied,[4–8] the reactivity of fluorinated triarylalanes $Al(Ar^F)_3$ is less explored, and a comparison between the two elements is missing. This perspective aims to fill this gap to discuss homoleptic fluorinated

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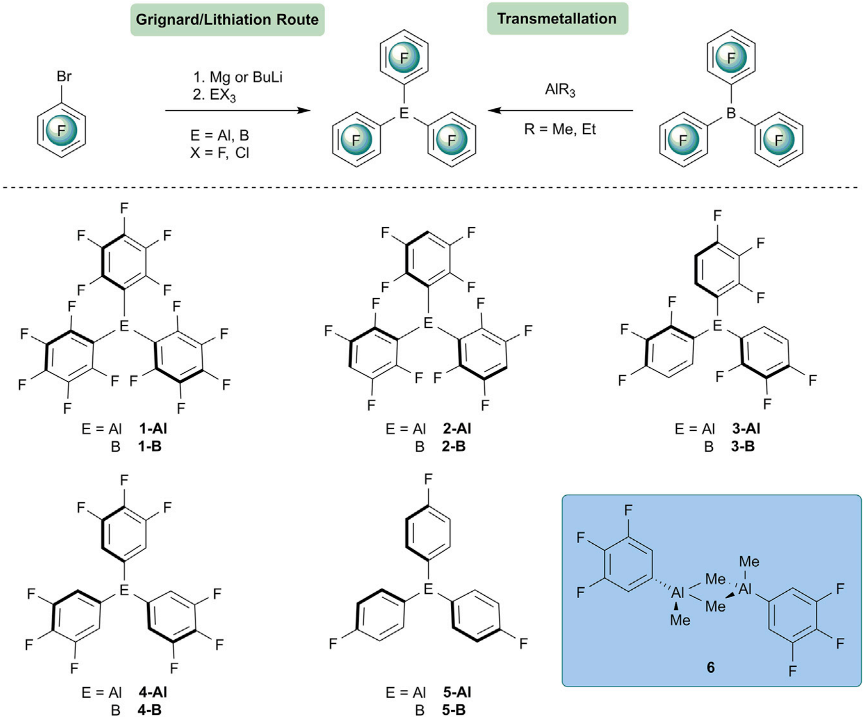

Figure 1. General synthesis and structures of the triarylalanes and triarylboranes descripted herein

The pictured alanes **1-Al**–**5-Al** and the boranes **1-B**–**5-B** can be synthesized either via a Grignard or lithiation route[10,11,14–16,18–28] or, in the case of **2-Al**·toluene and **3-Al**, via transmetalation of the respective boron congener.[13,14]

triarylalanes $Al(Ar^F)_3$ in direct comparison with their boron counterparts $B(Ar^F)_3$, examining their synthesis, properties, and reactivities.

Synthetic routes to $E(Ar^F)_3$ compounds

While many different fluorinated triarylboron compounds are reported, the variety of fluorinated triaryl aluminum compounds is much less pronounced, with just a handful of examples known (Figure 1, bottom). $Al(C_6F_5)_3$ **1-Al** (and its donor complexes **1-Al**·D [D = Et_2O, THF, toluene]) is the most investigated alane,[9–13] with only a few reports that describe the synthesis and properties of other fluorinated triarylalanes. Other reported alanes to date include $Al(2,3,5,6\text{-}F_4C_6H)_3$ **2-Al**,[14] $Al(2,3,4\text{-}F_3C_6H_2)_3$ **3-Al**,[15] $Al(3,4,5\text{-}F_3C_6H_2)_3$ **4-Al**,[15] and $Al(4\text{-}F\ C_6H_4)_3$ **5-Al**.[16,17] A few more fluorinated triaryl compounds, for example $Al(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_3$, are reported only in patents.[18] The borane congeners, on the other hand, have been more widely reported, with many articles on the synthesis and properties of the boron compounds $B(2,3,5,6\text{-}F_4C_6H)_3$ **2-B**,[19,20] $B(2,3,4\text{-}F_3C_6H_2)_3$ **3-B**,[15] and $B(4\text{-}FC_6H_4)_3$ **5-B**,[21–23] with $B(3,4,5\text{-}F_3C_6H_2)_3$ **4-B**[22,24–28] and $B(C_6F_5)_3$ **1-B**[5,29] being intensively studied. The boranes **1-B**–**5-B** and the alanes **1-Al**·D (D = Et_2O, THF), **4-Al**·OEt_2, and **5-Al** can all be synthesized via a lithiation or Grignard route through generation of an intermediate organolithium or Grignard reagent from a bromo aryl precursor. Subsequent treatment with a haloborane/-alane EX_3 (E = B, Al; X = F, Cl; Figure 1, top) generates the desired product, which is typically subjected to sublimation in the case of borane.[10,11,15–17,19–23,24–29] For alanes, sublimination is not advised due to the thermal instability of the product. An alternative route to generate the alane derivatives is through transmetalation. This method has the potential advantage of avoiding donor solvents such as Et_2O or THF, which may coordinate to the aluminum center in the product, thereby quenching its reactivity. The aluminum compounds **2-Al**·toluene and **3-Al** were both prepared through transmetalation of the boron congener **2-B** or **3-B** with AlR_3 (R = Me, Et; Figure 1, top).[14,15] In contrast, treatment of **4-B** with $AlMe_3$ resulted in incomplete aryl transfer, giving the dimeric structure **6**, in which two CH_3 groups bridge the aluminum centers through 2e,3c bonds.[15] The same type of dimeric structure can be observed by partial transmetalation of **1-B** with $AlMe_3$.[30] To date, **2-Al**·toluene and **4-Al**·OEt_2 only have been reported in their solvated structural form.[14,15] In general, it is advisable to synthesize the alanes with a solvent donor, since they have a tendency for a strong thermal induced decomposition (see later).[31,32]

Properties

Although both $B(Ar^F)_3$ and $Al(Ar^F)_3$ would be expected to have similar properties, there are several key differences. One of these is their stability, which is possibly a large factor that has hindered progress in the development of $Al(Ar^F)_3$ chemistry. While the borane **1-B** is largely thermally stable and can be sublimed (110°C, 1×10^{-3} mbar),[29] the first report on the synthesis of **1-Al** by Brinkmann et al.[10] mentioned violent detonations when the crude product from the reaction of $AlCl_3$ and C_6F_5MgBr in Et_2O was sublimed. The same observation was made when the reaction mixture of **1-B** and $AlEt_3$ in neat conditions reached a temperature of 70°C.[10] Since then, a note of caution regarding the shock and thermal sensitivity of **1-Al** has generally been applied in articles working with (*ortho*-)fluorinated triarylalanes.[31,32] The reason for this sensitivity is attributed to inter- or intramolecular F-abstractions, which result in the formation of reactive fluorobenzyne intermediates.[10] This view was supported after Chen et al.[9] synthesized the unsolvated alane **1-Al** in 2016 for the first time via transmetalation of **1-B** with $AlEt_3$ in hexane and analyzed the solid-state structure via X-ray crystallography analysis. In the solid state, **1-Al** forms a dimeric structure with strong Al···F interactions of the ortho-fluorine atoms of one alane molecule with the aluminum center of a neighboring alane molecule, which at the same time serves as a fluorine donor to the first alane (Figure 2, top). In the structure, short Al···F distances of 1.962(1) and 1.983(5) Å and elongated C–F bonds indicate a strong interaction between the Al and F atoms. The solid-state structure also reveals a shorter Al–C=C–F bond (highlighted bonds in Figure 2, top) compared to the other C=C bonds. These structural features suggest a decomposition pathway via Al–F bond formation and tetrafluorobenzyne generation likely (Figure 2, top).[9] This decomposition is akin to that noted with LiC_6F_5. The exothermic formation of strong Al–F bonds and generation of unstable benzynes accounts for the instability of the alanes relative to the boranes, where stronger E–C bonds exist (B–C = 448 $kJ \cdot mol^{-1}$ versus Al–C = 255 $kJ \cdot mol^{-1}$).[33] Such Al···F interactions with a Al···F distance of 2.034(3) Å can also be found in the solid-state structure of **3-Al** published recently in our group (Figure 2, bottom).[15] Additional evidence for the formation of Al–F bonds has also been presented in a recent study from Timoshkin et al.[34] on the thermal decomposition of $E(C_6F_5)_3$·pyridine complexes (E = Al, Ga, In). The mass-spectrum analysis of **1-Al**·py in the gas phase at 450–500 K showed $AlF_2C_5H_5N^+$ (100%) as the most intense ion, indicating that thermal decomposition proceeds via an exchange of C_6F_5 groups by F atoms at the aluminum center.[34] In contrast, in the mass spectrum of **1-B**·D (D = py or Et_2O), the free D^+ ion was found as the most intense peak as well as **1-B**$^+$ and other further decomposition fragments, including HC_6F_5, indicating that **1-B**·D most likely dissociates initially into the free donor molecule and **1-B**.[35,36]

Lewis acidity

The Lewis acidity of a compound correlates with its ability to accept an electron pair and therefore with its reactivity and catalytic activity (see later). Knowing the relative strength of a Lewis acid is therefore important for understanding its reactivity. There

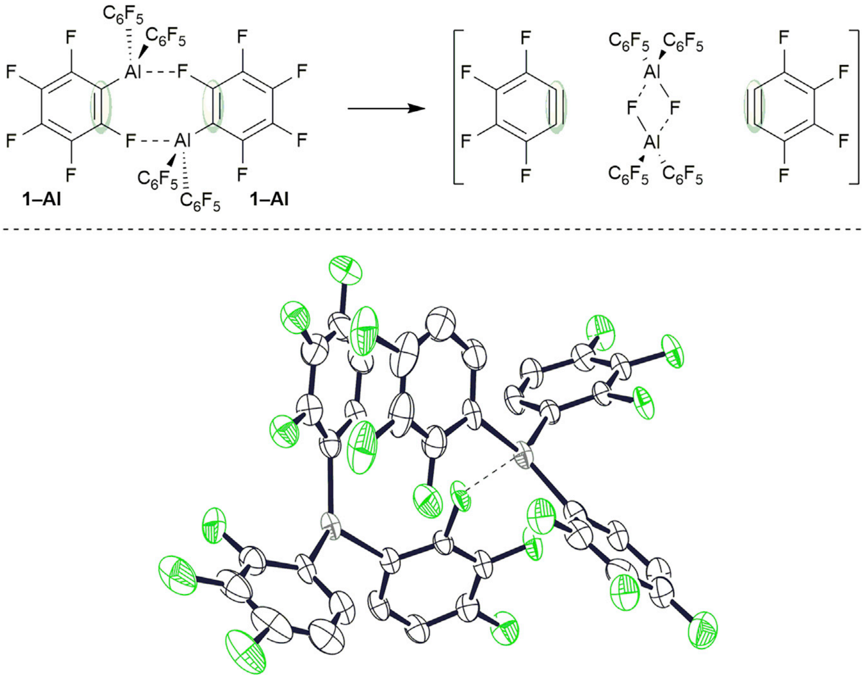

Figure 2. Proposed decomposition pathway of 1-Al and the solid-state structure of 3-Al in the unit cell

Short Al···F contacts between two **1-Al** molecules indicate a decomposition pathway via Al–F bond formation and tetrafluorobenzyne generation.[9] Such short Al···F interactions can also be found in the solid-state structure of **3-Al**. Dashed bond represents neighboring Al···F contact. H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Green, fluorine; gray, aluminum.[14]

are several methods used to calculate Lewis acidity both computationally and experimentally. Outcomes of these studies have led to much debate over the relative strength of $B(Ar^F)_3$ relative to $Al(Ar^F)_3$, although the general consensus is that the alanes are more Lewis acidic than the boranes. Indeed most studies support the view that **1-Al** is the stronger Lewis acid when compared to **1-B**.[37–41] This can be indicated by the observation that **1-Al** forms complexes with weak donor solvents like toluene or benzene, which **1-B** does not do.[37,42] According to fluoride ion affinity (FIA) calculations (CCSD(T)(FC)/double-ζ level plus MP2 extrapolation to quadruple-ζ), a method widely applied to determine Lewis acidity, **1-Al** with a FIA of 536 $kJ \cdot mol^{-1}$ is far more Lewis acidic than **1-B** with its FIA value of 452 $kJ \cdot mol^{-1}$.[39] With a lager FIA than SbF_5, **1-Al** is also categorized as a Lewis superacid.[38,41] However, when comparing the hydride ion affinity (HIA; RI-BP86/def2-TZVPP), **1-B** was found the better acceptor, with a value of 528 $kJ \cdot mol^{-1}$, than **1-Al**, with a HIA of 514 $kJ \cdot mol^{-1}$.[37] In addition, a very few reports on the experimental determination of the Lewis acidity of **1-Al** demonstrate the same trend.[12,43,44] Park et al.[12] investigated the C≡N stretching frequency of a benzonitrile/Lewis acid adduct using IR spectroscopy. Here the stronger Lewis acid would give a higher stretching frequency for the adduct. The spectroscopic results show that **1-B** is the strongest Lewis acid, with $v(CN) = 2{,}324\ cm^{-1}$, and that **1-Al** is weaker and only slightly more acidic than $AlMe_3$ ($v(CN)$ of 2,280 and 2,276 cm^{-1}, respectively).[12] The same trend can be observed in the stretching frequencies of **1-Al** and **1-B** with acetonitrile. **1-Al** coordinates two molecules of MeCN and forms a complex of the composition of [**1-Al**·2MeCN]·MeCN with $v(CN)$ of 2,311 and 2,340 cm^{-1}, whereas **1-B** and MeCN have a ratio of 1:1 and **1-B**·MeCN possesses a stretching frequency of

Table 1. Overview of the Lewis acidities of the alanes and boranes discussed herein

	Gutmann-Beckett [AN]	FIA [kJ·mol^{-1}]	HIA [kJ·mol^{-1}]	ν(CN) [cm^{-1}]	GEI [eV]
1-Al	-	536[c] 541[e]	514[d]	2,280[12] 2,311; 2,340[45]	–
1-B	77.5[b,22] 78.1–82.0[a,48]	452[c] 459[e]	528[d]	2,324[12] 2,366[45]	1.408[49]
2-Al	–	–	–	–	–
2-B	80.2[a,48]	432[49]	–	–	1.250[49]
3-Al	–	501[e]	–	–	–
3-B	–	404[e]	–	–	–
4-Al	–	511[e]	–	–	–
4-B	79.6[b,22]	427[e]	–	–	–
5-Al	–	–	–	–	–
5-B	57.0[b,22]	–	–	–	–

AN, acceptor number; FIA, fluorine ion affinity; HIA, hydride ion affinity; GEI, global electrophilicity index.

[a] Measured in CD_2Cl_2.

[b] Measured in $CDCl_3$.

[c] DFT calculations using the theory CCSD(T)(FC)/double-ζ level plus MP2 extrapolation to quadruple-ζ.[39]

[d] DFT calculations using the theory RI-BP86/def2-TZVPP.[37]

[e] DFT calculations using the theory M06-2X/cc-pVDZ.[15]

2,366 cm^{-1}.[45] In other experimental studies involving Zr-metallocene complex formation with **1-E** (E = B, Al), it was found that **1-B** forms a thermally more stable adduct with Cp_2ZrMe_2 (Cp = cyclopentadiene) compared to **1-Al**.[44] Additionally, calorimetry in solution showed the abstraction of methide from *rac*-(EBI)$ZrMe_2$ (EBI = ethylene-1,2-bis(1-indenyl)) by **1-Al** is less exothermic than abstraction by **1-B**, indicating **1-Al** is less Lewis acidic.[43] It should be noted that all of these studies where performed with the toluene adduct of **1-Al**, which could distort the results and have an effect on, for example, the methide abstraction enthalpies.[43] However, a theoretical study by Timoshkin et al.[40] on compounds **1-E**·NH_3 (E = Al, B) revealed that upon complexation, the trigonal planar central atom in **1-E** changes to a pyramidal confirmation under the need for reorganization energy. The reorganization energy for **1-B** is higher than that of **1-Al**, which results in the lower overall Lewis acidity for **1-B**, although the B–N donor-acceptor interaction in already-pyramidalized compounds is stronger than Al–N interactions of similar compounds.[40,41]

Describing the relative Lewis acidities for the boranes highly depends on the determination method applied.[46] For example, according to the Gutmann-Beckett method, where an acceptor number (AN) is obtained through monitoring the change in ^{31}P NMR chemical shift upon coordinating triethylphosphine oxide ($Et_3P{=}O$) to the borane,[47] **4-B** (AN = 79.57) is more Lewis acidic than **1-B** (AN = 77.49).[22] But when looking at the DFT calculated (M06-2X/cc-pVDZ) FIA, **4-B** is less Lewis acidic than **1-B** (427 and 459 kJ·mol^{-1}, respectively).[15] However, not every triarylborane has been investigated with the same methods (either computationally or experimentally). For example, the experimental methods often vary by external/other parameters (e.g., solvents) so that a number of different values for the same borane have been published, even when the same method was applied (see Table 1).[48]

Few investigations on the Lewis acidity of other triaryl aluminum derivatives have been performed, but according to FIA calculations (M06-2X/cc-pVDZ), the aluminum compounds **3-Al** and **4-Al** are more Lewis acidic than their boron counterparts **3-B** and **4-B**.[15] It has also been reported that **2-E** with four fluorine atoms per phenyl ring has a lower Lewis acidity compared to the fully fluorinated compounds

1-E (E = B, Al).[14,19] Of note, recently reported related aluminum compounds of the type $Al(OC(C_6F_5)_3)_3$ fall into the class of Lewis superacids.[38] Synthesized by treatment of $AlEt_3$ with the trityl alcohol $HOC(C_6F_5)_3$, they show a high thermal stability, which allows the adduct free isolation and storage under inert conditions at room temperature despite the fact that they possess a FIA value even higher than that of Krossing's benchmark compound $Al(OC(CF_3)_3)_3$.[50] For comparison, Krossing's aluminum derivative has never been isolated due to its limited thermal stability.[51]

Given that the values presented in the literature on Lewis acidities are so diverse (see Table 1 for comparison), a more uniform approach to predict Lewis acidity was made by Stephan et al. known as the global electrophilicity index (GEI).[49] Here, the computationally determined ability of an acid to accept electrons can be derived from the HOMO and LUMO energies of the Lewis acid and is, importantly, independent of the Lewis base.[49] According to the GEI, **1-B** is the most acidic borane and **2-B** is 11% less Lewis acidic.[49] However, to date, the GEI has not been applied to the aluminum congeners.

In short, in order to compare all the known alanes and boranes to the full extent, one method needs to be applied to all systems in which all the conditions are kept the same among different measurements.

Reactivity

The electron-deficient nature of trivalent boron and aluminum compounds renders them capable of accepting an electron pair from a donor to form a Lewis acid-base adduct.[2] By employing fluorinated triaryl substituents, not only is the Lewis acidity enhanced (see above), but also the steric bulk around the trial atom is increased. Thus, when reacted with a sterically encumbered base, no classical adduct formation is observed, and the acid-base pair becomes "frustrated."[52,53] The concept of frustrated Lewis pairs (FLPs) had led to unique reactivities and applications in organic synthesis in which $E(Ar^F)_3$ compounds have played a key role as the Lewis acid component.[53,54] **1-B**-based FLPs are commonly employed to activate H_2 and effectively transfer the hydride to reduce imines, nitriles, aziridines, enamines, and silylenolethers.[8] However, there are examples where it was not possible to deliver H_2 to an unactivated olefin with **1-B**/P*t*Bu$_3$, but changing the Lewis acid to the more reactive FLP system **1-Al**/P*t*Bu$_3$ made the hydrogen transfer achievable.[53,55] In general, the reaction of $B(Ar^F)_3/PR_3$ FLPs with H_2 forms salts of the type $[R_3PH][HB(Ar^F)_3]$, while treatment of the alane FLP $Al(Ar^F)_3/PR_3$ with H_2 yields $[R_3PH][(\mu\text{-}H)\{Al(Ar^F)_3\}_2]$, in which two fluorinated triaryl aluminum molecules are bridged by a hydrogen atom (Figure 3, top).[14,53] Although **2-B** is known to be ~3%–5% less Lewis acidic than **1-B** (measured by the Gutmann-Beckett and Childs method),[20] the FLP **2-B**/P(*o*-tol)$_3$ (tol, toluene) has the right balance of acidity and hydridicity (of the H_2 activated species) to allow reversible binding of H_2 at room temperature. Importantly, in **2-B**, there is no possibility for *para*-F attack and nucleophilic substitution reaction, which is a known possible side reaction when using **1-B**.[19,54] The alane FLP **2-Al**/P(*o*-tol)$_3$ can also activate H_2 to form the salt [(*o*-tol)$_3$PH][(μ-H){**2-Al**}$_2$]; however, this could not be isolated due to the slow activation and reversible loss of H_2. This was suggested to be due to the lower Lewis acidity of **2-Al** compared to **1-Al**. Experimentally, it was not possible to use **2-Al**/P(*o*-tol)$_3$ for the reduction of olefins.[14] A phosphine salt of the perfluoro biphenyl aluminum derivative $[(Mes_3PH][(\mu\text{-}H)\{Al(C_{12}F_9)_3\}_2]$ (Mes, mesityl) was also tested for the reduction of ethane; however, even after extensive heating, the insertion of the ethane into the aluminum-hydride bond was not observed. This was attributed to the steric bulk of

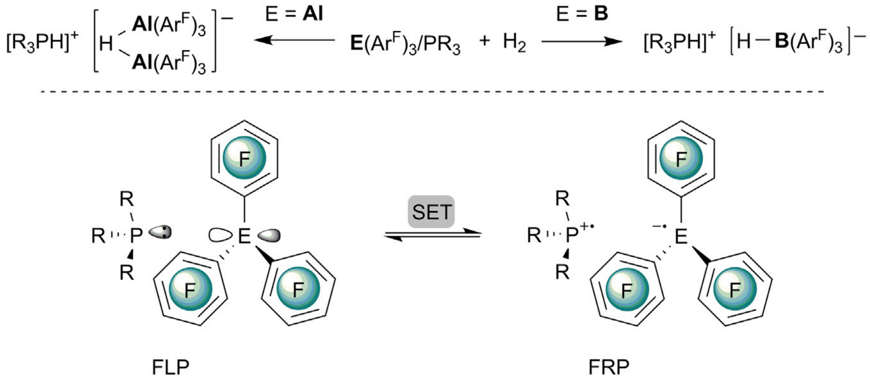

Figure 3. Products of FLPs $Al(Ar^F)_3/PR_3$ and $B(Ar^F)_3/PR_3$ with H_2, and SET equilibrium between an FLP and FRP

Reaction of $B(Ar^F)_3/PR_3$ with H_2 forms salts of the type $[R_3PH][HB(Ar^F)_3]$, while treatment of $Al(Ar^F)_3/PR_3$ with H_2 yields $[R_3PH][(\mu\text{-}H)\{Al(Ar^F)_3\}_2]$.[13,46] A postulated single-electron transfer (SET) equilibrium between the frustrated Lewis pair (FLP) and the frustrated radical pair (FRP) is based on the observation of a weak radical signal detected by electron paramagnetic resonance (EPR) spectroscopy of a solution containing Mes_3P and **1-Al** or **1-B**.[56]

the biphenyl group and the increased Lewis acidity, making the hydride inaccessible. The free triaryl aluminum compound $Al(C_{12}F_9)_3$ could not be isolated.[14]

In addition to H_2 activation, other FLP reactivity is common to both $B(Ar^F)_3$ and $Al(Ar^F)_3$. Examples involving **1-Al** FLPs include C–H activation reactions of terminal alkynes[57] or isobutylene,[56] and polymerization reactions.[58] Although the activation of CO_2 is commonly achieved with aluminum/phosphorus-based FLPs, the aluminum compounds involved in these reaction are typically not fluorinated triaryl aluminum compounds.[59,60]

While it is generally assumed that the reaction pathways involving FLPs in small-molecule activation are two-electron processes, only in recent years was a possible a radical pathway by a frustrated radical pair (FRP) considered.[61] The possibility for a homolytic H–H bond cleavage with the FLP **1-B**/P*t*Bu$_3$ was first postulated by Piers et al.[62]; however, the first aluminum-based FRP was reported by Stephan et al. in 2013.[63] The reaction of **1-Al**/PR_3 (R = *t*Bu, Mes, napthyl) with N_2O and a further equivalent of **1-Al** produces frustrated radical ion pairs of the composition $[R_3P^{\cdot}][(\mu\text{-}O^{\cdot})\{$**1-Al**$\}_2]$.[63] Stephan et al.[64] postulated further in 2017 a single-electron transfer (SET) equilibrium between the FLP and the FRP on the bases of an observed weak radical signal detected by electron paramagnetic resonance (EPR) spectroscopy of a solution containing Mes_3P and **1-B**. The signal that could be attributed to the phosphine radical cation ($Mes_3P^{\cdot+}$) became more intense when using **1-Al** as the Lewis acid. However, the radical anion **1-Al**$^{\cdot-}$ could not be detected via EPR because of its short lifetime.[64] To further confirm the formation of a FRP, **1-Al**/$PMes_3$ and **1-B**/$PMes_3$ were treated separately with Ph_3SnH and tetrachloro-1,4-benzoquinone (TCQ). In the former case, the formation of the salts $[Mes_3PH][(\mu\text{-}H)\{$**1-Al**$\}_2]$ or $[Mes_3PH][H$**1-B**$]$ was observed as well as the di-stannane $Ph_3Sn–SnPh_3$, indicating the generation of $H^{\cdot}$ and $Sn^{\cdot}$ intermediates via a homolytic cleavage of the Sn–H bond. The products resulting from a heterolytic cleavage of the Sn–H bond could be observed when the Lewis base was switched to P*t*Bu$_3$. Here, **1-Al**/P*t*Bu$_3$ or **1-B**/P*t*Bu$_3$ was treated with Ph_3SnH and $[tBu_3PSnPh_3][(\mu\text{-}H)\{$**1-Al**$\}_2]$ and $[tBu_3PSnPh_3][H$**1-B**$]$ were isolated, respectively, indicating that the reaction pathway (radical or diamagnetic) of the FLPs is dependent on the Lewis base employed. The same trend

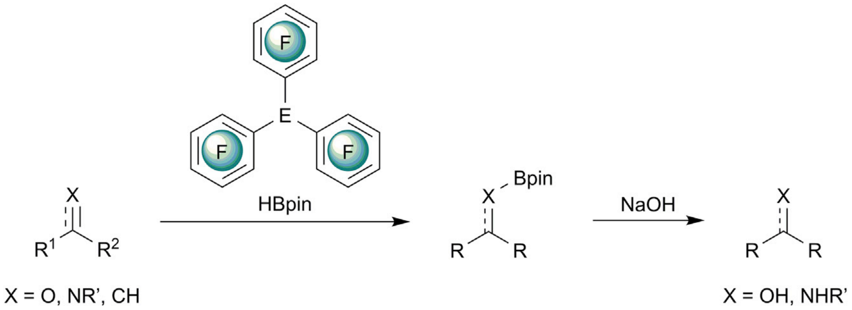

Figure 4. General reaction scheme for the E(Ar^F)$_3$-catalyzed hydroboration reaction
Reductive hydroboration reaction of unsaturated substrates with HBpin and **4-Al**●OEt$_2$ or **4-B** as catalysts. Basic, aqueous workup yields the reduced products.[14,23,24]

was found when reacting **1-E**/PMes$_3$ or **1-E**/P*t*Bu$_3$ (E = Al, B) with TCQ whereby Mes$_3$P promotes a radical pathway and *t*Bu$_3$P a two-electron pathway.[64] However, a recent study by Slootweg et al.[65] suggests that both reaction pathways with **1-B**/PMes$_3$ or **1-B**/P*t*Bu$_3$ and Ph$_3$SnH occur via a polar, heterolytic mechanism by showing that [*t*Bu$_3$PSnPh$_3$][H**1-B**] can convert into [*t*Bu$_3$PH][H**1-B**]. A higher energy barrier for the formation of [*t*Bu$_3$PH][H**1-B**] compared to [Mes$_3$PH][H**1-B**] explains the slow formation of [*t*Bu$_3$PH][H**1-B**] and therefore the possible isolation of [*t*Bu$_3$PSnPh$_3$][H**1-B**] as an intermediate.[65] From the reactions with TCQ and **1-B**/PR$_3$ (R = Mes, *t*Bu) in the dark, Slootweg et al.[65] concluded that the radicals observed are due to the binding of **1-B** to the carbonyl group of the substrate, which facilitates the SET instead of a direct SET between **1-B** and PR$_3$.[65] However, since the **1-B**/PR$_3$ radical ion pair can be generated via photo-induced SET (534 nm for R = Mes),[66] a small amount of the FRP, which is not majorly contributing to the reaction, seems to be formed when the reactions are carried out under light conditions.[65] An example to utilize the increased electron acceptor capacity and possible visible-light-induced SET by the coordination of **1-B** to a carbonyl compound was proposed by ourselves[67,68] and Ooi et al.[69] However, in our work, EPR and DFT studies showed that a diamagnetic pathway was most likely operative, but a one-electron process could also be possible with certain substrates. Considering that FRPs based on aluminum form in higher concentrations[64] and the radical anion **1-Al**$^{\cdot-}$ can be generated much easier than **1-B**$^{\cdot-}$ upon treatment with decamethylferrocene (Cp*$_2$Fe),[70] including aluminum-based Lewis acids in the exploration of FRPs for organic reactions could be beneficial for future studies.

Usage of E(Ar^F)$_3$ (E = Al, B) in catalysis and organic reactions

Since the use of B(Ar^F)$_3$ (in particular **1-B**) in catalysis and organic reactions is so well explored,[4–6,8] the focus herein lies on the alane derivatives Al(Ar^F)$_3$ in comparison to their borane equivalents. The most prominent reactions involving catalytic and stochiometric amounts of fluorinated triarylalanes and boranes are summarized in the following section.

The catalytic hydroboration of unsaturated substrates using group 13 catalysts is well explored and is often used as a test reaction when designing new main-group Lewis acid catalysts.[71] Both **4-Al**·OEt$_2$ and **4-B** have successfully been used as catalysts in reductive hydroboration reactions of aldehydes, ketones, aldimines, olefines, and terminal alkynes (10 mol% versus 2–5 mol%, respectively; Figure 4).[15,24,25] It was suggested that the 3,4,5-fluorine substitution pattern in the borane makes **4-B** particularly effective in these conversions.[24] Although the yields of the products from the treatment of aldehydes, ketones, and imines with HBpin and **4-Al**·OEt$_2$

or **4-B** do not differ significantly, it seems that the reactions catalyzed by borane are somewhat faster, and some of them proceed at room temperature, while the alane-catalyzed conversions only take place at 70°C.[15,25]

In 1996, Piers et al.[72] reported the hydrosilylation of C=O bonds with hydrosilanes via **1-B** promoted Si–H bond activation.[72] However, direct spectroscopic and structural evidence for the [Si–H···B] adduct could only be provided in 2014, when Piers et al.[73] exchanged **1-B** for a more Lewis acidic borane, meaning [Si–H···**1-B**] could never be isolated.[73,74] In contrast, mixing Et_3SiH with unsolvated **1-Al** in hexane and storing the solution at −30°C gave single crystals of the hydrosilane-alane complex [Et_3Si–H···**1-Al**].[74] In a study conducted by Chen et al.,[74] the silane-alane system showed a clear advantage over the silane-borane complex in catalytic transformations such as ligand redistribution of tertiary silanes into secondary and quaternary Si compounds, polymerization of conjugated polar alkenes, hydrosilylation of unactivated alkenes, and hydrodefluorination of fluoroalkanes. The ability to isolate to silane adduct [Et_3Si–H···**1-Al**] and the better performance of this complex in contrast to [Si–H···**1-B**] were attributed to the higher Lewis acidity of **1-Al** compared to **1-B**.[74] In a similar process, the highly selective reduction of CO_2 into CH_4 could be archived by using the mixed catalytic system **1-Al**/**1-B** in a tandem catalytic hydrosilylation reaction with Et_3SiH.[75] In this reaction, **1-Al** fixates CO_2 by forming a classical Lewis acid **1-Al**·O=C adduct and promotes the first reduction step by converting CO_2 into $HCOOSiEt_3$. **1-B** mediates the FLP-type Si–H activation and catalyzes the reductive reaction steps from $HCOOSiEt_3 \rightarrow H_2C(OSiEt_3)_2 \rightarrow H_3COSiEt_3$ and finally toward the end product, CH_4. The reason for the distinct catalytic behavior between the aluminum- and boron-based Lewis acids is due to the higher overall Lewis acidity of **1-Al**, which results in the formation of more stable **1-Al**·O=C (and intermediates) adducts. The roles of **1-Al** and **1-B** in the catalytic reduction of CO_2 to CH_4 are therefore complementary but cooperative. These findings are supported by the detection, characterization, and independent synthesis of each reaction intermediate as well as computational calculations.[75]

Another major field in which **1-Al** and **1-B** are used is as co-catalysts or activators in metallocene or Lewis pair-catalyzed polymerizations.[31,32,43,76–80] For example, Park et al.[12] used both **1-Al** and **1-B** to exchange a methyl group with a C_6F_5 group in methylaluminoxane (MAO), a well-known catalyst activator for ethylene polymerization. With both alane and borane, an increased reactivity of the Cp_2ZrCl_2 catalyst could be observed after treatment with the modified MAO. In case of **1-B**, boron also gets incorporated into the MAO framework, which is also known to be performance enhancing.[12] Further examples of Lewis-acid-catalyzed polymerizations involving **1-Al** and **1-B** can be found in the recent perspective article by Chen et al.[81]

Aryl transfer reactions such as carboborations[5] are also commonly explored in $B(Ar^F)_3$ chemistry; however, much less is known about similar reactions involving $Al(Ar^F)_3$, although examples exist. In particular, stochiometric amounts of **5-Al** have mostly been used as a nucleophile in aryl transfer reactions.[16,17,82] For example, *N*-substituted quaternary carbon centers in compound **8** could be generated via a retro-ene arylation reaction from the reaction of *N*-alkoxyenamides (**7**) with nucleophilic triaryl aluminum compounds (Figure 5A). The less Lewis acidic commercially available $AlPh_3$ performed poorly compared to the fluorinated triaryl aluminum compounds.[82] The boron counterpart **5-B** and **4-B** have been used by our group in aryl transfer reactions from $B(Ar^F)_3$ to α-diazocarbonylcompounds or iodonium ylides (cf. Figure 5B).[22,26] In case of the more Lewis acidic **4-B**, it was possible to transfer all of the aryl rings to the α-diazocarbonyl starting material.[22] Applying

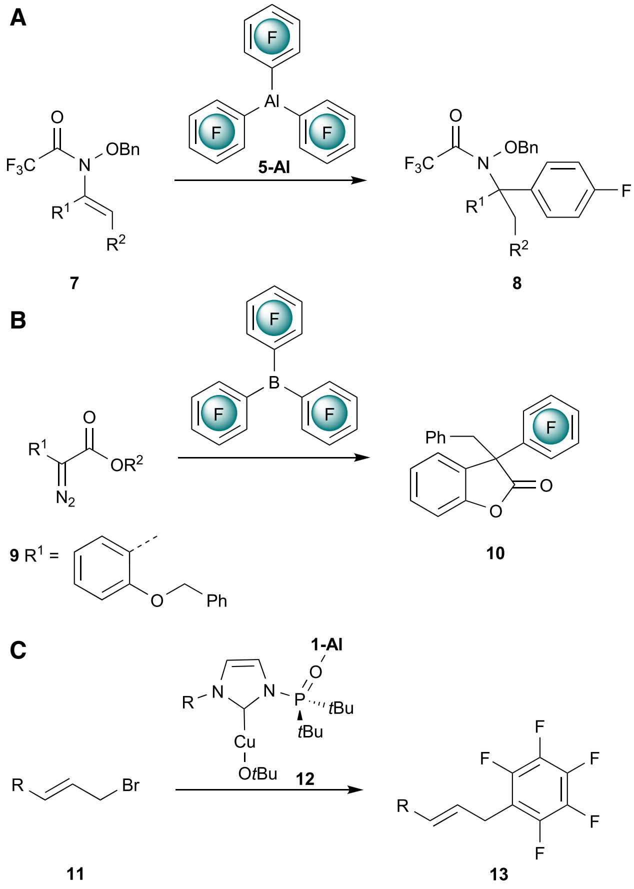

Figure 5. Overview of aryl transfer reactions with $Al(Ar^F)_3$ or $B(Ar^F)_3$

(A) A retro-ene arylation reaction of *N*-alkoxyenamide (**7**) with **5-Al** to produce a quaternary carbon center in compound **8**.[70]

(B) Aryl transfer reaction from **4-B** or **1-B** to the diazoester **9**, resulting in the formation of lactone **10**.[21]

(C) A new C–C bond was formed in compound **13** by aryl transfer to allyl bromide **11** by using Cu/**1-Al** complex **12**.[71]

the reaction protocol to the diazoester **9** with **4-B** or **1-B**, the generation of a lactones **10** bearing a quaternary carbon center was observed.[22] Ogoshi et al. have also demonstrated aryl transfer with the alane **1-Al** using a heterobimetallic Cu/**1-Al** N-heterocyclic carbene (NHC) complex **12** for a transmetalation between **1-Al** and Cu to form a Cu–C_6F_5 bond. This reactive intermediate can subsequently transfer the C_6F_5 group to an allyl bromide **11** to form a new C–C bond in **13** (Figure 5C).[83]

Conclusion and outlook

This overview of $B(Ar^F)_3$ and $Al(Ar^F)_3$ demonstrates a high degree of similarity between fluorinated triaryl aluminum compounds and their boron counterparts in terms of reactivity and applications in catalysis and organic synthesis. However, the chemistry of $Al(Ar^F)_3$ is much less represented in the literature. Albeit controversially discussed, a slightly enhanced Lewis acidity and therefore a higher reactivity is to be assumed for the alanes, which could impart higher activity in selected reactions. The usage of $Al(Ar^F)_3$ could also be more beneficial compared to $B(Ar^F)_3$ in the formation and reactivity of frustrated radical pairs (FRPs) owing to the higher stability of $Al(Ar^F)_3^{\cdot -}$. As the syntheses of fluorinated triaryl aluminum compounds are very similar to that of the more established boranes B(Ar^{F})$_3$, a large number of derivatives could potentially be synthesized easily. However, the shock and thermal sensitivity resulting in violent detonations of ortho fluorinated triaryl aluminum compounds always have to be considered and taken into account when synthesizing and working with such compounds. This in part has hampered progress in this area. In this regard, the use of alanes devoid of *o*-F (and potentially *p*-F) atoms may be useful in overcoming these hazards. Alternatively, other triarylalanes such as Al(C$_6$H$_3$-3,5-(CF$_3$)$_2$)$_3$ or derivatives of Krossing's aluminum compounds of the type Al(OC(Ar^{F})$_3$)$_3$ could be ways to circumvent such stability issues.

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AUTHOR CONTRIBUTIONS

T.K. and R.L.M. wrote and prepared the manuscript. Both authors proofread the manuscript and commented on the draft.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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