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CO_2 reduction *via* aluminum complexes of ammonia boranes†

Gabriel Ménard and Douglas W. Stephan*

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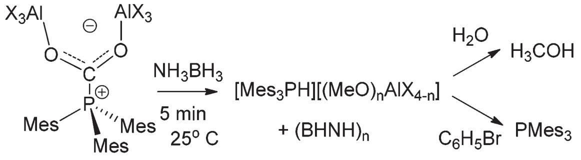
Reactions of amine-boranes NH_3BH_3, Me_2NHBH_3, or Me_3NBH_3 with AlX_3 (X = Cl, Br, I, C_6F_5) have been examined. The species $AlBr_3{\cdot}H_3BNMe_3$ **2**, $Al(C_6F_5)_3{\cdot}H_3BNMe_3$ **3**, $Al(C_6F_5)_3{\cdot}H_3BNHMe_2$ **4** and $Al(C_6F_5)_3{\cdot}H_3BNH_3$ **5** have been prepared and isolated. The analogous reaction of $B(C_6F_5)_3$ and H_3BNMe_3 results in C_6F_5-transfer and the formation of $(C_6F_5)BH_2{\cdot}NMe_3$ **6**. While the adduct **6** was unreactive to CO_2, species **3** reacts with CO_2 to give the formate linked $Al(C_6F_5)_3(HCO_2)H_2BNMe_3$ **8**. The species $R_3PC(OAl(C_6F_5)_3)_2$ (R = *o*-tol (**1′-C₆F₅**), R = Mes (**1-C₆F₅**)) were prepared, and **1′-C₆F₅** was shown to react with amine-boranes to effect the reduction of this bound-CO_2 to formate and methoxide-derivatives, proceeding through intermediates including **8** and $[(Me_3NBH_2)_2(\mu\text{-H})][(HCO_2)(Al(C_6F_5)_3)_2]$ **9**. The salt $[tBu_3PH][(HCO_2)(Al(C_6F_5)_3)_2]$ **10** was prepared independently.

Introduction

Carbon dioxide is ubiquitous in our environment and maintained in gentle balance through the combined actions of photosynthesis, animal respiration, decomposing organic material, *etc.* as part of the carbon cycle. However, since the industrial revolution, this balance has been altered with the rapid increase in CO_2 emission prompting global climate change.[1,2] While mitigation of emission through reduced consumption,[3] the use of renewables[4] and a shift away from C-based fuels[5–7] likely offer the best long-term remedies, strategies to carbon-neutral fuels, such as Olah's "Methanol Economy", are being explored.[8,9] Essential to such efforts are fundamental understanding of CO_2 activation and reduction chemistry.

Transition metal and main-group based reductions of CO_2 have recently been explored. A variety of metals, such as Zr,[10] Nb,[11] Re,[12] Fe,[13] Ru,[14] Ir,[15] Ni,[16,17] and Cu,[18,19] in conjunction with H_2 or an external reductant, have been used to reduce CO_2 to CO, formic acid, MeOH, and even methane. Non-metal mediated routes are also beginning to emerge. Use of such reagents to capture CO_2 has been demonstrated for carbenes, frustrated Lewis pairs (FLPs)[20] and most recently a seemingly benign dithiocarbamate.[21] Furthermore while catalytic reduction of CO_2 has been achieved employing carbenes,[22,23] stoichiometric reductions of CO_2 have been demonstrated employing FLPs affording reduction to formate, MeOH, CO, and CH_4 depending on the reductant used.[24–29] In an earlier report, we described the formation of Al-based FLP complexes of CO_2 of the form $Mes_3PC(OAlX_3)_2$ (**1-X**; X = Cl, Br, I) and their subsequent reaction with ammonia borane (AB = NH_3BH_3) to effect, upon quenching, the stoichiometric reduction to MeOH (eqn (1)).[24]

Herein, we examine the interaction of Al-based Lewis acids with several amine-boranes and explore the reactivity of these species with CO_2. This reactivity is also shown to have implications for the pathway for reduction of the CO_2 in **1-X**.



1-X (X = Cl, Br, I) (1)

Results and discussion

Reactions of amine-boranes with Lewis acids

Reactions of amine-boranes AB, Me_2NHBH_3 (^{Me2}AB), or Me_3NBH_3 (^{Me3}AB) with AlX_3 (X = Cl, Br, I, C_6F_5) have been examined. In the case of $AlBr_3$, an equimolar amount of $AlBr_3$ was combined with the soluble ^{Me3}AB in a J-Young tube in C_6D_5Br. An ^{27}Al NMR spectrum showed a single broad peak centered at 79 ppm and the ^{11}B and ^{1}H spectra showed only slightly shifted and broadened (for BH_3) signals in comparison

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Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario M5S 3H6. E-mail: dstephan@chem.utoronto.ca

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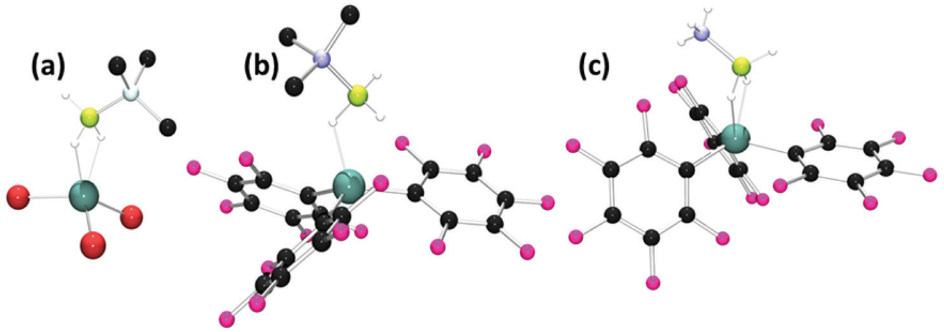


Fig. 1 POV-Ray depictions of (a) **2**; (b) **3**; and (c) **5**. C: black, N: blue, B: yellow-green, Al: teal, Br: scarlet, F: pink, H: white. Methyl H-atoms omitted for clarity.

to an authentic sample of ^{Me3}AB. The synthesis of this new species **2** was scaled up and **2** was isolated in 70% yield. Elemental analysis was consistent with the formulation of **2** as $AlBr_3{\cdot}H_3BNMe_3$ and an X-ray diffraction study confirmed the association of the B of ^{Me3}AB to the Al of $AlBr_3$ *via* two hydride bridges (Fig. 1a). Efforts to prepare an analogous adduct using AB and $AlBr_3$ gave a highly insoluble product, the nature of which could not be unambiguously determined.

The analogous synthesis employing $Al(C_6F_5)_3$ and ^{Me3}AB, gave the related species **3** after 15 min in 77% yield. While an ^{27}Al NMR signal was not observed, the ^{11}B and ^{1}H signals for the ^{Me3}AB fragment were again slightly shifted and broadened. Furthermore, the ^{19}F signals for $Al(C_6F_5)_3$ were also shifted. An X-ray structure confirmed **3** as $Al(C_6F_5)_3{\cdot}H_3BNMe_3$ (Fig. 1b). Similarly, the ^{Me2}AB and AB adducts of $Al(C_6F_5)_3$, **4** and **5** were prepared in 87% and 55% yield, respectively.

In the case of **5** the structure was again confirmed crystallographically (Fig. 1c).

The structural data for **2**, **3**, and **5**, reveal N–B distances of 1.577(5) Å, 1.589(2) Å, and 1.582(4) Å respectively. These are similar to the values reported for ^{Me3}AB (1.617(4) Å) and AB (1.58(2) Å) in the solid state.[30,31] This is attributable to polarization at B resulting from coordination of the B–H bonds to Al. The bridging hydrides give rise to differences in the B–Al distances in **2** and **3** being 2.312(5) Å and 2.498(3) Å, respectively. This presumably reflects the increased steric congestion between the C_6F_5 and Me groups of **3** in comparison to lesser interaction of the Br and Me substituents of **2**. Consistent with this notion, the B–Al distance in **5** is much shorter than in **3** and similar to **2** at 2.357(3) Å.

Interestingly, while Al has been used in the dehydrogenation chemistry of amine-boranes,[32,33] the present compounds represent rare examples of intermolecular B–H–Al bonds. This B–H–M bonding motif is reminiscent of several known early,[34,35] late,[36–41] and s-block main group[42–44] AB complexes. However, AB complexes of d^0 elements typically contain intramolecular B–H–M (M = Mg, Ca, Sc)[34,42–44] bonds derived from chelating anions $\{H_3BNMe_2BH_2Me_2N\}^-$ or $\{H_3BR_2N^-\}$ with both terminal B–H and amide (R_2N^-) groups bound to the same metal centre. In contrast, compounds **2–5** represent the first *intermolecular* group 13-AB adducts known, where no chelate is present.

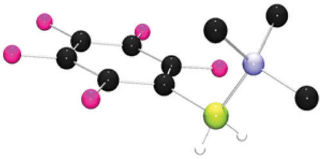
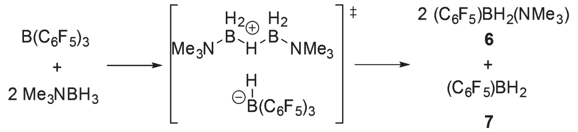


Fig. 2 POV-Ray depiction of **6**. C: black, N: blue, B: yellow-green, F: pink, H: white. Methyl H's omitted for clarity. B–N: 1.628(2) Å.

Compounds **2–5** are stable in solution for at least a day, however all compounds readily decompose when heated to 70 °C for several hours. The stability of these compounds stands in marked contrast to the analogous situation for $B(C_6F_5)_3$ in which the Lewis acid has been reported to catalyze the dehydrogenation of AB.[45] However, in the case of ^{Me3}AB and $B(C_6F_5)_3$, NMR data suggest an alternative reaction pathway. While a 1 : 1 reaction results in broad signals in the ^{11}B, ^{19}F, and ^{1}H NMR spectra, a 1 : 2 ratio of $B(C_6F_5)_3$ to ^{Me3}AB proceeds more cleanly. When monitored by NMR spectroscopy, the clean formation of $[(\mu_2\text{-}H)(H_2BNMe_3)_2][HB(C_6F_5)_3]$ was observed after 20 min. Spectral data were consistent with the presence of each of these ions.[46,47] Attempts to isolate this salt were unsuccessful as this species reacts further to give two new compounds **6** and **7**. Compound **6** was isolated by crystallization of a toluene–hexanes solution at −38 °C. The ^{11}B NMR spectrum of the product contained a broadened triplet (J_{B-H} = 95 Hz) at −10 ppm with corresponding peaks in the ^{19}F spectrum at −129, −157, and −164 ppm, indicative of a four-coordinate boron centre. The ^{1}H spectrum contained 2 peaks which integrated in a 9 : 2 ratio for the Me : B–H peaks. Furthermore, the B–H peaks formed a triplet (J_{H-F} = 7 Hz) in the $^{1}H\{^{11}B\}$ spectrum indicative of H–F coupling to the *ortho*-fluorines of the C_6F_5 ring. Single crystal X-ray crystallography confirmed the structure of **6** as $(C_6F_5)BH_2{\cdot}NMe_3$ (Fig. 2). The second product (**7**) is ascribed to the adduct-free $(C_6F_5)BH_2$ based on NMR spectroscopy; however, attempts to isolate this species have thus far failed.

The formation of **6** and **7** is the result of a redistribution reaction (eqn (2)) and stands in contrast to that seen for the corresponding reaction with $Al(C_6F_5)_3$. It should be noted that a similar combination of $B(C_6F_5)_3$ and $BH_3{\cdot}SMe_2$ has been reported to generate $(C_6F_5)BH_2{\cdot}SMe_2$.[48]



(2)

Reactions of Al–AB species with CO_2

While the adduct **6** was unreactive to CO_2, species **2–5** react with CO_2. In the case of **2** or **4** exposure to 1 atm of $^{13}CO_2$ leads to evidence of reduction to several formate and methoxy species as evidenced by the ^{13}C resonances in the 170–175 ppm and 50–70 ppm ranges, respectively. However no single species could be isolated from these mixtures. In contrast, **3** reacts with $^{13}CO_2$ to cleanly form a single formate derivative **8**. This species exhibits a resonance at 173 ppm in the ^{13}C NMR spectrum that correlates to a peak at 8.14 ppm in the ^{1}H NMR spectrum. While the corresponding ^{27}Al NMR spectrum again showed no discernible signal, the ^{11}B signal was shifted to 3.8 ppm. Compound **8** was isolated in 72% yield and subsequently crystallographically characterized (Fig. 3) and shown to be $Al(C_6F_5)_3(HCO_2)H_2BNMe_3$ in which a formate group links the $Al(C_6F_5)_3$ and Me_3NBH_2 fragments. Similar bis-boron formate derivatives have been reported by Piers[28] and by our group.[26] The C–O bond lengths in **8** are equal at 1.252(2) Å and the Al–O (1.823(1) Å) and B–O (1.536(2) Å) are similar to those in previous reports.[24–26,28] Compound **8** represents the first example, to our knowledge, of a formate moiety bound between two different group 13 elements.

While **8** is stable in solution, it is noteworthy that the corresponding reactions employing **5** with $^{13}CO_2$ show evidence of further reaction. A broad signal in the ^{13}C NMR spectrum at 172 ppm, typical for a formate fragment was observed 15 min after mixing. In addition, broad signals in the ^{11}B NMR spectrum at 34 and −15 ppm were attributed to the dehydrogenated species $(HNBH)_n$ and $(H_2NBH_2)_n$,[49] respectively. Quenching this sample with D_2O and subsequent ^{1}H NMR analysis showed a doublet (due to H–^{13}C coupling) at 3.34 ppm and a less intense doublet at 8.43 ppm consistent with methanol and formic acid, respectively. Attempts to experimentally identify intermediates in the conversion of formate to methanol were inconclusive.

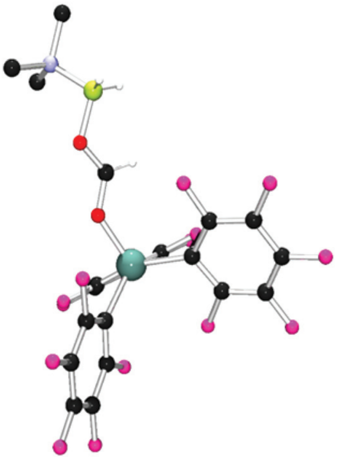
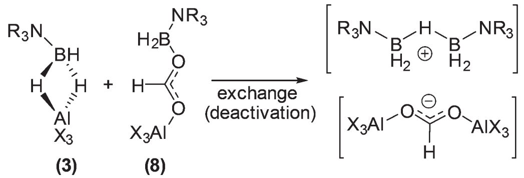
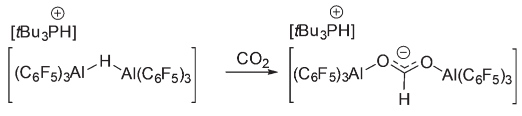


Fig. 3 POV-Ray depiction of **8**. C: black, N: blue, B: yellow-green, O: red, Al: teal, F: pink, H: white. Methyl H's omitted for clarity.



(3) (8) (9)

Scheme 1 Proposed reaction pathways of **3** and **8** (X = C_6F_5 and R = Me).



(10)

Scheme 2 Synthesis of **10**.

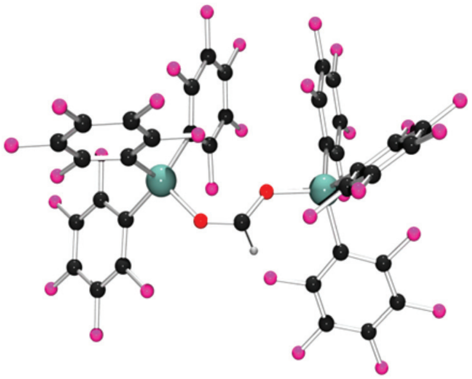


Fig. 4 POV-Ray depiction of the anion of **10**. C: black, O: red, Al: teal, F: pink, H: white.

Subsequently, the reaction of **8** with 1 equivalent of **3** was monitored over time by NMR spectroscopy. These data suggest a Lewis acid exchange reaction generates the species $[(\mu_2\text{-H})(H_2BNMe_3)_2][HCO_2(Al(C_6F_5)_3)_2]$ (**9**) although this species could not be isolated (Scheme 1). Nonetheless, the cation of **9** $[(\mu_2\text{-H})(H_2BNMe_3)_2]^+$ is known[47] and exhibits the expected resonances. The anion was independently synthesized by reacting the known salt[50] $[tBu_3PH][(\mu_2\text{-H})(Al(C_6F_5)_3)_2]$ with CO_2 to generate $[tBu_3PH][(HCO_2)(Al(C_6F_5)_3)_2]$ **10** (Scheme 2). The ^{1}H, ^{13}C and ^{19}F spectra for the anion of **10** were identical to those seen for **9**. The structure of **10** was unambiguously determined (Fig. 4), confirming the bridging nature of the formate fragment in the anion.

Reduction of CO_2 in $Mes_3PC(OAlX_3)_2$

Related to the above reductions of CO_2 with AB, we previously communicated that solutions of **1-Cl** or **1-Br** treated with excess (3 eq.) AB and subsequent water quench result in the

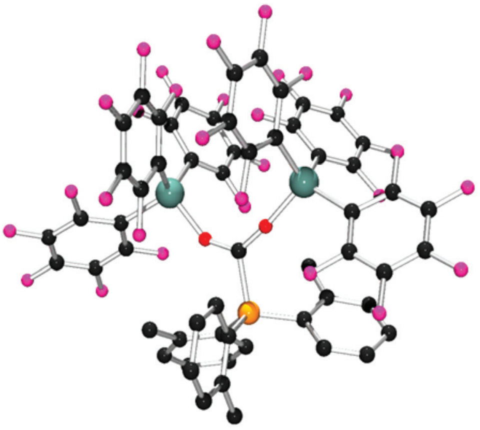
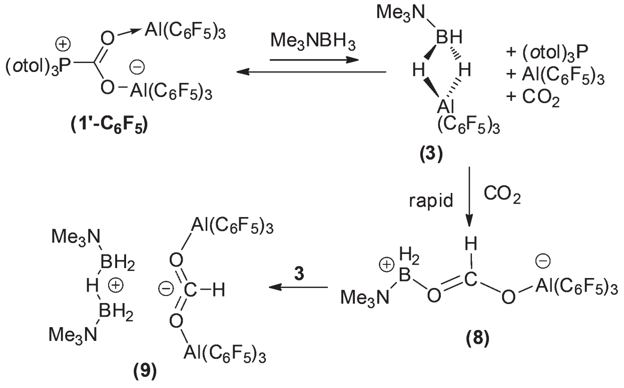


Fig. 5 POV-Ray depiction of **$1'$-C_6F_5**. C: black, O: red, Al: teal, F: pink, P: orange. H atoms omitted for clarity.

reduction of the CO_2 moiety to MeOH in 37–51% yield (eqn (1)).[24] However, the study of the reduction of CO_2 in complexes **1-X** (X = Cl, Br, I)[24] was plagued by the poor solubility of AB in bromobenzene, the very fast reaction rate, and the complex mixture of products formed. Nonetheless, treatment of **1-Cl** with increasing amounts of ^{Me2}AB or ^{Me3}AB to 1 equiv. results in increasing formation of methoxy species from an intermediate formate species.

To provide a further spectroscopic handle, the species $Mes_3PC(OAl(C_6F_5)_3)_2$ (**1-C_6F_5**) and *o*-tol$_3$PC(OAl(C_6F_5)$_3$)$_2$ (**$1'$-C_6F_5**) were prepared employing an analogous method to the one used for **1-X**.[24,25] The latter species was structurally characterized (Fig. 5) confirming the coordination of a $Al(C_6F_5)_3$ fragment coordinated to each of the O-atoms of the CO_2 moiety. The O–C–O angle in **$1'$-C_6F_5** (127.1(3)°) and O–Al bond lengths of 1.858(2) Å are similar to those reported for **1-X**. This stands in contrast to the reported complex[51] *t*Bu$_3$P(CO$_2$)Al(C_6F_5)$_3$ where only one Al centre is present. Indeed, although a 1 : 1-CO_2 complex could be observed by NMR spectroscopy, reaction mixtures of *o*-tol$_3$P and $Al(C_6F_5)_3$ in the presence of CO_2 led only to the isolation of **$1'$-C_6F_5** regardless of the stoichiometry.

The reaction of ^{13}C-labelled **$1'$-C_6F_5** (^{13}C-**$1'$-C_6F_5**) with 0.33 equiv. of ^{Me3}AB was monitored by NMR spectroscopy. The initial spectra show broadening of the ^{31}P peak attributable to **$1'$-C_6F_5**, as well as some free *o*-tol$_3$P, inferring an equilibrium involving dissociation of $Al(C_6F_5)_3$ from **$1'$-C_6F_5**. This was concurrent with the formation of the formate species **8** as evidenced by $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$ and ^{1}H NMR spectroscopy. The liberated alane also generates **3** *in situ* which can react with **8** to form the salt **9** (Scheme 3). After 12 h the reaction mixture is observed to contain ^{13}C-**$1'$-C_6F_5**, **9**, and the cation [*o*-tol$_3$P-BH$_2$NMe$_3$]$^+$. The identity of the latter species was confirmed by the independent reaction of the known salt[47] $[(\mu_2\text{-H})(H_2BNMe_3)_2][B(C_6F_5)_4]$ with excess *o*-tol$_3$P. Altering the stoichiometry to a full equivalent of ^{Me3}AB resulted in the consumption of **$1'$-C_6F_5** converting it to **8** and **9**. Heating this reaction mixture to 60 °C for several hours led to further reduction from formate to methoxy derivatives. Presumably the presence of Al acceptors on each oxygen of the formate in **9** prompts hydride transfer to the central carbon.



Scheme 3 Reaction of **$1'$-C_6F_5** with ^{Me3}AB.

Interestingly, treating **$1'$-C_6F_5** with the sterically less crowded amine-boranes ^{Me2}AB or AB led to more rapid reduction to methoxy derivatives under milder conditions. Space-filling models of **3** and **5** (Fig. S1†) show decreasing steric congestion around the B–H–Al moiety providing more accessible hydride centres. This is thought to facilitate further reduction consistent with the increasing reactivity of **2**, **4**, and **5** compared to **3** with CO_2, as well as observed in our initial report with **1-X** and AB.[24]

Conclusions

In this work, we have demonstrated that amine-boranes form adducts with Al-based Lewis acids and undergo subsequent reactions with CO_2 affording formate-bridged species. In addition, the reduction of the CO_2 fragment in **$1'$-C_6F_5** is shown to proceed through the formate species **9**, described above. This demonstrates that, while the species **1-X** are derived from FLP capture of CO_2,[24] these species serve only as stoichiometric sources of CO_2 and Lewis acid upon reaction with AB. The rapidity described for the reduction of **1-X**,[24] with AB is consistent with reduced reactivity observed for the more sterically demanding reagents ^{Me2}AB or ^{Me3}AB. Finally, Paul *et al.*[52] proposed a complex mechanism involving direct attack of AB on the CO_2 moiety of **1-X**, based on computational studies. The present experimental results stand in contrast and support a mechanism resulting from dissociative reactions of **1-X**.

Experimental section

General considerations

All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (Innovative Technology glovebox equipped with a −38 °C freezer). Hexanes, pentane, and toluene (Aldrich) were dried using an Innovative Technologies solvent system and degassed prior to use. Fluorobenzene and bromobenzene (–H_5 and –D_5) were purchased from Aldrich and dried over P_2O_5 for several days and vacuum distilled onto 4 Å molecular sieves prior to use. Dichloromethane-d_2 and toluene-d_8 were purchased from Aldrich, dried over CaH_2 and vacuum distilled onto 4 Å molecular sieves prior to use. D_2O was purchased from Cambridge Isotopes. NMR spectra were obtained on a Bruker Avance 400 MHz or a Varian 400 MHz and spectra were referenced to residual solvent of C_6D_5Br (${}^{1}H$ = 7.28 ppm for *meta* proton; ${}^{13}C$ = 122.4 ppm for *ipso* carbon), C_7H_8 (${}^{1}H$ = 2.08 ppm for methyl; ${}^{13}C$ = 20.43 ppm for methyl), D_2O (${}^{1}H$ = 4.79 ppm for residual HDO peak), and CD_2Cl_2 (${}^{1}H$ = 5.32 ppm; ${}^{13}C$ = 53.84 ppm), or externally (${}^{27}Al$: $Al(NO_3)_3$, ${}^{11}B$: $(Et_2O)BF_3$, ${}^{31}P$: 85% H_3PO_4, ${}^{19}F$: $CFCl_3$). Chemical shifts (δ) listed are in ppm and absolute values of the coupling constants are in Hz. NMR assignments are supported by additional 2D experiments. Elemental analyses (C, N, H) and X-ray crystallography were performed in house. $(o\text{-tol})_3P$ and Mes_3P were purchased from Strem and used without further purification. NH_3BH_3 was purchased from Aldrich and used without further purification. $AlBr_3$, Me_2NHBH_3, and Me_3NBH_3 were purchased from Strem and sublimed prior to use. ${}^{13}CO_2$ and $Me_2Si(H)Cl$ were purchased from Aldrich and used without further purification. $B(C_6F_5)_3$ was purchased from Boulder Scientific, sublimed under vacuum, then treated with excess $Me_2Si(H)Cl$ for 4 h and re-sublimed after removal of volatiles. CO_2 (grade 4.0) was purchased from Linde and passed through a Drierite column prior to use. $Al(C_6F_5)_3$·tol,[24a] $[tBu_3PH][H(Al(C_6F_5)_3)_2]$[50] and **1-X** (X = Cl, Br, I)[24,25] were prepared according to literature procedure.

Synthesis of $Mes_3PC(OAl(C_6F_5)_3)_2$ (1-C_6F_5). A Schlenk flask equipped with a Teflon screw cap was charged with Mes_3P (125 mg, 0.32 mmol), $Al(C_6F_5)_3$·tol (400 mg, 0.64 mmol) and bromobenzene (5 mL). The bomb was transferred to the Schlenk line equipped with a CO_2 outlet. The bomb was degassed, filled with CO_2 (1 atm), and sealed. The solution became a mixture and was stirred for 30 min. after which time the CO_2 atmosphere was removed and hexanes (*ca.* 5–10 mL) were added dropwise to the stirring mixture in the glovebox. The precipitate was filtered on a glass frit, washed with hexanes and dried *in vacuo* (410 mg, 0.27 mmol, 85%).

${}^{1}H$ NMR (400 MHz, CD_2Cl_2): δ 7.21 (d, ${}^{4}J_{H-H}$ = 4 Hz, 3H, *m*-Mes), 7.05 (d, ${}^{4}J_{H-H}$ = 4 Hz, 3H, *m*-Mes), 2.38 (s, 9H, CH_3), 2.28 (s, 9H, CH_3), 1.97 (s, 9H, CH_3). ${}^{31}P\{{}^{1}H\}$ NMR (161 MHz, CD_2Cl_2): δ 17.0. ${}^{27}Al$ NMR (104 MHz, CD_2Cl_2): blank. ${}^{19}F\{{}^{1}H\}$ NMR (376 MHz, CD_2Cl_2): δ −122.2 (dd, ${}^{3}J_{F-F}$ = 26 Hz, ${}^{4}J_{F-F}$ = 10 Hz, 12F, *o*-C_6F_5), −154.7 (bs, 6F, *p*-C_6F_5), −163.3 (m, 12F, *m*-C_6F_5). ${}^{13}C\{{}^{1}H\}$ NMR (100 MHz, CD_2Cl_2): δ 150.2 (dm, ${}^{1}J_{C-F}$ = 232 Hz), 146.8 (d, ${}^{4}J_{C-P}$ = 3 Hz, *p*-C_6H_2), 145.2 (d, ${}^{2}J_{C-P}$ = 11 Hz, *o*-C_6H_2), 144.2 (d, ${}^{2}J_{C-P}$ = 10 Hz, *o*-C_6H_2), 141.8 (dm, ${}^{1}J_{C-F}$ = 250 Hz), 136.9 (dm, ${}^{1}J_{C-F}$ = 252 Hz), 133.9 (d, ${}^{3}J_{C-P}$ = 12 Hz, *m*-C_6H_2), 133.3 (d, ${}^{3}J_{C-P}$ = 12 Hz, *m*-C_6H_2), 131.2 (d, ${}^{1}J_{C-P}$ = 135 Hz, CO_2), 117.6 (d, ${}^{2}J_{C-P}$ = 78 Hz, i-C_6H_2), 24.7 (d, ${}^{3}J_{C-P}$ = 4 Hz, *o*-CH_3^{Mes}), 24.2 (d, ${}^{3}J_{C-P}$ = 5 Hz, *o*-CH_3^{Mes}), 21.3 (s, *p*-CH_3^{Mes}). Anal. Calc. for $C_{64}H_{33}Al_2F_{30}O_2P$: C, 51.63; H, 2.23. Found: C, 51.24; H, 2.56.

Synthesis of $(o\text{-tol})_3PC(OAl(C_6F_5)_3)_2$ (1′-C_6F_5). Synthesized in an analogous fashion to **1-C_6F_5** using 76 mg (0.25 mmol) $(o\text{-tol})_3P$ and 311 mg (0.50 mmol) $Al(C_6F_5)_3$·tol. Isolated yield is 325 mg (0.22 mmol, 90%). Vapour diffusion of a bromobenzene solution of the compound with pentane yielded single crystals suitable for X-ray crystallography.

${}^{1}H$ NMR (400 MHz, C_6D_5Br): δ 7.60–6.85 (m, 12H), 1.81 (bs, 9H, *o*-CH_3), 1.27–1.13 (m, 4H, 0.5·($CH_3(CH_2)CH_3$)), 0.84 (t, ${}^{3}J_{H-H}$ = 7 Hz, 3H, 0.5·($CH_3(CH_2)CH_3$)). ${}^{31}P\{{}^{1}H\}$ NMR (161 MHz, C_6D_5Br): δ 30.0. ${}^{27}Al$ NMR (104 MHz, C_6D_5Br): blank. ${}^{19}F\{{}^{1}H\}$ NMR (376 MHz, C_6D_5Br): δ −121.8 (bd, ${}^{3}J_{F-F}$ = 19 Hz, 12F, *o*-C_6F_5), −152.5 (t, ${}^{3}J_{F-F}$ = 20 Hz, 6F, *p*-C_6F_5), −161.4 (m, 12F, *m*-C_6F_5). ${}^{13}C\{{}^{1}H\}$ NMR (100 MHz, C_6D_5Br): δ 167.3 (d, ${}^{1}J_{C-P}$ = 128 Hz, CO_2), 149.9 (dm, ${}^{1}J_{C-F}$ = 234 Hz), 144.2 (d, ${}^{2}J_{C-P}$ = 8 Hz, *C*-Me), 141.7 (dm, ${}^{1}J_{C-F}$ = 252 Hz), 136.7 (dm, ${}^{1}J_{C-F}$ = 253 Hz), 136.4 (d, J_{C-P} = 2 Hz), 135.2 (d, J_{C-P} = 12 Hz), 133.7 (d, J_{C-P} = 11 Hz), 127.7 (d, J_{C-P} = 14 Hz), 112.9 (m, i-C_6F_5), 112.1 (d, ${}^{1}J_{C-P}$ = 78 Hz, i-C_6H_4), 31.8 (s, C_6H_{14}), 22.9 (s, C_6H_{14}), 22.4 (bs, *o*-CH_3), 14.4 (s, C_6H_{14}). Anal. Calc. for $C_{61}H_{28}Al_2F_{30}O_2P$ (4 + 0.5·C_6H_{14}): C, 50.61; H, 1.95. Found: C, 50.36; H, 2.06.

Synthesis of Me_3NBH_3·$AlBr_3$ (2). $AlBr_3$ (300 mg, 1.1 mmol) and Me_3NBH_3 (82 mg, 1.1 mmol) were combined in bromobenzene (5 mL) in a screw cap vial. After stirring for 5 min, hexanes (*ca.* 10 mL) were added to precipitate a product. The product was filtered on a glass frit, washed with pentane and dried (265 mg, 0.78 mmol, 70%). Vapour diffusion of a bromobenzene solution of the compound with pentane yielded single crystals suitable for X-ray crystallography.

${}^{1}H$ NMR (400 MHz, C_6D_5Br): δ 2.62 (bq, ${}^{1}J_{H-B}$ = 89 Hz, 3H, BH_3), 2.07 (s, 9H, 3 × CH_3). ${}^{11}B$ NMR (128 MHz, C_6D_5Br): δ −10.2 (bq, ${}^{1}J_{B-H}$ = 89 Hz). ${}^{27}Al$ NMR (104 MHz, C_6D_5Br): 78.5 (bs). ${}^{13}C\{{}^{1}H\}$ NMR (100 MHz, C_6D_5Br): δ 53.5. Anal. Calc. for $C_3H_{12}BAlBr_3N$: C, 10.61; H, 3.56; N, 4.12. Found: C, 10.83; H, 3.22; N, 4.11.

Synthesis of Me_3NBH_3·$Al(C_6F_5)_3$ (3). $Al(C_6F_5)_3$·tol (750 mg, 1.2 mmol) and Me_3NBH_3 (88 mg, 1.2 mmol) were combined in toluene (10 mL) in a 50 mL Schlenk flask. After stirring for 5 min, pentane (*ca.* 30 mL) was added to precipitate a product. The product was filtered on a glass frit, washed with pentane and dried (560 mg, 0.93 mmol, 77%). Slow cooling a saturated toluene solution to −38 °C yielded single crystals suitable for X-ray crystallography.

${}^{1}H$ NMR (400 MHz, C_6D_5Br): δ 2.14 (overlapping s (3 × CH_3) and bs (BH_3), 12H). ${}^{11}B$ NMR (128 MHz, C_6D_5Br): δ −9.1 (bs). ${}^{27}Al$ NMR (104 MHz, C_6D_5Br): blank. ${}^{19}F\{{}^{1}H\}$ NMR (376 MHz, C_6D_5Br): δ −122.4 (dd, ${}^{3}J_{F-F}$ = 26 Hz, ${}^{4}J_{F-F}$ = 11 Hz, 6F, *o*-C_6F_5), −152.4 (t, ${}^{3}J_{F-F}$ = 19 Hz, 3F, *p*-C_6F_5), −161.3 (m, 6F, *m*-C_6F_5). ${}^{13}C\{{}^{1}H\}$ NMR (100 MHz, C_6D_5Br): δ 150.0 (dm, ${}^{1}J_{C-F}$ = 235 Hz), 141.9 (dm, ${}^{1}J_{C-F}$ = 253 Hz), 136.9 (dm, ${}^{1}J_{C-F}$ = 253 Hz), 113.2 (m, i-C_6F_5), 53.3 (s, $N(CH_3)_3$). Anal. Calc. for $C_{21}H_{12}BAlF_{15}N$: C, 41.96; H, 2.01; N, 2.33. Found: C, 41.72; H, 1.99; N, 2.36.

Synthesis of Me_2NHBH_3·$Al(C_6F_5)_3$ (4). This compound was synthesized in an analogous fashion to **3** using $Al(C_6F_5)_3$ (500 mg, 0.8 mmol), Me_2NHBH_3 (47 mg, 0.8 mmol), and toluene (5 mL). Following filtration of the solid, the filtrate was stored at −38 °C to obtain a second crop (410 mg (total), 0.70 mmol, 87%).

^{1}H NMR (400 MHz, C_6D_5Br): δ 3.73 (bs, 1H, N*H*), 2.15 (overlapping d ($^3J_{H-H}$ = 5.6 Hz, N(CH_3)$_2$) and bs (BH_3), 9H total). ^{11}B NMR (128 MHz, C_6D_5Br): δ −16.5 (bs). ^{27}Al NMR (104 MHz, C_6D_5Br): blank. ^{19}F{^{1}H} NMR (376 MHz, C_6D_5Br): δ −123.2 (dd, $^3J_{F-F}$ = 26 Hz, $^4J_{F-F}$ = 8 Hz, 6F, *o*-C_6F_5), −151.5 (t, $^3J_{F-F}$ = 21 Hz, 3F, *p*-C_6F_5), −160.0 (m, 6F, *m*-C_6F_5). ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): δ 149.7 (dm, $^1J_{C-F}$ = 234 Hz), 141.7 (dm, $^1J_{C-F}$ = 252 Hz), 136.9 (dm, $^1J_{C-F}$ = 255 Hz), 113.5 (m, i-C_6F_5), 43.8 (s, N(*C*H_3)$_2$). Anal. Calc. for $C_{20}H_{10}BAlF_{15}N$: C, 40.92; H, 1.72; N, 2.39. Found: C, 40.58; H, 1.70; N, 2.39.

Synthesis of $NH_3BH_3{\cdot}Al(C_6F_5)_3$ (5). $Al(C_6F_5)_3$ (300 mg, 0.48 mmol) and H_3NBH_3 (15 mg, 0.48 mmol) were combined in fluorobenzene (10 mL) in a vial. After stirring for 20 min, the mixture was filtered through Celite. The solvent volume was reduced to *ca.* 2–3 mL and pentane (*ca.* 10 mL) was added to precipitate a product. The product was filtered on a glass frit, washed with pentane and dried (150 mg, 0.27 mmol, 55%). Slow cooling a fluorobenzene/pentane solution to −38 °C yielded single crystals suitable for X-ray crystallography.

^{1}H NMR (400 MHz, C_6D_5Br): δ 2.99 (bs, 3H, NH_3), 2.10 (bs, 3H, BH_3). ^{11}B NMR (128 MHz, C_6D_5Br): δ −24.0 (bs). ^{27}Al NMR (104 MHz, C_6D_5Br): blank. ^{19}F{^{1}H} NMR (376 MHz, C_6D_5Br): δ −123.1 (dd, $^3J_{F-F}$ = 28 Hz, $^4J_{F-F}$ = 19 Hz, 6F, *o*-C_6F_5), −151.6 (t, $^3J_{F-F}$ = 19 Hz, 3F, *p*-C_6F_5), −159.9 (m, 6F, *m*-C_6F_5). ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): δ 149.7 (dm, $^1J_{C-F}$ = 235 Hz), 141.7 (dm, $^1J_{C-F}$ = 252 Hz), 136.9 (dm, $^1J_{C-F}$ = 255 Hz), 113.5 (m, i-C_6F_5). Anal. Calc. for $C_{18}H_6AlBF_{15}N$: C, 38.67; H, 1.08; N, 2.51. Found: C, 38.30; H, 0.95; N, 3.26.

Synthesis of $(Me_3N){\cdot}H_2B(C_6F_5)$ (6). In a vial in the glovebox were combined $B(C_6F_5)_3$ (200 mg, 0.39 mmol) and Me_3NBH_3 (57 mg, 0.78 mmol) in a 1 : 2 solution of toluene (5 mL) and hexanes (10 mL). Precipitation initially occurs but the mixture becomes a solution after stirring overnight. The next morning, the solution was put in the −38 °C freezer. The crystals that formed were filtered on a glass frit and washed with minimal cold hexanes and dried *in vacuo* (100 mg, 0.42 mmol, 54%). Slow cooling a concentrated toluene–hexanes solution of the compound to −38 °C yielded single crystals suitable for X-ray crystallography.

^{1}H NMR (400 MHz, C_6D_5Br): δ 2.49 (bq, 2H, (C_6F_5)BH_2), 2.07 (s, 9H, N(CH_3)$_3$). ^{11}B{^{1}H} NMR (128 MHz, C_6D_5Br): −9.9 (s). ^{19}F{^{1}H} NMR (376 MHz, C_6D_5Br): δ −129.0 (dd, $^3J_{F-F}$ = 26 Hz, $^4J_{F-F}$ = 11 Hz, 2F, *o*-C_6F_5), −157.4 (t, $^3J_{F-F}$ = 21 Hz, 1F, *p*-C_6F_5), −163.6 (m, 2F, *m*-C_6F_5). ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): δ 148.8 (dm, $^1J_{C-F}$ = 236 Hz), 139.9 (dm, $^1J_{C-F}$ = 249 Hz), 137.0 (dm, $^1J_{C-F}$ = 249 Hz), 117.4 (bs, i-C_6F_5), 51.7 (s, N(*C*H_3)$_3$). Anal. Calc. for $C_9H_{11}BF_5N$: C, 45.23; H, 4.64; N, 5.86. Found: C, 45.27; H, 4.92; N, 5.99.

Synthesis of $Al(C_6F_5)_3(HCO_2)H_2BNMe_3$ (8). $Me_3NBH_3{\cdot}Al(C_6F_5)_3$ (155 mg, 0.26 mmol) was dissolved in toluene (5 mL) in a 50 mL Schlenk flask. The flask was transferred to the Schlenk line equipped with a CO_2 outlet. The bomb was degassed, filled with CO_2 (1 atm), and sealed. The solution was stirred for 30 min after which time the CO_2 atmosphere was removed and pentane (*ca.* 20 mL) was added. After stirring rapidly for several minutes, a product precipitated and was filtered, washed with pentane, and dried (120 mg, 0.19 mmol, 72%). Slow cooling a toluene–pentane solution to −38 °C yielded single crystals suitable for X-ray crystallography.

^{1}H NMR (400 MHz, C_7D_8): δ 7.55 (s, 1H, *H*-CO_2), 2.17 (bs, 2H, BH_2), 12H), 1.33 (s, 9H, 3 × CH_3). ^{11}B NMR (128 MHz, C_7D_8): δ 3.2 (bs). ^{27}Al NMR (104 MHz, C_7D_8): 121 (bs, $\nu_{1/2}$ = *ca.* 2000 Hz). ^{19}F{^{1}H} NMR (376 MHz, C_7D_8): δ −124.1 (dd, $^3J_{F-F}$ = 26 Hz, $^4J_{F-F}$ = 11 Hz, 6F, *o*-C_6F_5), −154.0 (t, $^3J_{F-F}$ = 21 Hz, 3F, *p*-C_6F_5), −162.7 (m, 6F, *m*-C_6F_5). ^{13}C{^{1}H} NMR (100 MHz, C_7D_8): δ 173.3 (s, H*C*O_2), 150.5 (dm, $^1J_{C-F}$ = 235 Hz), 142.0 (dm, $^1J_{C-F}$ = 251 Hz), 137.3 (dm, $^1J_{C-F}$ = 253 Hz), 48.1 (s, 3 × *C*H_3). Anal. Calc. for $C_{22}H_{12}BAlF_{15}NO_2$: C, 40.96; H, 1.87; N, 2.16. Found: C, 40.37; H, 1.94; N, 2.17.

Synthesis of [*t*Bu_3PH][$HCO_2(Al(C_6F_5)_3)_2$] (10). A Schlenk flask was charged with [*t*Bu_3PH][$H(Al(C_6F_5)_3)_2$] (400 mg, 0.32 mmol) dissolved in fluorobenzene (*ca.* 5 mL). The bomb was transferred to the Schlenk line equipped with a CO_2 outlet, degassed and filled with CO_2 (1 atm). The solution was stirred for 12 h after which the solvent was removed *in vacuo*. Hexanes (*ca.* 10 mL) were added to the residue and the precipitate that forms was stirred in hexanes for 30 min before being filtered on a glass frit (260 mg, 0.20 mmol, 63%). Vapour diffusion of a bromobenzene solution of the compound with hexanes yielded single crystals suitable for X-ray crystallography.

^{1}H NMR (400 MHz, C_6D_5Br): δ 8.65 (s, 1H, *H*CO_2–), 4.12 (d, $^1J_{H-P}$ = 426 Hz, 1H, P-*H*), 0.96 (d, $^3J_{H-P}$ = 16 Hz, 27H, *t*Bu). ^{31}P{^{1}H} NMR (161 MHz, C_6D_5Br): δ 60.0. ^{27}Al NMR (104 MHz, C_6D_5Br): blank. ^{19}F{^{1}H} NMR (376 MHz, C_6D_5Br): δ −122.4 (dd, $^3J_{F-F}$ = 26 Hz, $^4J_{F-F}$ = 11 Hz, 12F, *o*-C_6F_5), −153.6 (t, $^3J_{F-F}$ = 21 Hz, 6F, *p*-C_6F_5), −161.6 (m, 12F, *m*-C_6F_5). ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br), partial: δ 172.8 (s, H*C*O_2–), 150.1 (dm, $^1J_{C-F}$ = 235 Hz), 141.4 (dm, $^1J_{C-F}$ = 250 Hz), 136.7 (dm, $^1J_{C-F}$ = 252 Hz), 114.5 (m, i-C_6F_5), 36.9 (d, $^1J_{C-P}$ = 26.4 Hz, P*C*Me_3), 29.3 (s, PC*Me*$_3$). Anal. Calc. for $C_{49}H_{29}Al_2F_{30}O_2P$: C, 45.11; H, 2.24. Found: C, 44.58; H, 2.40.

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