^{19}F NMR Investigations of the Reaction of B(C$_6$F$_5$)$_3$ with Different Tri(alkyl)aluminum Compounds

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Summary: Tris(pentafluorophenyl)borane, B(C$_6$F$_5$)$_3$ reacts with triethylaluminum, AlEt$_3$ to a mixture of Al(C$_6$F$_5$)$_{3-n}$Et$_n$ and Al$_2$(C$_6$F$_5$)$_{6-n}$Et$_n$ compounds depending on the B/Al ratio. From excess borane to excess AlEt$_3$ the species Al(C$_6$F$_5$)$_3$ → Al(C$_6$F$_5$)$_2$Et ⇋ Al$_2$(C$_6$F$_5$)$_4$Et$_2$ → Al$_2$(C$_6$F$_5$)$_3$Et$_3$ → Al$_2$(C$_6$F$_5$)$_2$Et$_4$ → Al$_2$(C$_6$F$_5$)Et$_5$ are formed and differentiated by their *para*-F signal in ^{19}F NMR. The reaction between B(C$_6$F$_5$)$_3$ and the higher aluminum alkyls, tri(*iso*-butyl)aluminum and tri(*n*-hexyl)aluminum AlR$_3$ (R = *i*-Bu, *n*-C$_6$H$_{13}$) is slower and requires AlR$_3$ excess to shift the C$_6$F$_5$ ↔ R exchange equilibria to almost complete formation of Al(C$_6$F$_5$)R$_2$ and BR$_3$. At equimolar ratio the equilibrium lies on the side of the unchanged borane together with its boranate [B(C$_6$F$_5$)$_3$R]$^-$ anion. For tri(*n*-octyl)aluminum even at large Al(*n*-C$_8$H$_{17}$)$_3$ excess no C$_6$F$_5$ ↔ alkyl exchange can be observed, but boranate anions form.

Keywords: aluminium alkyl; borane; cocatalyst; ^{19}F NMR perfluorated

Introduction

The synthesis of tris(pentafluorophenyl)-borane, B(C$_6$F$_5$)$_3$ was first described in the 1960s[1] but the properties of B(C$_6$F$_5$)$_3$ including the strong Lewis acidity were not investigated further and no applications of C$_6$F$_5$-substituted boranes were reported. Beginning in the early 1990s it was discovered [2] that group 4 metallocene alkyls in combination with B(C$_6$F$_5$)$_3$ led to highly active catalysts for olefin polymerization and opened the possibility to isolate crystallographically characterizable cationic metallocene complexes.[2–4] As an alternative to methylalumoxane (MAO),[5] perfluorated boranes and boranates B(C$_6$F$_5$)$_3$,[2] [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$,[6] and [HNRR'$_2$]$^+$ [B(C$_6$F$_5$)$_4$]$^{-[7]}$ can be key components of homogeneous single-site olefin polymerization catalyst systems.[3,4,8] Furthermore, aluminum alkyls which are less efficient

activators themselves, are often added to such a single-site borane-containing polymerization system and used as scavengers or *in-situ* alkylating reagents.[4] The B(C$_6$F$_5$)$_3$/AlEt$_3$ cocatalytic system is known from the activation process of early transition-metal group 4 metallocene catalysts in olefin polymerization.[4,9] The application of perfluorated boranes with aluminum alkyls as a two-component cocatalytic system raises the question of the actual constitution of the activator. An intricate knowledge on the cocatalytic composition is a prerequisite to investigate the activation process and to determine the structure of the active species in the polymerization. Reactions of boranes with aluminum alkyls, AlR$_3$ or zinc dialkyls, ZnR$_2$ have been observed.[10,11] The combination of B(C$_6$F$_5$)$_3$ and AlMe$_3$ reacts by a facile aryl/alkyl group exchange to give Al(C$_6$F$_5$)$_3$ and BMe$_3$ as the main products (eq. 1).[12,13] Comparable exchange reactions have been observed between E(C$_6$F$_5$)$_3$ (E = Al, B) and MAO[14] and in the reaction of AlR$_3$ with [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^{-}$.[12] These exchange reactions between the main group alkyls are different from the reactions of (perfluoroaryl)boron compounds, B(Ar^F)$_3$

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with group 4 metallocene alkyls, Cp_2MR_2 (M = Ti, Zr, Hf) which result in the formation of ionic or zwitterionic products $[Cp_2MR]^+[R-B(Ar^F)_3]^-$ from alkyl abstraction.[3,4,8,15]

of $AlEt_3$ to $B(C_6F_5)_3$ was difficult, hence, for spectra b) to e) in Figure 1 the noted B:Al ratio is meant to reflect the trend.

Reaction of $B(C_6F_5)_3$ with $AlEt_3$ leads to an exchange of the C_6F_5 and ethyl

$$B(C_6F_5)_3 + AlMe_3 \xrightarrow{\text{fast}} B(C_6F_5)_2Me + 1/2\ Al_2(C_6F_5)_2Me_4 \rightleftharpoons B(C_6F_5)Me_2 + 1/2\ Al_2(C_6F_5)_4Me_2 \rightleftharpoons BMe_3 + Al(C_6F_5)_3 \quad (1)$$

Concomitant with our interest in the vinyl addition norbornene polymerization, where we use nickel and palladium complexes with MAO or $B(C_6F_5)_3/AlEt_3$ cocatalysts,[16,17] we followed the interactions between $B(C_6F_5)_3$ and different aluminum trialkyls to elucidate the composition of the activator for the transition-metal pre-catalysts. The $B(C_6F_5)_3/AlEt_3$ cocatalytic system was recently also applied by others to activate late transition-metal complexes for the (co)polymerization of cyclopentene,[18] ethene,[19] norbornene and norbornene derivatives.[20,21]

Here we report the results of ^{19}F NMR investigations on the interaction between $B(C_6F_5)_3$ and the aluminum trialkyls tri(ethyl)aluminum (TEA, $AlEt_3$), tri(iso-butyl)aluminum (TIBA, $Al(i-Bu)_3$), tri(-hexyl)aluminum (THA, $Al(n-C_6H_{13})_3$) and tri(octyl)aluminum (TOA, $Al(n-C_8H_{17})_3$). The ^{19}F NMR investigations were carried out with different molar $B(C_6F_5)_3$:AlR_3 ratios (R = C_2H_5, $i-C_4H_9$, $n-C_6H_{13}$, and $n-C_8H_{17}$) which cover the range applied in polymerization procedures.[16,21]

Reaction Between $B(C_6F_5)_3$ and $AlEt_3$

A molar ratio of $B(C_6F_5)_3$:$AlEt_3$ = 1:9 is typically reported when $B(C_6F_5)_3$ is applied in combination with $AlEt_3$ as a cocatalyst to activate late transition metal complexes.[16,21] The ^{19}F NMR spectra for the reaction between $B(C_6F_5)_3$ and $AlEt_3$ at different molar ratios $B(C_6F_5)_3$:$AlEt_3$ between 10:3 and 1:10 are depicted in Figure 1. The interpretation is provided in Figure 1 in combination with Figure 2. The assignment of the signals is based on ^{19}F NMR literature[10–13] with consideration of the applied molar B:Al ratios. It should be note that the exact addition of low amounts

groups. It can clearly be differentiated if the C_6F_5 group is bonded to boron or aluminum by the chemical shift region of the ortho- and para-F signal. Only the meta-F signal for B-C_6F_5 and Al-C_6F_5 overlap. Also, different $B(C_6F_5)_{3-n}Et_n$ species show quite different chemical shifts for the ortho- and para-F signal. For the $Al(C_6F_5)_{3-n}Et_n$ species the differentiation occurs mainly in the para-F and somewhat in the meta-F region. Ortho-F signals of $Al(C_6F_5)_{3-n}Et_n$ species appear all between −122.1 and −122.4 ppm (Figure 1). The signals itself are multiplets from F-F coupling which could only be partly resolved because of peak overlap. With excess $B(C_6F_5)_3$ the aluminum species $Al(C_6F_5)_3$ (**Al**) and $Al(C_6F_5)_2Et$ (**Al***) are observed (Figure 1 c-d, Figure 2).

When the B:Al ratio approaches 1:1, the signal attributed to (**Al²***) $Al_2(C_6F_5)_4Et_2 \leftrightharpoons Al(C_6F_5)_2Et$ (**Al***) is the only one remaining and broadens (Figure 1 d → f) either due to the high concentration or because the rate of the monomer-dimer equilibrium of tri(alkyl,aryl)aluminum compounds falls into the NMR time scale.[22] Evidently, the exchange reaction between $B(C_6F_5)_3$ and $AlEt_3$ does not go to completion under the conditions of the NMR experiment to form $Al(C_6F_5)_3$ in a pure form. This behaviour has also been observed for the reaction between $B(C_6F_5)_3$ and $AlMe_3$.[13]

Noteworthy, the inital spectrum of neat $B(C_6F_5)_3$ also exhibits broad peaks (Fig. 1a) which sharpen and shift slightly upon addition of $AlEt_3$ (Fig. 1b). The broad peaks may be due to concentration (0.105 mmol = 53.8 mg/0.5 ml CD_2Cl_2). However, broad peaks may also originate from the presence of Lewis-base (L) impurities, such
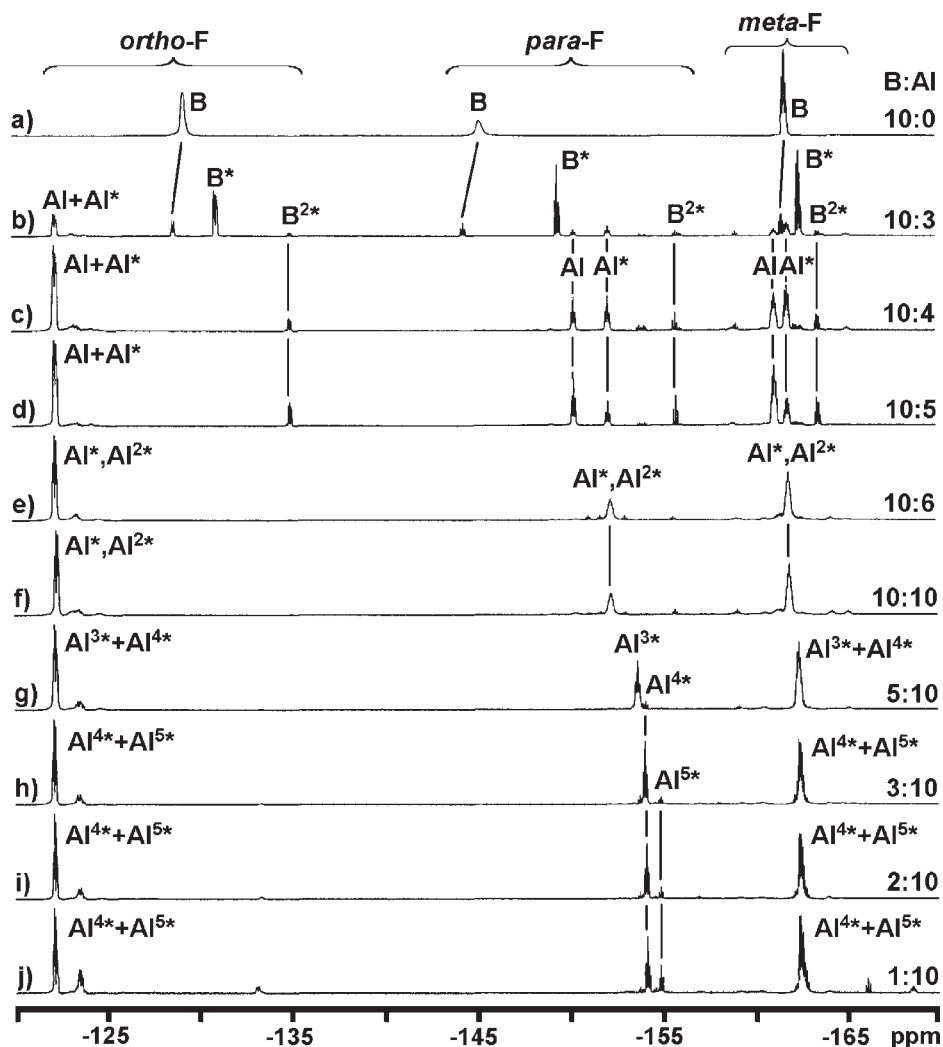
Figure 1.
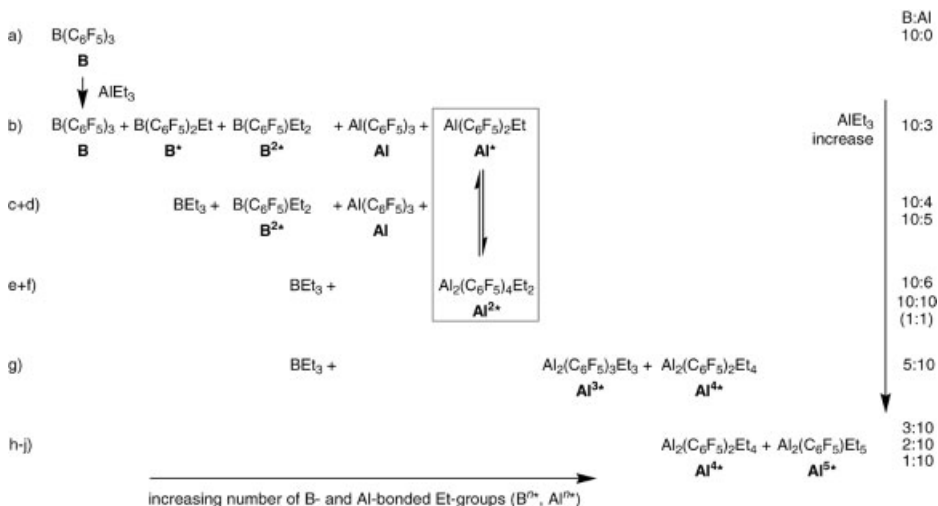^{19}F NMR spectra of $B(C_6F_5)_3$/$AlEt_3$ mixtures with increasing $AlEt_3$ content (decreasing B:Al ratio) from top to bottom. In the spectral assignments **B^{n*}** and **Al^{n*}**n indicates the number of ethyl groups. For the spectral interpretation and exact symbol designations (**B**, **B***, **Al**, **Al*** etc.) see Figure 2; further details in experimental section.

as, water which form adducts to $B(C_6F_5)_3$ without decomposition [23] and enter in a fast equilibrium with free borane according to eq. 2, so that a weighted/averaged signal between the one for free $B(C_6F_5)_3$ and L-$B(C_6F_5)_3$ is measured.[17] With the advent of the stronger Lewis acidic $Al(C_6F_5)_{3-n}Et_n$ species the Lewis-base impurities are removed from boron, so that the signals sharpen and shift.

$$L + B(C_6F_5)_3 \underset{}{\overset{fast}{\rightleftharpoons}} L-B(C_6F_5)_3 \qquad (2)$$
$$\text{(excess)}$$
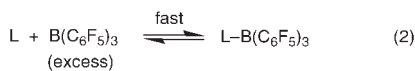
With excess $AlEt_3$ the average number of C_6F_5 groups bonded to aluminum must decrease. Starting from the B:Al ratio of about 10:10 (1:1) where the peaks are assigned to the dimeric species $Al_2(C_6F_5)_4Et_2$ (**Al^{2*}**) in equilibrium with

B:Al
10:0

a) $B(C_6F_5)_3$
     B

b) $B(C_6F_5)_3 + B(C_6F_5)_2Et + B(C_6F_5)Et_2$ $+ Al(C_6F_5)_3 +$ $Al(C_6F_5)_2Et$ AlEt$_3$ 10:3
     B   **B***   **B$^{2\bullet}$**   **Al**   **Al***   increase

c+d) $BEt_3 + B(C_6F_5)Et_2$ $+ Al(C_6F_5)_3 +$ 10:4
                     B$^{2\bullet}$ **Al**   10:5

e+f) $BEt_3 +$ $Al_2(C_6F_5)_4Et_2$ 10:6
                                      Al$^{2\bullet}$ 10:10 (1:1)

g) $BEt_3 +$ $Al_2(C_6F_5)_3Et_3 + Al_2(C_6F_5)_2Et_4$ 5:10
                                               Al$^{3\bullet}$ **Al$^{4\bullet}$**

h-j) $Al_2(C_6F_5)_2Et_4 + Al_2(C_6F_5)Et_5$ 3:10
                                               Al$^{4\bullet}$ **Al$^{5\bullet}$**   2:10
                                                                                         1:10

increasing number of B- and Al-bonded Et-groups ($B^{n\bullet}$, $Al^{n\bullet}$)

Figure 2.
Interpretation of the ^{19}F NMR spectral changes upon increasing AlEt$_3$ content (decreasing B:Al ratio) in Figure 1. In the spectral assignments B^{n*} and $Al^{n*}n$ indicates the number of ethyl groups. Note that BEt$_3$ and AlEt$_3$ do not give a signal in ^{19}F NMR.

its monomer Al(C$_6$F$_5$)$_2$Et (**Al***), three different *para*-F peaks develop consecutively when going to a B:Al ratio of 1:10 (that is increasing AlEt$_3$) (Figure 1 f-j). Unfortunately, there is no species differentiation in the *ortho*- and *meta*-F signals. Going from Fig. 1f with B:Al = 10:10 to Fig. 1g with B:Al = 5:10 the *para*-signal assigned to (**Al^{2*}**) Al$_2$(C$_6$F$_5$)$_4$Et$_2$ ⇋ Al(C$_6$F$_5$)$_2$Et (**Al***) disappears and a new major and minor multiplet occur at higher field. The major one is assigned to the sesqui compound Al$_2$(C$_6$F$_5$)$_3$Et$_3$ (**Al^{3*}**). Its signal disappears again when progressing to Fig. 1h with B:Al = 3:10 where the previously minor multiplett grows in intensity and now becomes the major one. This signal is assigned to Al$_2$(C$_6$F$_5$)$_2$Et$_4$ (**Al^{4*}**). Also in Fig. 1h a new minor *para*-signal develops at higher field from the major signal which continues to increase in intensity at the expense of its low-field neighbor when going over Fig 1i (B:Al = 2:10) to Fig 1j with B:Al = 1:10. This last signal seems to be due to Al$_2$(C$_6$F$_5$)Et$_5$ (**Al^{5*}**). Note the steady high-field shift of the *para*-F signal with increasing number of ethyl groups in the series Al(C$_6$F$_5$)$_3$ → Al(C$_6$F$_5$)$_2$Et ⇋ Al$_2$-

(C$_6$F$_5$)$_4$Et$_2$ → Al$_2$(C$_6$F$_5$)$_3$Et$_3$ → Al$_2$(C$_6$F$_5$)$_2$-Et$_4$ → Al$_2$(C$_6$F$_5$)Et$_5$.

In the typical B(C$_6$F$_5$)$_3$:AlEt$_3$ cocatalyst with a B:Al ratio of 1:9 [16,21] the active Lewis base species have to be formulated as Al$_2$(C$_6$F$_5$)$_2$Et$_4$ and Al$_2$(C$_6$F$_5$)Et$_5$ together with the monomeric form Al(C$_6$F$_5$)Et$_2$. Furthermore, the systematic ^{19}F NMR experiments have demonstrated that different C$_6$F$_5$-substituted borane and aluminum species can be observed depending on the molar B(C$_6$F$_5$)$_3$:AlEt$_3$ ratio.

Reaction Between B(C$_6$F$_5$)$_3$ and AlR$_3$ (R = *i*-Bu, n-C$_6$H$_{13}$, *n*-C$_8$H$_{17}$)

The ^{19}F NMR spectra for the reactions between B(C$_6$F$_5$)$_3$ and AlR$_3$ at 1:1 molar ratios are presented in Figure 3. The spectrum of B(C$_6$F$_5$)$_3$ and Al(*i*-Bu)$_3$ in Figure 3a is dominated by the signals of unreacted B(C$_6$F$_5$)$_3$ (**B**) at −128.7 ppm (*ortho*-F), −144.3 ppm (*para*-F), and −161.3 ppm (*meta*-F) (cf. Figure 1a). In addition, two sets of weak ^{19}F NMR signals are found in the spectrum which can be assigned to the borane species B(C$_6$F$_5$)$_2$(*i*-Bu) (**B***) and [B(C$_6$F$_5$)$_3$(*i*-Bu)]$^-$ (**B^{*-}**) by comparison to B(C$_6$F$_5$)$_2$Et and [B(C$_6$F$_5$)$_3$Et]$^-$ from
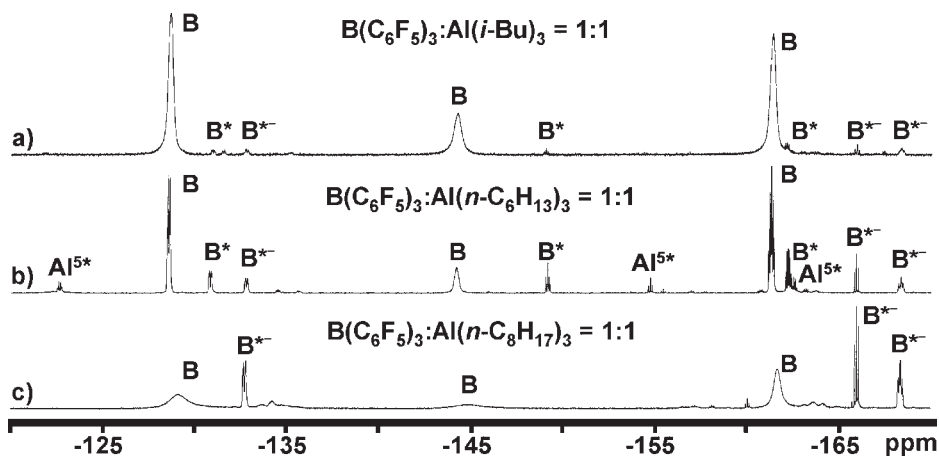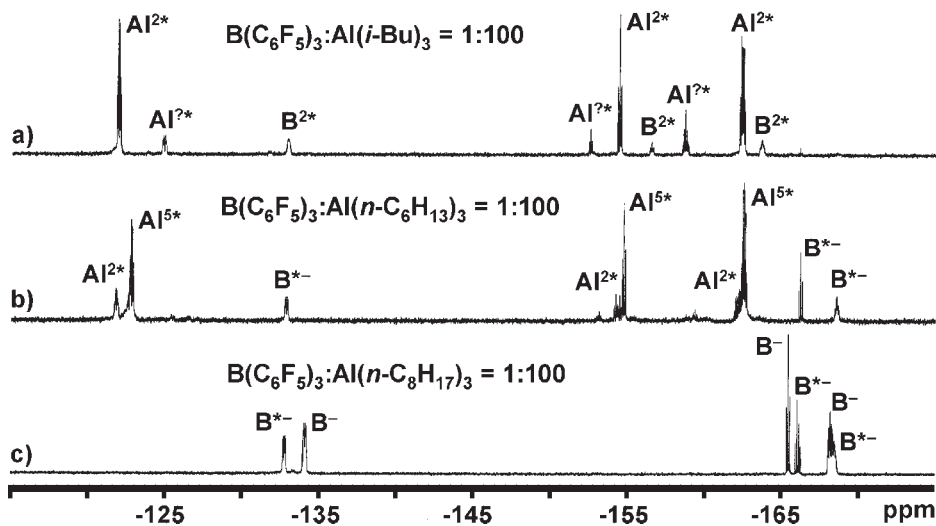
Figure 3.
^{19}F NMR spectra of $B(C_6F_5)_3/AlR_3$ mixtures at 1:1 molar ratios. The spectra were measured 12 min (a) and 10 min (b and c) after the addition of AlR_3 at room temperature. For the spectral interpretation and exact symbol designations (**B**, **B***, **Al^{5*}** etc.) see text and equations 3a-c; further details in experimental section.

$ZnEt_2/B(C_6F_5)_3$.[11] For the anionic bora-nate $[B(C_6F_5)_3(i\text{-}Bu)]^-$, **B***$^-$ the sequence *ortho – para – meta* from low to high field is retained, despite the substantial shift of the *para*-F signal with respect to those of the neutral boranes. Very weak signals for an $Al\text{-}C_6F_5$ species can be seen upon spectral enlargement. The reaction between $B(C_6F_5)_3$ and $Al(i\text{-}Bu)_3$ is summarized in eq. 3a. The cation required for **B***$^-$ is tentatively for-mulated as $[Al(i\text{-}Bu)_2]^+$ although $[AlR_2]^+$ species free of donor ligands are not known. It is intriguing if such species with $R = i\text{-}Bu$, *n*-hexyl or *n*-octyl could be stabilized by $[B(C_6F_5)_3R]^-$ (**B***$^-$). A transient species "$[AlMe_2]^+\text{-} [B(C_6F_5)_4]^-$" was formulated

Figure 4.
^{19}F NMR spectra of $B(C_6F_5)_3/AlR_3$ mixtures at 1:100 molar ratios. The spectra were measured 1h 7min (a), 1h 29min (b), and 1h 19min (c) after the addition of AlR_3 at room temperature. For the spectral interpretation and exact symbol designations (**B^{2*}**, **Al^{2*}** etc.) see text and equations 4a-c; further details in experimental section.
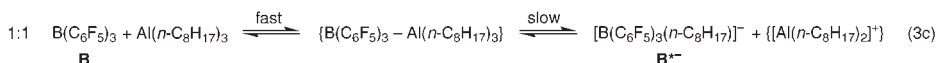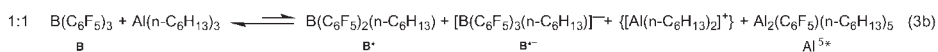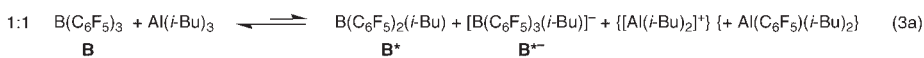
as part of the reaction between $AlMe_3$ and $[CPh_3]^+\text{-}[B(C_6F_5)_4]^-$ but found to immediately decompose to $B(C_6F_5)_3$ and $Al(C_6F_5)Me_2$. Yet, with more bulky R groups and in the presence of excess AlR_3 more stable $[Al_nR_{3n-1}]^+$ clusters may be envisaged.[12]

The ^{19}F NMR spectrum of $B(C_6F_5)_3$ and $Al(n\text{-}C_6H_{13})_3$ (1:1) in Figure 3b is again dominated by the signals of unreacted $B(C_6F_5)_3$ (**B**), albeit with sharper peaks than in Figure 3a. As in Figure 3a, two sets of now more intense ^{19}F NMR signals can be assigned to the borane species $B(C_6F_5)_2(n\text{-}C_6H_{13})$ (**B***) and $[B(C_6F_5)_3(n\text{-}C_6H_{13})]^-$ (**B***−). An additional set of signals at -122.7 ppm (*ortho*-F), -154.7 ppm (*para*-F), and -162.4–162.6 ppm (*meta*-F) can be identified by the low-field shift in the area of the *ortho*-F atom to an $Al\text{-}C_6F_5$ species. This provides evidence for a minor ligand exchange reaction. Based on the chemical shift of the *para*-F signal of -154.7 ppm the species is assigned as $Al_2(C_6F_5)(n\text{-}C_6H_{13})_5$ (**A^{5*}**) in comparison to $Al_2(C_6F_5)(Et)_5$ (-154.9 ppm). Higher aluminum tri(*n*-alkyls), AlR_3 still dimerize in solution with little difference in the thermodynamic data for the monomer-dimer equilibria from $R = n$-propyl to *n*-dodecyl.[22] Unlike with $AlEt_3$, no complete exchange reaction could be achieved with $Al(n\text{-}C_6H_{13})_3$ at equimolar ratio. Even after a reaction time of 15 h the spectrum was still dominated by the signals of unreacted $B(C_6F_5)_3$. The reaction between $B(C_6F_5)_3$ and $Al(n\text{-}C_6H_{13})_3$ is formulated in eq. 3b.

The spectrum of $B(C_6F_5)_3$ and $Al(n\text{-}C_8H_{17})_3$ (1:1) in Figure 3c shows only signals of unreacted $B(C_6F_5)_3$ and of $[B(C_6F_5)_3(n\text{-}C_8H_{17})]^-$ (**B***−). The signals of $B(C_6F_5)_3$ are significantly broadened which indicates that $B(C_6F_5)_3$ is part of an equilibrium system whose rate constant lies within the NMR time scale. We suggest an interaction in a pre-equilibrium with $Al(n\text{-}C_8H_{17})_3$ for the subsequent octyl group abstraction by the borane to yield **B***−. During a reaction time of about 14 h no changes in the number and position of the signals including their intensity ratio were observed. The formation of $Al\text{-}C_6F_5$ species could not been detected from the reaction of $B(C_6F_5)_3$ and $Al(n\text{-}C_8H_{17})_3$. The reaction between $B(C_6F_5)_3$ and $Al(n\text{-}C_8H_{17})_3$ is given in eq. 3c.

The ^{19}F NMR spectra for the reactions between $B(C_6F_5)_3$ and AlR_3 at 1:100 molar ratios are collected in Figure 4. The spectrum of $B(C_6F_5)_3$ and $Al(i\text{-}Bu)_3$ in Figure 4a now shows the result of the ligand exchange reaction in the form of two $Al\text{-}C_6F_5$ species, identified from the low field signals (<-125 ppm) in the *ortho*-F region. Based on the excess of $Al(i\text{-}Bu)_3$ the major group of signals at -121.9 ppm (*ortho*-F), -154.4 ppm (*para*-F), and -161.4 ppm (*meta*-F) is assigned to $Al(C_6F_5)(i\text{-}Bu)_2$ (**Al^{2*}**) since $Al(i\text{-}Bu)_3$ (TIBA) is largely monomeric in solution and dimeric mostly in the solid state.[22] The origion of the minor set of aluminum signals at -124.9 ppm (*ortho*-F), -152.6 ppm (*para*-F), and -158.7 ppm (*meta*-F) (**Al$^{?*}$**) is not quite clear. Possible species might be $[Al(C_6F_5)(i\text{-}Bu)_3]^-$ or $[Al(C_6F_5)(i\text{-}Bu)H]$ (from β-H elimination and *iso*-butylene formation). In addition weak signals of $B(C_6F_5)(i\text{-}Bu)_2$ (**B^{2*}**) could still be seen which indicates that the ligand exchange

1:1 $\quad B(C_6F_5)_3 + Al(i\text{-}Bu)_3 \;\rightleftharpoons\; B(C_6F_5)_2(i\text{-}Bu) + [B(C_6F_5)_3(i\text{-}Bu)]^- + \{[Al(i\text{-}Bu)_2]^+\} \{+ Al(C_6F_5)(i\text{-}Bu)_2\} \quad$ (3a)
$\qquad\quad$ **B** $\qquad\qquad\qquad\qquad\qquad\qquad$ **B*** $\qquad\qquad$ **B***−

1:1 $\quad B(C_6F_5)_3 + Al(n\text{-}C_6H_{13})_3 \;\rightleftharpoons\; B(C_6F_5)_2(n\text{-}C_6H_{13}) + [B(C_6F_5)_3(n\text{-}C_6H_{13})]^- + \{[Al(n\text{-}C_6H_{13})_2]^+\} + Al_2(C_6F_5)(n\text{-}C_6H_{13})_5 \quad$ (3b)
$\qquad\quad$ **B** $\qquad\qquad\qquad\qquad\qquad\qquad$ **B*** $\qquad\qquad$ **B***− $\qquad\qquad\qquad\qquad$ **Al^{5*}**

1:1 $\quad B(C_6F_5)_3 + Al(n\text{-}C_8H_{17})_3 \;\underset{\text{fast}}{\rightleftharpoons}\; \{B(C_6F_5)_3 - Al(n\text{-}C_8H_{17})_3\} \;\underset{\text{slow}}{\rightleftharpoons}\; [B(C_6F_5)_3(n\text{-}C_8H_{17})]^- + \{[Al(n\text{-}C_8H_{17})_2]^+\} \quad$ (3c)
$\qquad\quad$ **B** $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ **B***−

does not rapidly go to completion. However the signals of $\mathbf{B^{2*}}$ almost disappeared over a period of about 14 h whereas the intensity ratio between $\mathbf{Al^{2*}}$ and the uncertain species $\mathbf{Al^{?*}}$ stayed nearly constant over this period. The reaction between $B(C_6F_5)_3$ and excess $Al(i\text{-}Bu)_3$ is given in eq. 4a.

Also, an excess of $Al(n\text{-}C_6H_{13})_3$ resulted in a nearly complete transfer of the C_6F_5 group from boron to aluminium according to the spectrum in Figure 4b. Two Al-C_6F_5 species can be identified. The major one is assigned to $Al_2(C_6F_5)(n\text{-}C_6H_{13})_5$ ($\mathbf{A^{5*}}$) and was already seen in the 1:1 spectrum in Figure 3b. The signal intensities of $\mathbf{A^{5*}}$ increase with time at the expense of those of the minor Al-C_6F_5 species whose nature is again not fully clear. Its chemical shifts are typical for $Al(C_6F_5)R_n$. Perhaps the monomer-dimer equilibrium formation is slow on the NMR time scale so that the monomeric form $Al(C_6F_5)(n\text{-}C_6H_{13})_2$ ($\mathbf{A^{2*}}$) as the direct reaction product from the group transfer continuous to exist independently. Only a small amount of C_6F_5 groups remained bonded to boron as the species $[B(C_6F_5)_3(n\text{-}C_6H_{13})]^-$ ($\mathbf{B^{*-}}$). This boranate anion probably forms quickly after mixing of the reagents and is then kinetically inert because of its tetrahedral shape. Its signal intensities decreased only slowly over a period of 14 h. Equation 4b summarizes the reaction.
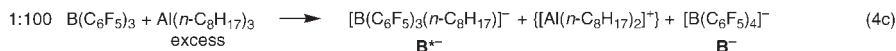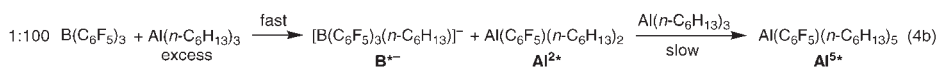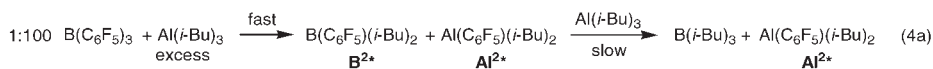
Surprisingly, the spectrum of $B(C_6F_5)_3$ and $Al(n\text{-}C_8H_{17})_3$ (1:100) in Figure 4c shows only two sets of B-C_6F_5 boranate signals: One set corresponds to $[B(C_6F_5)_3(n\text{-}C_8H_{17})]^-$ ($\mathbf{B^{*-}}$, as seen in Figure 3c) and the second, more intense set of signals is at -134.2 ppm (*ortho*-F), -165.3 ppm (*para*-F), and -168.1 ppm (*meta*-F, overlapping with *meta*-F of $\mathbf{B^{*-}}$). These latter chemical shifts are close to those reported for $[B(C_6F_5)_4]^-$ ($\mathbf{B^-}$) with $[RZn(OEt_2)_3]^+$ cations (-133.6, -164.1, and -168.0 ppm), so that they are tentatively assigned to this species.[11] The spectrum does not change over a time of 14 h. The formation of $[B(C_6F_5)_4]^-$ must somehow be catalyzed by $Al(n\text{-}C_8H_{17})_3$ or a derived $\{[Al(n\text{-}C_8H_{17})_2]^+\}$ cation but remains somewhat elusive. No transfer of a C_6F_5 group to aluminum can be observed. Following eq. 3c, the equilibria are now shifted to $\mathbf{B^{*-}}$ with excess $Al(n\text{-}C_8H_{17})_3$ (eq. 4c)

Experimental Part

General Procedures and Materials

All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk or drybox techniques. NMR spectra were recorded with a Bruker Avance DPX 200 at 300 K and 188 MHz (^{19}F NMR, calibration against an external standard of $CDFCl_2$ check). The NMR experiments with air-sensitive materials were performed under inertgas-atmosphere using NMR tubes with screw caps (Wilmad) and Teflon-covered septa (Wheaton) and CD_2Cl_2 as solvent. Chemicals were supplied as follows and

$$1{:}100 \quad B(C_6F_5)_3 + \underset{\text{excess}}{Al(i\text{-}Bu)_3} \xrightarrow{\text{fast}} \underset{\mathbf{B^{2*}}}{B(C_6F_5)(i\text{-}Bu)_2} + \underset{\mathbf{Al^{2*}}}{Al(C_6F_5)(i\text{-}Bu)_2} \xrightarrow[\text{slow}]{Al(i\text{-}Bu)_3} B(i\text{-}Bu)_3 + \underset{\mathbf{Al^{2*}}}{Al(C_6F_5)(i\text{-}Bu)_2} \quad (4a)$$

$$1{:}100 \quad B(C_6F_5)_3 + \underset{\text{excess}}{Al(n\text{-}C_6H_{13})_3} \xrightarrow{\text{fast}} \underset{\mathbf{B^{*-}}}{[B(C_6F_5)_3(n\text{-}C_6H_{13})]^-} + \underset{\mathbf{Al^{2*}}}{Al(C_6F_5)(n\text{-}C_6H_{13})_2} \xrightarrow[\text{slow}]{Al(n\text{-}C_6H_{13})_3} \underset{\mathbf{Al^{5*}}}{Al(C_6F_5)(n\text{-}C_6H_{13})_5} \quad (4b)$$

$$1{:}100 \quad B(C_6F_5)_3 + \underset{\text{excess}}{Al(n\text{-}C_8H_{17})_3} \longrightarrow \underset{\mathbf{B^{*-}}}{[B(C_6F_5)_3(n\text{-}C_8H_{17})]^-} + \{[Al(n\text{-}C_8H_{17})_2]^+\} + \underset{\mathbf{B^-}}{[B(C_6F_5)_4]^-} \quad (4c)$$

used as received: CD_2Cl_2 by Deutero GmbH, $B(C_6F_5)_3$ by Aldrich, $AlMe_3$ solution in toluene or heptane ($2 \ mol \cdot L^{-1}$) by Aldrich, $AlEt_3$ as a $1 \ mol \cdot L^{-1}$ solution in hexane by Merck-Schuchardt, neat $Al(i\text{-}Bu)_3$, $Al(n\text{-}C_6H_{13})_3$ and $Al(n\text{-}C_8H_{17})_3$ by Schering AG. A $0.5 \ mol \cdot L^{-1}$ toluene solution was prepared for the use of $Al(i\text{-}Bu)_3$, $Al(n\text{-}C_6H_{13})_3$ and $Al(n\text{-}C_8H_{17})_3$. Toluene was dried over sodium metal, distilled and stored under argon. Hexane was dried over potassium.

NMR Investigations of $B(C_6F_5)_3$ in Combination with $AlEt_3$

(a) Molar Ratio $B(C_6F_5)_3$:$AlEt_3$ = 10:X
(X = 0, 3, 4, 5, 6, 10, 20).
$B(C_6F_5)_3$ (0.105 mmol, 53.8 mg) was dissolved in CD_2Cl_2 (0.5 mL) and the corresponding amount of $AlEt_3$ ($1 \ mol \cdot L^{-1}$ solution in hexane) was added via syringe. The ^{19}F NMR spectra were recorded approximately 10 min after the addition of $AlEt_3$.

(b) Molar Ratio $B(C_6F_5)_3$:$AlEt_3$ = X:10 (X = 1, 2, 3).
$Al(C_2H_5)_3$ (0.21 mmol, 0.21 mL of a $1 \ mol \cdot L^{-1}$ solution in hexane) was added via syringe to the corresponding amount of $B(C_6F_5)_3$ dissolved in CD_2Cl_2 (0.5 mL). The ^{19}F NMR spectra were recorded approximately 10 min after the addition of $AlEt_3$.

NMR Investigations of $B(C_6F_5)_3$ in Combination with $Al(i\text{-}Bu)_3$ (TIBA), $Al(n\text{-}C_6H_{13})_3$ (THA) and $Al(n\text{-}C_8H_{17})_3$ (TOA)

(a) Molar Ratio $B(C_6F_5)_3$:AlR_3 = 1:1
The aluminum alkyl (0.05 mmol, 0.1 mL of a $0.5 \ mol \cdot L^{-1}$ solution in toluene) was added via syringe to a solution of $B(C_6F_5)_3$ (0.05 mmol, 25.6 mg) in CD_2Cl_2 (0.5 mL). The ^{19}F NMR spectra were recorded 12 min, 42 min, 1 h 40 min, 2 h 19 min after the addition of $Al(i\text{-}Bu)_3$, 10 min, 16 min, 36 min, 1 h 6 min, 2 h 24 min, 15 h 20 min after the addition of $Al(n\text{-}C_6H_{13})_3$, and 10 min, 16 min, 36 min, 57 min, 1 h 54 min, 14 h 25 min after the addition of $Al(n\text{-}C_8H_{17})_3$.

(b) Molar Ratio $B(C_6F_5)_3$:AlR_3 = 1:100
The neat aluminum alkyl (1.00 mmol, $d_{TIBA} = 0.789 \ g \cdot mL^{-1} \Rightarrow 0.25$ mL, $d_{THA} = 0.830 \ g \cdot mL^{-1} \Rightarrow 0.34$ mL, $d_{TOA} = 0.832 \ g \cdot mL^{-1} \Rightarrow 0.44$ mL) were added via syringe to a solution of $B(C_6F_5)_3$ (0.01 mmol, 2.6 mg) in CD_2Cl_2 (0.3 mL for TIBA and THA, 0.2 mL for TOA). NMR spectra were recorded 1 h 7 min, 1 h 40 min, 2 h 9 min, 14 h 35 min after the addition of $Al(i\text{-}Bu)_3$, 20 min, 59 min, 1 h 29 min, 1 h 59 min, 14 h 5 min after the addition of $Al(n\text{-}C_6H_{13})_3$, and 12 min, 18 min, 48 min, 1 h 19 min, 13 h 35 min after the addition of $Al(n\text{-}C_8H_{17})_3$.

There were no changes in the peak positions over time only in their relative intensities. A complete listing of the chemical shifts and FF coupling constants for all spectra will be included in a full publication elsewhere.

Conclusions

Systematic ^{19}F NMR experiments have demonstrated that different C_6F_5-substituted borane and aluminum species can be observed from the reaction of $B(C_6F_5)_3$ with $AlEt_3$. From excess borane to excess $AlEt_3$ the species $Al(C_6F_5)_3 \rightarrow Al(C_6F_5)_2$-$Et \leftrightarrows Al_2(C_6F_5)_4Et_2 \rightarrow Al_2(C_6F_5)_3Et_3 \rightarrow Al_2(C_6F_5)_2Et_4 \rightarrow Al_2(C_6F_5)Et_5$ are formed and differentiated by their *para*-F signal. At a $B(C_6F_5)_3$:$AlEt_3$ ratio of 1:9, which is often used as cocatalytic system, the active Lewis base species have to be formulated as $Al_2(C_6F_5)_2Et_4$ and $Al_2(C_6F_5)Et_5$ together with the monomeric form $Al(C_6F_5)Et_2$.

The reaction between $B(C_6F_5)_3$ and higher aluminum alkyls AlR_3 (R = *i*-Bu, *n*-C_6H_{13}, *n*-C_8H_{17}) is not only thermodynamically but also kinetically controlled. At an equimolar ratio the (thermodynamic) equilibrium lies on the side of the unchanged borane together with its boranate $[B(C_6F_5)_3R]^-$ anion. At large AlR_3 excess the equilibrium is shifted to the group-exchange products BR_3 and $Al(C_6F_5)R_2$ for

R = i-Bu and n-C$_6$H$_{13}$. Yet, the exchange is not quickly completed and the intermediate B(C$_6$F$_5$)(i-Bu)$_2$ or the side product [B(C$_6$F$_5$)$_3$(n-C$_6$H$_{13}$)]$^-$ can still be seen for some hours after mixing. For R = n-C$_8$H$_{17}$ even at large Al(n-C$_8$H$_{17}$)$_3$ excess no C$_6$F$_5$ ↔ alkyl exchange can be observed, but there is indication that a [B(C$_6$F$_5$)$_4$]$^-$ anion forms beside [B(C$_6$F$_5$)$_3$(n-C$_8$H$_{17}$)]$^-$.

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