 DOI: 10.1002/masy.200650407

^{19}F NMR Investigations of the Reaction of $B(C_6F_5)_3$ with Different Tri(alkyl)aluminum Compounds

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Summary: Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ reacts with triethylaluminum, $AlEt_3$ to a mixture of $Al(C_6F_5)_{3-n}Et_n$ and $Al_2(C_6F_5)_{6-n}Et_n$ compounds depending on the B/Al ratio. From excess borane to excess $AlEt_3$ the species $Al(C_6F_5)_3 \rightarrow Al(C_6F_5)_2Et \leftrightharpoons Al_2(C_6F_5)_4Et_2 \rightarrow Al_2(C_6F_5)_3Et_3 \rightarrow Al_2(C_6F_5)_2Et_4 \rightarrow Al_2(C_6F_5)Et_5$ are formed and differentiated by their *para*-F signal in ^{19}F NMR. The reaction between $B(C_6F_5)_3$ and the higher aluminum alkyls, tri(*iso*-butyl)aluminum and tri(*n*-hexyl)aluminum AlR_3 (R = *i*-Bu, *n*-C_6H_{13}) is slower and requires AlR_3 excess to shift the $C_6F_5 \leftrightarrow R$ exchange equilibria to almost complete formation of $Al(C_6F_5)R_2$ and BR_3. At equimolar ratio the equilibrium lies on the side of the unchanged borane together with its boranate $[B(C_6F_5)_3R]^-$ anion. For tri(*n*-octyl)aluminum even at large $Al(n\text{-}C_8H_{17})_3$ excess no $C_6F_5 \leftrightarrow$ 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, $B(C_6F_5)_3$ was first described in the 1960s[1] but the properties of $B(C_6F_5)_3$ including the strong Lewis acidity were not investigated further and no applications of C_6F_5-substituted boranes were reported. Beginning in the early 1990s it was discovered [2] that group 4 metallocene alkyls in combination with $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$,[2] $[Ph_3C]^+[B(C_6F_5)_4]^-$,[6] and $[HNRR'_2]^+[B(C_6F_5)_4]^-$[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 $B(C_6F_5)_3$/$AlEt_3$ 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 $B(C_6F_5)_3$ and $AlMe_3$ reacts by a facile aryl/alkyl group exchange to give $Al(C_6F_5)_3$ and BMe_3 as the main products (eq. 1).[12,13] Comparable exchange reactions have been observed between $E(C_6F_5)_3$ (E = Al, B) and MAO[14] and in the reaction of AlR_3 with $[Ph_3C]^+[B(C_6F_5)_4]^-$.[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 $[Cp_2MR]^+[R\text{-}B(Ar^F)_3]^-$ 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

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

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, $Al(i\text{-}Bu)_3$), tri(-hexyl)aluminum (THA, $Al(n\text{-}C_6H_{13})_3$) and tri(octyl)aluminum (TOA, $Al(n\text{-}C_8H_{17})_3$). The ^{19}F NMR investigations were carried out with different molar $B(C_6F_5)_3$:AlR_3 ratios (R = C_2H_5, $i\text{-}C_4H_9$, $n\text{-}C_6H_{13}$, and $n\text{-}C_8H_{17}$) 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***) $Al_2(C_6F_5)_4Et_2 \leftrightarrows Al(C_6F_5)_2Et$ (**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

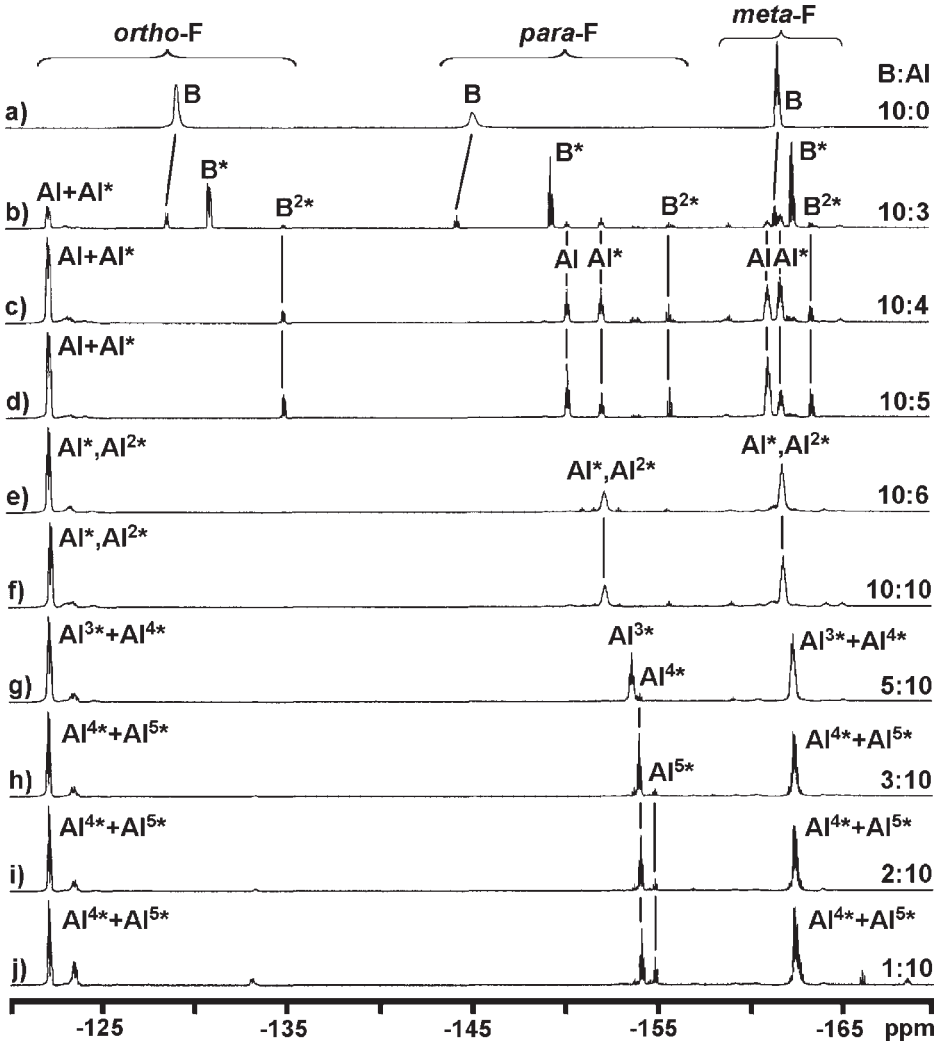


Figure 1.
^{19}F NMR spectra of $B(C_6F_5)_3/AlEt_3$ mixtures with increasing $AlEt_3$ content (decreasing B:Al ratio) from top to bottom. In the spectral assignments $\mathbf{B}^{n*}$ and $\mathbf{Al}^{n*}n$ indicates the number of ethyl groups. For the spectral interpretation and exact symbol designations (**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.

$$L + \underset{\text{(excess)}}{B(C_6F_5)_3} \overset{\text{fast}}{\rightleftharpoons} L{-}B(C_6F_5)_3 \qquad (2)$$

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 $Al_2(C_6F_5)_4Et_2$ ($\mathbf{Al}^{2*}$) in equilibrium with

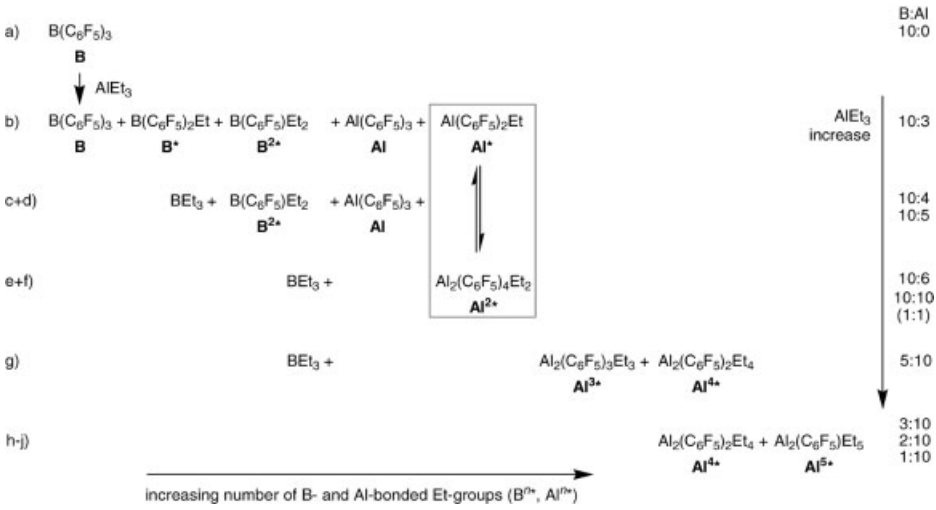


Figure 2.
Interpretation of the ^{19}F NMR spectral changes upon increasing $AlEt_3$ content (decreasing B:Al ratio) in Figure 1. In the spectral assignments $\mathbf{B}^{n*}$ and $\mathbf{Al}^{n*}\boldsymbol{n}$ indicates the number of ethyl groups. Note that BEt_3 and $AlEt_3$ do not give a signal in ^{19}F NMR.

its monomer $Al(C_6F_5)_2Et$ (**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*}) $Al_2(C_6F_5)_2Et_4 \leftrightarrows Al(C_6F_5)_2Et$ (**Al***) disappears and a new major and minor multiplet occur at higher field. The major one is assigned to the sesqui compound $Al_2(C_6F_5)_3Et_3$ (**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 $Al_2(C_6F_5)_2Et_4$ (**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 $Al_2(C_6F_5)Et_5$ (**Al**^{5*}). Note the steady high-field shift of the *para*-F signal with increasing number of ethyl groups in the series $Al(C_6F_5)_3 \rightarrow Al(C_6F_5)_2Et \leftrightarrows Al_2(C_6F_5)_4Et_2 \rightarrow Al_2(C_6F_5)_3Et_3 \rightarrow Al_2(C_6F_5)_2Et_4 \rightarrow Al_2(C_6F_5)Et_5$.

In the typical $B(C_6F_5)_3$:$AlEt_3$ cocatalyst with a B:Al ratio of 1:9 [16,21] the active Lewis base species have to be formulated as $Al_2(C_6F_5)_2Et_4$ and $Al_2(C_6F_5)Et_5$ together with the monomeric form $Al(C_6F_5)Et_2$. Furthermore, the systematic ^{19}F NMR experiments have demonstrated that different C_6F_5-substituted borane and aluminum species can be observed depending on the molar $B(C_6F_5)_3$:$AlEt_3$ ratio.

Reaction Between $B(C_6F_5)_3$ and AlR_3 (R = *i*-Bu, n-C_6H_{13}, *n*-C_8H_{17})

The ^{19}F NMR spectra for the reactions between $B(C_6F_5)_3$ and AlR_3 at 1:1 molar ratios are presented in Figure 3. The spectrum of $B(C_6F_5)_3$ and $Al(i\text{-Bu})_3$ in Figure 3a is dominated by the signals of unreacted $B(C_6F_5)_3$ (**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 $B(C_6F_5)_2(i\text{-Bu})$ (**B***) and $[B(C_6F_5)_3(i\text{-Bu})]^-$ (**B***$^-$) by comparison to $B(C_6F_5)_2Et$ and $[B(C_6F_5)_3Et]^-$ from

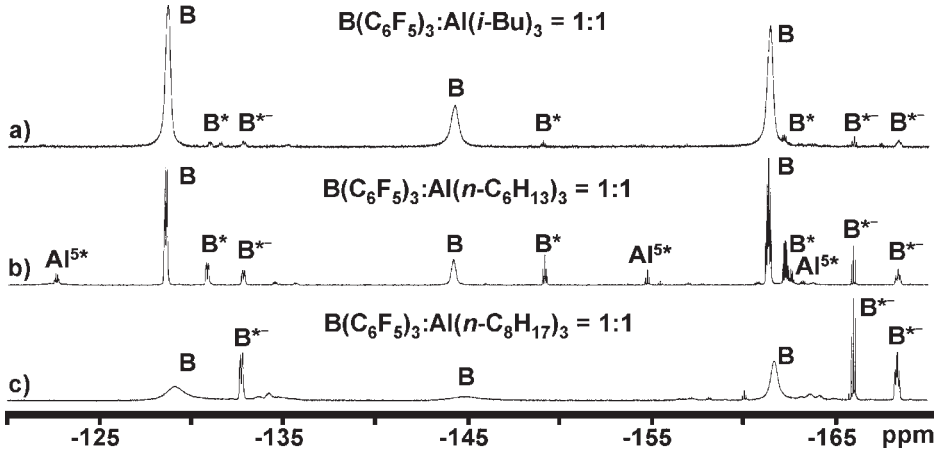


Figure 3.
^{19}F NMR spectra of $B(C_6F_5)_3/AlR_3$ mixtures at 1:1 molar ratios. The spectra were measured 12 min (a) and 10 min (b and c) after the addition of AlR_3 at room temperature. For the spectral interpretation and exact symbol designations (**B**, **B***, **Al**^{5*} etc.) see text and equations 3a-c; further details in experimental section.

$ZnEt_2/B(C_6F_5)_3$.[11] For the anionic borate $[B(C_6F_5)_3(i\text{-Bu})]^-$, **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-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 formulated 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*-Bu, *n*-hexyl or *n*-octyl could be stabilized by $[B(C_6F_5)_3R]^-$ (**B**$^{*-}$). A transient species "$[AlMe_2]^+$- $[B(C_6F_5)_4]^-$" was formulated

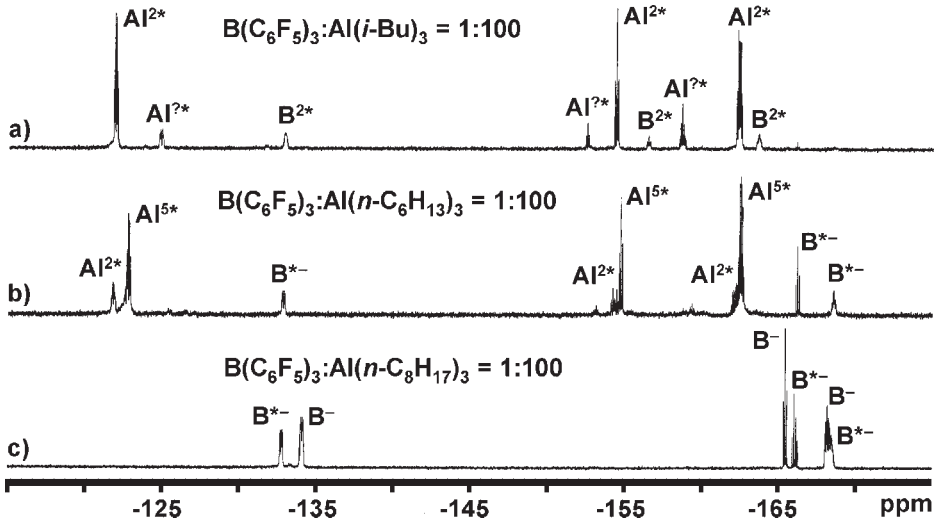


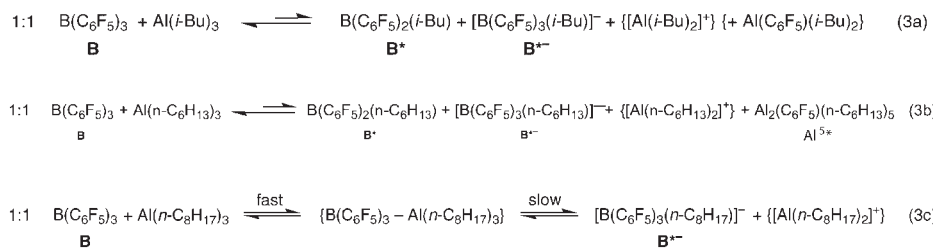
Figure 4.
^{19}F NMR spectra of $B(C_6F_5)_3/AlR_3$ mixtures at 1:100 molar ratios. The spectra were measured 1h 7min (a), 1h 29min (b), and 1h 19min (c) after the addition of AlR_3 at room temperature. For the spectral interpretation and exact symbol designations (**B**^{2*}, **Al**^{2*} etc.) see text and equations 4a-c; further details in experimental section.

as part of the reaction between $AlMe_3$ and $[CPh_3]^+$-$[B(C_6F_5)_4]^-$ 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-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-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-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



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.

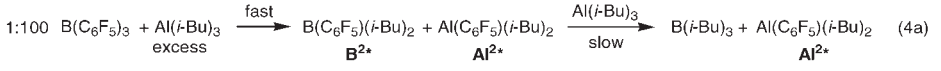
Also, an excess of $Al(n\text{-}C_6H_{13})_3$ resulted in a nearly complete transfer of the C_6F_5 group from boron to aluminium according to the spectrum in Figure 4b. Two Al-C_6F_5 species can be identified. The major one is assigned to $Al_2(C_6F_5)(n\text{-}C_6H_{13})_5$ ($\mathbf{A^{5*}}$) and was 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.

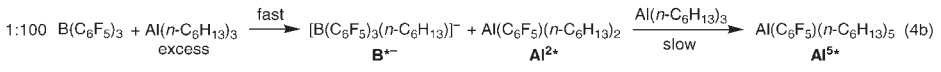
Surprisingly, the spectrum of $B(C_6F_5)_3$ and $Al(n\text{-}C_8H_{17})_3$ (1:100) in Figure 4c shows only two sets of B-C_6F_5 boranate signals: One set corresponds to $[B(C_6F_5)_3(n\text{-}C_8H_{17})]^-$ ($\mathbf{B^{*-}}$, as seen in Figure 3c) and the second, more intense set of signals is at −134.2 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)

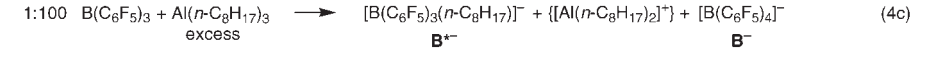
Experimental Part

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







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 · L^{-1}) by Aldrich, $AlEt_3$ as a 1 mol · L^{-1} solution in hexane by Merck-Schuchardt, neat Al(*i*-Bu)$_3$, Al(*n*-C_6H_{13})$_3$ and Al(*n*-C_8H_{17})$_3$ by Schering AG. A 0.5 mol · L^{-1} toluene solution was prepared for the use of Al(*i*-Bu)$_3$, Al(*n*-C_6H_{13})$_3$ and Al(*n*-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 · 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 · 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*-Bu)$_3$ (TIBA), Al(*n*-C_6H_{13})$_3$ (THA) and Al(*n*-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 · 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*-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*-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*-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 · $mL^{-1} \Rightarrow 0.25$ mL, $d_{THA} = 0.830$ g · $mL^{-1} \Rightarrow 0.34$ mL, $d_{TOA} = 0.832$ g · $mL^{-1} \Rightarrow 0.44$ 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*-Bu)$_3$, 20 min, 59 min, 1 h 29 min, 1 h 59 min, 14 h 5 min after the addition of Al(*n*-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*-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_6H_{13}. Yet, the exchange is not quickly completed and the intermediate $B(C_6F_5)(i\text{-Bu})_2$ or the side product $[B(C_6F_5)_3(n\text{-}C_6H_{13})]^-$ can still be seen for some hours after mixing. For R = *n*-C_8H_{17} even at large $Al(n\text{-}C_8H_{17})_3$ excess no $C_6F_5 \leftrightarrow$ alkyl exchange can be observed, but there is indication that a $[B(C_6F_5)_4]^-$ anion forms beside $[B(C_6F_5)_3(n\text{-}C_8H_{17})]^-$.

[1] A. G. Massey, A. J. Park, F. G. A. Stone, *Proc. Chem. Soc.* **1963**, 212. A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245. A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1966**, *5*, 218.

[2] X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1991**, *113*, 3623. X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015.

[3] R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325. M. Bochmann, S. J. Lancaster, M. B. Hursthouse, K. M. A. Malik, *Organometallics* **1994**, *13*, 2235. M. Bochmann, *Dalton Trans.* **1996**, 255. Y. X. Chen, C. L. Stern, S. Yang, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 12452. W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* **1997**, *127*, 144.

[4] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391.

[5] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99.

[6] J. C. W. Chien, W.-M. Tsai, M. D. Rausch, *J. Am. Chem. Soc.* **1991**, *113*, 8570.

[7] X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1991**, *10*, 840.

[8] Reviews: H. H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem. Int. Ed.* **1995**, *34*, 1143. C. Janiak, "*Metallocenes*", (ed. A. Togni, R.L. Halterman) Wiley-VCH, Weinheim, **1998**, ch. 9, 547. R. F. Jordan, *J. Mol. Catal.* **1998**, *128*, 1–337. A. L. McKnight, R. M. Waymouth, *Chem. Rev.* **1998**, *98*, 2587. W. E. Piers, *Chem. Eur. J.* **1998**, *4*, 13. T. J. Marks, J. C. Stevens, *Top. Catal.* **1999**, *7*, 1. G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* **1999**, *38*, 428. H. G. Alt, A. Köppl, *Chem. Rev.* **2000**, *100*, 1205. G. G. Hlatky, *Coord. Chem. Rev.* **2000**, *199*, 235. G. W. Coates, *J. Chem. Soc., Dalton Trans.* **2002**, 467. C. Janiak, *Metallocene Catalysts in Kirk-Othmer Encyclopedia of Chemical Technology Online Edition* 2002, DOI: 10.1002/0471238961.1305200110011409.a01, http://www.mrw.interscience.wiley.com/kirk/articles/metajani.a01/frame.html

[9] G. H. Hlatky, H. W. Turner, R. R. Eckman, *J. Am. Chem. Soc.* **1989**, *111*, 2728. G. H. Hlatky, R. R. Eckman, H. W. Turner, *Organometallics* **1992**, *11*, 1413. US 5668234 (1997) B.F. Goodrich Company, USA, invs. S. Collins, L. F. Rhodes, B. L. Goodall, *Chem. Abstr.* **1997**, *127*, 263591s. I. Tritto, R. Donetti, M. C. Sacchi, P. Locatelli, G. Zannoni, *Macromolecules* **1997**, *30*, 1247.

[10] J. S. Kim, L. M. Wojcinski, S. Liu, J. C. Sworen, A. Sen, *J. Am. Chem. Soc.* **2000**, *122*, 5668.

[11] D. A. Walker, T. J. Woodmann, D. L. Hughes, M. Bochmann, *Organometallics* **2001**, *20*, 3772.

[12] M. Bochmann, M. J. Sarsfield, *Organometallics* **1998**, *17*, 5908.

[13] J. Klosin, G. R. Roof, E. Y. X. Chen, K. A. Abboud, *Organometallics* **2000**, *19*, 4684.

[14] C. H. Lee, S. J. Lee, J. W. Park, K. H. Kim, B. Y. Lee, J. S. Oh, *J. Mol. Catal., A: Chem.* **1998**, *132*, 231.

[15] G. Erker, *Acc. Chem. Res.* **2001**, *34*, 309.

[16] C. Janiak, P.-G. Lassahn, *J. Mol. Catal. A: Chem.* **2001**, *166*, 193. P.-G. Lassahn, C. Janiak, J. S. Oh, *Z. Naturforsch. B* **2001**, *56b*, 1289. C. Janiak, P.-G. Lassahn, *Polym. Bull.* **2002**, *47*, 539. Berchtold, V. Lozan, P.-G. Lassahn, C. Janiak, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 3604. P.-G. Lassahn, C. Janiak, J. S. Oh, *Macromol. Rapid Commun.* **2002**, *23*, 16. V. Lozan, P.-G. Lassahn, C. Zhang, B. Wu, C. Janiak, G. Rheinwald, H. Lang, *Z. Naturforsch. B* **2003**, *58b*, 1152. P.-G. Lassahn, C. Tzschucke, W. Bannwarth, C. Janiak, *Z. Naturforsch. B* **2003**, *58*, 1063. P.-G. Lassahn, V. Lozan, G. A. Timco, P. Christian, C. Janiak, R. E. P. Winpenny, *J. Catalysis* **2004**, *222*, 260. C. Janiak, P.-G. Lassahn, V. Lozan, *Macromol. Symp.* **2006**, this issue.

[17] P.-G. Lassahn, V. Lozan, C. Janiak, *Dalton Trans.* **2003**, 927. P.-G. Lassahn, V. Lozan, B. Wu, A. S. Weller, C. Janiak, *Dalton Trans.* **2003**, 4437.

[18] S. J. McLain, J. Feldman, E. F. McCord, K. H. Gardner, M. F. Teasley, E. B. Coughlin, K. J. Sweetman, L. K. Johnson, M. Brookhart, *Macromolecules* **1998**, *31*, 6705.

[19] B. Y. Lee, G. C. Bazan, J. Vela, Z. J. A. Komon, X. Bu, *J. Am. Chem. Soc.* **2001**, *123*, 5352.

[20] D. A. Barnes, G. M. Benedikt, B. L. Goodall, S. S. Huang, H. A. Kalamarides, S. Lenhard, L. H. McIntosh III, K. T. Selvy, R. A. Shick, L. F. Rhodes, *Macromolecules* **2003**, *36*, 2623.

[21] US 5912313 (1999), B.F. Goodrich Company, USA, invs. L. H. McIntoshIII, B. L. Goodall, R. A. Shick, J. Saikumar; *Chem. Abstr.* **1997**, *127*, 110414m. US 5705503 (1998), B.F. Goodrich Company, USA, invs. B. L. Goodall, W. Risse, J. P. Mathew; *Chem. Abstr.* **1997**, *126*, 104553u. US 5677405 (1997), B.F. Goodrich Company, USA, invs. B. L. Goodall, L. H. McIntoshIII, D. A. Barnes; *Chem. Abstr.* **1997**, *126*, 104554v. WO 9856839, (1998), B.F. Goodrich Company, USA, invs. B. L. Goodall, L. H. McIntosh III; *Chem. Abstr.* **1999**, *130*, 66911g. US 6232417 (2001), B.F. Goodrich Company, USA, invs. J.-H. Lipian, A. Bell, B. L. Goodall, L. F. Rhodes, R. A. Shick, J. Saikumar; *Chem. Abstr.* **1999**, *130*, 252843m. US 6265506 (2001), B.F. Goodrich Company, USA, invs. B. L. Goodall, L. H. McIntosh III; *Chem. Abstr.* **2001**, *135*, 122919h.

[22] J. J. Eisch, *Comprehensive Organometallic Chemistry* **1982**, *1*, 555. M. E. O'Neill, K. Wade, *Comprehensive Organometallic Chemistry* **1982**, *1*, 1.

[23] C. Janiak, L. Braun, T. G. Scharmann, F. Girgsdies, *Acta Crystallogr. C* **1998**, *54*, 1722. R. T. Stibany, P. Brant, *Acta Crystallogr. C* **2001**, *57*, 644. C. Bergquist, B. M. Bridgewater, C. J. Harian, J. R. Norton, R. A. Friesner, G. Parkin, *J. Am. Chem. Soc.* **2000**, *122*, 10581.

