

Modification of Methylaluminoxane-Activated *ansa*-Zirconocene Catalysts with Triisobutylaluminum—Transformations of Reactive Cations Studied by NMR Spectroscopy

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Abstract: When triisobutylaluminum ($\text{Al}i\text{Bu}_3$) is added to solutions containing methylaluminoxane (MAO) and $\text{rac}[\text{Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2]$ (ind: indenyl) in C_6D_6 , NMR spectra show that methyl-bridged mixed-alkylaluminum dimers $\text{Al}(\mu\text{-Me})_2\text{Me}_{4-x}i\text{Bu}_x$ predominate. These dimers react with MAO under partial transfer of isobutyl groups and

induce a conversion of the initially prevailing cationic trimethylaluminum adduct $\text{rac}[\text{Me}_2\text{Si}(\text{ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2^+]$ to $\text{rac}[\text{Me}_2\text{Si}(\text{ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}i\text{Bu}^+]$ and $\text{rac}[\text{Me}_2\text{Si}(\text{ind})_2\text{Zr}(\mu\text{-Me})_2\text{Al}i\text{Bu}_2^+]$. These species are unstable and release isobutene under formation of zirconocene hydrides.

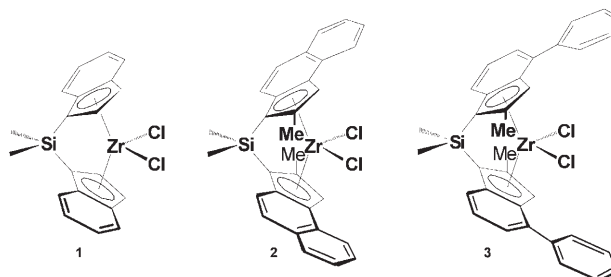
Keywords: aluminum alkyls • metallocenes • methylaluminoxane • polymerization • structure–activity relationships

Introduction

Activation of zirconocene precatalysts for application in olefin polymerization catalysis is most often achieved by reaction with a large excess of methylalumoxane (MAO).^[1] This activator can be partly replaced, without loss of activity, by less expensive aluminum alkyls, such as triisobutylaluminum ($\text{Al}i\text{Bu}_3$).^[2–9] It would, therefore, be of substantial practical interest to clarify the effects of $\text{Al}i\text{Bu}_3$ additions to MAO-activated zirconocene catalyst systems. NMR spectroscopic studies have shown that these catalyst systems predominantly contain the C_2 -symmetric AlMe_3 adduct of the respective methyl zirconocene cation, $[\text{Cp}^x_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$ (Cp^x_2 : a pair of substituted and/or bridged C_5 -ring ligands), in outer-sphere association with MAO-derived $\text{Me}\text{-MAO}^-$ anions.^[10–15]

A primary task would be to clarify the way in which species of this type react with added $\text{Al}i\text{Bu}_3$. In continuation of

previous inquiries,^[16–20] we have investigated in detail, by use of ^1H and ^{13}C NMR spectroscopic methods, which transformations these cationic zirconocene complexes undergo upon addition of alkylaluminum compounds to MAO-activated catalyst systems derived primarily from $\text{rac}[\text{Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2]$ (**1**) (ind: indenyl).



Results and Discussion

^1H NMR spectra of solutions containing **1** (3.8 mM) and MAO (dried to reduce the content of trimethylaluminum)^[21] in an $[\text{Al}]_{\text{MAO}}/[\text{Zr}]$ ratio of ≈ 600 in C_6D_6 (see the Experimental Section) were recorded. In addition to a broad $\text{MAO}\text{-CH}_3$ signal in the range of $\delta \approx 0$ to -0.5 ppm and a sharp Al_2Me_6 signal at -0.33 ppm, most of the remaining signals displayed can be attributed to the cationic species $\text{rac}[\text{Me}_2\text{Si}(\text{ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$ (species **III**).^[10–13] Rather weak, broadened signals at $\delta = 5.7\text{--}6.0$, $5.1\text{--}5.2$, and -1.6 to

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–1.8 ppm indicate that 5–10% of the zirconocene units are present in the form of contact ion-pairs of the type $\text{rac-}[\text{Me}_2\text{Si}(\text{ind})_2\text{ZrMe}]^+[\text{Me-MAO}]^-$ (species **IV**).^[12,13] Integral ratios of the NMR signals due to the zirconocene and methylaluminum species show that such a solution typically contains, for each zirconocene unit, a total of ≈ 1000 Al-bound Me groups, of which $\approx 10\%$ are due to trimethylaluminum.

Upon addition of $\text{Al}i\text{Bu}_3$ to such a solution, by using $[\text{Al}i\text{Bu}_3]_{\text{add}}/[\text{Zr}]$ ratios that increase from 3.6 to 108 (and corresponding $[i\text{Bu}]/[\text{Me}]_{\text{tot}}$ ratios from 0.01 to 0.32) by means of successive additions of 0.1–0.2 mL aliquots of a 1 M stock solution of $\text{Al}i\text{Bu}_3$ in $[\text{D}_6]$ benzene, one observes NMR spectral changes as shown in Figures 1 and 2, which are complete

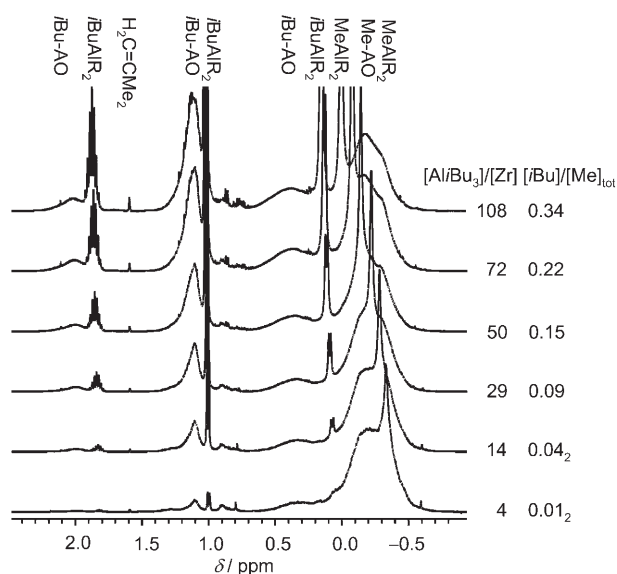
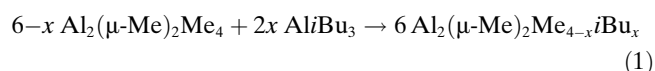


Figure 1. Alkylaluminum region of the ^1H NMR spectra of solutions of **1** (3.1 mM) in C_6D_6 containing MAO ($[\text{Al}]_{\text{MAO}}/[\text{Zr}] \approx 600$) and increasing proportions of $\text{Al}i\text{Bu}_3$.

within the time required ($t \approx 5$ min) to record a NMR spectrum. As noted in related studies,^[3,19,22,23] the signal assigned to the trialkyl dimer $\text{Al}_2(\mu\text{-Me})_2\text{Me}_4$ moves from its position at $\delta = -0.33$ ppm—an average of terminal (Me_{term}) and bridging Me groups—to successively lower fields, that is, toward the position of the bridging Me groups, due to a fast and essentially complete consumption of monomeric, three-coordinate $\text{Al}i\text{Bu}_3$ by reaction with $\text{Al}_2(\mu\text{-Me})_2\text{Me}_4$ to form mixed-trialkylaluminum dimers of the type $\text{Al}_2(\mu\text{-Me})_2\text{Me}_{4-x}i\text{Bu}_x$ [Eq. (1)]. In these dimers all of the aluminum centers acquire a coordination number of four by retaining Me groups in both bridging positions, while all of the $i\text{Bu}$ residues bind to the terminal positions.



For all of the mixed-trialkylaluminum dimers present, the CH, CH_2 , and CH_3 protons of the $i\text{Bu}$ residues give rise to two sharp doublets at $\delta = 0.08$ and 1.00 ppm and a sharp

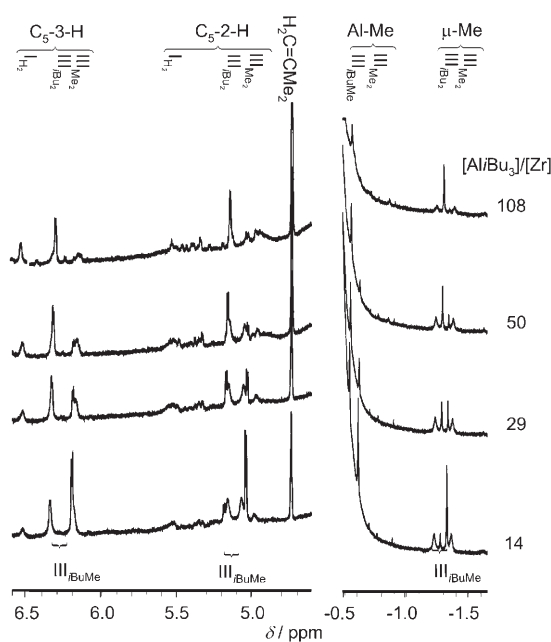
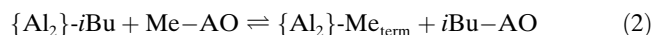


Figure 2. Ligand CH and $[\text{Zr}(\mu\text{-CH}_3)\text{-Al}]$ regions of the ^1H NMR spectra of solutions of **1** (3.1 mM) containing MAO ($[\text{Al}]_{\text{MAO}}/[\text{Zr}] \approx 600$) in C_6D_6 and increasing proportions of $\text{Al}i\text{Bu}_3$ (see Figure 1, with gain increased ≈ 20 -fold).

nonet at $\delta = 1.86$ ppm with an integral ratio of 2:6:1. As the Al-bound $i\text{Bu}$ groups in each of these mixed-trialkylaluminum dimers do not have distinguishable NMR signals, they will be summarily referred to as $\{\text{Al}_2\}\text{-}i\text{Bu}$.

Adjacent to these $i\text{Bu}$ signals we observed three broadened signals at somewhat lower fields ($\delta \approx 0.35$, 1.1 and 2.0 ppm), which also have an integral ratio close to 2:6:1. These we assign to the $i\text{Bu}$ residues attached to MAO clusters, which are likely to cause substantial signal broadening as a result of their chemical inhomogeneity. This confirms our previous observations that the prevailing mixed-trialkylaluminum dimers $\text{Al}_2(\mu\text{-Me})_2\text{R}_3i\text{Bu}_x$ transfer their $i\text{Bu}$ residues to MAO in exchange for a transferable Me group,^[19] presumably in a reversible reaction, as shown in Equation (2), in which Me-AO and $i\text{Bu-AO}$ are MAO clusters with exchangeable Me and $i\text{Bu}$ groups, respectively ($\{\text{Al}_2\} = (\mu\text{-Me})_2$ -bridged trialkylaluminum dimers)



Steady-state concentrations for the species involved in Equation (2) can be determined from their signal intensities. From these data, we can now estimate the ratios of $i\text{Bu}$ to Me groups in the terminal-alkyl positions of trialkylaluminum dimers and in the alkyl positions of MAO, respectively, based on the assumption that all bridging dimer positions are occupied by methyl groups. The results (Table 1) show that, according to Equation (2), the propensity of MAO to accept $i\text{Bu}$ in place of Me is rather low. At the highest isobutyl loading studied, not even half of the alkyl positions of MAO, yet about 90% of the terminal alkylalu-

Table 1. Ratios of *i*Bu to Me in terminal-alkyl positions of trialkylaluminum dimers, $[(Al_2-iBu)/[(Al_2)Me_{term}]]$, and in alkyl positions of MAO, $[iBu-AO]/[Me-AO]$, and equilibrium constant K_2 with respect to the isobutyl loading, $[iBu]/[Me]_{tot}$.

$[iBu]/[Me]_{tot}$	0.042	0.09	0.15	0.22	0.34
$[(Al_2-iBu)/[(Al_2)Me_{term}]]$	0.09	0.40	1.00	3.25	8.1
$[iBu-AO]/[Me-AO]$	0.009	0.038	0.09	0.23	0.40
K_2	0.10	0.095	0.09	0.07	0.05

minum dimer positions, are occupied by *i*Bu groups. For low $[iBu]/[Me]_{tot}$ loadings, the value of the equilibrium constant $K_2 = [Al-Me_{term}][iBu-AO]/([Al-iBu][Me-AO])$ is $\approx 1/10$; it is reduced even further if *i*Bu groups occupy more than $\approx 20\%$ of the alkyl positions of MAO (Table 1). It is apparent that the alkyl positions in typical MAO clusters are sterically more encumbered than those in a trialkylaluminum dimer, with major parts of the methyl positions in MAO not being accessible for *i*Bu groups at all.

The changes caused by the addition of Al_iBu_3 to the reaction system **1**/MAO, which initially contains the cationic $AlMe_3$ adduct $rac-[Me_2Si(ind)_2Zr(\mu-Me)_2AlMe_2]^+$ (species **III**_{Me₂}, see Scheme 1) as the main component, can be observed in Figure 2. At low ratios of $[Al_iBu_3]_{add}/[Zr] \approx 10-20$ ($[Al_iBu_3]_{add}$: concentration of Al_iBu_3 added), the weak, broadened signals associated with contact ion-pairs of the type $rac-[Me_2Si(ind)_2ZrMe]^+[Me-MAO]^-$ (species **IV**, see Table 2) are diminished below detection limits. It is apparent that small additions of Al_iBu_3 are sufficient to convert species **IV** almost completely to a trialkylaluminum adduct of type **III**. This conversion might be due to the release of a

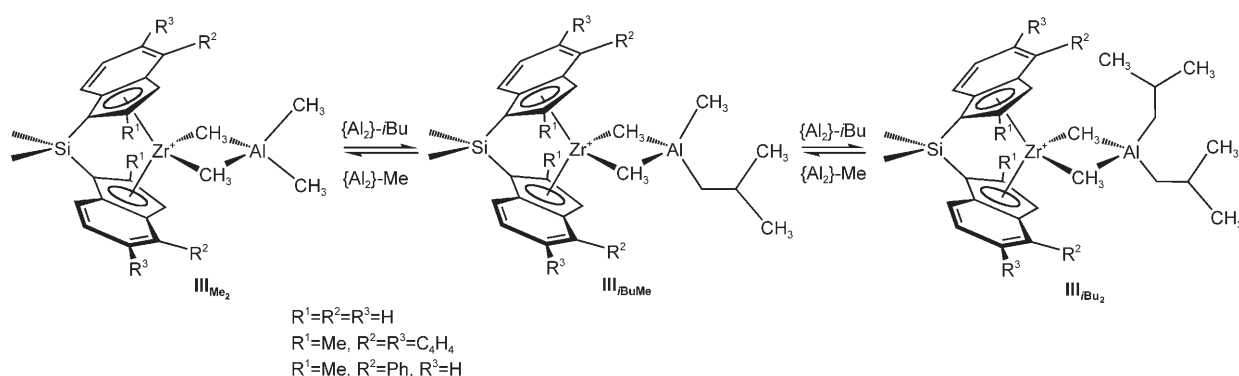
methyl-aluminum species by the reaction of Al_iBu_3 with $Me-AO$ according to Equation (2), and/or the formation of more Lewis acidic MAO sites,^[19] that is, of less strongly coordinating $R-MAO^-$ anions, by Me/iBu exchange.

The increase of the $[Al_iBu_3]_{add}/[Zr]$ ratios causes the signals of the initially prevailing C_2 -symmetric $AlMe_3$ adduct $rac-[Me_2Si(ind)_2Zr(\mu-Me)_2AlMe_2]^+$ (now denoted as species **III**_{Me₂}) to give way to a set of two $\mu-Me$, one terminal $Al-Me$, and four ligand-CH signals that have an integral ratio of 3:3:3:1:1:1:1 (Table 2). These signals must belong to a less-symmetric species, most probably the cationic Me_2Al_iBu adduct $rac-[Me_2Si(ind)_2Zr(\mu-Me)_2AlMe_iBu]^+$ (**III**_{iBuMe}). The broadening of the diastereotopic $\mu-Me$ and ligand-CH signals is probably a result of positional interchange of the terminal Me and *i*Bu groups. At $[Al_iBu_3]_{add}/[Zr]$ ratios greater than 20, this set of signals is replaced by another set, comprising one sharp $\mu-Me$ and two sharp ligand-CH signals (3:1:1), without any terminal $Zr-Me$ signal, which must be associated with of the cationic C_2 -symmetric $MeAl_iBu_2$ adduct $rac-[Me_2Si(ind)_2Zr(\mu-Me)_2Al_iBu_2]^+$ (**III**_{iBu₂}).^[24,25]

When $Al_2(^{13}CH_3)_6$ (99% isotopic enrichment) is added to **1**/MAO solutions containing Al_iBu_3 ($[Al_iBu_3]_{add}/[Zr] = 108$) in such an amount that $\approx 60\%$ of all CH_3 groups present are isotopically labeled, the previously prevailing $Zr(\mu-Me)_2Al$ signal of species **III**_{iBu₂} at $\delta = -1.292$ ppm is diminished in favor of species **III**_{Me₂}, which is now centered at $\delta = -1.342$ ppm with two ^{13}C satellites ($^1J_{H,^{13}C} = 113.5$ Hz). This signal also correlates with a ^{13}C signal at $\delta = 34.79$ ppm,^[26] and with two proton signals from $Zr(\mu-Me)_2Al$ of species **III**_{iBuMe} (centered at $\delta = -1.382$ and -1.242 ppm with two ^{13}C satellites, $^1J_{H,^{13}C} = 113$ Hz), which, in turn, correlates with ^{13}C signals at $\delta = 34.34$ and 34.81 ppm (Figure 3). Partial removal of isotopically mixed $Al_2(^{12,13}CH_3)_6$ in vacuo leads to partial regeneration of the $\mu-Me$ signal of species **III**_{iBu₂}, which is now isotopically shifted to $\delta = -1.303$ ppm (two ^{13}C satellites, $^1J_{H,^{13}C} = 113.4$ Hz), and correlated with a ^{13}C signal at $\delta = 33.83$ ppm. These relatively high ^{13}C shifts and low $^1J_{H,^{13}C}$ coupling constants coincide with previously established values for $[Cp_2Zr(\mu-Me)_2AlMe_2]^+$,^[12] and constitute unequivocal proof for the assignments of these signals to bridging Me groups in species **III**_{Me₂}, **III**_{iBuMe}, and **III**_{iBu₂} (Table 1).

Table 2. 1H NMR signals of $rac-Me_2Si(ind)_2Zr$ derivatives (δ in ppm).

	H(3)	H(2)	Zr-Me	Al-Me _{term}
ZrCl ₂	6.80	5.74	-	-
ZrMe ₂	6.69	5.68	-0.97	-
Zr($\mu-Me$) ₂ AlMe ₂ ⁺ (III _{Me₂})	6.20	5.03	-1.34	-0.62
Zr($\mu-Me$) ₂ Al <i>i</i> BuMe ⁺ (III _{iBuMe})	6.18, 6.35	5.05, 5.15	-1.37, -1.23	-0.55, -
Zr($\mu-Me$) ₂ Al <i>i</i> Bu ₂ ⁺ (III _{iBu₂})	6.33	5.17	-1.28	-
ZrMe ⁺ MeMAO ⁻ (IV)	5.7 to 6.0	5.1 to 5.2	-1.6 to -1.8	-



Scheme 1.

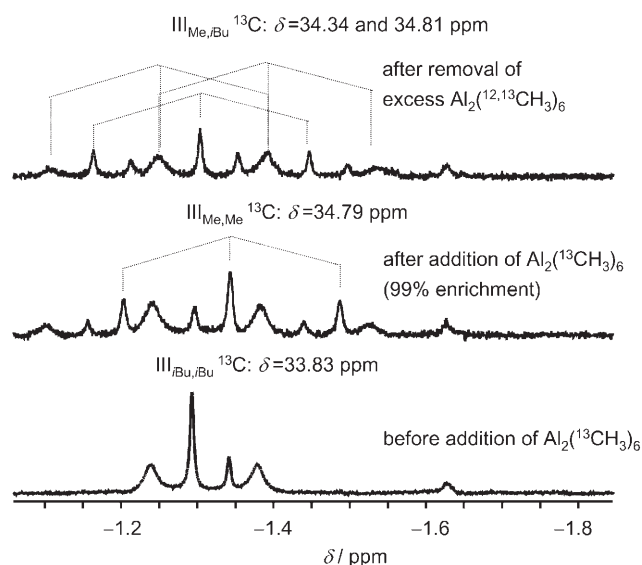
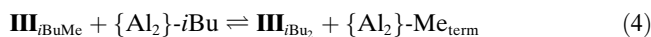
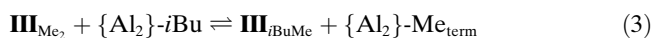


Figure 3. ^{13}C NMR spectra (terminal Al-CH₃ region of species **III**) of a solution containing **1** (3.1 mM), MAO ([Al]_{MAO}/[Zr] \approx 600), and Al*i*Bu₃ ([Al*i*Bu₃]_{add}/[Zr] = 108) in C₆D₆, before and after addition of Al₂(¹³CH₃)₆ and after removal of excess Al₂(CH₃)₆.

The three species **III**_{Me₂}, **III**_{iBuMe}, and **III**_{iBu₂} must be present in these reaction systems in sequential equilibria with each other and with the various trialkylaluminum dimers prevalent at different initial [Al*i*Bu₃]_{add}/[Zr] ratios, as described by Equations (3) and (4):



Relative concentrations of species **III**_{Me₂}, **III**_{iBuMe}, and **III**_{iBu₂} can be determined for varying [Al*i*Bu₃]_{add}/[Zr] ratios by integration of the signals shown in Figure 2. Using these values and the ratios of $[\{\text{Al}_2\}\text{-}i\text{Bu}]/[\{\text{Al}_2\}\text{-Me}_{\text{term}}]$ obtained above, equilibrium constants K_3 and K_4 pertaining to the equilibria in Equations (3) and (4), respectively, can be determined (Supporting Information). The experimental value of $K_3 = 1.8 \pm 0.2$ thus obtained is close to the statistical value ($K_3 = 2$) expected for the reaction in Equation (3). Whereas, the value of $K_4 = 0.16 \pm 0.02$ appears to be significantly smaller than the statistical value ($K_4 = 0.5$) expected for the reaction in Equation (4).^[27]

While these data are burdened by some error margins, associated with the relative concentrations of the prevailing trialkylaluminum dimers, no such uncertainties pertain to the comproportionation equilibrium involving **III**_{Me₂}, **III**_{iBu₂}, and **III**_{iBuMe} [Eq. (5)].



Direct evaluation of the associated equilibrium constant K_5 from the concentration data for the relevant species (see Supporting Information) does indeed give an invariant value

of $K_5 = 11.2 \pm 0.4$ for all [Al*i*Bu₃]_{add}/[Zr] ratios at which all three species (**III**_{Me₂}, **III**_{iBu₂}, and **III**_{iBuMe}) are simultaneously present in adequate concentrations.^[28] This experimental value is significantly higher than a value of $K_5 = 4$ expected for a statistical distribution of Me and *i*Bu groups among all three type **III** species. This indicates a slight enthalpy gain for the formation of the mixed-alkyl species, which avoid some of the steric crowding that is expected for **III**_{iBu₂}.

Pronounced steric effects are apparent from analogous studies with reaction systems that contain one of the *ansa*-zirconocene complexes *rac*-[Me₂Si(2-Me-benz[e]ind)₂ZrCl₂] (**2**) or *rac*-[Me₂Si(2-Me-4-Ph-ind)₂ZrCl₂] (**3**) instead of **1**.^[29,30] In both cases, the monobutylated species **III**_{iBuMe} predominates even at the highest isobutyl loadings studied, and contains only minimal (if any) traces of the dibutylated species **III**_{iBu₂}.

The reaction system **3**/MAO in C₆D₆ displays a further peculiarity in that it evolves methane at a much faster rate than any of the other reaction systems discussed so far. At room temperature, the very sharp signal of CH₄ begins to appear soon after preparing these solutions, and in the course of a few hours one observes a new 1:1:1 set of ¹H NMR signals at $\delta = -1.03$, -1.52 , and -1.78 ppm, which can be assigned to the Me groups of a methylene complex of the type [Zr(μ -CH₂)(μ -Me)AlMe₂]. The formation of this complex, which proceeds with a half-life of ≈ 15 h, is reminiscent of similar reactions that involve related titanocene complexes and, under certain conditions, also zirconocene systems.^[31–33]

In addition to the interconversion between different type **III** species, by exchange of terminal methyl groups against isobutyl groups, a significant reduction of their total concentrations at elevated [Al*i*Bu₃]_{add}/[Zr] ratios is apparent from Figure 2. The appearance of new ligand signals (denoted as I_{H₂} in Figure 2) and of the signals of isobutylene at $\delta = 1.59$ and 4.73 ppm, as well as previous observations on related reaction systems,^[17,34,35] suggest that the isobutylated adducts **III**_{iBuMe} and **III**_{iBu₂} are partly converted to some hydride species. Results of more direct studies on these hydride species, in reaction systems containing [Me₂Si(ind)₂ZrCl₂], MAO and diisobutylaluminum hydride, will be reported in a separate communication.^[36]

Conclusions

The absence of Zr-bound isobutyl groups in the reaction systems studied above documents that the alkyl exchange of cationic alkylaluminum adducts of type **III** with Al*i*Bu₃ is restricted to the terminal alkyl positions of these species. The negligible tendency of isobutyl groups to bridge between the aluminum and metallocene centers, which has been noted before for isoelectronic ytrocene species *rac*-[Me₂Si(2-Me-ind)₂Y(μ -R)₂AlR₂],^[37] supports the notion that aluminum alkyl adducts of type **III** are much less likely to form when a growing polymer chain is bound to the metal center of a metallocene catalyst.^[11]

When terminal methyl groups in a cationic AlMe_3 adduct III_{Me_2} are exchanged for the *i*Bu groups of alkylaluminum dimers of the type $\text{Al}_2(\mu\text{-Me})_2\text{Me}_x\text{iBu}_{4-x}$, the transfer of a second *i*Bu group to the type III species appears to be particularly sensitive to steric interactions with the zirconocene ligand framework: Even for the rather open species $\text{rac}[\text{Me}_2\text{Si}(\text{ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMeiBu}]^+$ introduction of another *i*Bu group according to Equation (4) is disfavored, relative to a statistical process, by a factor of ≈ 3 . For sterically more encumbered type III species, such as $\text{rac}[\text{Me}_2\text{Si}(2\text{-Me-4-Ph-ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMeiBu}]^+$ and $\text{rac}[\text{Me}_2\text{Si}(2\text{-Me-benzind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMeiBu}]^+$, the tendency to exchange the last terminal Me group for another *i*Bu group appears to be almost nonexistent. This is undoubtedly due to the space limitations caused by the extended ligand frameworks of these complexes and by the restriction that not both of the isobutyl residues can adopt a transoid conformation with respect to the metallocene (see Scheme 1).

Similar steric interactions, which might facilitate the expulsion of $\text{AlMe}_2\text{iBu}_{3-x}$ from a cation of type III in exchange for an olefin substrate are, therefore, likely to contribute to the exceptionally high olefin-polymerization activities reported for the sterically crowded catalyst systems $\text{rac}[\text{Me}_2\text{Si}(2\text{-Me-4-Ph-ind})_2\text{ZrCl}_2]/\text{MAO}$ and $\text{rac}[\text{Me}_2\text{Si}(2\text{-Me-benzind})_2\text{ZrCl}_2]/\text{MAO}$,^[27,28] and to the beneficial effects of $\text{Al}i\text{Bu}_3$ additions to catalyst systems of this kind.

Effects of the equilibria between species of the types III_{Me_2} , $\text{III}_{i\text{BuMe}}$, and $\text{III}_{i\text{Bu}_2}$ on the stereochemical pathway of propene polymerizations will be reported in a forthcoming publication.^[38]

Experimental Section

All experiments were carried out under an atmosphere of dry nitrogen or argon, using either Schlenk or glove box techniques. The solvents $[\text{D}_8]\text{toluene}$, $[\text{D}_6]\text{benzene}$, and unlabeled toluene were dried over molecular sieves (4 Å) prior to use, with unlabeled toluene being subsequently distilled from molten sodium metal, and stored under argon. $[\text{Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2]$ was prepared according to ref. [39].

Alkylaluminum reagents: A solution of MAO in toluene (1.3 M in Al, Al_2Me_6 content ca. 30%) was evaporated to dryness in vacuo at room temperature and the solid residue was kept in a dynamic vacuum at 50 °C for 3 h to give free-flowing solid MAO.^[21] Solid MAO (1.37 g) was dissolved in C_6D_6 (9 mL), to give a MAO stock solution ($[\text{Al}]_{\text{MAO}} = 2.1 \text{ M}$, based on an assumed MAO composition close to $\text{Al}_4\text{Me}_6\text{O}_3$ and an AlMe_3 content comprising 10% of all AlMe ^1H NMR signals, i.e., 5% of the $[\text{Al}]_{\text{MAO}}$ content).

Triisobutylaluminum ($\text{Al}i\text{Bu}_3$, 1 M in toluene, Aldrich) was evaporated in vacuo and the residue was redissolved in C_6D_6 to give an $\text{Al}i\text{Bu}_3$ stock solution with the same volume as the original solution.

NMR spectroscopy: To a MAO solution (10 mL, C_6D_6) contained within a Schlenk vessel, solid $\text{rac}[\text{Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2]$ (15 mg, 31 μmol) was added. Integration of the ^1H NMR signals of the Al-bound CH_3 groups and of the zirconocene ligand protons gave a calculated $[\text{Al}]_{\text{MAO}}/[\text{Zr}]$ ratio of ≈ 600 . Small aliquots of the stock solution of $\text{Al}i\text{Bu}_3$ in C_6D_6 were added to the Schlenk vessel, to give the $[\text{Al}i\text{Bu}_3]_{\text{add}}/[\text{Zr}]$ ratios indicated in Table 1. After each addition, a sample ($\approx 0.5 \text{ mL}$) of the reaction mixture was transferred under argon to an NMR tube to record its ^1H NMR spectra. After the time required to obtain the first NMR spectrum (ca. 5 min), no further spectral changes were observed.

All NMR spectra were recorded on a Varian INOVA-400 spectrometer. The ^1H NMR spectra were recorded at $T = 22^\circ\text{C}$ in standard 5 mm NMR tubes. ^1H NMR operating conditions: spectrometer frequency 399.76 MHz; spectral width 6.4 kHz; pulse width 5.2 μs (45°); delay between pulses $T = 6.74 \text{ s}$, 80–600 transients. ^{13}C NMR parameters: spectrometer frequency 100.53 MHz; spectral width 28 kHz; pulse width $T = 4.9 \mu\text{s}$ (45°); delay between pulses $T = 5.3 \text{ s}$; broad-band decoupling, 4000–25 000 transients. To determine chemical shifts, C_6D_6 solvent peaks were taken as $\delta = 7.15 \text{ ppm}$ (^1H) and 128.00 ppm (^{13}C). For each solution, the $[\text{Al}]_{\text{MAO}}/[\text{Zr}]_{\text{tot}}$ ratio was determined by comparing the combined integrated intensity of the CH_3 ligand signals at $\delta = 1.54, 1.7,$ and 1.8 ppm with the combined integrals of the broad CH_3 signal of MAO centered at $\delta = -0.2 \text{ ppm}$ (assuming a MAO composition of $(\text{Al}_4\text{Me}_6\text{O}_3)_n$) and of the CH_3 signal of Al_2Me_6 at $\delta = -0.33 \text{ ppm}$.

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- [25] ^1H NMR signals previously assigned to species III' are therefore actually not those of $\text{III}_{i\text{BuMe}}$, as was implied in ref. [19], but those of $\text{III}_{i\text{Bu}}$.
- [26] By double-resonance experiments.
- [27] Alkyl exchange according to Equations (3) and (4) actually involves four different reactions each, depending on the number of $i\text{Bu}$ groups (1 to 4) present in the trialkylaluminum dimer reagent. The statistical factors for $i\text{Bu}$ transfer from any one of these dimers is equal to the ratio of $i\text{Bu}$ to Me terminal groups in the reagent and product $\{\text{Al}_2\}$ dimers, respectively. Substitution of the concentrations of each of the dimers by the concentration values $[\{\text{Al}_2\}\text{-}i\text{Bu}]$ and $[\{\text{Al}_2\}\text{-Me}_{\text{term}}]$ will just cancel these statistical factors, such that the statistical factors for the reactions in Equations (3) and (4) are determined solely by the numbers of $i\text{Bu}$ to Me terminal groups in the complexes of type III involved.
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