Investigations on Ternary Metallocene-Based Catalyst Systems

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SUMMARY: The influence of the cocatalyst triisobutyl aluminium (TiBA) on the two step reaction of the ternary activation of the metallocene precursor $Ph_2C(CpFlu)ZrCl_2$ with TiBA and the activator N,N-dimethylanilinium-tetrakis(pentafluorophenyl)borat (DMAB) was investigated by means of NMR spectroscopy. More than 5 equivalents of TiBA are required for a total conversion of $Ph_2C(CpFlu)ZrCl_2$. The reaction exclusiveley leads to the monoalkyl complex $Ph_2C(CpFlu)ZrClBu^i$, independent of the Al / Zr ratio. The reaction of the $Ph_2C(CpFlu)ZrCl_2$ / TiBA mixtures, using 10, 20 and 50 equivalents of TiBA with DMAB, generates two cationic metallocene species. Using 100 equivalents of TiBA exclusiveley leads to the formation of the cationic heterodinuclear metallocene complex $[Ph_2C(CpFlu)Zr\text{-}(\mu\text{-}H)\text{-}(\mu\text{-}C_4H_7)\text{-}AlBu^i_2]^+$. In no case was the degradation or complexation of $[B(C_6F_5)_4]^-$ detected, whereas the direct reaction between TiBA and DMAB gives $AlBu^i_{3-x}(C_6F_5)_x$ compounds. A mechanism was postulated to explain the formation of $[Ph_2C(CpFlu)Zr\text{-}(\mu\text{-}H)\text{-}(\mu\text{-}C_4H_7)\text{-}AlBu^i_2]^+$. The catalyst system $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAB was used for continuous high pressure polymerizations of ethylene at 150 MPa and 180 °C. To investigate the influence of additional TiBA and triethyl aluminium (TEA) in the reactor, their concentrations were varied over a wide range. Highest productivities and molecular weights were obtained with low concentrations of TiBA in the reactor. Up to a concentration of 30 molppm Al in the reactor, unimodal polymers were formed with Mw / Mn between 2 and 3. With higher aluminium concentrations, the products formed contained small amounts of waxes. This was due to oligomerization catalyzed by the aluminium alkyl compounds. Using the Schulz-Zimm distribution all MWDs were analyzed with regard to the amount of waxes produced by ethylene oligomerization and with regard to the influence of chain transfer reactions to the aluminium. The rate constants of chain transfer to aluminium in relation to the rate constants of insertion of ethylene were estimated.

Introduction

Ternary catalyst systems based on a metallocene dichloride L_2MCl_2 (M = Ti, Zr, Hf; L = cyclopentadienyl-based bridged or non-bridged ligands), a large excess of an aluminium alkyl

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compound (AlR_3) and one to two equivalents of a cation-forming agent such as $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ or $[PhNHMe_2][B(C_6F_5)_4]$ (DMAB) are relatively insensitive to impurities because the excess aluminium alkyl compound reacts with impurities, thus protecting the active sites.[1-7] It is for that reason that ternary catalyst systems are preferably used in technical polymerization processes.[8-11]

Little is known about the activation mechanism of ternary catalyst systems. This is why the parameters of the activation procedure have to be empirically adjusted. The activation mechanism involves at least two steps. They are assumed to be an alkylation of the metallocene dichloride, followed by the formation of the cationic metallocene species.[5, 6] Further investigations related to this topic were carried out by Sinn and Kaminsky[12], Brintzinger et al.[13] and Bochmann et al.[14]

It was of interest to determine, whether the [Al] / [Zr] ratio has an influence on the formation of active sites in ternary catalyst systems. In this paper some of the results that describe the role of excess TiBA on the alkylation step and the activation step, as determined by NMR-spectroscopy, using the *ansa*-metallocene $Ph_2C(CpFlu)ZrCl_2$, are described.[15, 16]

Some work was done to investigate the influence of the excess aluminium alkyl compound on the polymerization of olefins and polymer properties below 1 MPa[17, 18, 19] but little is known about the effects under high pressure and high temperature conditions. Thus, the influence of the aluminium alkyl compounds TIBA and TEA in the reactor on the metallocene-catalyzed high-pressure polymerization of ethylene at 150 MPa and 180 °C, using $Ph_2C(CpFlu)ZrCl_2$ as catalyst precursor (which was preactivated with TiBA and DMAP outside the reactor) was also investigated and is reported here.[16, 20]

NMR Investigations. Reaction of $Ph_2C(CpFlu)ZrCl_2$ with Bu^iMgCl and TiBA

As can be seen in Figure 1 and Figure 2, the reaction of $Ph_2C(CpFlu)ZrCl_2$ with one equivalent of Bu^iMgCl or various amounts of TiBA always forms the mono-*iso*-butyl complex $Ph_2C(CpFlu)ZrClBu^i$. $Ph_2C(CpFlu)ZrCl_2$ is C_s-symmetric whereas $Ph_2C(CpFlu)ZrClBu^i$ has a chiral metal center due to four different ligands attached to the zirconium. Thus the methylene group and the methyl groups are diastereotopic. Consequently, the ^1H NMR data indicates two sets of resonances for the CH_3 groups (not seen in Figures 1 and 2) and the signals of the CH_2 group appear as an ABX pattern at –0.80 and -1.11 ppm, with a coupling constant of $^2J_{AB}$ of 13.0 Hz.

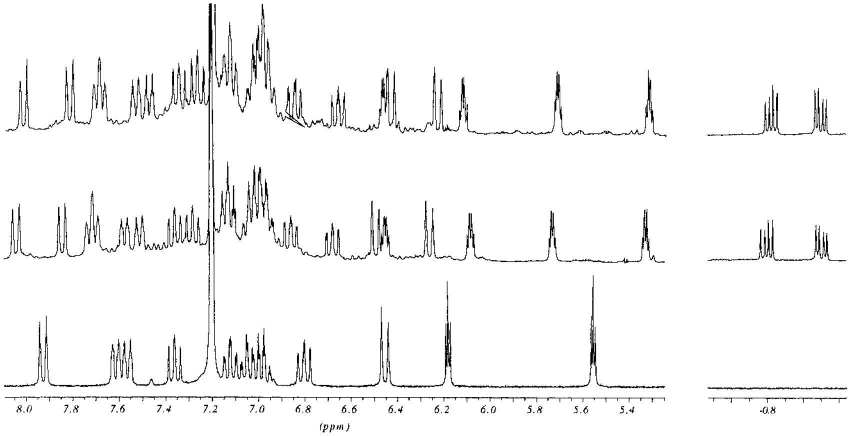


Fig. 1: Aromatic and methylene group ^{1}H NMR resonances of $Ph_2C(CpFlu)ZrCl_2$ (below), $Ph_2C(CpFlu)ZrClBu^i$ (from reaction of $Ph_2C(CpFlu)ZrCl_2$ with one equivalent Bu^iMgCl) (middle) and $Ph_2C(CpFlu)ZrClBu^i$ (from reaction of $Ph_2C(CpFlu)ZrCl_2$ with one equivalent Bu^iMgCl) + 3 equivalents of TiBA (above). Aluminium alkyl signals omitted.

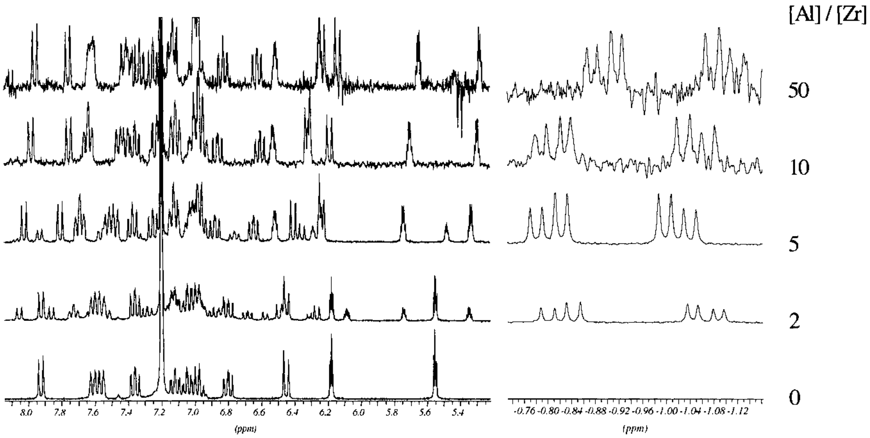


Fig. 2: Aromatic and methylene group ^{1}H NMR resonances of $Ph_2C(CpFlu)ZrCl_2$ reacted with 0, 2, 5, 10 and 50 equivalents of TiBA (bottom to top). Aluminium alkyl signals omitted.

Spectra recorded of $Ph_2C(CpFlu)ZrCl_2$ reacted with [TiBA] / [Zr] ratios of 2 and 5 still show the resonances of $Ph_2C(CpFlu)ZrCl_2$ whereas with [TiBA] / [Zr] ratios of 10 and 50 total conversion of $Ph_2C(CpFlu)ZrCl_2$ is observed (Figure 2). These results can be attributed to an equilibrium of the *iso*-butyl exchange reaction between $Ph_2C(CpFlu)ZrCl_2$ and TiBA (Formula 1).

$$Ph_2C(CpFlu)ZrCl_2 + AlBu^i_3 \rightleftharpoons Ph_2C(CpFlu)ZrClBu^i + AlBu^i_2Cl$$

Formula 1

The NMR data obtained from ^{13}C spectra show a large stepwise shift of the CH_2 resonance of $Ph_2C(CpFlu)ZrClBu^i$ from 73.6 to 85.4 ppm, if the [TiBA] / [Zr] ratio is increased from 0, over 2 and 5, to 10. This can be explained by an equilibrium as shown in Formula 2. It is proposed that formation of $Ph_2C(CpFlu)ZrClBu^i \cdot AlBu^i_3$ or $Ph_2C(CpFlu)ZrClBu^i \cdot AlBu^i_2Cl$ can lower the electron density of the metal center via Zr-Cl-Al bridges.

$$Ph_2C(CpFlu)ZrClBu^i + AlBu^i_3 \rightleftharpoons Ph_2C(CpFlu)ZrClBu^i \cdot AlBu^i_3$$

Formula 2

The slight change in the shifts ($\Delta < 0.1$ ppm) of the ^1H resonances of $Ph_2C(CpFlu)ZrCl_2$ and $Ph_2C(CpFlu)ZrClBu^i$ with increasing [TiBA] / [Zr] ratio (Figure 2) is too small to be a reliable indicator for the formation of $LLZrClBu^i \cdot AlR_3$ associates.

NMR Investigations of $Ph_2C(CpFlu)ZrCl_2$/TiBA/DMAB and TiBA/DMAB Systems

A slurry of $Ph_2C(CpFlu)ZrCl_2$ in benzene-d_6 was treated with 10, 20, 50 and 100 equivalents of TiBA and the resulting mixtures were reacted with one equivalent of DMAB. The second reaction step was accompanied by the evolution of gas that could be trapped by a gas mouse. It was identified by means of NMR spectroscopy as a mixture of *iso*-butane and *iso*-butene. During the evolution of the gas a dark green or brownish-yellow oil, containing the resulting ionic metallocene species, precipitates. Three extractions of the oil with benzene-d_6 removed excess TiBA and $PhNMe_2$ which was formed during the reaction. After purification the oil was directly used for NMR analysis.

The precipitation of oils during the formation of cationic metallocene complexes in benzene is known in the literature.[21-23] The two-phase solutions obtained show a behaviour similar to systems that Atwood defined as „liquid clathrates“.[24, 25] In our two-phase system the NMR spectra show that the top phase only contains the non-ionic compounds $PhNMe_2$, aluminium alkyls and most of the benzene-d_6. The bottom phase contains the ionic compounds and some benzene-d_6, but no free or complexed *N,N*-dimethylaniline.

The ^1H NMR spectra of the bottom phase always show two cationic metallocene species with [TiBA] / [Zr] ratios of 10, 20 and 50, whereas with 100 equivalents of TiBA only one species could be detected (Figure 3). In the ^1H NMR spectra one of these metallocene species shows only two Cp resonances, at 5.83 and 5.03 ppm, indicating a C_s symmetric metallocene complex. The signals of the C_s symmetric complex diminish with increasing [Al] / [Zr] ratios and disappear when 100 equivalents of TiBA are used. Further identification was not possible due to overlap with signals of the second species, identified as $[Ph_2C(CpFlu)Zr\text{-}\mu\text{-}H\text{-}\mu\text{-}(C_4H_7)\text{-}AlBu^i_2][B(C_6F_5)_4]\cdot AlBu^i_3$ (**A**). The signals of this species are visible in all the spectra and increase with increasing [Al] / [Zr] ratios. When the reaction is performed with an excess of 100 equivalents of TiBA, the spectra only show the signals assigned to **A**.

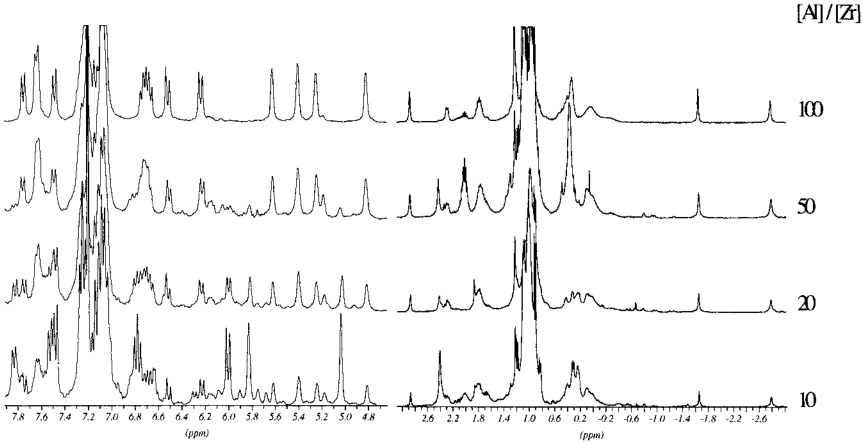


Fig. 3: ^1H NMR spectra of the lower phase resulting from mixtures of $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAB prepared in C_6D_6 with various quantities of TiBA.

Using 2D NMR experiments an assignment of all the signals in the ^1H and the ^{13}C NMR spectra (Figure 4) was possible. This lead to a remarkable bridged structure, as shown in Figure 4. An $AlBu^i_2$ fragment is bound to the Zr center via a Zr-H-Al bridge and an allylic $Zr\text{-}C_4H_7\text{-}Al$ group, forming a sixmembered ring. The resonance for the bridged hydride is found as a singlet at –2.78 ppm (peak 36). The allylic framework was be unambigously proved with C, H correlated (Figure 5) and long range C, H correlated (not shown here[15]) 2D NMR spectra. The C, H correlation spectra in Figure 5 yield cross signals for all protons and ^{13}C nuclei which are connected by a ^{13}C, ^1H coupling over one bond ($^1J_{C,H}$). The connected lines in Figure 5 show the coupling of the allylic CH_2 proton signals with ^{13}C resonances, which are identified as methylene groups in the ^{13}C DEPT spectra. As expected, no cross signal is obtained for the bridged Zr-*H*-Al hydrogen.

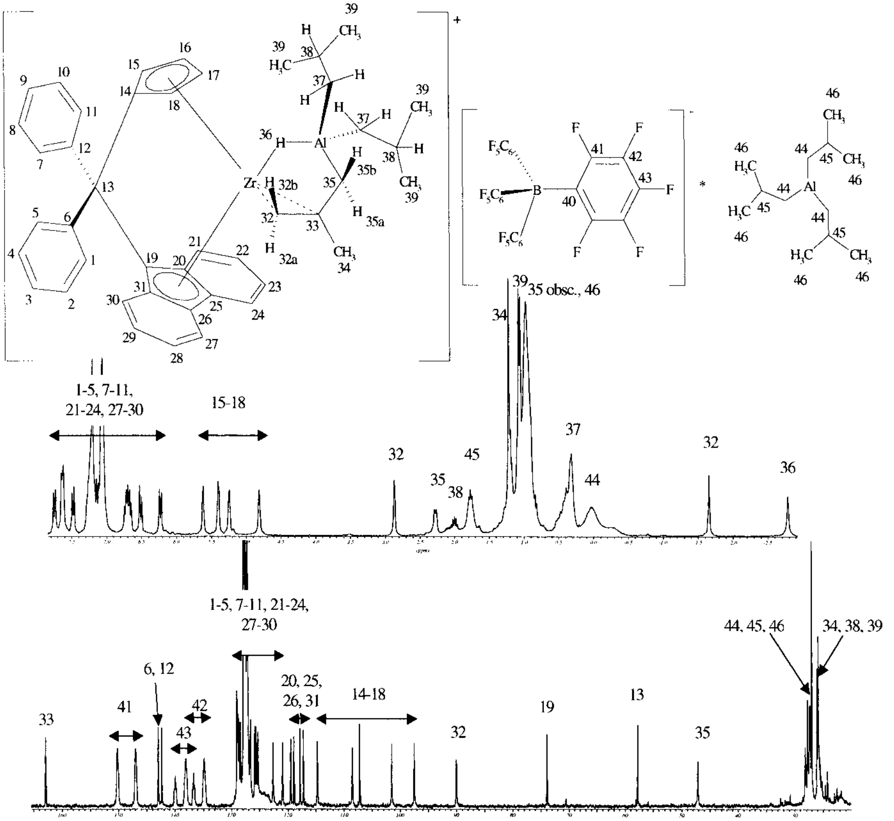


Fig. 4: [$Ph_2C(CpFlu)Zr$-μ-H-μ-(C_4H_7)-$AlBu^i_2$][$B(C_6F_5)_4$]·$AlBu^i_3$ (**A**). ^1H and ^{13}C NMR spectra. Assignment of signals.

The diastereotopic methylene group Zr-CH_2 of the allyl ligand shows characteristic signals for each proton at 2.87 and -1.66 ppm in the ^1H NMR spectrum (Figure 4, peaks 32a and 32b). Alt et al. described and explained similar shifts.[26] Accordingly, the diastereotopic methylene group Al-CH_2 shows the same pattern of singlets at 2.28 ppm and around 1 ppm, but with a smaller upfield shift of the high field resonance (peaks 35a and 35b). The corresponding resonances of the carbon atoms are found at 90.5 ppm, assigned to Zr-CH_2 with a $^1J_{C,H}$ coupling constant of 157.5 Hz, and at 47.7 ppm, assigned to Al-CH_2 with a $^1J_{C,H}$ coupling constant of 129.4 Hz. These data indicate the non-symmetric bonding of the bridging allyl ligand.[27] The chemical shifts and coupling constants are evidence for the sp^2-hybridized nature of the Zr-CH_2 carbon atom, whereas the Al-CH_2 carbon has a strong sp^3 character. There is no evidence for α-agostic interactions with the metal centers because, in this case, the coupling constants would be expected to be lower than 100 Hz.[28]

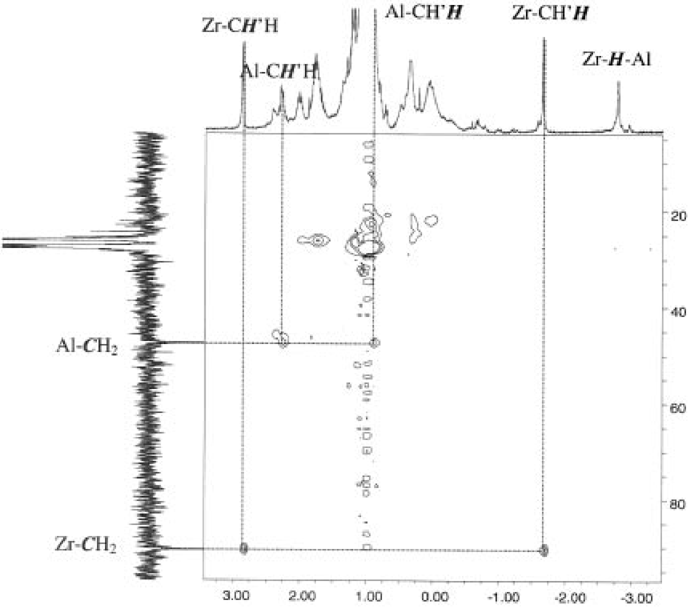


Fig. 5: C, H correlated spectra of **A** (^1H vs ^{13}C DEPT spectra). Assignment of CH_2-allylic resonances.

Results of high temperature NMR experiments, up to 70 °C, showed no change in the resonances in the spectra. No coalescence was detected for the methylene resonances, i.e. there is no rotation nor fluxional ligand exchange (π-allyl / σ-allyl ligand exchange) of the allylic group. Characteristic for a methallylic structure is the resonance at 163.4 ppm (peak 33) of the quarternary allyl carbon atom.[23, 29, 30] The allylic methyl group appears as a singlet at 1.22 ppm in the ^1H NMR and at 26.6 ppm in the ^{13}C NMR (peak 34). Resonances for the two *iso*-butyl groups appear as a multiplet at 2.00 ppm for the methine, as a doublet at 1.06 ppm for the methyl and as a broad signal at 0.32 ppm for the methylene protons (peaks 37 – 39).

Interestingly, there is another $AlBu^i_3$ present in the bottom phase, as can be clearly seen from coupling patterns in the two-dimensional NMR spectra and from integration of the ^1H NMR (peaks 44 – 46). It was not possible to obtain **A** as a solid by removing this unit of TiBA under vacuum. All efforts lead to the decomposition of **A**. The anion $[B(C_6F_5)_4]^-$ does not coordinate to the metallocene cation. In any case, the ^{19}F NMR spectra only show the resonances of non-coordinated $[B(C_6F_5)_4]^-$.[15]

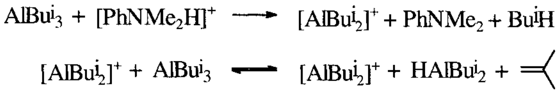
The formation a **A** from a mixture of $Ph_2C(CpFlu)ZrClBu^i$ / TiBA with DMAB must be a multistep reaction and it is assumed that the initial step is the reaction of DMAB and TiBA. The direct reaction of DMAB with 2 or 4 equivalents of TiBA lead to complete degradation of $[B(C_6F_5)_4]^-$ (Formula 3).[15]

$$\begin{tikzcd} \mathrm{AlBu^i_3} + [\mathrm{PhNMe_2H}]^+[\mathrm{B(C_6F_5)_4}]^- \arrow[r] & [\mathrm{AlBu^i_2}]^+[\mathrm{B(C_6F_5)_4}]^- + \mathrm{PhNMe_2} + \mathrm{Bu^iH} \arrow[d] \\ & \mathrm{AlBu^i_{3-x}(C_6F_5)_x} + \mathrm{BBu^i_x(C_6F_5)_{3-x}} \end{tikzcd}$$

Formula 3

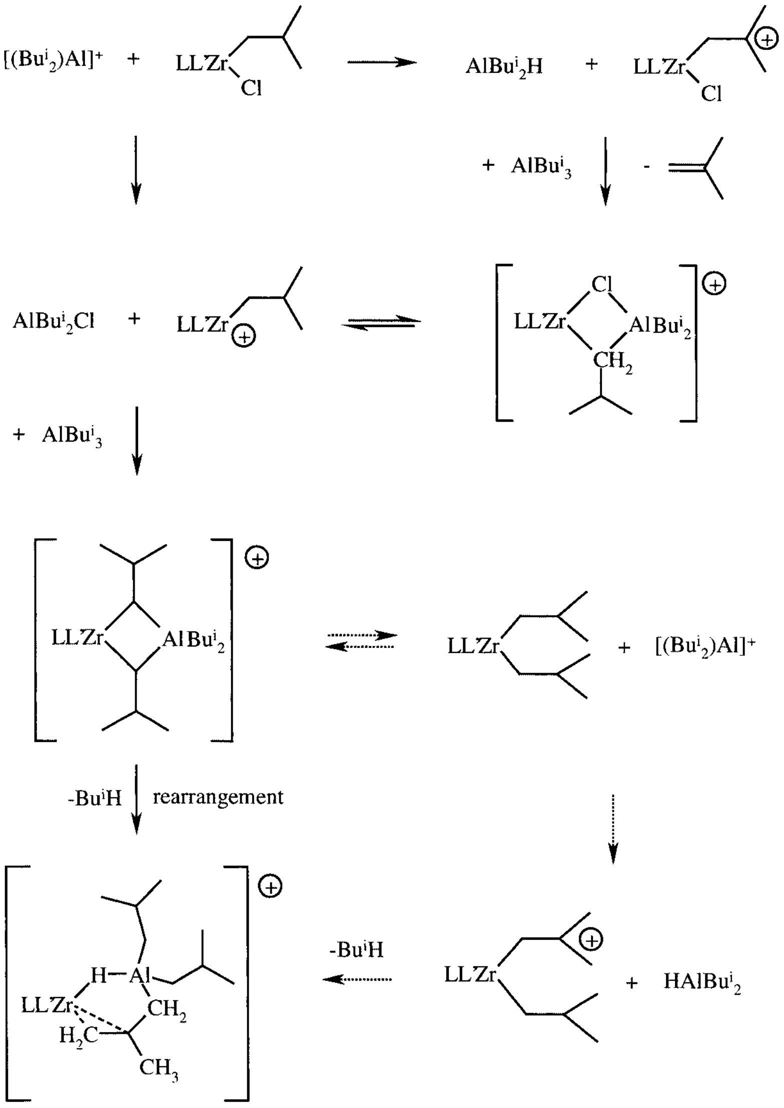
As shown in Formula 3, the formation of $AlBu^i_{3-x}(C_6F_5)_x$ compounds can be attributed to a transient $[Bu^i_2Al]^+$ cation. Bochmann et al. described a similar formation of transient $[AlBu^i_2]^+$ by reaction of $AlBu^i_3$ with $[Ph_3C][B(C_6F_5)_4]$.[14] However, in the $Ph_2C(CpFlu)ZrClBu^i$ / TiBA / DMAB system we observed no degradation of the anion, which may be due to the presence of $Ph_2C(CpFlu)ZrClBu^i$ and high excess TiBA.

The following mechanism is therefore proposed. In a first step, protonation of TiBA leads to evolution of *iso*-butane and generates a transient $[Bu^i_2Al]^+$ cation. It can be assumed that $[Bu^i_2Al]^+$ easily reacts with further TiBA. β-hydride abstraction results in $AlBu^i_2H$ and $[Bu^i_2AlCH_2CMe_2]^+$ which, after the loss of *iso*-butene, regenerates $[Bu^i_2Al]^+$ (Formula 4).



Formula 4

Transient $[AlBu^i_2]^+$ can abstract the chloride or a β-hydride from $Ph_2C(CpFlu)ZrClBu^i$, which is the only metallocene product of the alkylation step independent of the excess $AlBu^i_3$ used. As shown in Scheme 1, both abstractions can lead to $[Ph_2C(CpFlu)ZrBu^i]^+$. In the presence of excess TiBA the dinuclear complex $[Ph_2C(CpFlu)ZrBu^i{\cdot}AlBu^i_3]^+$ can be formed. With the loss of *iso*-butane, this complex can rearrange to form $[Ph_2C(CpFlu)Zr\text{-}\mu\text{-}H\text{-}\mu\text{-}(C_4H_7)\text{-}AlBu^i_2]^+$, as determined by NMR. The rearrangement can be illustrated as shown with dotted arrows in Scheme 1. A similar rearrangement has been described by Bochmann and coworkers.[30] The cationic complex $[Ph_2C(CpFlu)Zr\text{-}\mu\text{-}H\text{-}\mu\text{-}(C_4H_7)\text{-}AlBu^i_2]^+$ that we found can also be seen as the allyl complex $[Ph_2C(FluCp)Zr(\eta^3\text{-methallyl})]^+$ stabilized by $HAlBu^i_2$.



Scheme 1. Proposed formation of $[Ph_2C(CpFlu)Zr\text{-}\mu\text{-}H\text{-}\mu\text{-}(C_4H_7)\text{-}AlBu^i_2]^+$.[a, b]
[a] LL'= $Ph_2C(CpFlu)$. [b] The anion, $[B(C_6F_5)_4]^-$ has been omitted.

High-Pressure Polymerizations of Ethylene

In two series of experiments, the concentrations of TiBA and TEA in the continuously operated reactor were varied. $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAP was used as the catalyst system. It was preactivated outside the reactor with a Zr / Al / B ratio of 1 / 200 / 1.3. The ternary catalyst systems were prepared according to an optimized standard procedure.[20, 31] The setup used for the polymerization of ethylene is described elsewhere.[10, 16, 31] For the experiments described here, the pressure was set to 150 ± 1 MPa, the temperature to 180 ± 3 °C and the residence time to 240 ± 3 s. 90 mol-% of ethylene and 10 mol-% of hexane were continuously fed into the reactor.

With 3 molppm TIBA in the reactor the catalyst system produces about 2500 kg PE/g Zr. Increasing the TiBA concentration to 10 molppm resulted in a sharp increase in productivity, to 10000 kg PE/g Zr. A further increase in the TiBA concentration lead to a decrease in productivity, so that with 420 molppm TiBA, 2000 kg PE/g Zr was obtained. With additional TEA in the reactor, productivity dropped from 2500 to 850 kg PE/g Zr (Figure 6).

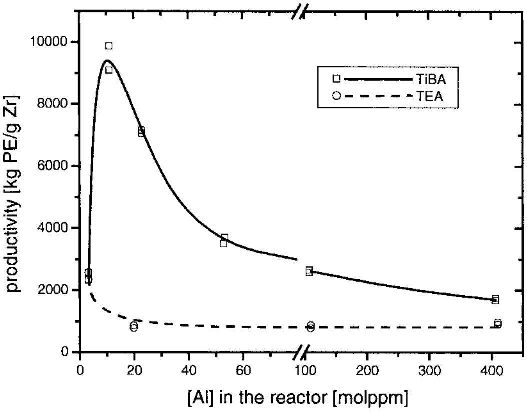


Fig. 6: Influence of [Al] in the reactor on productivity of $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAB (1 / 200 / 1.3).

The polymer samples obtained using $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAB have the highest Mn (42000 g/mol), with a TiBA concentration of 3 to 10 molppm in the reactor of. Up to an [Al] of ca. 30 molppm the polymers show narrow molecular weight distributions (MWDs) with Mw / Mn ≈ 2, typical for single-site catalysts (Figure 7). The Mn of the polymers obtained with TEA were slightly lower and the polydispersities were significantly higher than the molecular weights and polydispersities of the polymers obtained with TiBA (Figure 8). Naga et al. found similar results in propylene polymerizations catalyzed by ternary metallocene catalysts, using TEA and TIBA as cocatalysts.[17]

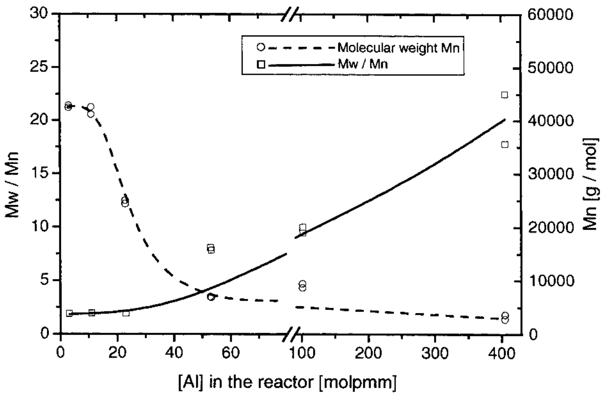


Fig. 7: Influence of [TiBA] in the reactor on Mw / Mn and molecular weight of polyethylene samples obtained with $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAB (1 / 200 / 1.3).

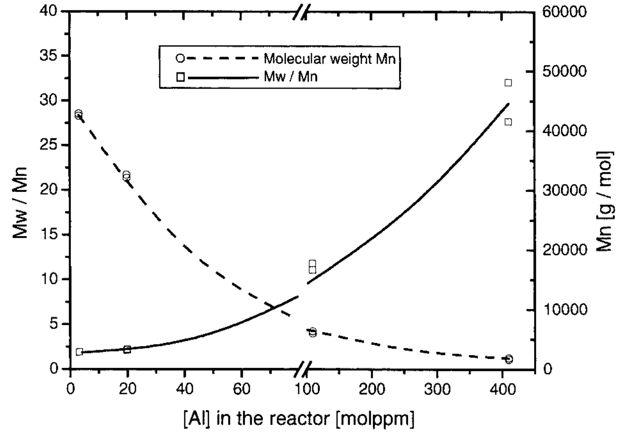


Fig. 8: Influence of [TEA] in the reactor on Mw / Mn and molecular weight of polyethylene samples obtained with $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAB (1 / 200 / 1.3).

At concentrations of more than 400 molppm aluminium alkyl compound in the reactor the molecular weights were below 5000 g/mol and the polydispersity was between 20 and 40 (Figures 7 and 8). Increasing TiBA or TEA concentrations lead to increasing formation of waxes in the reactor, due to ethylene oligomerization at aluminium centers. Therefore with increasing aluminium concentration, the MWDs became bimodal. The MWDs were fitted using the Schulz-Zimm distribution (the function is explained elsewhere[20, 32]). The MWDs of the polymers containing waxes can be described as a superposition of two Schulz-Zimm distributions. The fit of the experimental data was performed by adjusting all parameters of the two Schulz-Zimm distributions by iteration. From these results it is possible to seperately calculate the low- and high molecular mass parts of a MWD (Figure 9).

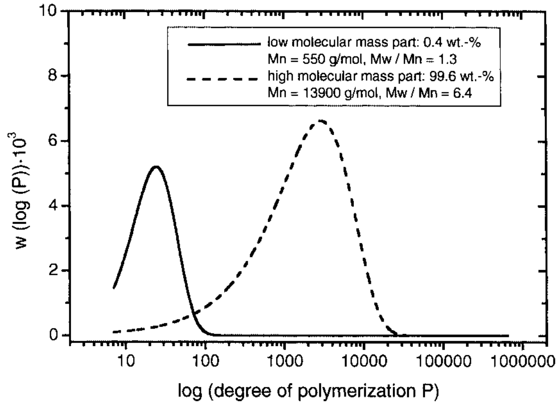


Fig. 9: Calculated wax and polymer peaks with [Al] = 420 molppm in the reactor using two Schulz-Zimm distributions.

The average results of the calculations for different aluminium alkyl compound concentrations in the reactor are summarized in Table 1. The tabulated results show that even for high aluminium concentrations in the reactor the fraction of waxes in the polymer (the low molecular mass part) is very low (<0.5 wt.-%). The amount of oligomers obtained with TEA was twice as high as with TiBA. This proves that TEA has a stronger inclination towards oligomerization of ethylene than TiBA. In all cases the Mn of the high molecular mass part of the MWDs decreased with increasing aluminium concentration and the Mw / Mn ratio increased slightly. This can be attributed to the increasing number of chain transfer reactions to the aluminium. The results show that with TEA, more chain transfer reactions occur than with TiBA. From a linear fit of the reciprocal degree of polymerization ($1/P$) of the high molecular mass part against the concentration of aluminium in the reactor (*[Al]*), the ratio of chain transfer to aluminium and insertion of ethylene, k_{trA} / k_P, can be estimated.[17, 20, 33] The results in Table 2 show that ethylene insertion is much faster than chain transfer to the aluminium. With TEA in the reactor the catalyst system $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAB showed 83300 ethylene insertions before one chain transfer reaction occured. With TiBA in the reactor this ratio increased to 500000 ethylene insertions before one chain transfer reaction occured.

Table 1. Calculations of the high- and low molecular mass parts of polyethylene samples obtained with $Ph_2C(CpFlu)ZrCl_2$ / TiBA / DMAB (1 / 200 / 1.3).

[Al] in the reactor [molppm]		High molecular mass part			Low molecular mass part		
		wt.-%	Mn [g/mol]	Mw/Mn	wt.-%	Mn [g/mol]	Mw/Mn
TiBA	11	100	39800	2.0	-	-	-
	102	99.88	36200	2.3	0.12	750	1.3
	406	99.79	35300	2.2	0.21	620	1.3
TEA	20	100	27000	2.6	-	-	-
	110	99.82	25100	3.7	0.13	790	1.4
	410	99.60	19600	3.5	0.40	510	1.3

Table 2. Estimation of rate constants of chain transfer.

[Al] in the reactor [molppm]		Mn [g/mol]	P	$1/P\cdot10^4$	[ethylene] [mol/l]	$k_{trA}/(k_P\cdot[ethylene])$ [l/mol]	k_{trA}/k_P
TiBA	11	39800	1421	7.0	11.1	$1.88\cdot10^{-7}$	$0.2\cdot10^{-5}$
	102	36200	1293	7.7	12.0		
	406	35300	1261	7.9	11.2		
	$[ethylene]_m^{(a)} = 11.4$						
TEA	20	27000	964	10.4	11.7	$1.00\cdot10^{-6}$	$1.2\cdot10^{-5}$
	110	25100	896	11.2	11.7		
	410	19600	700	14.3	11.3		
	$[ethylene]_m^{(a)} = 11.6$						

(a) averaged ethylene concentration

Conclusions

The NMR results show that the amount of cocatalyst used has a strong influence on the products formed in ternary activated metallocene-based catalyst systems. It is very interesting that the reaction of $Ph_2C(CpFlu)ZrCl_2$ even with high excess of TiBA only leads to monoalkylation and not to dialkylation. The amount of TiBA also influences the formation of the precursor of the active complex. Only mixtures of $Ph_2C(CpFlu)ZrCl_2$ with 100 equivalents of TiBA react with DMAB to only one heterodinuclear metallocene cation indentified as [$Ph_2C(CpFlu)Zr$-μ-H-μ-(C_4H_7)-$AlBu^i{}_2]^+$. It should be mentioned this is not a general result. The type of the aluminium alkyl compound as well as the ligand system of the metallocene precursor play an important role regarding which intermediate and endproducts are formed.[12, 13, 15] The polymerization results make clear that the type and the concentration of the aluminium alkyl compounds used in the reactor strongly influence the productivity and the polymer properties. Interestingly the highest productivities and unique polymers with high molecular masses are obtained with very small amounts of TiBA. This is an important aspect related to reduce costs in industrial applications and clearly shows that every polymerization process still needs to be empirically optimized. From evaluating the MWDs it becomes clear that chain transfer reactions to aluminium centers compared to ethylene insertion only play a minor role in high pressure polymerizations.

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