Activation of *rac*-Me₂Si(ind)₂ZrCl₂ by Methylalumoxane Modified by Aluminum Alkyls: An EPR Spin-Probe, ¹H NMR, and Polymerization Study

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Introduction

Methylalumoxane (MAO), which remains the most widely used co-catalyst for olefin polymerizations with metallocene and post-metallocene catalysts,^[1–3] has been shown to act as a Lewis acid in removing an alkyl ligand from a pre-catalyst

species under formation of a cationic active site.^[4–12] To be effective, MAO must be used in large excess over the transition metal component. For practical applications, it would thus be desirable to decrease the amount of MAO activator. This can be achieved by replacing it—at least in part—by triisobutylaluminum (TIBA): According to results

of Fink and co-workers, the addition of TIBA increases the catalytic activity of several zirconocene/MAO systems.^[13,14] Similar effects of TIBA on propene polymerizations were also reported for some constrained geometry titanium catalysts,^[15,16] while for the system $\text{Me}_2\text{Si}(2\text{-Me-4-PhInd})_2\text{ZrCl}_2/\text{MAO}$, partial replacement of MAO with TIBA prolonged the catalyst activity.^[17] The addition of TIBA increases the activity of several homogeneous zirconocene/MAO systems in the copolymerization of propylene with hex-1-ene.^[18] For gas-phase ethene polymerization with the catalyst system $(^n\text{BuCp})_2\text{ZrCl}_2/\text{MAO}$ on various organic supports, additions of TIBA gave prolonged catalytic activities; at relatively low $[\text{Al}]_{\text{MAO}}/[\text{Zr}]$ ratios they also led to increased activities.^[19] For the catalyst system $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ on a silica gel support, the addition of TIBA has recently likewise been observed to cause a substantial increase of activities for ethene polymerization.^[20]

It would thus appear worthwhile to investigate the mechanisms by which addition of TIBA and other aluminum alkyls affect the co-catalytic action of MAO. In this work, we have set out to characterize, by means of ^1H NMR spectroscopy, the species present in MAO solutions containing added TIBA or triethylaluminum (TEA), and in commercially available modified MAO (MMAO), prepared by hydrolysis of mixtures of TIBA and trimethylaluminum (TMA). The Lewis acidity of these species is studied by the use of electron paramagnetic resonance (EPR) spin-probe techniques.^[11] Finally, we have tried to determine, by ^1H NMR, which cationic complexes are formed upon activation of $(\text{SBI})\text{ZrCl}_2$ ($\text{SBI} = \text{rac-Me}_2\text{Si}(\text{Ind})_2$) with various modified MAO samples, in order to correlate their relative abundance with the effects of these activators on the activity of $(\text{SBI})\text{ZrCl}_2$ -based catalyst systems toward ethene polymerization.

Results and Discussion

^1H NMR Studies of MAO–TIBA Mixtures and of MMAO

The MAO used in our study is prepared from commercial MAO by removal of the solvent and of most of the trimethylaluminum content under vacuum at 20 °C for 20 h and then at 50 °C for 2 h. The solid product obtained is hitherto referred to as MAO. The ^1H NMR spectrum of MAO in toluene- d_8 exhibits a broad signal in the range of 0 to –0.5 ppm, which is attributable to CH_3 protons of $(\text{AlMe}_{(1+2x)}\text{O}_{(1-x)})_n$ clusters, while a more narrow signal at –0.38 ppm belongs to Al_2Me_6 (Figure 1a).^a In MAO–

Figure 1. ^1H NMR spectra (toluene- d_8 , 20 °C, $[\text{Al}] = 0.8 \text{ M}$) of MAO (see Experimental Part) (a) and MAO–TIBA at $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}}$ ratios of 1:10 (b), 1:3 (c), and 1:1 (d), and the ^1H NMR spectrum (toluene- d_8 , 20 °C) of commercial MMAO (AKZO) (e).

TIBA mixtures with $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}}$ ratios of 1:10 to 1:1, the position of this signal shifts from its value of –0.38 ppm in MAO to the value of ca. +0.1 ppm, i.e., towards a position characteristic of bridging Al–Me–Al groups (Figure 1b–d).^[21] MAO–TIBA mixtures at $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}}$ ratios of 1:3 or 1:1 are thus likely to contain mainly species with bridging methyl and terminal isobutyl groups, i.e., mixed dimers of the type $^i\text{Bu}_2\text{Al}(\mu\text{-Me})_2\text{Al}^i\text{Bu}_2$.^[22,23]

In the ^1H NMR spectra of MMAO samples commercially prepared by hydrolysis of TMA/TIBA mixtures (MMAO from AKZO, Figure 1e), this Me signal appears at ca. 0.0 ppm, i.e., close to that of an MAO–TIBA mixture with $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}} = 1:3$. Since the position of this signal can serve as an indicator of the ratio between Al–Me and Al– ^iBu groups in dimers of the type $\text{Al}_2\text{Me}_{(6-x)}(^i\text{Bu})_x$, similar $[\text{Al-Me}]/[\text{Al-}^i\text{Bu}]$ ratios are apparent for these two samples.

Concomitantly with the formation of these mixed $^i\text{Bu}_2\text{Al}(\mu\text{-Me})_2\text{Al}^i\text{Bu}_2$ dimers, some of the Me groups of the MAO clusters, with composition $(\text{AlMe}_{(1+2x)}\text{O}_{(1-x)})_n$,^[24–26] are likely to be replaced by ^iBu groups upon addition of TIBA. Formation of modified MAO clusters of the type $(\text{AlMe}_{(1+2x-y)}^i\text{Bu}_y\text{O}_{(1-x)})_n$ is supported by the observation that, in addition to a broad Me signal and the sharp signals of TIBA, MAO samples to which TIBA

^a A single ^1H NMR resonance is observed at room temperature as a result of fast exchange between bridging and terminal Me groups in Al_2Me_6 . At –70 °C, this peak de-coalesces to separate bridging and terminal methyl signals at 0.03 and –0.53 ppm, respectively, see ref.^[21]

has been added show broad ^1H signals at 1.12 ppm and 0.34 ppm, which are assigned to the methyl and methylene protons, respectively, of ^iBu groups transferred by TIBA to MAO clusters in exchange for Me groups (Figure 1b–d). These two signals are also observed in ^1H NMR spectra of commercially prepared MMAO samples (Figure 1e). Both of these activator systems thus seem to contain rather similar $(\text{AlMe}_{(1+2x-y)}^i\text{Bu}_y\text{O}_{(1-x)})_n$ species.

In distinction to commercial MMAO, however, freshly prepared MAO–TIBA mixtures give rise to some additional signals, marked by asterisks in Figure 1b–d. The relative intensity of these signals increases with increasing $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}}$ ratio. Their smaller line widths, as compared to that of the signals at 1.12 and 0.34 ppm, indicate that these peaks are associated with isobutylaluminumoxane oligomers of a smaller size than those exhibiting the broad peaks at 1.12 and 0.34 ppm.^b The absence of their ^1H NMR signals in MMAO solutions (Figure 1e) would thus indicate that these small oligomeric molecules are present in MMAO in much smaller proportions than in freshly prepared MAO–TIBA mixtures. It remains to be understood in which way their presence and that of the mixed $(\text{AlMe}_{(1+2x-y)}^i\text{Bu}_y\text{O}_{(1-x)})_n$ clusters affect the activation process.

EPR Spin-Probe Study of MAO and MMAO Samples

The TEMPO–MAO System

The Lewis acidic sites of MAO have been characterized in a previous study by use of the stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) and it has been revealed that MAO contains two types of acidic sites, I and II, which give rise to TEMPO adducts with distinct EPR signals.^[11] In order to further characterize the species responsible for these signals, the conditions of our low-temperature experiments have now been changed such that appropriate amounts of TEMPO and of a MAO in toluene are directly and rapidly mixed at ca. -20°C in an EPR tube, and then frozen by immersion into liquid nitrogen and placed into the resonator of the EPR spectrometer. The sample is then allowed to melt and to warm to room temperature over a period of ca. 30 min, with EPR spectra being periodically recorded.

As previously observed, the EPR signal of TEMPO coordinated to Lewis acidic site I dominates in the spectra immediately after interaction between TEMPO and MAO ($[\text{TEMPO}]/[\text{Al}]_{\text{MAO}} = 1:20$, $[\text{Al}]_{\text{MAO}} = 0.2\text{ M}$) (Figure 2a). The present sample preparation method yields EPR spectra of TEMPO coordinated to sites I with better resolution than

Figure 2. EPR spectra (toluene) of MAO–TEMPO with $[\text{TEMPO}]/[\text{Al}]_{\text{MAO}} = 1:20$, $[\text{Al}]_{\text{MAO}} = 0.2\text{ M}$, recorded 5 min after melting in the resonator (a, solid line) and after 20 min at 20°C (b). Simulation of the experimental spectrum with $a_N = 18.6\text{ G}$, $a_{\text{Al}} = 1.0\text{ G}$, line width = 1.0 G (a, dashed line).

those previously reported,^c and with characteristic inflection points, which unambiguously document the existence of hyperfine splitting (hfs) from aluminum (Figure 2a). This spectrum is accurately simulated by a theoretical spectrum (dashed line) with a hfs constant of $a_{\text{Al}} = 1.0 \pm 0.1\text{ G}$.

As previously noted, this signal rapidly disappears at room temperature, and after 15 min only the EPR signal arising from TEMPO coordinated to acidic sites II is observed, which displays an Al hfs with $a_{\text{Al}} = 1.9 \pm 0.1\text{ G}$ (Figure 2b).^d This signal is smaller than that assigned to TEMPO at sites I, but is quite stable at room temperature. Apparently, coordination to sites II stabilizes TEMPO against destruction by aluminum alkyls more efficiently than coordination to sites I. Based on their greater Al hfs, it is proposed that sites II are more Lewis acidic than sites I. Since a similar trend is apparent in the series TEMPO– AlCl_3 ($a_{\text{Al}} = 9.8\text{ G}$), TEMPO– AlCl_2Et ($a_{\text{Al}} = 6.9\text{ G}$), and TEMPO– AlClEt_2 ($a_{\text{Al}} = 3.7\text{ G}$),^[11] sites II ($a_{\text{Al}} = 1.9\text{ G}$) have been assigned to coordinatively unsaturated Al centers in an AlO_2Me environment and sites I ($a_{\text{Al}} = 1.0\text{ G}$) to Al centers in an AlOMe_2 environment.

^c The existence of Al hyperfine splitting for TEMPO coordinated to sites I was tentatively assumed in a previous study,^[11] based on a broadening of the corresponding EPR signal compared to that of uncoordinated TEMPO.

^d Interaction of TEMPO with Al_2Me_6 , TEA, or TIBA in the absence of MAO leads to rapid disappearance of the EPR signal of TEMPO with no other signals being observed.

^b Bravaya et al. have assigned similar sets of signals to relatively small isobutyl alumoxane molecules of the type $(^i\text{Bu})_2\text{Al}-\text{O}-\text{Al}(^i\text{Bu})_2$.^[27]

Figure 3. EPR spectra (toluene) of MAO-TIBA-TEMPO with $[Al]_{TIBA}/[Al]_{MAO} = 1:10$ and $[TEMPO]/[Al] = 1:100$, recorded 2 min after melting in the resonator (a) and after 15 min at 20 °C (b).

The TEMPO-MAO-TIBA System

In MAO-TIBA mixtures prepared with various $[Al]_{MAO}/[Al]_{TIBA}$ and $[TEMPO]/[Al]$ ratios, where $[Al]$ is the total Al concentration, EPR spin probe studies likewise show the presence of two types of Lewis acidic sites, which are denoted here as I_{TIBA} and II_{TIBA} .

First, solutions with $[Al]_{TIBA}/[Al]_{MAO} = 1:10$ are considered. Upon interaction with TEMPO ($[TEMPO]/[Al] = 1:100$), an adduct of TEMPO with site I_{TIBA} is initially observed as the major species in solution, which is characterized by a triplet signal with $a_N = 19.5$ G and an unresolved hfs from aluminum (Figure 3a). This adduct then decays and only a smaller signal attributable to the

adduct of TEMPO with site II_{TIBA} remains observable (Figure 3b). This signal, which is thermally less stable than in the case of TEMPO and MAO alone, shows a multiplet with $a_N = 19.5$ G and $a_{Al} = 4.0$ G (Table 1).

Both types of Lewis acidic sites present in the MAO-TIBA system are thus different from those present in MAO ($a_N = 18.6$ G for I and $a_N = 19.5$ G for I_{TIBA} ; $a_{Al} = 1.9$ G for II and $a_{Al} = 4.0$ G for II_{TIBA}). Relatively small amounts of TIBA (10%) thus appear to change the Lewis acidic sites of MAO substantially. The acidic sites II_{TIBA} in MAO-TIBA mixtures, in particular, appear to be more strongly Lewis acidic than sites II in MAO alone, based on the increased value of $a_{Al} = 4$ G for TEMPO at site II_{TIBA} versus $a_{Al} = 1.9$ G for TEMPO at site II . By analogy with the assignment of the MAO sites II , sites II_{TIBA} can be assigned to coordinatively unsaturated $AlO_2(^iBu)_2$ centers present in mixed $(AlMe_{(1+2x-y)}^iBu_yO_{(1-x)})_n$ clusters.

When the proportions of TIBA are increased from $[Al]_{TIBA}/[Al]_{MAO} = 1:10$ to $[Al]_{TIBA}/[Al]_{MAO} = 1:3$, the value of a_{Al} for the acidic sites II_{TIBA} increases from 4.0 ± 0.1 G to 4.5 ± 0.1 G (Table 1). Apparently, the Lewis acidity of mixed $(AlMe_{(1+2x-y)}^iBu_yO_{(1-x)})_n$ clusters present in these MAO-TIBA mixtures increases further with increasing iBu contents.

According to their respective 1H NMR spectra (Figure 1), the acidic sites of commercially available MMAO are expected to be similar to those in MAO-TIBA systems with an $[Al]_{TIBA}/[Al]_{MAO} = 1:3$ ratio. In agreement with this expectation, TEMPO coordinated to MMAO ($[TEMPO]/[Al] = 1:100$, $[MMAO] = 0.2$ M) exhibits EPR spectra from adducts of TEMPO with acidic sites I_{MMAO} ($a_N = 19.6$ G and unresolved hfs from Al) similar to those for I_{TIBA} . The rather unstable signals of type II_{MMAO} , which become observable after the decay of most of the type I_{MMAO}

Table 1. EPR parameters of TEMPO adducts with Lewis acidic sites of MAO, MAO + alkyl aluminum mixtures, and MMAO.

Sample	Adduct	$g (\pm 0.001)$	$a_N (\pm 0.1)$	$a_{Al} (\pm 0.1)$	$\tau_c \cdot (\times 10^{10})^a$	$R \cdot (\times 10^{10})^b$	n^c
			G	G		m	
MAO	I_{MAO}	2.005	18.6	≤ 1.0	2	6	20
MAO-TIBA (1:10)	II_{MAO}	2.005	19.6	1.9	5.5	8.6	60–65
	I_{TIBA}	2.005	19.5	— ^{d)}			
MAO-TIBA (1:3)	II_{TIBA}	2.005	19.5	4.0	7	9.4	77–87
	I_{TIBA}	2.005	19.4	— ^{d)}			
MMAO (AKZO)	II_{TIBA}	— ^{e)}	— ^{e)}	4.5	7.6	9.6	82–92
	I_{MMAO}	2.005	19.6	— ^{d)}			
MAO-TEA (1:3)	II_{MMAO}	2.005	— ^{e)}	4.4	5.4	8.6	59–67
	I_{TEA}	2.005	19.6	— ^{d)}			
	II_{TEA}	2.005	19.4	2.9			
	II'_{TEA}	— ^{e)}	— ^{e)}	4.2			

^{a)} Correlation time.

^{b)} Radius of MAO oligomers.

^{c)} Mean oligomerization number.

^{d)} Splitting unresolved.

^{e)} Not measured because of interference from (stronger) EPR signals of other adducts.

signals, show a hfs from Al with $a_{\text{Al}} = 4.4$ G, and are thus similar again to those assigned to II_{TIBA} (Table 1).

High $[\text{Al}]_{\text{MAO}}/[\text{Zr}]$ ratios are necessary for an effective activation of metallocene-based catalysts, undoubtedly because of the necessity to provide sufficient amounts of the more strongly Lewis-acidic but less abundant sites II of MAO. The increased Lewis acidity of sites II_{TIBA} in MAO–TIBA mixtures, as compared to that of sites II in MAO alone, is thus likely to contribute to the positive effects of TIBA additions on the co-catalytic activity of MAO.

The TEMPO–MAO–TEA System

A sample with $[\text{Al}]_{\text{TEA}}/[\text{Al}]_{\text{MAO}} = 1:10$ and $[\text{TEMPO}]/[\text{Al}] = 1:100$ displays mainly Lewis acidic sites like those in pure MAO. New acidic sites are observable under these conditions only in minor amounts but become dominant when the proportion of TEA is increased to $[\text{Al}]_{\text{TEA}}/[\text{Al}]_{\text{MAO}} = 1:3$ (Figure 4). They are characterized by the EPR parameters listed in Table 1. Even without precise knowledge concerning the nature of these sites, their larger a_{Al} values indicate that at least sites II'_{TEA} and II''_{TEA} are stronger than sites II of MAO. The addition of TEA, like that of TIBA, thus appears to increase the Lewis acidity of MAO.

Size Evaluation of MAO and MMAO Oligomers

The coordination of TEMPO with large molecules will increase its rotational correlation time τ_c , and will hence change the relative widths and intensities of its EPR signal. Thus the average radius R of MAO oligomers can be estimated by its effect on τ_c , see Equation (1), from the relative

intensities and line widths of the EPR spectrum.^[28,29]

$$\tau_c = \frac{4\pi R^3 \eta}{3kT}, \quad \text{with } \eta \text{ being the solution viscosity} \quad (1)$$

Assuming that a volume of $40\text{--}45 \text{ \AA}^3$ is associated with one Al unit of each $(\text{AlMe}_{(1+2x-y)}\text{Bu}_y\text{O}_{(1-x)})_n$ cluster,^[30] average oligomerization numbers n can be obtained for the species in which TEMPO is coordinated to sites I in MAO and in MAO–TIBA solutions (Table 1). It is seen that the average size of these oligomers is larger for the sample $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}} = 1:10$ than for that with MAO alone, and is even larger for the sample with $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}} = 1:3$.

The n values estimated from the spectra of TEMPO adducts with acidic sites I in a given reaction system correlate with the respective Lewis acidities of sites II , as judged by their a_{Al} values (Table 1). This observation would suggest that acidic sites of both types I and II are present on the same clusters in MAO solutions, and that this is also the case for the solutions of MAO–TIBA, where a higher Lewis acidity of sites II appears to be associated with clusters of greater size.

At any rate, the results of our EPR spin-probe study show with unexpected clarity that rather uniform Lewis acidic sites with distinct a_{Al} values—rather than distributions of these parameters—are present in each of the co-catalyst systems studied.

^1H NMR of $(\text{SBI})\text{ZrCl}_2/\text{MAO}/\text{TIBA}$ and $(\text{SBI})\text{ZrCl}_2/\text{MMAO}$ Systems

In agreement with earlier data,^[7] activation of $(\text{SBI})\text{ZrCl}_2$ with MAO ($[\text{Al}]/[\text{Zr}] = 50$) results in the formation of a mainly heterobinuclear ion pair $[(\text{SBI})\text{Zr}(\mu\text{-Me})_2\text{-AlMe}_2]^+ \cdot [\text{MeMAO}]^-$ (**III**) that is stable for several days at room temperature (Figure 5a, Table 2). Note that in the sample

Figure 4. EPR spectra (toluene) of MAO–TEA–TEMPO with $[\text{Al}]_{\text{TEA}}/[\text{Al}]_{\text{MAO}} = 1:3$ and $[\text{TEMPO}]/[\text{Al}] = 1:100$, recorded after 10 min (a) and after 15 min at 20°C (b). Spectrum (a) is a superposition of the spectra of TEMPO adducts with sites I_{TEA} and II_{TEA} .

Figure 5. ^1H NMR spectra (toluene- d_8 , 20°C) of $(\text{SBI})\text{ZrCl}_2$ –MAO with $[\text{Al}]/[\text{Zr}] = 1:50$ (a) and of $(\text{SBI})\text{ZrCl}_2$ –MAO–TIBA with $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}} = 1:10$ and $[\text{Al}]/[\text{Zr}] = 50$ (b), and $[\text{Al}]/[\text{Zr}] = 200$ (c).

Table 2. Selected ^1H NMR signals for zirconocenium cations **III**, **III'**, and **IV'** (δ , toluene- d_8 , room temperature).

Species	Cp-H	Si(CH ₃) ₂	Al-CH ₃	Zr-CH ₃ -Al
$[\text{rac-SiMe}_2(1\text{-Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$ (III)	6.25, 5.12	0.83	-0.59	-1.26
$[\text{rac-SiMe}_2(1\text{-Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}^i\text{Bu}]^+[\text{Me-(MAO-TIBA)}]^-$ (III')	6.45, 5.30	NF	-0.53	-1.20
$\{[\text{rac-SiMe}_2(1\text{-Ind})_2\text{ZrMe}]^+[\text{Me-(MAO-TIBA)}]^- \}$ (IV')	5.8, 5.2	NF	-	-1.7

in Figure 5a, contact ion pairs $[(\text{SBI})\text{ZrMe}^+ \cdots \text{MeMAO}]^-$ (**IV**) are not observed.

When $(\text{SBI})\text{ZrCl}_2$ is activated with a MAO-TIBA mixture ($[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}} = 1:10$, $[\text{Al}]/[\text{Zr}] = 50$), broadened signals at ca. -1.7 and at 5.3 and 5.8 ppm are assigned to contact ion pairs $[(\text{SBI})\text{ZrMe}^+ \cdots \{\text{Me-(TIBA-MAO)}\}^-]$ (**IV'**) (Figure 5b), where $\{\text{Me-(TIBA-MAO)}\}^-$ denotes the counter ion formed upon Me^- abstraction by modified MAO. Thus, compared to the corresponding system without TIBA (Figure 5a), one observes a dramatic increase of the characteristically broad signals of the contact ion pair **IV'**. This effect can be explained by the TIBA-induced conversion of most of the Al_2Me_6 content of MAO into the mixed species $^i\text{BuMeAl}(\mu\text{-Me})_2\text{Al}^i\text{BuMe}$ and $^i\text{Bu}_2\text{Al}(\mu\text{-Me})_2\text{Al}^i\text{Bu}_2$ mentioned above. Because of their sensitivity to steric interactions with the zirconocene ligand framework,^[31] adducts of the cation $[(\text{SBI})\text{ZrMe}]^+$ with mixed aluminum alkyls such as Al^iBuMe_2 and, in particular, with $\text{Al}^i\text{Bu}_2\text{Me}$ will undoubtedly be less stable than those with AlMe_3 (Figure 7), such that the cation $[(\text{SBI})\text{ZrMe}]^+$ will remain preferentially associated with its MAO-derived counter anion.

When the $[\text{Al}]/[\text{Zr}]$ ratio is increased to 200 with $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}}$ remaining at 1:10 (Figure 5c), the proportion of ion pairs denoted as **III** and **III'** increases at the expense of contact ion pairs **IV'**, presumably because of the increased concentration of mixed Al alkyls, which eventually overcomes their disadvantage with respect to adduct formation with $[(\text{SBI})\text{ZrMe}]^+$. Species **III'** dominates, especially at $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}} = 1:3$ and $[\text{Al}]/[\text{Zr}] = 200$ –500 and in solutions containing MMAO (Figure 6c–e). Based on its similarity to the signal set of **III**, species **III'** is assigned to a heterobinuclear cation $[(\text{SBI})\text{Zr}(\mu\text{-Me})_2\text{AlMe}^i\text{Bu}]^+$ where one of the terminal methyl groups has been replaced by an ^iBu group (Table 2).^c The formation of such a cation would be expected in these TIBA-containing reaction systems, where AlMe_x units tend to be converted into mixed $\text{AlMe}_{(x-1)}^i\text{Bu}$ species.

In addition, the presence of isobutene, apparent from its characteristic signals at 4.74 and 1.63 ppm, indicates that metal hydrides, i.e., Zr-H and/or Al-H species, are also

likely to be present in these reaction systems. Further analysis of these polymerization activities is to be focused, however, on the metal alkyl species.

Polymerization Studies

The kinetics of ethylene polymerization catalyzed by $(\text{SBI})\text{ZrCl}_2$ activated by MAO, MMAO, MAO-TIBA, and MAO-TEA has been studied by measuring the ethylene consumption by each of the catalyst systems in toluene solution at 50 °C (see Experimental Part). For all activators used, the catalytic activity decreases with time (Figure 8). The deactivation time and the initial maximum activity remarkably depend on the type of the activator. The $(\text{SBI})\text{ZrCl}_2/(\text{MAO-TEA})$ system exhibits the highest initial activity ($600 \text{ kg PE} \cdot (\text{mol Zr} \cdot \text{h})^{-1}$) as compared to

Figure 6. ^1H NMR spectra (toluene- d_8 , 20 °C) of $(\text{SBI})\text{ZrCl}_2$ -MMAO (AKZO) with $[\text{Al}]/[\text{Zr}] = 20$ (a), 50 (b), 200 (c), and 500 (d), and of $(\text{SBI})\text{ZrCl}_2$ -MAO-TIBA with $[\text{Al}]_{\text{TIBA}}/[\text{Al}]_{\text{MAO}} = 1:3$ and $[\text{Al}]/[\text{Zr}] = 500$ (e). Asterisks mark peaks of $(\text{SBI})\text{ZrClMe}$.

^c The presence of one terminal Me group in species **III'** is indicated by a ^1H NMR signal at ca. -0.53 ppm. The presence of two terminal ^iBu groups appears to be unfavorable, because of their steric interactions with the ligand framework (c.f. Figure 7).

Figure 7. Steric interactions in adducts of (SBI)ZrMe⁺ with AlMe₃ (left), with Me₂Al^{*i*}Bu (middle) and with MeAl^{*i*}Bu₂ (right).

that for (SBI)ZrCl₂/MAO (290 kg PE · (mol Zr · h)⁻¹) and (SBI)ZrCl₂/(MAO–TIBA) (400 kg PE · (mol Zr · h)⁻¹). However, for (SBI)ZrCl₂/(MAO–TEA) the initial activity drops by a factor of 10 within 1 min, whereas for (SBI)ZrCl₂/MAO and (SBI)ZrCl₂/(MAO–TIBA) this drop takes 2 and 5 min, respectively (Figure 8).

As could be expected from the similarities of the ¹H NMR spectra of the respective catalyst systems (Figure 6d,e), the kinetic curves for (SBI)ZrCl₂/(MAO–TIBA) and (SBI)ZrCl₂/MMAO are rather similar (Figure 8). However, the activity of (SBI)ZrCl₂/MMAO is somewhat smaller than that for (SBI)ZrCl₂/(MAO–TIBA). The reason of this difference is still unclear.

We have further investigated the effect of additions of TEA and TIBA to MAO on the polyethylene yield for the first 3 min of polymerization (Table 3), by calculation from the ethylene consumption. It is seen that the maximum polyethylene yield is observed at a [Al]_{TIBA}/[Al]_{MAO} ratio of 1:3 and a [Al]_{total}/[Zr] ratio of 200. The increase of the [Al]_{total}/[Zr] ratio from 200 to 400 at [Al]_{TIBA}/[Al]_{MAO} = 1:3, however, decreases the polymer yield (Table 3, entries 3

and 7). In general, at a [Al]_{total}/[Zr] ratio of 400, the effect of added trialkylaluminum becomes rather small (cf. Table 3, entries 6, 7, and 11).

At a [Al]_{TEA}/[Al]_{MAO} ratio of 1:10, no pronounced effect of TEA on the co-catalytic activity of MAO is observed, whereas at [Al]_{TEA}/[Al]_{MAO} = 1:3, the co-catalytic activity increases by a factor of 40 (Table 3, entries 8 and 9). These data are in agreement with EPR spin-probe studies, where for a MAO–TEA sample, the new Lewis acidic sites different from those present in neat MAO were observed only at [Al]_{TEA}/[Al]_{MAO} = 1:3 (Figure 4). With regard to practical applications, however, the use of TEA as a MAO modifier is hardly possible because of the rapid decay of the zirconocene catalyst. Only TIBA appears to be of primary interest as a co-catalyst additive under practical aspects. Our polymerization data are in good agreement with the previous results on the effect of TIBA on the polymerization activity of various zirconocene/MAO systems.^[13–20]

Figure 8. The kinetic profile of ethylene polymerization with (SBI)ZrCl₂, activated with (1) MAO, (2) MAO–TEA ([Al]_{TEA}/[Al]_{MAO} = 1:3), (3) MAO–TIBA ([Al]_{TIBA}/[Al]_{MAO} = 1:3), and (4) MMAO.

Table 3. Effects of TIBA and TEA additions on the activity of Me₂SiInd₂ZrCl₂/MAO catalyst systems for the polymerization of ethene.

Entry ^{a)}	[Al] _{MAO} /[Zr]	AlR ₃ added	[Al](AlR ₃)/[Al](MAO)	PE yield ^{d)} g
1	200	–	0	0.1
2	200	TIBA	1:10	2.4
3	200	TIBA	1:3	8.7
4	200	TIBA	1:1	5.7
5	0	TIBA ^{b)}	–	0
6	400	–	0	4.6
7	400	TIBA	1:3	5.7
8	200	TEA	1:10	0.1
9	200	TEA	1:3	4.2
10	400	TEA	1:3	4.6
11	500 ^{c)}	–	–	4.7

^{a)} Polymerization conditions: [(SBI)ZrCl₂] = 20 μmol · L⁻¹, 120 mL of toluene, 50 °C, P_{C₂H₄} = 2 bar.

^{b)} TIBA/Zr = 200.

^{c)} MMAO was used.

^{d)} PE yield was calculated from the ethene consumption for the first 3 min of polymerization.

Experimental Part

Materials

Toluene was dried over molecular sieves (4 Å), purified by refluxing over sodium metal, and distilled under dry nitrogen. Other solvents were distilled over sodium or sodium-benzophenone under nitrogen and degassed under vacuum. All experiments were carried out in sealed high-vacuum systems using breakseal techniques. *rac*-(SBI)ZrCl₂ was synthesized as described.^[32] 2,2,6,6-Tetramethyl-piperidine-*N*-oxide (TEMPO) was purchased from Aldrich and used as a 10⁻²–10⁻³ M toluene solution. Triisobutylaluminum (TIBA) in toluene solution (commercial product, ≤2% Al as DIBAH, total Al content 1.6 M) was diluted prior to use to obtain a 0.16 M toluene solution. Trimethylaluminum (TMA) was purchased from Aldrich. Methylaluminoxane (MAO) was obtained from Crompton GmbH (Bergkamen) as a toluene solution (total Al content 1.8 M, Al as AlMe₃ 0.5 M). MMAO (MAO, modified with TIBA) was purchased from AKZO as a solution in heptane (total Al content 7.1 wt.-%).

¹H NMR spectra were recorded at 250.130 MHz, on a Bruker DPX-250 MHz NMR spectrometer. Typical operating conditions for ¹H NMR measurements: spectral width 5 kHz, spectrum accumulation frequency 0.5–0.2 Hz, number of transients 32–64, ca. 30° pulse at 2 μs. For calculations of ¹H shifts, the resonance of the CD₂H-group of the toluene solvent was taken to be 2.11 ppm.

EPR spectra were recorded on a Bruker ER-200D spectrometer at 9.3 GHz, with a modulation frequency of 100 kHz, and a modulation amplitude of 1 G. Measurements were performed in glass tubes (*d* = 5 mm). Periclase crystal (MgO) with impurities of Mn²⁺ and Cr³⁺, which served as a side reference, was placed into the second compartment of the dual cavity. EPR spectra were simulated using the EPR1 program described in ref.^[33]

Preparation of MAO Samples

(MAO-TEA) and (MAO-TIBA) Samples

The solid product prepared from commercial MAO by removal of the solvent and of most of the trimethylaluminum content under vacuum at 20 °C for 20 h and then at 50 °C for an additional 2 h (polymeric MAO with a total Al content of 40 wt.-% and a residual AlMe₃ content of ca. 1 wt.-%) was used for the preparation of the samples. The obtained solid product was dissolved in toluene solutions of TIBA (TEA) to obtain mixtures with the desired Al_{MAO}/Al_{TIBA} or Al_{MAO}/Al_{TEA} molar ratios. The thus prepared mixtures proved to be rather stable and could be used for NMR and EPR measurements within 1–2 d of preparation. For NMR investigations, toluene was replaced with toluene-*d*₈ by drying the prepared (MAO-TIBA(TEA)) samples and re-dissolving the solid residue in toluene-*d*₈.

Ethylene Polymerization Studies

Polymerization was performed in a 1.0 L steel reactor, equipped with magnetic stirrer, a water jacket for temperature control,

and an automatic computer-controlled system for ethylene feed and for recording the ethylene consumption vs time. The error bars for the repeated measurements were typically within the range of ±10%.

The reactor was evacuated at 80 °C, cooled to 20 °C, and then charged with 120 mL of a toluene solution containing (SBI)ZrCl₂ (2.4 μmol) and the required amount of the activator (MAO, MAO-TEA (TIBA)). The reaction mixture was heated to 50 °C, saturated with ethylene to a total pressure of 2 bar, and the ethylene consumption measurement was started. During the reaction time (10 min) the ethylene pressure, stirring speed, and temperature were kept constant. After 10 min, the reactor was vented, and the polymer was isolated by filtration and dried to constant weight at ambient temperature.

Conclusion

From our results we can conclude that the positive effects of TIBA additions on the activity of the catalyst system (SBI)ZrCl₂/MAO are likely to result from a combination of at least two factors:

- The formation of mixed aluminum alkyl dimers such as ⁱBu₂Al(μ-Me)₂AlⁱBu₂ in which all Al centers acquire a coordination number of 4, and the reduced tendency of the arising mixed aluminum alkyls MeAlⁱBu₂ and Me₂AlⁱBu to convert the cation [(SBI)ZrMe]⁺ from its contact ion pair **IV'** into the presumably less reactive heterobinuclear species **III** and **III'**.
- The formation of mixed MAO clusters of the type (AlMe_(1+2x-y)Sup_(1-x))_n, which contain Al centers of higher Lewis acidity than the corresponding clusters of MAO alone. These mixed MAO clusters are thus likely to afford less coordinating counter ions than their unmodified MAO counterparts upon abstraction of Me⁻ or ⁱBu⁻ anions from (SBI)ZrClMe or (SBI)ZrClⁱBu present in the reaction solution. While in many respects the commercially prepared MMAO resembles MAO-TIBA mixtures with [Al]_{TIBA}/[Al]_{MAO} = 1:3, some differences are apparent, e.g., with respect to the absence of relatively sharp signals indicative of smaller ⁱBuAl clusters. Implications of these observations with respect to the nature of the species particular for each of these activator systems and their respective role in catalyst activation thus deserve further study.

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