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^{1}H and ^{13}C NMR Studies of Cationic Intermediates Formed upon Activation of "Oscillating" Catalyst (2-PhInd)$_2$ZrCl$_2$ with MAO, MMAO, and AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$

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The conformationally dynamic unbridged metallocene (2-PhInd)$_2$ZrCl$_2$ (**1-Cl**) was activated with methylaluminoxane (MAO), modified methylaluminoxane (MMAO), and AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$. The following ion pairs were characterized by ^{1}H and ^{13}C NMR: [(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**III**), [(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**III′**), [(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe^{i}Bu]$^+$[Me-MAO]$^-$ (**III$_{\mathbf{Me}i\mathbf{Bu}}$**), [(2-PhInd)$_2$Zr($\mu$-Me)$_2$Al^{i}Bu$_2$]$^+$[Me-MAO]$^-$ (**III$_{i\mathbf{Bu}i\mathbf{Bu}}$**), and [(2-PhInd)$_2$ZrMe$^+$···Me-MAO$^-$] (**IV**). In the temperature range −50 to 20 °C, the rotation of indenyl ligands of complexes **III**, **III′**, and **III$_{\mathbf{Me}i\mathbf{Bu}}$** is faster than the evaluated rate of propylene insertion, whereas for **III$_{i\mathbf{Bu}i\mathbf{Bu}}$** the rate of indenyl ligand rotation is comparable to or slower than the rate of propylene insertion. The ion pair **III$_{i\mathbf{Bu}i\mathbf{Bu}}$** demonstrates the fundamental possibility of the existence of intermediates with the "locked" conformation of 2-PhInd ligands in **1-Cl**/MAO or **1-Cl**/MMAO systems. For the catalytic system **1-Cl**/MAO, both outer sphere ion pair **III** and inner sphere ion pair **IV** are present in the reaction solution at high [Al]$_{\mathrm{MAO}}$/[Zr] ratios. For the catalytic system **1-Cl**/MMAO, the concentration of inner sphere ion pairs of type **IV** is much smaller (below the NMR detection limit), and only outer sphere ion pairs **III$_{\mathbf{Me}i\mathbf{Bu}}$** and **III$_{i\mathbf{Bu}i\mathbf{Bu}}$** are observed.

Introduction

The so-called "oscillating" catalysts (bis(2-Ar-indenyl)zirconocenes), which produce elastomeric polypropylenes, are an intriguing class of olefin polymerization catalysts.[1−3] Apparently, formation of stereoblock elastomeric plastics is a result of the dynamic character of the active species, the cation of general formula [(2-Ar-indenyl)$_2$ZrP]$^+$ (Ar = aryl; P = polymeryl).[1−4] According to the hypothesis of Waymouth, the active species "oscillates" between a "*rac*-like" (isotactic-selective) and a "*meso*-like" (nonstereoselective) conformation at a frequency intermediate between those of monomer insertion and chain transfer.[1,2,5] Alternatively, Busico has proposed that the achiral *meso*-isomer can be disregarded as a source of the atactic stereosequences, and the generation of isotactic and atactic stereosequences is a result of the interconversion of chiral *rac*-isomers at a rate competitive with propylene insertion.[4] For one of the *rac*-isomers, the rate of indenyl ring rotation is faster than propylene insertion (atactic block is formed); for another *rac*-isomer, this rotation is slower than propylene insertion (isotactic block is formed). The key point of this hypothesis is the assumption that isomers differ by the nature of the counterions. For some counterions, their association with [(2-Ar-indenyl)$_2$ZrP]$^+$ leads to a locked conformation (the ligand rotation is restricted), leading to long isotactic sequences.

To provide more evidence for the accessible isomers and their conformational dynamics, direct observation of the active species would be highly informative. However, detection of the propagating species [(2-Ar-indenyl)$_2$ZrP]$^+$ (P = polymeryl) is complicated by rapid chain transfer and β-hydride elimination.[5] Nevertheless, one can expect that the important information on the dynamics of cationic intermediates could be derived from the study of the conformational behavior of the initiating active species of the type [(2-Ar-indenyl)$_2$ZrMe]$^+$. Recently, the conformationally dynamic unbridged metallocene bis(2-phenylindenyl)dimethylzirconium (2-PhInd)$_2$ZrMe$_2$ (**1-Me**) has been activated with trispentafluorophenylborane (B(C$_6$F$_5$)$_3$) or trityl tetrakispentafluorophenylborate ([Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$) to yield ion pairs [(2-PhInd)$_2$ZrMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**2a**) and [(2-PhInd)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**2b**), respectively. NMR analysis of metallocene cations of **2a** and **2b** provides no evidence that the association of the anions with the (2-PhInd)$_2$ZrMe$^+$ cations leads to locked conformations at temperatures above −40 °C.[5]

However, in the case of MAO as activator, ion pairs different from **2a** and **2b** are expected: heterobinuclear ion pair [(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**III**) and contact ion pair [(2-PhInd)$_2$ZrMe$^+$···Me-MAO$^-$] (**IV**).[6−9] It is important

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(1) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217.

(2) Lin, S.; Waymouth, R. M. *Acc. Chem. Res.* **2002**, *35*, 765.

(3) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(4) Busico, V.; Castelli, V. V. A.; Aprea, P.; Cipullo, R.; Segre, A.; Talarico, G.; Vacatello, M. *J. Am. Chem. Soc.* **2003**, *125*, 5451.

(5) Lincoln, A. L.; Wilmes, G. M.; Waymouth, R. M. *Organometallics* **2005**, *24*, 5828.

(6) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247.

(7) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2000**, *201*, 558.

(8) Bryliakov, K. P.; Semikolenova, N. V.; Yudaev, D. V.; Zakharov, V. A.; Brintzinger, H.-H.; Ystenes, M.; Rytter, E.; Talsi, E. P. *J. Organomet. Chem.* **2003**, *683*, 92.

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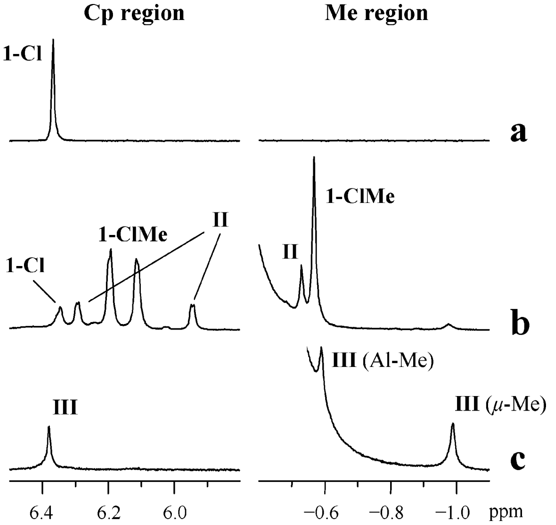

Figure 1. ^{1}H NMR spectra of **1-Cl** (a) and **1-Cl**/MAO samples (b, c): Al:Zr = 10 (b), Al:Zr = 100 (c) ([**1-Cl**] = 0.02 M (a), [**1-Cl**] = 0.04 M (b), [**1-Cl**] = 8×10^{-3} M (c), toluene-d_8, 20 °C).

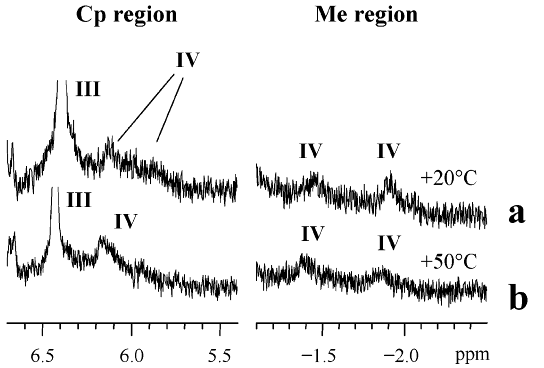

Figure 2. ^{1}H NMR spectra of the **1-Cl**/MAO sample at 20 °C (a) and 50 °C (b) ([**1-Cl**] = 8×10^{-3} M, Al:Zr =100, toluene-d_8).

to study the conformational behavior of **III** and **IV**. It was shown previously that **1-Me** and (2-PhInd)$_2$ZrCl$_2$ (**1-Cl**), when activated with modified MAO (MMAO) containing isobutylaluminum groups, yielded higher tacticity polypropylenes than **1-Me** and **1-Cl** activated by MAO (containing only methylaluminum groups).[10] It is interesting to compare the conformational behavior of cationic intermediates formed upon activation of **1-Cl** with MAO and MMAO. In this work, we have undertaken a ^{1}H and ^{13}C NMR study of ion pairs formed in the catalytic systems **1-Cl**/MAO, **1-Cl**/MMAO, and **1-Cl**/AlMe$_3$/[CPh$_3$]$^+$-[B(C$_6$F$_5$)$_4$]$^-$ in order to evaluate the possibility of the formation of intermediates with a locked conformation of the 2-PhInd ligands.

Results and Discussion

Catalytic Systems 1-Cl/MAO and 1-Cl/AlMe$_3$/[Ph$_3$C]$^+$-[B(C$_6$F$_5$)$_4$]$^-$. The ^{1}H NMR spectrum of **1-Cl** exhibits a singlet (4H) at δ ~6.4 ppm for the cyclopentadienyl (Cp) protons in the temperature range −50 to 50 °C (Figure 1a). This observation is consistent with the known rapid rotation of the indenyl ligands in this temperature range. Even for the bulkier precatalyst bis[2-(3,5-di-*tert*-butylphenyl)indenyl]dimethylzirconium, indenyl ligands rotate at a rate of 94 700 s^{-1} at −78 °C.[11]

The addition of a relatively small amount of MAO ([Al]$_{MAO}$/[Zr] = 10) to the solution of **1-Cl** in toluene leads mainly to the monomethylation of the starting complex with the formation of complex (2-PhInd)$_2$ZrClMe (**1-ClMe**). At 20 °C this complex exhibits two signals for the Cp protons at δ 6.19 (d, 2H, J_{HH} = 1.7 Hz) and 6.11 (d, 2H, J_{HH} = 1.7 Hz) due to nonequivalence of η^5-ligands, and a signal at δ −0.57 (s, 3H) for Zr-CH$_3$ protons (Figure 1b, Table 1).[12] **1-ClMe** was prepared quantitatively *in situ* upon interaction of **1-Cl** with a 10-fold excess of AlMe$_3$. In the temperature range −50 to 50 °C, the positions of two Cp signals of the **1-ClMe** only slightly change. In the case of the locked conformation of ligands, four peaks for the Cp protons of **1-ClMe** should be observed. Thus, rapid rotation of indenyl ligands takes place in complex **1-ClMe** in the temperature range considered.

Noteworthy, besides the peaks of **1-ClMe**, the ^{1}H NMR spectrum of Figure 1b exhibits weaker peaks of complex **II** at δ 6.29 (d, 2H, J_{HH} = 1.6 Hz) and 5.94 (d, 2H, J_{HH} = 1.6 Hz) for the Cp protons and a signal at δ −0.53 (s, 3H) for Zr-CH$_3$ protons. **II** was not observed upon interaction of **1-Cl** with AlMe$_3$. Interaction of zirconocenes (L$_2$ZrMe$_2$) with MAO at low [Al]$_{MAO}$/[Zr] ratios is known to give homobinuclear ion pairs [L$_2$ZrMe(μ-Me)L$_2$ZrMe]$^+$[Me-MAO]$^-$.[6,7] For the catalytic system Cp$_2$TiCl$_2$/MAO at low [Al]$_{MAO}$/[Ti] ratios, homobinuclear ion pairs of the type [Cp$_2$TiMe(μ-Cl)Cp$_2$TiCl]$^+$[Me-MAO]$^-$ (**II$_1$**), [Cp$_2$TiMe(μ-Cl)Cp$_2$TiMe]$^+$[Me-MAO]$^-$ (**II$_2$**), and [Cp$_2$TiMe(μ-Me)Cp$_2$TiMe]$^+$[Me-MAO]$^-$ (**II$_3$**) can be observed.[9] On the basis of relative integral intensities of Cp and Zr-CH$_3$ peaks, **II** could be assigned to the ion pair [(2-PhInd)$_2$ZrMe-(μ-Cl)(2-PhInd)$_2$ZrMe]$^+$[Me-MAO]$^-$. Further studies are needed to verify this assumption.

In conditions approaching those of real polymerization ([Al]$_{MAO}$/[Zr] > 100), heterobinuclear ion pair [(2-PhInd)$_2$Zr-(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**III**) and contact ion pair [(2-PhInd)$_2$ZrMe$^+$···Me-MAO$^-$] (**IV**) became the predominant species in solution (Figures 1c and 2). The proportion of **III** increases with the increase of the [Al]$_{MAO}$/[Zr] ratio, and at [Al]$_{MAO}$/[Zr] ≈ 500, complex **III** prevailed in the reaction solution. The ^{1}H NMR spectrum of **III** (toluene-d_8, 20 °C) displays a singlet (4H) at δ 6.39 for the Cp protons and singlets at δ −0.58 (6H) and −0.97 (6H) for Al-Me and Zr-Me-Al protons, respectively (Figure 1c, Table 1). The ^{13}C NMR spectrum of **III** exhibits a sharp peak of the Zr-Me-Al carbon at δ 41.20 (J^1_{CH} = 113 Hz) (see Supporting Information). The ^{1}H NMR spectrum of **III** is similar to that of [(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**III′**) prepared by interaction of **1-Cl** with AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ ([Zr]:[Al]:[B] = 1:50:1.2) in toluene-d_8 at 20 °C (Table 1). In the temperature range −50 to 50 °C, no decoalescence of the resonances of **III** and **III′** Cp protons was observed. We conclude that indenyl ligands of **III** and **III′** rapidly rotate in the temperature range −50 to 50 °C.

In contrast to the outer sphere ion pair **III** exhibiting relatively sharp and well-observed NMR signals, the ^{1}H and ^{13}C NMR resonances of the contact ion pair **IV** are broadened due to direct interaction of (2-PhInd)$_2$ZrMe$^+$ with nonuniform [Me-MAO]$^-$ counterions (Figure 2). At 20 °C, **IV** exhibits broadened signals from Cp protons at about δ 6.1 and 5.9 and broadened signals from Zr-CH$_3$ protons at about δ −1.4 and −1.9 (Figure 2a).

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(9) Bryliakov, K. P.; Talsi, E. P.; Bochmann, M. *Organometallics* **2004**, *23*, 149.

(10) Wilmes, G. M.; Polse, J. L.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 6766.

(11) Wilmes, G. M.; France, M. B.; Lynch, S. R.; Waymouth, R. M. *Organometallics* **2004**, *23*, 2405.

(12) Table 1 incorporates also the ^{1}H NMR data for ion pairs formed in the (SBI)ZrCl$_2$/MAO system (SBI = *rac*-Me$_2$Si(Ind)$_2$) for comparison.

Table 1. Selected ^{1}H NMR Chemical Shifts (ppm, 20 °C, toluene-d_8) for Complexes Formed upon Activation of (2-PhInd)$_2$ZrCl$_2$ and *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ with MAO and AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$

no.	species	Cp	Zr-Me	μ-Me	Al-Me
1	(2-PhInd)$_2$ZrCl$_2$ (**1-Cl**)	6.37			
2	(2-PhInd)$_2$ZrClMe (**1-ClMe**)	6.19^a, 6.11^a	−0.57		
3	[(2-PhInd)$_2$ZrMe(μ-Cl)(2-PhInd)$_2$ZrMe]$^+$[Me-MAO]$^-$ (**II**)	6.29^b, 5.94^b	−0.53		
4	[(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ (**III**)	6.39		−0.97^c	−0.58
5	[(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**III′**)	6.45		−1.01	−0.67
6	[(2-PhInd)$_2$ZrMe$^+$···Me-MAO$^-$] (**IV**)^d	6.1, 5.9	−1.4^e, −1.9^e		
7	[*rac*-Me$_2$Si(Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$	6.27^f, 5.14^f		−1.28	−0.62
8	[*rac*-Me$_2$Si(Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$	6.10^g, 5.00^g		−1.39	−0.72
9	[*rac*-Me$_2$Si(Ind)$_2$ZrMe$^+$···Me-MAO$^-$]^d	5.8^h, 5.2^i	−1.6^j		

[a] Doublet with $J_{HH} = 1.7$ Hz. [b]Doublet with $J_{HH} = 1.6$ Hz. [c]Respective ^{13}C peak of μ-Me carbons is at 41.20 (q, $J^1_{CH} = 113$ Hz). [d]Broad signals. [e]$\Delta\nu_{1/2} \approx 30$ Hz. [f]Doublet with $J_{HH} = 2.8$ Hz. [g]Doublet with $J_{HH} = 3.0$ Hz. [h]$\Delta\nu_{1/2} \approx 20$ Hz. [i]$\Delta\nu_{1/2} \approx 45$ Hz. [j]$\Delta\nu_{1/2} \approx 60$ Hz.

Table 2. Selected ^{1}H NMR Chemical Shifts, δ, for Complexes Formed upon Activation of (2-PhInd)$_2$ZrCl$_2$ with MMAO in Toluene-d_8 and *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ with MAO/Al^{i}Bu$_3$ in Benzene-d_6

no.	species	T, °C	Cp	μ-Me	Al-Me
1	[(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe^{i}Bu]$^+$[Me-MAO]$^-$ (**III$_{\mathbf{Me}\boldsymbol{i}\mathbf{Bu}}$**)	−10	6.43, 6.31	−0.95, −1.08	−0.53
		0	6.45, 6.33	−0.92, −1.05	−0.53
		10	6.47, 6.35	−0.90, −1.03	−0.54
		20	6.49, 6.37	−0.88, −1.00	−0.54
2	[(2-PhInd)$_2$Zr(μ-Me)$_2$Al^{i}Bu$_2$]$^+$[Me-MAO]$^-$ (**III$_{\boldsymbol{i}\mathbf{Bu}\boldsymbol{i}\mathbf{Bu}}$**)	−10	6.38, 6.34^a	−1.00	
		0	6.40, 6.37^b	−0.98	
		10	6.40^c	−0.95	
		20	6.42^d	−0.93	
3	[*rac*-Me$_2$Si(Ind)$_2$Zr(μ-Me)$_2$AlMe^{i}Bu]$^+$[Me-MAO]$^{-e}$	20	6.35, 6.18 5.15, 5.05	−1.23, −1.37	−0.55
4	[*rac*-Me$_2$Si(Ind)$_2$Zr(μ-Me)$_2$Al^{i}Bu$_2$]$^+$[Me-MAO]$^{-e}$	20	6.33 5.17	−1.28	

[a] Distance between peaks is about 9.0 Hz. [b]Distance between peaks is about 6.5 Hz. [c]$\Delta\nu_{1/2} \approx 8$ Hz. [d]$\Delta\nu_{1/2} \approx 7$ Hz. [e]NMR data from ref 16.

Such a complex picture shows that species **IV** with various [Me-MAO]$^-$ counterions displays resonances with different chemical shifts and the exchange of various [Me-MAO]$^-$ counterions in **IV** is slow on the NMR time scale. Several distinct types of [Me-MAO]$^-$ anions in contact with a zirconocenium cation were recently observed by ^{13}C NMR in the catalytic system (MeC$_5$H$_4$)$_2$ZrMe$_2$/MAO.[13] With the increase of temperature up to 50 °C, the signal of Cp protons of **IV** at δ 6.1 ppm noticeably increases at the expense of that at δ 5.9 (Figure 2b). It is tempting to ascribe this effect to increased mobility of indenyl ligands with increasing temperature. However, other explanations are possible. One of them is the change of the nature of [Me-MAO]$^-$ counterions. It was shown previously that the size of oligomeric molecules of MAO reversibly decreases with increasing temperature.[14] Thus, for **IV** (as well as for **III**) there is no evidence in favor of the locked conformation of indenyl ligands in the temperature range −50 to 50 °C.

As mentioned above, the replacement of MAO by MMAO as activator results in the increase of the tacticity of polypropylenes produced with **1-Me** and **1-Cl** catalysts.[10] Thus, it is reasonable to search the intermediates with locked conformation of 2-PhInd ligands in **1-Cl**/MMAO system.

Catalytic System 1-Cl/MMAO. Recently, on the basis of the analysis of the ^{1}H NMR spectra of the (SBI)ZrCl$_2$/MMAO system (SBI = *rac*-Me$_2$Si(Ind)$_2$), we have assumed that when (SBI)ZrCl$_2$ is reacted with MMAO, the mixed heterobinuclear cation [(SBI)Zr(μ-Me)$_2$AlMe^{i}Bu]$^+$ is formed, together with its methyl congener [(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$.[15] Then, on the basis of the detailed ^{1}H and ^{13}C NMR study of (SBI)ZrCl$_2$/MAO/Al^{i}Bu$_3$ system in benzene-d_6, Babushkin and Brintzinger have shown that with increasing [Al^{i}Bu$_3$]/Zr ratio from 14 to 100 ([Al]$_{MAO}$/[Zr] ≈ 600) first ion pairs [(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$[Me-MAO]$^-$ and [(SBI)Zr(μ-Me)$_2$AlMe^{i}Bu]$^+$[Me-MAO]$^-$ then ion pairs [(SBI)Zr(μ-Me)$_2$AlMe^{i}Bu]$^+$[Me-MAO]$^-$ and [(SBI)Zr(μ-Me)$_2$Al^{i}Bu$_2$]$^+$[Me-MAO]$^-$ became the predominant species in solution (Table 2).[16] They have also shown that the ^{1}H NMR signals assigned in ref 15 to ion pair [(SBI)Zr(μ-Me)$_2$AlMe^{i}Bu]$^+$[Me-MAO]$^-$ actually belong to ion pair [(SBI)Zr(μ-Me)$_2$Al^{i}Bu$_2$]$^+$[Me-MAO]$^-$. These results helped us to assign the ^{1}H NMR peaks of similar heterobinuclear ion pairs in the **1-Cl**/MMAO system.

It was found that at relatively low [Al]$_{MMAO}$/Zr ratios of 30−70 ([Zr] = 8 × 10^{-3} M), mainly monomethylated complex **1-ClMe** is present in the reaction solution. With the increase of the [Al]$_{MMAO}$/Zr ratio, the concentration of mixed heterobinuclear ion pairs [(2-PhInd)$_2$Zr(μ-Me)$_2$AlMe^{i}Bu]$^+$[Me-MAO]$^-$ (**III$_{\mathbf{Me}\boldsymbol{i}\mathbf{Bu}}$**) and [(2-PhInd)$_2$Zr($\mu$-Me)$_2$Al^{i}Bu$_2$]$^+$[Me-MAO]$^-$ (**III$_{\boldsymbol{i}\mathbf{Bu}\boldsymbol{i}\mathbf{Bu}}$**) increases.[17] Figure 3 shows the ^{1}H NMR spectra of the catalytic system **1-Cl**/MMAO in toluene-d_8 at various temperatures ([Zr] = 6 × 10^{-3} M, [Al]$_{MMAO}$/[Zr] = 200). Resonances of Cp and Zr-Me-Al protons of **III$_{\mathbf{Me}\boldsymbol{i}\mathbf{Bu}}$** and **III$_{\boldsymbol{i}\mathbf{Bu}\boldsymbol{i}\mathbf{Bu}}$** are marked in Figure 3. Their spectral parameters are collected in Table 2 in comparison with those for similar species in the (SBI)ZrCl$_2$/MAO/Al^{i}Bu$_3$ system.[16] Besides the ^{1}H NMR resonances of **III$_{\mathbf{Me}\boldsymbol{i}\mathbf{Bu}}$** and **III$_{\boldsymbol{i}\mathbf{Bu}\boldsymbol{i}\mathbf{Bu}}$**, the ^{1}H NMR spectra of Figure 3 show two broad and intense peaks in the Cp region that could be assigned to neutral complex (2-PhInd)$_2$ZrClR, where R is

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(13) Babushkin, D. E.; Naundorf, C.; Brintzinger, H.-H. *Dalton Trans.* **2006**, 4539.

(14) Babushkin, D. E.; Semikolenova, N. V.; Panchenko, V. N.; Sobolev, A. P.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **1997**, *198*, 3845.

(15) Bryliakov, K. P.; Semikolenova, N. V.; Panchenko, V. N.; Zakharov, V. A.; Brintzinger, H.-H.; Talsi, E. P. *Macromol. Chem. Phys.* **2006**, *207*, 327.

(16) Babushkin, D. E.; Brintzinger H.-H. *Chem.−Eur. J.* **2007**, accepted.

(17) For simplicity, we use the same notation of the counter anion [Me-MAO]$^-$ for MAO- and MMAO-based systems. Apparently, for these two systems, the counter anions are different. The counter anion incorporates only Me groups in the case of MAO and both Me and ^{i}Bu groups in the case of MMAO.

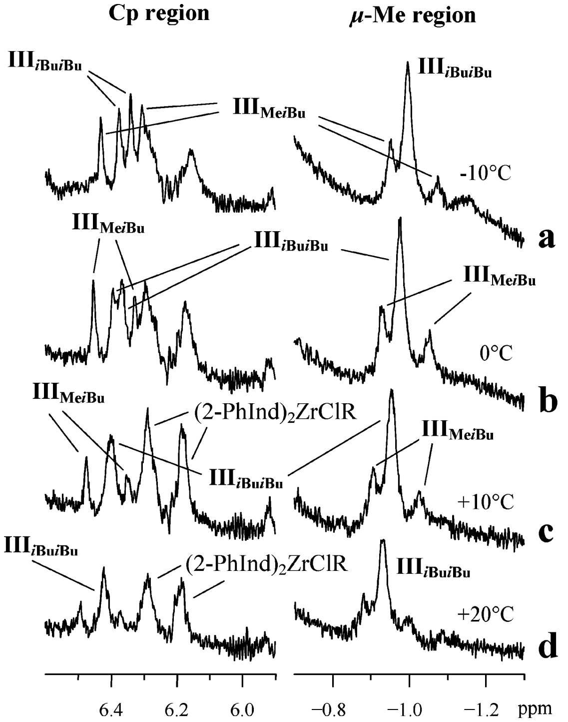

Figure 3. ^{1}H NMR spectra of the **1-Cl**/MMAO sample at differing temperatures: −10 °C (a), 0 °C (b), +10 °C (c), +20 °C (d) ([**1-Cl**] = 6 × 10^{-3} M, Al:Zr = 200, toluene-d_8).

^{i}Bu or Me. The ligand R of (2-PhInd)$_2$ZrClR exchanges rapidly (on the NMR time scale) at room temperature. The relative concentration of (2-PhInd)$_2$ZrClR decreased with an increase of the [Al]$_{\text{MMAO}}$/[Zr] ratio up to 400.

It is very important that **III$_{iBuiBu}$** exhibits two peaks from Cp protons at low temperatures (Figures 3a, b) that coalesce at higher temperatures (Figures 3c,d, Table 2). The distance between unperturbed Cp peaks of **III$_{iBuiBu}$** at low temperature is about 10 Hz. To fulfill the conditions of rapid exchange, the characteristic time of indenyl ligand rotation should be about 10^{-2} s at 20 °C. This time is comparable with the characteristic time of propylene insertion (10^{-2} to 10^{-3} s).[11] Thus, **III$_{iBuiBu}$** is the first example of an intermediate with restricted rotation of indenyl ligands at room temperature found for the "oscillating" catalyst.[18] For less sterically hindered intermediate **III$_{MeiBu}$**, no decoalescence of Cp peaks at low temperature was observed. For this intermediate, the rotation of indenyl ligands remains fast even at −30 °C (Figures 3 and 4).

The coalescence of Cp peaks of **III$_{iBuiBu}$** is reversible: when the sample of Figure 3d was cooled again to −10 °C, the observed spectrum closely resembled that of Figure 3a. The only difference was the slightly lower intensity of the ^{1}H NMR peaks. This is caused by the decrease of the concentration of Zr(IV) species due to partial reduction of Zr(IV) to Zr(III). In Figure 5 one can see the EPR spectrum recorded 2 h after onset of the reaction of **1-Cl** with MMAO at room temperature ([Zr] = 6 × 10^{-3} M, [Al]$_{\text{MMAO}}$/[Zr] = 200). The major peak at $g = 1.968$ and the minor one at $g = 1.983$ are in the typical range reported for zirconium(III) species.[19,20] The integration shows that up to 40% of the starting Zr(IV) complex is converted into Zr(III) species upon interaction with MMAO for 2 h at room temperature. The nature of these species is still unclear.

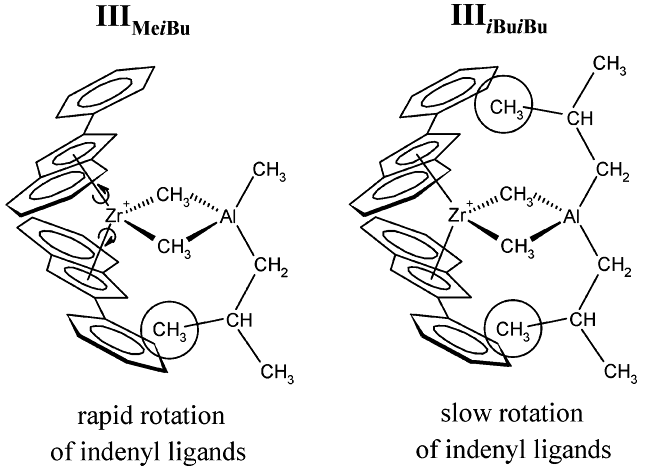

Figure 4. Proposed structures of **III$_{MeiBu}$** and **III$_{iBuiBu}$**.

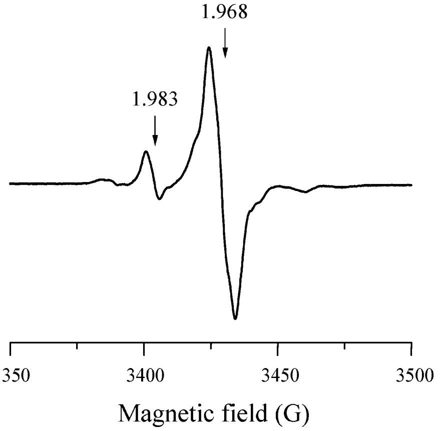

Figure 5. EPR spectrum of the **1-Cl**/MMAO sample recorded 2 h after mixing of reagents at 20 °C ([**1-Cl**] = 6 × 10^{-3} M, Al:Zr = 200, toluene-d_8).

Tight ion pairs of the type **IV** were not observed in the catalytic system **1-Cl**/MMAO. Similarly, species of the type **IV** did not arise in the catalytic system (SBI)ZrCl$_2$/MMAO.[16] Thus, concentration of tight ion pairs is much lower for the **1-Cl**/MMAO system than for the **1-Cl**/MAO analogue. An EPR-spin probe study has shown that the oligomeric molecules of MMAO are bulkier than oligomeric molecules of MAO.[15] The bulkiness of MMAO could prevent the tight contact of the [Me-MAO]$^-$ counterion with zirconium and thus disfavor formation of ion pairs of the type **IV**.

Our polymerization study confirms the higher tacticity of polypropylene produced by the **1-Cl**/MMAO system than by the **1-Cl**/MAO analogue, previously reported by Waymouth and co-workers.[10] The polymers produced by the **1-Cl**/MMAO system display higher isotacticity ([mmmm] = 30% by ^{13}C NMR) than those produced by the **1-Cl**/MAO system ([mmmm] = 18%) (Table 3).

Mechanism of the "Oscillating Catalysts" Performance. As mentioned, rotation of indenyl ligands in the active intermediate should be slow as compared to the rate of propylene insertion for the formation of long isotactic stereosequences. In this work we have shown that restricted indenyl ligand rotation could be observed for the mixed heterobinuclear ion pair **III$_{iBuiBu}$**. The proposed active intermediate of the **1-Cl**/MAO system seems to be the ion pair [(2-PhInd)$_2$ZrP]$^+$[Me-MAO]$^-$ (**V**) with the vacant coordination site of zirconium

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(18) Very recently, the restricted rotation of ligands at 20 °C was reported for unbridged amine-functionalized zirconocene [1-(p-Me$_2$NC$_6$H$_4$)-3,4-Me$_2$C$_5$H$_2$]$_2$ZrMe$_2$ activated with MAO. Kim, S. K.; Kim, H. K.; Lee, M. H.; Yoon, S. W.; Do, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 6163.

(19) Fryzuk, M. D.; Jafarpour, L.; Rettig, S. J. *Organometallics* **1999**, *18*, 4050.

(20) Williams, G. M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1122.

Table 3. Propylene Polymerizations with (2-PhInd)$_2$ZrCl$_2$[a]

entry	activator	PP yield, g	productivity[b]	[mmmm][c]
1	MAO	3.1	25.8	18
2	MMAO	2.7	22.5	30

[a] Polymerization conditions: [Zr] = 13.5 μmol/L, 150 mL of toluene, $P(C_3H_6)$ = 6 bar, polymerization temperature 30 °C, time 10 min, Al_{MAO}:Zr = 2500. [b] In kg of PP/(mol of Zr bar min). [c] Determined by ^{13}C NMR.

occupied by AlMe$_3$ or [Me-MAO]$^-$. Waymouth et al. have obtained practically amorphous polypropylene with the **1-Cl**/MAO system rich in "free" AlMe$_3$.[21] Thus, species **V** with a vacant coordination site of zirconium occupied by AlMe$_3$ can be responsible for the atactic stereosequences, and species **V** with a vacant coordination site occupied by [Me-MAO]$^-$ for the isotactic stereosequences. This is possible if the indenyl ligand rotation is fast in the first case and slow in the second one. Apparently, steric restrictions for the indenyl ligand rotation are smaller for AlMe$_3$ than for [Me-MAO]$^-$. For the insertion of propylene, AlMe$_3$ or [Me-MAO]$^-$ ligands in **V** should be replaced by the monomer molecule. Then, the corresponding coordination site is again occupied by AlMe$_3$ or [Me-MAO]$^-$ before the next insertion. The switch from atactic to isotactic stereoblock formation occurs when AlMe$_3$ in **V** is replaced by [Me-MAO]$^-$.

The concentration of inner sphere ion pairs **IV** for the **1-Cl**/MMAO system is lower than for the **1-Cl**/MAO counterpart, whereas the former system produces more isotactic polypropylene than the latter one (Table 3). These data evidence indirectly against the involvement of species **V** with inner sphere coordination of [Me-MAO]$^-$ in the formation of the long isotactic stereosequences by the catalytic system **1-Cl**/MMAO. In the case of MMAO, ion pairs of the type **V** with vacant coordination sites occupied by Al^{i}BuMe$_2$ and Al^{i}Bu$_2$Me can be responsible for the atactic and isotactic stereosequences, respectively. Further studies are needed to verify this model.

Conclusions

The study of conformational behavior of ion pairs formed upon activation of "oscillating" catalyst (2-PhInd)$_2$ZrCl$_2$ with MAO, MMAO, and AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ has shown that for the ion pair [(2-PhInd)$_2$Zr(μ-Me)$_2$Al^{i}Bu$_2$]$^+$[Me-MAO]$^-$ the rate of indenyl ligand rotation at 20 °C is comparable with the rate of propylene insertion. This demonstrates the fundamental possibility of the existence of *rac*-intermediates with the restricted rotation of 2-arylindenyl ligands for the (2-ArInd)$_2$ZrCl$_2$/MAO catalysts. The interconversion between *rac*-intermediates with locked and unlocked conformations of the indenyl ligands (the hypothesis of Busico) seems to be a plausible explanation of the "oscillating catalysts" performance.

Experimental Section

Toluene was dried over molecular sieves (4 Å), purified by refluxing over sodium metal, and distilled under dry nitrogen. Toluene-*d*$_8$ was dried over molecular sieves (4 Å), degassed in vacuo, and stored under dry argon. All experiments were carried out in sealed high-vacuum systems using breakseal techniques. (2-PhInd)$_2$ZrCl$_2$,[1] (SBI)ZrCl$_2$,[22] and [CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ [23] were synthesized as described. Trimethylaluminum (AlMe$_3$) was purchased from Aldrich. Methylaluminoxane (MAO) was obtained from Crompton GmbH (Bergkamen) as a toluene solution (total Al concentration 1.8 M, Al as AlMe$_3$ 0.5 M). MMAO (MAO, modified with TIBA) was purchased from AKZO as a heptane solution (total Al content 7.1 wt %).

^{1}H and ^{13}C NMR spectra were recorded at 250.130 and 62.89 MHz, on a Bruker DPX-250 MHz NMR spectrometer. Typical operating conditions for ^{1}H 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. Typical operating conditions for ^{13}C NMR measurements: spectral width 20 kHz; spectrum accumulation frequency 0.2−0.1 Hz; 100−2000 transients; 45° pulse at 5 μs. ^{13}C,^{1}H-correlations were established by using standard Bruker HXCOBI pulse programs. For calculations of ^{1}H and ^{13}C chemical shifts, the resonances of the methyl group of the toluene-*d*$_8$ solvent were taken as 2.09 and 20.40 ppm, respectively.

EPR spectra were measured on a Bruker ER-200D spectrometer at 9.3 GHz, modulation frequency 100 kHz, modulation amplitude 1 G. Measurements were performed in glass tubes (d = 5 mm). A periclase crystal (MgO) with impurities of Mn^{2+} and Cr^{3+}, which served as a side reference, was placed into the second compartment of the dual cavity. EPR spectra were quantified by double integration with TEMPO toluene solution as standard.

Preparation of MAO Samples. MAO samples used for NMR studies were prepared from commercial MAO by removal of the solvent and of most of the trimethylaluminum content in vacuo at 20 °C for 2 h. Thus prepared dry polymeric MAO contained 40 wt % of total Al and ca. 3 wt % of residual AlMe$_3$. ^{13}C-enriched MAO (MAO-^{13}C) was prepared by ligand exchange of 99% ^{13}C-enriched AlMe$_3$ (30 mol % of total Me groups) and solid MAO (70 mol % of total Me groups) in toluene solution followed by subsequent removal of volatiles under vacuum at room temperature to give a sample of MAO-^{13}C (65−70% ^{13}C) with desired AlMe$_3$ content (polymeric MAO with total Al content of 40% and Al as residual AlMe$_3$ ca. 5 wt %). A more detailed description is presented in ref 7.

Propylene Polymerization Studies. Polymerization was performed in a 1.0 L steel reactor, equipped with magnetic stirrer, a water jacket for temperature control, and automatic computer-controlled system for propylene feed.

(2-PhInd)$_2$ZrCl$_2$ (0.0011 g, 2.0 × 10^{-6} mol) was introduced into the autoclave in a vacuum-sealed glass ampule. The reactor was evacuated at 80 °C, cooled to 20 °C, and then charged with 150 mL of toluene solution containing the required amount of the activator (MAO, MMAO). The reaction mixture was warmed to 30 °C, saturated with propylene to a total pressure of 6 bar. The reaction was started by breaking the ampule with the complex. During the reaction time (10 min) propylene 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.

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Supporting Information Available: ^{13}C NMR spectrum of **1-Cl**/MAO-^{13}C sample and ^{13}C NMR spectra of polypropylenes synthesized by **1-Cl**/MAO and **1-Cl**/MMAO catalytic systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] Petoff, J. L.; Myers, C. L.; Waymouth, R. M. *Organometallics* **1999**, *32*, 7984.

[22] Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1511.

[23] Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1.