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^{1}H NMR characterization of intermediates formed by the activation of zirconocenes with methylaluminoxane at high Al/Zr ratios

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Cation-like intermediates formed by the activation of zirconocenes L_2ZrCl_2 [L_2 are cyclopentadienyl (Cp), indenyl (Ind) and fluorenyl (Flu) ligands] with methylaluminoxane (MAO) at high Al/Zr ratios were characterised by ^{1}H NMR spectroscopy.

The spectroscopic monitoring of cationic intermediates formed upon activation of metallocenes with methylaluminoxane (MAO) is crucial for the elucidation of the mechanisms of olefin polymerization.[1–5] Recent NMR studies[6,7] provided important information on the structures of cation-like intermediates formed upon the activation of Cp_2ZrMe_2 with MAO in toluene (Figure 1). The cationic complexes $[Cp_2Zr(\mu\text{-Me})_2AlMe_2]^+$ $Me\text{–}MAO^-$ **3** and $Cp_2ZrMe^+ \leftarrow Me^-\text{–}Al{\equiv}MAO$ **4** were the major species at high Al/Zr ratios (200–4000). Complexes **3** and **4** were proposed to be the precursors of active centres for polymerization.[7] In order to extend such studies to more complex and practically attractive zirconocene catalysts, we report here on the ^{1}H NMR characterization of cation-like intermediates $[L_2Zr(\mu\text{-Me})_2AlMe_2]^+$ $Me\text{–}MAO^-$ **3**, where L_2 are various cyclopentadienyl (Cp), indenyl (Ind) and fluorenyl (Flu) ligands. The following catalysts were studied: $(Cp\text{-R})_2ZrCl_2$ (R = Me, 1,2-Me_2, 1,2,3-Me_3, 1,2,4-Me_3, Me_4, Me_5, Bu, Bu^t), *rac*-ethanediyl$(Ind)_2ZrCl_2$, *rac*-$Me_2Si(Ind)_2ZrCl_2$, *rac*-Me_2Si(1-Ind-2-Me)$_2ZrCl_2$, *rac*-ethanediyl(1-Ind-4,5,6,7-H_4)$_2ZrCl_2$, (Ind-2-Me)$_2ZrCl_2$, $Me_2C(Cp)(Flu)ZrCl_2$, Me_2C(Cp-3-Me)(Flu)$ZrCl_2$, $Me_2Si(Flu)_2ZrCl_2$. Further notations **3** and **4** will be used irrespective of the nature of L just to show that outer-sphere ion pair of type **3** or inner-sphere ion pair of type **4** is considered.

All operations were carried out in a dry nitrogen atmosphere (99.999%) using standard Schlenk techniques. Solids and [$^2H_8$]toluene were handled and stored in a glovebox. L_2ZrCl_2 samples (Boulder Scientific Comp.) were used as received. Commercial MAO (Witco) was used after the removal of the solvent *in vacuo* at 20 °C. The solid product (polymeric MAO with a total Al content of 40 wt% and Al as residual $AlMe_3$ of a 5 wt%) was used for the preparation of the samples. NMR tubes with appropriate amounts of L_2ZrCl_2, solid MAO and [$^2H_8$]toluene were closed by septum stoppers inside a glovebox.

^{1}H NMR spectra were recorded on a Bruker DPX400 instrument and referenced to the residual resonance of the CD_2H group of the toluene solvent, which was taken as 2.09 ppm.

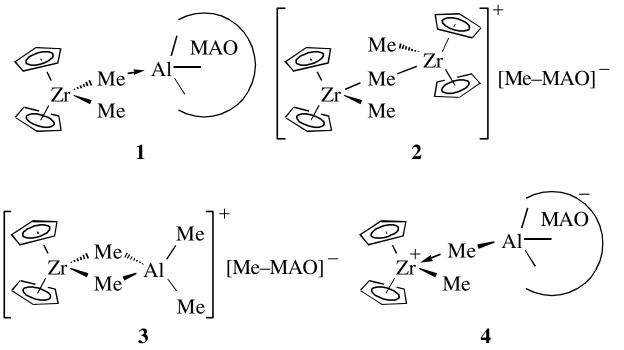

Figure 1 Proposed structures of main intermediates formed in the catalytic system Cp_2ZrMe_2/MAO in toluene.

The analysis of ^{1}H NMR spectra of the test systems (zirconocene concentrations, 10^{-3}–10^{-2} mol dm^{-3}; Al/Zr ratios 100–500; [$^2H_8$]toluene; 20 °C) shows that for the $(Cp\text{-R})_2ZrCl_2$/MAO (R = Me, 1,2-Me_2, Bu) systems at low Al/Zr ratios of about 100, mainly broad signals are observed, which can be attributed to complex **4** by analogy with the Cp_2ZrMe_2/MAO system.[7] With increasing the Al/Zr ratio, sharp resonances of complex **3** increased, but broad peaks of **4** were present in these systems even at an Al/Zr ratio of 500. For all other catalysts studied, broad resonances of **4** were not detected at all or were observed only at low Al/Zr ratios, whereas only the cation-like complex $[L_2Zr(\mu\text{-Me})_2AlMe_2]^+$ $Me\text{–}MAO^-$ **3** was observed in the reaction solution at the highest Al/Zr ratios. The *ansa*-Zirconocene/MAO systems displayed mainly the signals of **3** even at Al/Zr = 100. Probably, the substituents and bulkiness of ligands disfavoured the anion–cation contacts in complex **4** due to steric or electronic effects. Complexes **3** exhibited sharp ^{1}H NMR resonances ($\Delta\nu_{1/2}$ 0.5 Hz); this simplified their detection even in the presence of large excesses of MAO. As an example, the

Table 1 ^{1}H NMR signals of the complexes $[(Cp\text{-R})_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$ and $[(Cp\text{-R})_2Zr(\mu\text{-Me})_2AlMe_2]^+[B(C_6F_5)_4]^-$ (R = H, Me, 1,2-Me_2, 1,2,3-Me_3, 1,2,4-Me_3, Me_4, Me_5, Bu, Bu^t).

Species	Cp	Cp–Me	μ-Me	Al–Me
$[Cp_2Zr(\mu\text{-Me})_2AlMe_2]^+[B(C_6F_5)_4]^-$ (ref. 9)	5.44 (s, 10)		–0.40 (s, 6)	–0.73 (s, 6)
$[(Cp\text{-Bu})_2Zr(\mu\text{-Me})_2AlMe_2]^+[B(C_6F_5)_4]^-$ (ref. 9)	5.62 (t, 4), 5.68 (t, 4), *J* 2.6 Hz		–0.26 (s, 6)	–0.52 (s, 6)
$[(Cp\text{-Bu}^t)_2Zr(\mu\text{-Me})_2AlMe_2]^+[B(C_6F_5)_4]^-$ (ref. 9)	5.59 (t, 4), 5.99 (t, 4), *J* 2.6 Hz		–0.18 (s, 6)	–0.47 (s, 6)
$[(Cp\text{-1,2,3-Me}_3)Zr(\mu\text{-Me})_2AlMe_2]^+[B(C_6F_5)_4]^-$ (ref. 9)	5.33 (s, 4)	1.42 (s, 12), 1.48 (s, 6)	—[a]	–0.70 (s, 6)
$[Cp_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$	5.50 (s, 10)		–0.27 (s, 6)	–0.58 (s, 6)
$[(Cp\text{-Bu})_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$	5.58 (t, 4), 5.61 (t, 4), *J* 2.6 Hz		–0.23 (s, 6)	–0.72 (s, 6)
$[(Cp\text{-Bu}^t)_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$	5.54 (t, 4), 6.22 (t, 4), *J* 2.6 Hz		—[a]	—[a]
$[(Cp\text{-Me})_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$	5.38[b,8]	—[c]	—[a]	—[a]
$[(Cp\text{-1,2-Me}_2)_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$	5.57 (d, 4), 5.45 (t, 2), *J* 2.9 Hz	1.49 (s, 12)	—[a]	–0.64 (s, 6)
$[(Cp\text{-1,2,3-Me}_3)_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$	5.36 (s, 4)	1.40 (s, 12), 1.53 (s, 6)	–0.51 (s, 6)	–0.62 (s, 6)
$[(Cp\text{-1,2,4-Me}_3)_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$	5.42 (s, 4)	1.42 (s, 12), 1.46 (s, 6)	–0.50 (s, 6)	–0.61 (s, 6)
$[(Cp\text{-Me}_4)_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$	5.54 (s, 2)	1.38 (s, 12), 1.49 (s, 12)	–0.59 (s, 6)	–0.62 (s, 6)
$[(Cp\text{-Me}_5)_2Zr(\mu\text{-Me})_2AlMe_2]^+Me\text{–}MAO^-$		1.74 (s, 30)	—[a]	—[a]

[a]Not found. [b]Broad singlet ($\Delta\nu$ 6 Hz). [c]Masked by the peak of toluene.

Table 2 ^{1}H NMR signals of the complexes [*rac*-R^1(Ind-R)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^-$ and [*rac*-R^1(Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (R = H, 2-Me; R^1 = none, C$_2$H$_4$, SiMe$_2$).

Species	Ind-C$_5$	C$_2$H$_4$	SiMe$_2$	μ-Me	Al–Me
[*rac*-ethanediyl(Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^{-\,a}$	6.44 (dd, 2), J 3.3 and 0.7 Hz, 6.20 (d, 2), *J* 3.3 Hz	4.04 (s, 4)		–0.58 (s, 6)	–0.63 (s, 6)
[*rac*-Me$_2$Si(Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^{-\,a}$	6.92 (d, 2), *J* 3.3 Hz; 5.91 (d, 2), *J* 3.3 Hz		1.29 (s, 6)	–0.61 (s, 6)	–0.81 (s, 6)
[*rac*-ethanediyl(Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^{-\,b}$	5.61 (dd, 2), *J* 3.3 and 0.7 Hz; 5.26 (d, 2), *J* 3.3 Hz	3.22 (s, 4)		–0.75 (s, 6)	–1.22 (s, 6)
[*rac*-Me$_2$Si(Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^{-\,b}$	6.16 (d, 2), *J* 3.3 Hz; 5.03 (d, 2), *J* 3.3 Hz		0.85 (s, 6)	–0.65 (s, 6)	–1.35 (s, 6)
[*rac*-Me$_2$Si(1-Ind-2-Me)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^{-\,b,c}$	5.86 (s, 2)		0.9 (s, 6)	–0.65 (s, 6)	–1.39 (s, 6)
[(2-Me-Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^{-\,b,d}$	5.80 (s, 4)			–0.53 (s, 6)	–1.1 (s, 6)
[*rac*-ethanediyl(1-Ind-4,5,6,7-H$_4$)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^{-\,b}$	5.48 (d, 2), *J* 2.9 Hz; 4.76 (d, 2), *J* 2.9 Hz	2.84 (m, 2); 2.57 (m, 2)		–0.26 (s, 6)	–0.62 (s, 6)

[a]In CD$_2$Cl$_2$ at 20 °C.[8] [b]In [^{2}H$_8$]toluene at 20 °C. [c]2-Me peak at 1.53 (s, 6). [d]2-Me peak at 1.82 (s, 6).

^{1}H NMR spectrum of complex **3** observed in the *rac*-ethanediyl(Ind)$_2$ZrCl$_2$/MAO system at an Al/Zr ratio of 300 is presented in Figure 2. A spin–spin coupling constant of 0.7 Hz is resolved for one of the Ind-C$_5$ protons of **3**. Complexes **3** were stable for weeks at 20 °C in the test samples, while the time typically required for the recording of a spectrum did not exceed 3 h.

The ^{1}H NMR parameters of cation-like species **3** are collected in Tables 1–3 in comparison with data available for the related complexes [L$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and [L$_2$Hf(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ detected in [CPh$_3$][B(C$_6$F$_5$)$_4$]-based systems.[8,9] The assignment of Al–Me and Zr–Me–Al peaks of **3** in MAO-based systems was made by analogy with [CPh$_3$][B(C$_6$F$_5$)$_4$]-based systems, since cationic parts of **3** and [L$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ are the same. It can be seen that, despite the nonuniformity of their Me–MAO$^-$ counterions, the cationic parts of complexes **3** can be adequately characterised by ^{1}H NMR spectroscopy, as well as the related complexes in reaction systems based on [CPh$_3$][B(C$_6$F$_5$)$_4$]. The ^{1}H NMR spectra of **3** are not so sensitive to variations in the nature of their Me-MAO$^-$ counter anions as the ^{1}H NMR spectra of the ion pair **4**, since in **3** the perturbing Me-MAO$^-$ anion is only in an outer-sphere contact to the coordinatively saturated zirconocene cation. Besides, Me–MAO$^-$ anions can rapidly exchange between various species **3**; thus, the cationic part of **3** displays one sharp NMR pattern. However, there are several exceptions. For example, complex **3** formed in the catalytic system (Cp-Me)$_2$ZrCl$_2$/MAO displays only one broadened Cp resonance instead of an expected doublet of triplets, and its AlMe$_2$ and Zr–Me–Al peaks are not observed (Table 1). Probably, the widths of the ^{1}H NMR peaks of **3** are affected by the exchange of their Me–MAO$^-$ counterions. For some of zirconocenes in Table 1 corresponding AlMe$_2$ and Zr–Me–Al peaks (marked by *a*) are insufficiently sharp to be detected against a background of intense and broad resonances of MAO and AlMe$_3$ in the range 0.7 to –0.7 ppm.

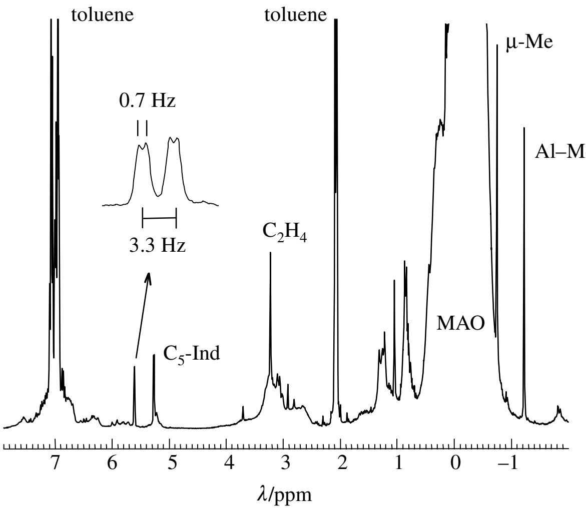

Figure 2 ^{1}H NMR spectrum of [ethanediyl(Ind)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$ Me–MAO$^-$ in toluene at 20 °C. ([Zr] = 3×10^{-3} mol dm^{-3}, Al/Zr = 300).

Thus, we found that the cationic part of cation-like complexes **3** dominating at high Al/Zr ratios in the majority of the zirconocene/MAO test systems can be reliably characterised by ^{1}H NMR spectroscopy. Based one these results, we can expect that, for any zirconocene/MAO system with Me-substituted or bulky ligands, ^{1}H NMR spectroscopy will be fruitful for the characterization and monitoring of cation-like complexes **3** dominating in these systems at high Al/Zr ratios.

The data obtained for the L$_2$ZrCl$_2$/MAO systems correlate with those for the highly active catalytic systems L$_2$ZrCl$_2$/AlMe$_3$CPh$_3^+$ B(C$_6$F$_5$)$_4^-$. In the latter, ^{1}H NMR spectroscopy indicates the presence of only the intermediates [L$_2$ZrMe(μ-Me)$_2$-AlMe$_2$]$^+$B(C$_6$F$_5$)$_4^-$ (refs. 8, 9) containing the same cations as those in intermediates **3** in the MAO-based systems, thus confirming the role of complex **3** as the precursor of the crucial catalyst species.

Table 3 ^{1}H NMR signals of the complexes [Me$_2$C(Cp)(Flu)Hf(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$, [Me$_2$C(Cp-R)(Flu)Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^-$ and [Me$_2$Si(Flu)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^-$ (R = H, 3-Me).

Species	Flu	C$_5$	CMe$_2$	μ-Me	Al–Me
[Me$_2$C(Cp)(Flu)Hf(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (ref. 8)	8.22 (d, 2), *J* 8.58 Hz; 7.96 (d, 2), *J* 8.91 Hz; 7.75 (t, 2), *J* 8.58 Hz; 7.34 (t, 2), *J* 8.91 Hz	6.32 (t, 2), *J* 2.6 Hz; 5.58 (t, 2), *J* 2.6 Hz	2.49 (s, 6)	–0.57 (s, 6)	–0.72 (s, 3) –0.63 (s, 3)
[Me$_2$C(Cp)(Flu)Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^-$	7.52 (d, 2), *J* 8.5 Hz; 7.28 (t, 2), *J* 8.5 Hz; 7.01 (t, 2), *J* 8.5 Hz^a	5.60 (t, 2), *J* 2.6 Hz; 4.68 (t, 2), *J* 2.6 Hz	1.89 (s, 6)	–0.76 (s, 6)	–1.51 (s, 6)
[Me$_2$C(3-Me-Cp)(Flu)Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^{-\,b}$	7.57 (t, 2), *J* 8.5 Hz^a	5.55 (t, 2), *J* 2.6 Hz; 5.31 (t, 1), *J* 2.6 Hz	1.86 (s, 6)	–0.71 (s, 6)	–1.73 (s, 3) –1.57 (s, 3)
[Me$_2$Si(Flu)$_2$Zr(μ-Me)$_2$AlMe$_2$]$^+$Me–MAO$^{-\,c}$	6.65 (t, 4), *J* 8 Hz^a			–0.72 (s, 6)	–2.46 (s, 6)

[a]Masked by the signal of toluene. [b]Peak of 3-Me at 1.92 (s, 6). [c]Peak of Me$_2$Si at 1.37 (s, 6).

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