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Journal of Organometallic Chemistry 677 (2003) 10–14

Journal of Organometallic Chemistry

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^{1}H-NMR spectroscopic study of cationic intermediates in solvent and oil constituents of the catalytic systems $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ and $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ in benzene

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Received 12 January 2003; received in revised form 20 March 2003; accepted 21 March 2003

Abstract

Using ^{1}H-NMR spectroscopy, mutual transformations and stability of cationic complexes $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$ (**1**), $[Cp_2ZrMe^+\cdots B(C_6F_5)_4^-]$ (**2**) and $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (**3**) formed in catalytic systems $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ and $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ in benzene were studied both in the solution and in the oil deposit formed whenever the total zirconocene concentration is high enough. It was shown that at high zirconocene concentrations, the decay rate of complexes **1** and **2** in the oil constituent of the reaction mixture is at least a factor ten lower than that in the solvent. Complexes **1**–**3** are close in energy to each other and can be readily converted to one another by changing the ratio between Cp_2ZrMe_2, $[CPh_3][B(C_6F_5)_4]$ and $AlMe_3$. Complex **1** reacts with excess $[CPh_3][B(C_6F_5)_4]$ to yield **2** with first order rate constant of $4\times10^{-4}\ s^{-1}$ at 20 °C. Complex **3** reacts with excess $[CPh_3][B(C_6F_5)_4]$ to yield **2** with a half-life of 1 h at 20 °C. Addition of 1-hexene to samples containing various relative amounts of complexes **1**–**3**, and further ^{1}H-NMR spectroscopic monitoring of the polymer/monomer ratio, showed that **1**–**3** have comparable polymerization activities.

Keywords: Metallocene polymerization; Mechanism; Cationic intermediates

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1. Introduction

The in situ monitoring of cationic intermediates formed upon activation of metallocenes by co-catalysts is crucial for the elucidation of the mechanism of olefin polymerization [1–6].

Recently, Bochmann and co-workers reinvestigated the reaction of $[CPh_3][B(C_6F_5)_4]$ with L_2ZrMe_2 ($L = Cp_2$ or SBI; SBI = rac-Me_2-$Si(Ind)_2$) in benzene at room temperature using ^{1}H-NMR spectroscopy [7]. It was shown that treatment of $[CPh_3][B(C_6F_5)_4]$ with excess L_2ZrMe_2 generates the binuclear zirconocene cations $[(L_2ZrMe_2)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$. Reaction of $[\{(SBI)ZrMe\}_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$ with excess of $[CPh_3][B(C_6F_5)_4]$ proceeds cleanly to give the ion pair $[(SBI)ZrMe^+\cdots B(C_6F_5)_4^-]$ and follows pseudo-first-order kinetics, $k = 3\times10^{-4}\ s^{-1}$ (20 °C). The mononuclear complex is stable in benzene under these conditions.

Bochmann and co-workers kept the zirconocene concentration low ($0.6 < [Zr] < 2.5$ mmol l^{-1}) to prevent the formation of higher aggregates and the precipitation of ionic species as an oil phase. In the present work, using low (~1 mmol l^{-1}) and high (~50 mmol l^{-1}) concentrations of zirconocene, we have found that it is possible to monitor with ^{1}H-NMR spectroscopy the cationic complexes both in the solvent and the oil phases, for both the catalytic systems $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ and $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$, in benzene. Mutual transformations of the following cationic complexes $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$ (**1**), $[\{Cp_2ZrMe^+\cdots B(C_6F_5)_4^-]$ (**2**)

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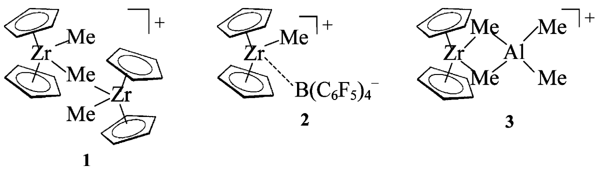
doi:10.1016/S0022-328X(03)00319-X



Scheme 1. Proposed structures for complexes **1**–**3**.

and $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (**3**) (Scheme 1), both in solvent and oil constituents of the reaction mixtures, were studied. Oily phase separations are encountered in zirconocene catalyst systems activated either by MAO or by borane or borate co-catalysts at elevated concentrations. Thus, it is interesting to elucidate nature and properties of these hitherto almost totally ignored objects.

2. Experimental

All operations were carried out under dry nitrogen atmosphere (99.999%) by standard Schlenk technique. Solids and benzene-d_6 were handled and stored in a glovebox. Solutions were transferred and dosed with lubricant free disposable syringes or gastight micro syringes. Benzene-d_6 was dried by reflux over sodium. Cp_2ZrMe_2 (Strem Chemicals, Inc.), and $[Ph_3C][B(C_6F_5)_4]$ (Albemarle Corp.) were used as received. 1-hexene was obtained from Borealis, as sampled after the purification step.

NMR tubes with appropriate amounts of Cp_2ZrMe_2, $[Ph_3C][B(C_6F_5)_4]$, and benzene-d_6 were closed by septum stoppers inside glovebox. Further addition of $AlMe_3$ and 1-hexene was, if necessary, performed outside glovebox with lubricant free disposable syringes or gastight micro syringes in the flow of nitrogen.

^{1}H-NMR spectra were recorded on a Bruker DPX300 instrument and referenced to residual solvent peaks relative to TMS.

3. Results and discussion

3.1. *Characterization of cationic complexes **1**–**3** in oil and solvent constituents of the catalytic systems $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ and $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ in benzene*

3.1.1. *$[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$ (1)*

When 0.014 g of Cp_2ZrMe_2 and 0.034 g of $[CPh_3][B(C_6F_5)_4$ (to make their ratio 2:1) were mixed with 1 ml of benzene-d_6 at room temperature directly in a 5 mm NMR tube, a two-phase system was formed with an oil layer in the bottom. The ^{1}H-NMR spectrum of this mixture recorded 10 min after sample preparation, exhibits two different patterns of cationic complex **1** (Fig. 1a). One pattern with more sharp peaks belongs to **1** dissolved in solution layer and the other one to the same complex (or aggregates of complexes) present in the oil layer. Further, these complexes will be referred to as complexes **1s** and **1o**, s and o referring to solvent and oil, respectively. Their ^{1}H-NMR peaks are marked in Fig. 1a by corresponding symbols.

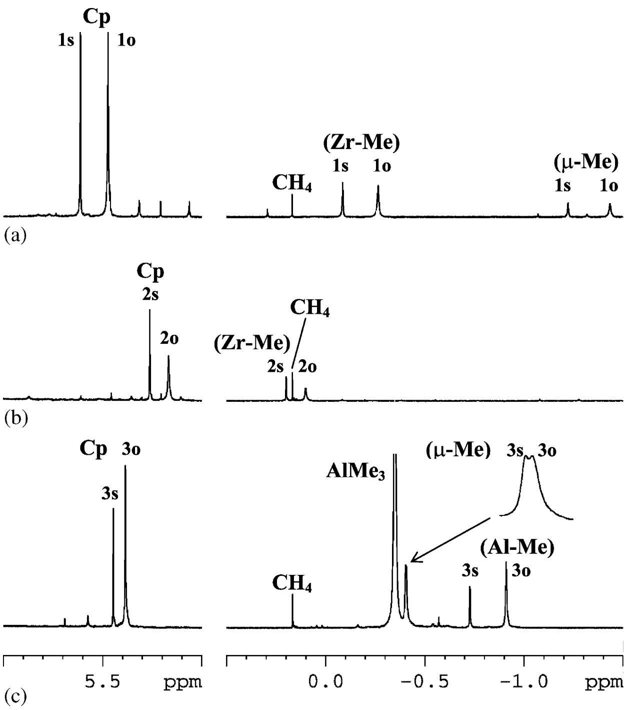


Fig. 1. ^{1}H-NMR spectra of cationic species recorded 5 min after sample preparations in benzene at 20 °C at various $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]/AlMe_3$ ratios: Zr/B/Al = 2:1:0 (a), Zr/B/Al = 2:2:0 (b) and Zr/B/Al = 2:2:2 (c). All samples contained 0.014 mg Cp_2ZrMe_2 in 1 ml benzene-d_6.

The ^{1}H-NMR spectrum of the solution layer decanted from the NMR tube showed mainly peaks of **1s**. When the sample of Fig. 1a was held 15–30 min within the NMR spectrometer, the relative concentration of **1o** decreased dramatically by a factor of 5–10, in parallel with precipitation of oil particles to the bottom of the tube. This precipitation thus decreased the amount of **1o** in the measuring region of the NMR tube. Shaking the NMR tube just before recording of ^{1}H-NMR spectra restored the initial ratio between **1s** and **1o**. Hence, the two sets of ^{1}H resonances observed must belong to complex **1** in the solvent and oil constituents of the reaction mixture, respectively. The ^{1}H chemical shifts of **1s** are close to those reported for complex **1** in diluted benzene solution ([7], Table 1).

Two types of dinuclear cationic complexes $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[Me\text{–}B(C_6F_5)_3]^-$ were previously observed by Beck et al. in the reaction of Cp_2ZrMe_2 with $B(C_6F_5)_3$ in benzene-d_6, and were assigned by the authors to associated and separated ion pairs [8]. In a later work the same authors assigned the second set of

Table 1
^{1}H-NMR signals of cationic species formed via activation of Cp_2ZrMe_2 with $B(C_6F_5)_3$, $[CPh_3][B(C_6F_5)_4]$, and $AlMe_3/[CPh_3][B(C_6F_5)_4]$ in benzene

Species	Cp	Zr–Me	μ-Me	Al–Me	Reference
Cp_2ZrMe_2	5.70 (s, 10)	−0.12 (s, 6)	–	–	
$[Cp_2ZrMe^+\cdots Me{-}B(C_6F_5)_3^-]$	5.39 (s, 10)	0.28 (s, 3)	–	–	
$[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[Me{-}B(C_6F_5)_3]^-$ (s)	5.62 (s, 20)	−0.12 (s, 6)	−1.19 (s, 3)	–	[8]
$[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[Me{-}B(C_6F_5)_3]^-$ (a)	5.52 (s, 20)	−0.19 (s, 6)	−1.39 (s, 3)	–	
$[Cp_2ZrMe^+\cdots B(C_6F_5)_4^-]$	5.20 (s, 10)	0.15 (s, 3)			[7]
$[Cp_2ZrMe^+\cdots B(C_6F_5)_4^-]$ (**2s**)	5.26 (s, 10)	0.20 (s, 3)	–	–	this work
$[Cp_2ZrMe^+\cdots B(C_6F_5)_4^-]$ (**2o**)	5.17 (s, 10)	0.10 (s, 3)	–	–	
$[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$	5.56 (s, 20)	−0.13 (s, 6)	−1.27 (s,3)	–	[7]
$[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$ (**2s**)	5.61 (s, 20)	−0.09 (s, 6)	−1.22 (s, 3)	–	this work
$[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$ (**2o**)	5.47 (s, 20)	−0.27 (s, 6)	−1.44 (s, 3)	–	
$[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (**3s**)	5.44 (s, 10)	–	−0.40 (s, 6) [a]	−0.73 (s, 6)	this work
$[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (**3o**)	5.38 (s, 10)	–	−0.41 (s, 6)	−0.91 (s, 6)	
$[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me{-}MAO]^-$	5.5 (s, 10)	–	−0.27 (s, 6)	−0.58 (s, 6)	[10]

[a] The chemical shift of this signal depends on the concentration of $AlMe_3$.

^{1}H peaks observed for $[Cp_2ZrMe(PR_3)]^+[Me{-}B(C_6F_5)_3]^-$ (PR_3 is triaryl phosphine) in benzene to the same species, but in a more highly aggregated form, possibly in a colloidal microphase [9]. Comparing the chemical shifts for the two sets of peaks observed for $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[Me{-}B(C_6F_5)_3]^-$ by Beck et al., [8] with those for complexes **1s** and **1o** (Table 1), reveals that in both cases cationic intermediates are present both in the solvent and the oil constituents.

3.1.2. $[Cp_2ZrMe^+\cdots B(C_6F_5)_4^-]$ (2)

A highly concentrated sample containing Cp_2ZrMe_2 and $[CPh_3][B(C_6F_5)_4]$ in 1:1 ratio in benzene-d_6 at room temperature displays two sets of ^{1}H resonances of cationic complex **2**. As in the previous case, these two sets of NMR peaks were assigned to **2** present in solvent (**2s**) and oil (**2o**) constituents of the reaction mixture based on the same experimental evidences (Fig. 1b, Table 1). Chemical shifts of **2s** were close to those reported for **2** in diluted benzene solution [7].

3.1.3. $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (3)

Addition of 20-fold excess of trimethylaluminium ($AlMe_3$) to the sample of Fig. 1b, containing Cp_2ZrMe_2 and $[CPh_3][B(C_6F_5)_4]$ in 1:1 ratio, gave rise to the formation of the heterodinuclear cation **3**. Separate sets of ^{1}H-NMR resonances were observed for **3** present in solution and oil phases of the reaction mixture (**3s** and **3o**, Fig. 1c, Table 1). ^{1}H-NMR data for **3s** in benzene-d_6 are so far not reported. However, its chemical shifts resemble those for cationic complex $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me\text{-}MAO]^-$ in MAO based system ([10], Table 1). The data obtained have allowed us to identify and thus monitor the cationic species **1**–**3** in the solvent and the oil constituents of the catalytic systems concerned.

3.2. $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ and $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ systems in diluted benzene solutions

For the study of the stability of **1s** in benzene at 20 °C, a sample with 2:1 $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ ratio was prepared ($[Cp_2ZrMe_2] = 1.5$ mmol l^{-1}). In this sample only **1s** is present in the reaction solution and decomposes with a half-life of about 3 h.

In the sample with 1.5:1 Zr/B ratio ($[Cp_2ZrMe_2] = 1.5$ mmol l^{-1}), a strikingly different picture was observed. Just after sample preparation, complex **1s** predominated in solution, then it is almost cleanly converted into complex **2s** with a first order rate constant of 4×10^{-4} s^{-1} at 20 °C. This value is close to that reported for similar reaction in $(SBI)ZrMe_2$ based system (3×10^{-4} s^{-1}, [7]). The half-life for further decomposition of complex **2s** was about 5 h.

We have tried to compare qualitatively activities of **1s** and **2s** towards polymerization of 1-hexene. For this goal, the same amounts of 1-hexene (to make its concentration 0.5 M) were added to two similar samples 5 and 100 min after sample preparation (Zr/B = 1.5, $[Cp_2ZrMe_2] = 1.5$ mmol l^{-1}). According to ^{1}H-NMR, in the first sample **1s** dominates in the reaction solution before addition of 1-hexene, while in the second sample complex **2s** is the major species. The concentrations of **1s** and **2s**, respectively, were similar within ±30%. After addition of 1-hexene, ^{1}H-NMR resonances of complexes **1s** and **2s** disappeared within 3 min (the time of acquisition of the ^{1}H-NMR spectrum). Polymerization of 1-hexene can be monitored by the decrease of the ^{1}H resonances of the monomer and the corresponding growth of polymer peaks. The polymerization rate is high during the first minutes after reaction onset, then it slowly (during 1–2 h) proceeds towards a complete conversion of the monomer. Ratios between concentrations of monomer and polymer were measured by ^{1}H-

NMR 10 min after onset of the reaction with 1-hexene in samples with **1s** and **2s** as predominant species. These ratios (monomer/polymer = 1:1–1:2) differed for two samples by not more than a factor of two, an evidence in favor of close activity levels of **1s** and **2s** towards polymerization of 1-hexene. For samples containing only complex **2s**, a lower concentration of **2s** gave lower polymerization rate, as determined by the ratio between polymer and monomer 10 min after reaction onset. No polymerization activity was observed for samples exhibiting no resonances of complexes **1s** or **2s**. Thus, the activities of complexes **1s** and **2s** are comparable.

It has previously been shown that the reaction of $[CPh_3][B(C_6F_5)_4]$ with Cp_2ZrMe_2 in dichloromethane at −60 °C formed **1**, even in the presence of the excess trityl salt. Conversion to **2** occurred only on warming [11]. Our results are in agreement with this observation. Probably, coordination of the neutral molecule Cp_2ZrMe_2 to the vacant coordination site of Cp_2ZrMe^+ to yield **1** is kinetically preferred to coordination of the bulky $B(C_6F_5)_4^-$ to yield **2**. Further, conversion of **1**–**2** evidences that a complex between Cp_2ZrMe^+ and $B(C_6F_5)_4^-$ is more stable than a complex between Cp_2ZrMe^+ and Cp_2ZrMe_2, with $B(C_6F_5)_4^-$ in outer sphere.

In order to elucidate the effect of $AlMe_3$ on the stability of cationic species in the catalytic system $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$, two samples with 1.5:1 Zr/B ratio were prepared. To make samples equivalent, appropriate amounts of solid Cp_2ZrMe_2 and $[CPh_3][B(C_6F_5)_4]$ were thoroughly mixed on a spot plate. Then the same amounts of this mixture were placed into two NMR tubes and 0.5 ml of benzene-d_6 were added to each tube ($[Cp_2ZrMe_2] = 1.5\ \text{mmol}\ l^{-1}$). The sample in the first tube was used for comparison, whereas to the second tube, five equivalents of $AlMe_3$ with respect to $[CPh_3][B(C_6F_5)_4]$ were added. In the first tube, **1s** was converted to **2s**, and subsequently **2s** decayed with a half-life of 4 h. In the samples containing $AlMe_3$, the observed picture differed dramatically. For the cationic complexes **1s**, **3s** detected in the sample containing five equivalents of $AlMe_3$ no pronounced changes in their concentrations were observed during 48 h at room temperature, hence they were all more stable than in sample with no additives of $AlMe_3$. Complex **3s** was the predominant species in the $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ system at $Al/Zr > 20$. Its reactivity towards 1-hexene, evaluated by the described procedure, was close to those of **1s** and **2s**. Thus activities of **1s**, **2s** and **3s** towards polymerization of 1-hexene are of the same order of magnitude.

An interesting picture was observed when one equivalent of $AlMe_3$ was added to the sample with 1:1 Zr/B ratio ($[Cp_2ZrMe_2] = 1.5\ \text{mmol}\ l^{-1}$). First predominantly complex **3s** formed (minor amounts of complexes **1s** and **2s** were also detected), then with a half-life of 1 h the signals of **3s** disappeared and those of **2s** grew. This is similar to the conversion of **1s**–**2s** described above. Thus, complexes **1s**–**3s** are close in energy to each other, and can be readily converted to one another by changing the ratio between Cp_2ZrMe_2, $[CPh_3][B(C_6F_5)_4]$ and $AlMe_3$. Complexes **1s**–**3s** are formed via coordination of Cp_2ZrMe_2, $[B(C_6F_5)_4]$ and $AlMe_3$ to the Cp_2MeZr^+ cation, respectively. The comparable activities of **1s**–**3s** towards polymerization of 1-hexene suggest that an olefin molecule readily replaces all these ligands to produce the actual reactive intermediate, Cp_2MeZr^+(olefin).

$AlMe_3$ increases noticeably the stability of cationic species in the catalytic system $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ through capturing of impurities.

3.3. $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ system in concentrated benzene solution

For comparison of the stabilities of cationic intermediates **1** and **2** in solution and oil constituents of the $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ system, a sample with 1.5:1 $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ ratio was prepared in 1 ml of benzene-d_6 directly in 5 mm NMR tube ($[Cp_2ZrMe_2] = 0.05$ M). The upper 0.5 ml of the mixture was decanted into another tube 20 min after sample preparation. Then concentrations of complexes **1** and **2** were monitored in both tubes.

Complexes **1s** and **2s** dominated in the sample containing the upper part of the reaction mixture, their concentrations estimated to be about 1 mmol l^{-1} just after sample preparation. Then ^{1}H-NMR resonances of **1s** and **2s** disappeared during 3 h after onset of the reaction as in the case of independently prepared diluted sample with 1.5:1 $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ ratio.

In contrast, in the sample containing the lower part of reaction mixture, complex **1s** decayed with a half-life of 20 h, while complex **2s** was stable at room temperature.

The ratio between the concentrations of **1s** and **2s** followed the ratio between the concentrations of **1o** and **2o**. The latter ratio can be readily obtained by shaking the sample before recording of the ^{1}H-NMR spectrum. This means that the cationic species exchange rather rapidly between solvent and oil phases. Characteristic time for this exchange must be between 10^{-1} s (to fulfil conditions of slow exchange in the ^{1}H-NMR time scale between **1s** and **1o**, **2s** and **2o**) and 10^2 s (to be noticeably smaller than characteristic time of the conversion of **1s**–**2s** in the solution phase).

Thus, complexes **1** and **2** are far more stable in the oil phase than in the solvent constituent of the catalytic system $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$.

Experiments similar to those described for $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4$ system were made for the catalytic system $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$, $Al/Zr = 50$, $[Cp_2ZrMe_2] = 0.05$ M. It was shown that complex **3** is very stable both in solvent and oil constituents of the reaction mixture, its concentration did not change noticeably during several days at 50 °C. The sample containing complex **3** was still able to polymerize 1-hexene 4 days after storing at 50 °C.

A main result of the presented study is the assignment of the NMR signals due to oil droplet formation in cationic zirconocene species, as opposed to their assignments to different types of ion pairs, and qualitative assessment of the stabilities of these species under different conditions. The observed differences in the stabilities of the complexes in the oil and the solvent phases are by themselves important as they may hint to new approaches on how to handle the catalysts in order to optimize their output.

4. Conclusions

Using ^{1}H-NMR spectroscopy, mutual transformations and stability of cationic complexes $[(Cp_2ZrMe)_2(\mu\text{-}Me)]^+[B(C_6F_5)_4]^-$ (**1**), $[Cp_2ZrMe^+\cdots B(C_6F_5)_4^-]$ (**2**) and $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (**3**) formed in catalytic systems $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ and $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ in benzene were studied both in solution and in the oil deposit formed whenever the total zirconocene concentration is high enough.

It is shown that, at high zirconocene concentrations, the decay rate of complexes **1** and **2** in the oil constituent of the reaction mixture is at least a factor ten lower than that in the solvent constituent.

Complex **1** reacts with excess of $[CPh_3][B(C_6F_5)_4]$ to yield **2** with first order rate constant of 4×10^{-4} s^{-1} at room temperature. Addition of small amounts of $AlMe_3$ to the system $Cp_2ZrMe/[CPh_3][B(C_6F_5)_4]$, $Al/Zr = 1$ gives rise to formation of **3** and a noticeable increase in the stability of the cationic species **1** and **2**. Complex **3** reacts with excess $[CPh_3][B(C_6F_5)_4]$ to yield **2** with a half-life of 1 h at 20 °C. Complexes **1**–**3** are close in energy to each other and can be readily converted to one another by changing the ratio between Cp_2ZrMe_2, $[CPh_3][B(C_6F_5)_4]$ and $AlMe_3$. Addition of 1-hexene to samples containing varying relative amounts of complexes **1**–**3** and ^{1}H-NMR monitoring of the polymer/monomer ratio, showed that **1**–**3** exhibit comparable polymerization activities.

Acknowledgements

Funding from the Norvegian Research Council under the Polymer Science program is acknowledged. EPT appreciate support of INTAS grant 00-0841. Albemarle Corp. is acknowledged for donation of the sample of $[CPh_3][B(C_6F_5)_4]$.

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