Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 859–868
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Formation and structures of cationic zirconium complexes in ternary systems *rac*-(SBI)$ZrX_2/AlBu^i_3/[CPh_3][B(C_6F_5)_4]$ (X = Cl, Me)

Konstantin P. Bryliakov [a,b,*], Evgenii P. Talsi [a,b], Nina V. Semikolenova [b], Vladimir A. Zakharov [b], Jörg Brand [c], Carlos Alonso-Moreno [d], Manfred Bochmann [d,*,1]

[a] *Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation*
[b] *Department of Natural Sciences, Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[c] *Fachbereich Chemie, University of Konstanz, D-78457 Konstanz, Germany*
[d] *Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, United Kingdom*

Received 12 September 2006; received in revised form 9 October 2006; accepted 16 October 2006

Abstract

Using ^{13}C, ^1H and ^{19}F NMR spectroscopy, formation of cationic species was studied in ternary systems $(SBI)ZrX_2/AlBu^i_3/[CPh_3][B(C_6F_5)_4]$, where X = Cl, Me [(SBI) = *rac*-$Me_2Si(Ind)_2$]. In the first system (X = Cl), the ion pair $[(SBI)Zr(\mu\text{-}Cl)_2Zr(SBI)][B(C_6F_5)_4]_2$ (**IV**) predominates at low Al/Zr ratios (Al/Zr < 10), whereas at higher Al/Zr ratios (⩾20) in the absence of monomer mainly $[(SBI)Zr(\mu\text{-}H)(\mu\text{-}C_4H_7)AlBu^i_2]\,[B(C_6F_5)_4]$ (**V**) is formed. The binuclear complex $[(SBI)Zr(\mu\text{-}Cl)_2Zr(SBI)][B(C_6F_5)_4]_2$ has been characterized crystallographically. Species **V** is also formed in the system X = Me at high Al/Zr ratios. In the presence of $AlBu^i_3$, **IV** displays activity in propylene polymerization and is the most likely precursor of the polymerizing species. Consistent mechanisms have been proposed for the reactions in these catalytic systems.

Keywords: Metallocenes; Catalysis; Activation; Intermediate; Triisobutyl aluminum; NMR

1. Introduction

Mixtures of triisobutyl aluminum (TIBA) and cation generating agents are widely used as co-catalysts in ternary systems for olefin polymerizations based on group IV metallocene complexes [1–9]. In some cases these TIBA-based activator systems are capable of increasing catalyst activities by 1–2 orders of magnitude compared to methylalumoxane (MAO) activation [10–13]. It is now generally accepted that the active species in metallocene-based catalysts are electron-deficient alkyl complexes [LL'MR$^+$] (where R = alkyl) paired with weakly coordinating counteranions, and it is thought that TIBA serves to generate a highly reactive metal alkyl species [14–18]. On the other hand, TIBA is known to be in equilibrium with $HAlBu^i_2$ which could act as a hydride source [19], and the precise nature of the reaction products of TIBA with metallocenes under catalytic conditions is unknown.

Recently, Götz and co-workers have reported an NMR investigation of the products of successive reaction of Cp_2ZrCl_2 and $Ph_2C(Cp)(Flu)ZrCl_2$ with Al^iBu_3 and $[PhNMe_2H][B(C_6F_5)_4]$ at elevated temperature (60 °C) [20]. They found the surprising formation of hydrido-bridged Zr–Al binuclear species, although some intermediates could only be tentatively identified. In view of our earlier studies of the kinetics of the high-activity catalysts $(SBI)ZrX_2/TIBA/[CPh_3][B(C_6F_5)_4]$ (SBI = *rac*-$Me_2Si(Ind)_2$, X = Cl or Me) [18,21] we were therefore interested in elucidating the role of TIBA under these conditions. In this paper, ^1H, ^{13}C and ^{19}F NMR spectroscopic study of this system is

---

[*] Corresponding authors. Tel.: +7 383 3306877; fax: +7 383 3308056.
E-mail addresses: bryliako@catalysis.ru (K.P. Bryliakov), m.bochmann@uea.ac.uk (M. Bochmann).

[1] Fax: +44 1603 592044.

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.10.037

presented, and several types of cationic zirconium species have been detected and characterized.

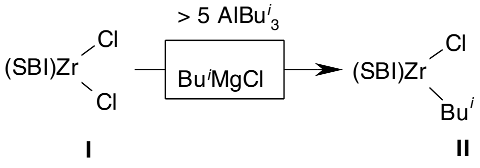
2. Results and discussion

2.1. The system $(SBI)ZrCl_2/AlBu^i_3/[CPh_3][B(C_6F_5)_4]$

Reaction of $(SBI)ZrCl_2$ (**I**) with $AlBu^i_3$ at room temperature in an Al/Zr ratio of 2:1 in toluene lead to a mixture of **I** and $(SBI)ZrClBu^i$ (**II**) (**I**/**II** ratio 2.3:1). At Al/Zr = 5:1, 90% conversion to **II** was the case (see Section 4). No other species (i.e. Zr hydrides, etc.) rather than **I** and **II** were observed in the mixture. The identity of **II** was confirmed by independent synthesis via reaction of **I** with ^{i}BuMgCl in toluene at 0–10 °C (see Section 4). An orange solid was formed almost quantitatively (Scheme 1). The complex is unstable in toluene and decays within hours at room temperature at Al/Zr = 5:1.

Addition of $[CPh_3][B(C_6F_5)_4]$ to $(SBI)ZrClBu^i$ formed in situ at room temperature rapidly produces a blue or green-blue oily residue as the lower phase, which contains the target ionic compounds, and a clear supernatant which contains TIBA, $HCPh_3$ and isobutene. NMR spectra were run either directly on the oily liquid, or 20 vol% of a polar solvent (i.e. 1,2-difluorobenzene or 1,2-dichlorobenzene) was added to the samples to obtain a homogeneous solution. Two zirconium species were detected in the NMR spectra of the oily phase, their ratio depending on the Al/Zr ratio used.

At low Al/Zr ratios (5–10) a new zirconium species **IV** was detected as a major product. In principle, under these conditions one might expect the formation of a cationic methallyl complex $[(SBI)Zr(\eta_3\text{-}CH_2CMeCH_2)][B(C_6F_5)_4]$ similar to those described previously [22,23]. However, no spectroscopic evidence for the formation of such species was obtained. Compound **IV** displays two characteristic doublets for the cyclopentadienyl protons of the SBI ligand in the ^{1}H spectra, at δ 5.39 and 6.42 (with the corresponding ^{13}C peaks at δ 121.6 and 122.6, Fig. 1), and a single resonance for Si–Me groups at δ 0.84. Apparently, **IV** is an ionic product with $[B(C_6F_5)_4]^-$ as counter-anion (^{19}F NMR: δ −133.3, −163.9, −167.7) (cf. [22,23]), its cationic part displaying C_2-symmetry. No coordination of the anion to Zr was observed in the ^{19}F NMR spectra. The C_5 part of **IV** is also characterized by a single ^{13}C peak at δ 88.2 (2C, assigned to Si–*C*(Cp) carbons on the basis of long range C,H-correlated spectra). Based on these spectral data, and taking into account the documented capability of cyclopentadienyl zirconium derivatives to form bis(μ-chloro) bridged dications [24,25], **IV** could be identified as $[(SBI)Zr(\mu\text{-}Cl)_2Zr(SBI)][B(C_6F_5)_4]_2$ ion pair. No spectroscopic evidence for the formation of *meso*- and *rac*-like diastereomers (as in the case of $[\{(SBI)ZrMe\}_2(\mu\text{-}Me)][B(C_6F_5)_4]$ for example [26]) was obtained. Apparently, one of the diastereomers strictly prevails in our case. On the basis of the spectroscopic and literature data [20], a possible route for the formation of **IV** was derived (Scheme 2).



Scheme 1. Preparation of complex **II**.

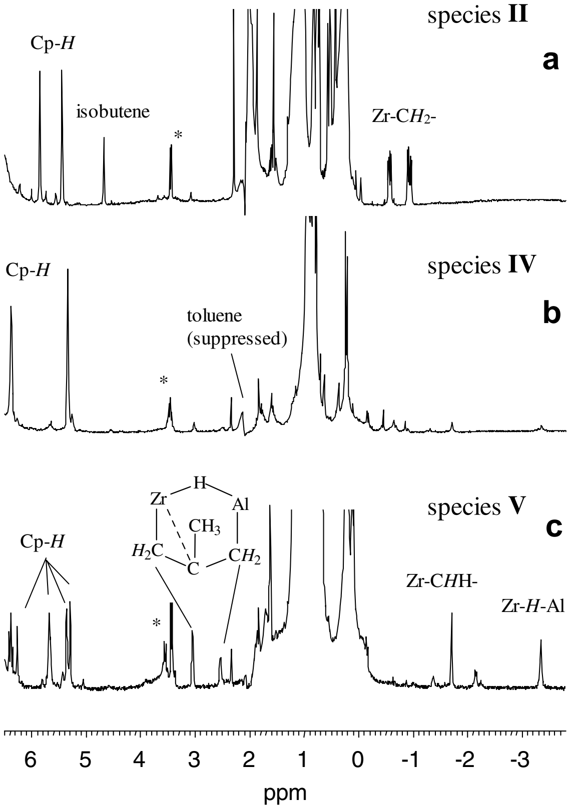


Fig. 1. ^{1}H NMR spectra (20 °C) of the systems $(SBI)ZrCl_2$/TIBA = 1:5, toluene (a), $(SBI)ZrCl_2/TIBA/[CPh_3][(C_6F_5)_4]$ = 1:5:1, toluene/1,2-dichlorobenzene (b), sample (b) after 30 min stirring with extra 25-fold excess of TIBA (c). Asterisks mark impurities in TIBA.

The formation of **IV** can be explained by β-hydride abstraction by CPh_3^+ from **II**, presumably to give the labile cation $[(SBI)Zr(Cl)\text{–}CH_2C^{(+)}(CH_3)_2]$, followed by loss of isobutene and generation of **IV**. The NMR spectra showed that **IV** does not react with isobutene when the latter is present in the sample. By contrast, injection of 10 mL of propylene gas into the NMR sample containing a slightly pre-cooled solution of complex **IV** with residual TIBA (see Section 4) showed fast (within seconds) gas consumption, followed by the formation of solid polymer in the upper part of the sample (^{13}C: δ 46.4 (CH_2), 27.8 (CH), 22.0 (CH_3)).

To corroborate our assignment of the species **IV**, we prepared it independently. Taking into account the well documented tendency of $[CPh_3][B(C_6F_5)_4]$ to abstract a methyl-anion from methylated metal complexes, one could expect the reaction of (SBI)ZrClMe with $[CPh_3][B(C_6F_5)_4]$