

Formation and structures of cationic zirconium complexes in ternary systems $rac\text{-(SBI)ZrX}_2/\text{AlBu}_3^i/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{X} = \text{Cl}, \text{Me}$)

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Abstract

Using ^{13}C , ^1H and ^{19}F NMR spectroscopy, formation of cationic species was studied in ternary systems $(\text{SBI})\text{ZrX}_2/\text{AlBu}_3^i/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, where $\text{X} = \text{Cl}, \text{Me}$ [$(\text{SBI}) = rac\text{-Me}_2\text{Si}(\text{Ind})_2$]. In the first system ($\text{X} = \text{Cl}$), the ion pair $[(\text{SBI})\text{Zr}(\mu\text{-Cl})_2\text{Zr}(\text{SBI})][\text{B}(\text{C}_6\text{F}_5)_4]_2$ (**IV**) predominates at low Al/Zr ratios ($\text{Al/Zr} < 10$), whereas at higher Al/Zr ratios (≥ 20) in the absence of monomer mainly $[(\text{SBI})\text{Zr}(\mu\text{-H})(\mu\text{-C}_4\text{H}_7)\text{AlBu}_2^i][\text{B}(\text{C}_6\text{F}_5)_4]$ (**V**) is formed. The binuclear complex $[(\text{SBI})\text{Zr}(\mu\text{-Cl})_2\text{Zr}(\text{SBI})][\text{B}(\text{C}_6\text{F}_5)_4]_2$ has been characterized crystallographically. Species **V** is also formed in the system $\text{X} = \text{Me}$ at high Al/Zr ratios. In the presence of AlBu_3^i , **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.

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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 $[\text{LL}'\text{MR}^+]$ (where $\text{R} = \text{alkyl}$) paired with weakly coordinating count-

erions, 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_2^i 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 $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ with Al^iBu_3 and $[\text{PhN-Me}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ 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 $(\text{SBI})\text{ZrX}_2/\text{TIBA}/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{SBI} = rac\text{-Me}_2\text{Si}(\text{Ind})_2$, $\text{X} = \text{Cl}$ 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

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

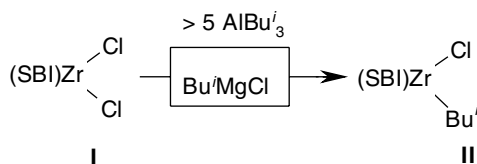
2. Results and discussion

2.1. The system (SBI)ZrCl₂/AlBu₃ⁱ[CPh₃][B(C₆F₅)₄]

Reaction of (SBI)ZrCl₂ (**I**) with AlBu₃ⁱ at room temperature in an Al/Zr ratio of 2:1 in toluene lead to a mixture of **I** and (SBI)ZrClBuⁱ (**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 ⁱBuMgCl 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 [CPh₃][B(C₆F₅)₄] to (SBI)ZrClBuⁱ 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, HCPH₃ 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(η³-CH₂CMeCH₂)] [B(C₆F₅)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 ¹H spectra, at δ 5.39 and 6.42 (with the corresponding ¹³C 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(C₆F₅)₄][−] as counter-anion (¹⁹F NMR: δ −133.3, −163.9, −167.7) (cf. [22,23]), its cationic part displaying C₂-symmetry. No coordination of the anion to Zr was observed in the ¹⁹F NMR spectra. The C₅ part of **IV** is also characterized by a single ¹³C 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 cyclopen-



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

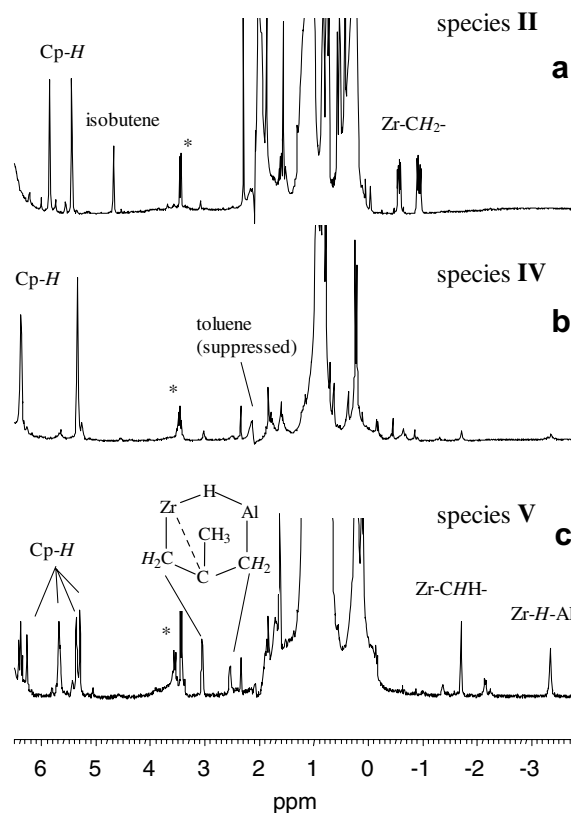
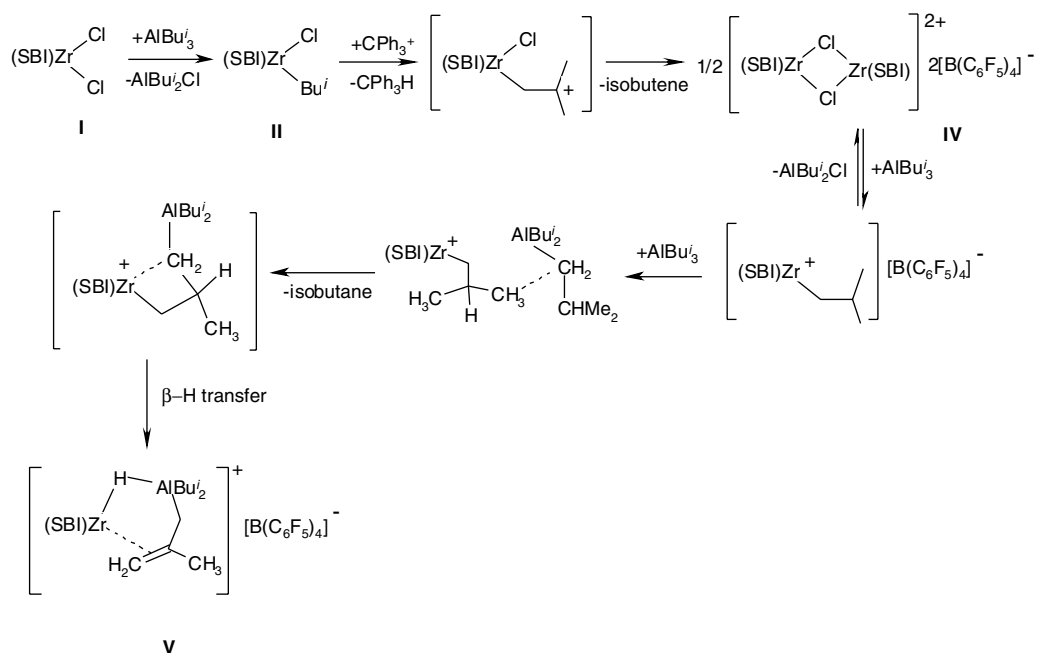


Fig. 1. ¹H NMR spectra (20 °C) of the systems (SBI)ZrCl₂/TIBA = 1:5, toluene (a), (SBI)ZrCl₂/TIBA/[CPh₃][B(C₆F₅)₄] = 1:5:1, toluene/1,2-dichlorobenzene (b), sample (b) after 30 min stirring with extra 25-fold excess of TIBA (c). Asterisks mark impurities in TIBA.

tadienyl zirconium derivatives to form bis(μ-chloro) bridged dications [24,25], **IV** could be identified as [(SBI)Zr-(μ-Cl)₂Zr(SBI)] [B(C₆F₅)₄]₂ ion pair. No spectroscopic evidence for the formation of *meso*- and *rac*-like diastereomers (as in the case of [(SBI)ZrMe]₂(μ-Me)] [B(C₆F₅)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).

The formation of **IV** can be explained by β-hydride abstraction by CPh₃⁺ from **II**, presumably to give the labile cation [(SBI)Zr(Cl)-CH₂C⁽⁺⁾(CH₃)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 (¹³C: δ 46.4 (CH₂), 27.8 (CH), 22.0 (CH₃)).

To corroborate our assignment of the species **IV**, we prepared it independently. Taking into account the well documented tendency of [CPh₃][B(C₆F₅)₄] to abstract a methyl-anion from methylated metal complexes, one could expect the reaction of (SBI)ZrCIME with [CPh₃][B(C₆F₅)₄]

Scheme 2. Suggested routes for the formation of intermediates **IV** and **V**.

to lead to species **IV**. The monomethylated zirconocene complex was prepared in situ by dissolution of (SBI)ZrCl₂ in toluene solution of AlMe₃ at an Al/Zr ratio of 7.5 (at this particular ratio, in agreement with the work of Brintzinger and Beck [27], we obtained 90% conversion of the starting Zr complex to the monomethyl product). Then, [CPh₃][B(C₆F₅)₄] was added (Zr/B = 1:1). As expected, the situation was somewhat complicated by the excess of AlMe₃ due to its ability to form heterobinuclear complexes with Zr [26]. Indeed, a mixture of two cationic Zr complexes was obtained. The major one (ca. 60%) was the heterobinuclear Zr complex [(SBI)Zr(μ-Me)₂AlMe₂][B(C₆F₅)₄] (for NMR characterization of heterobinuclear zirconocene complexes see [26,28,29]), while the minor one (ca. 40%) was the target species **IV**. This experiment confirms clearly that **IV** does not contain any alkyl ligands at the Zr atom. Species **IV** is not unusual and can be obtained with aluminum alkyls other than TIBA [24,25] (see Fig. 2).

Alternatively, **IV** was successfully generated by the synthetic procedure described by Jordan et al. for similar zirconocene complexes [25]. At the first stage, (SBI)ZrMe₂ was reacted with 1.0 equiv. of [CPh₃][B(C₆F₅)₄] to obtain [(SBI)ZrMe(S)][B(C₆F₅)₄] **III** (cf. [11]), (where S stands for solvent molecule), followed by the addition of Me₃SiCl to produce the expected species **IV** (Scheme 3).

Complex **IV** can be stored in a refrigerator for several days both in the oily phase and in toluene/1,2-dichlorobenzene or toluene/1,2-difluorobenzene solution. However, when species **IV** formed in the system (SBI)ZrCl₂AlBu₃ⁱ-[CPh₃][B(C₆F₅)₄] = 1:5:1 (see Section 4) was exposed to ambient temperature for ca. 1 week, single crystals formed. X-ray diffraction revealed the [(SBI)Zr(μ-Cl)₂Zr(SBI)][B(C₆F₅)₄]₂ structure for **IV** (Fig. 3), similar

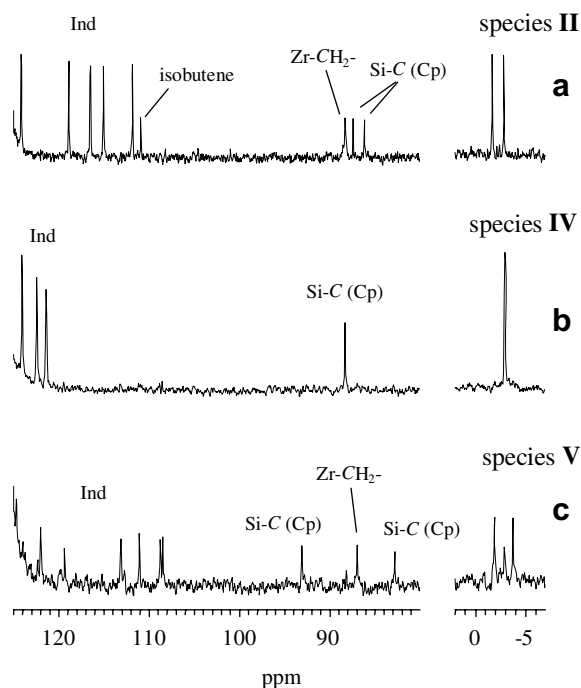


Fig. 2. ¹³C NMR spectra (20 °C) of the systems (SBI)ZrCl₂/TIBA = 1:10, toluene (a), (SBI)ZrCl₂/TIBA/[CPh₃][B(C₆F₅)₄] = 1:5:1 toluene/1,2-dichlorobenzene (b), sample (b) after 30 min stirring with extra 25-fold excess of TIBA (c). In the higher-field part, signals of Si-CH₃ carbons are presented.

to the previously reported [(Cp^R)₂Zr(μ-Cl)₂][B(C₆F₅)₄]₂ (Cp^R = Cp, C₅H₄Me) [25].

At higher Al/Zr ratios, magnetic stirring at room temperature for 10–30 min afforded a brown oily phase containing a new cationic species **V**, along with toluene,

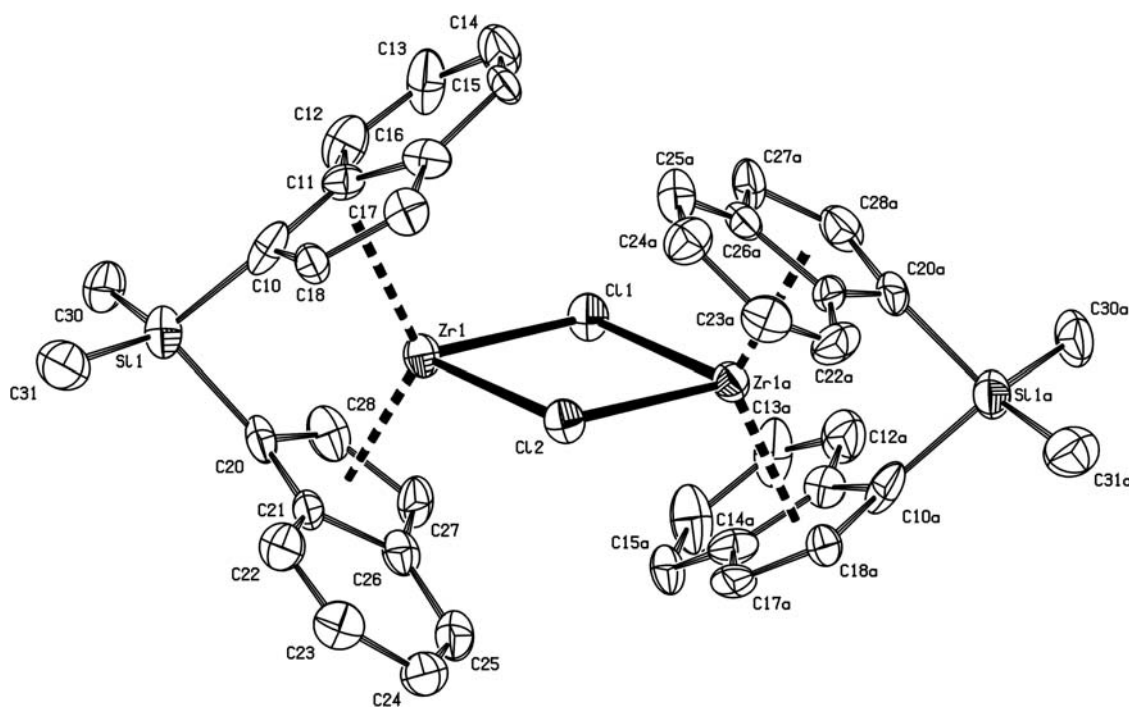
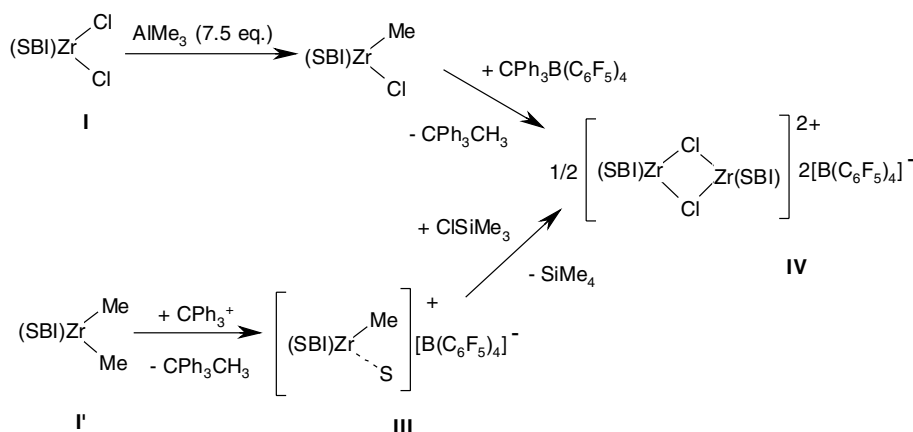


Fig. 3. ORTEP [30] plot of the μ_2 -Cl bridged dication $[(\text{SBI})\text{Zr}(\mu\text{-Cl})_2\text{Zr}(\text{SBI})][\text{B}(\text{C}_6\text{F}_5)_4]_2$ (IV). H atoms omitted for clarity (displacement ellipsoids 50%). Symmetry operation for atoms whose labels are marked with an a: $(-x, y, 0.5 - z)$.

residual IV and aluminum alkyls. For example, at an Al/Zr ratio of 30, the [IV]/[V] ratio amounted to 1:4 after 30 min stirring. The NMR spectra of V provide evidence for an allyl-bridged heterobinuclear complex, similar to the structure proposed by Götz for a $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})$ complex [20]. Species V displays C_1 symmetry, according to two ^{13}C resonances for two non-equivalent Si-CH₃ groups at $\delta -1.99$ and -3.82 . The Zr-CH₂ and Al-CH₂ peaks were found at $\delta 86.9$ and 53.8 , respectively, and the CH₂=CMe-signal was observed at $\delta 166.6$, i.e. at a chemical shift characteristic of a methallylic structure. The NMR data for the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion in V are as expected (^{19}F : $\delta -133.0, -163.7, -167.5$) [22,23]. This methallylic complex is stable for at least 1 day at room temperature. The route proposed for the conver-

sion of IV–V remains hypothetical, since no direct spectroscopic evidence for the elusive intermediates (placed in square brackets in Scheme 2) was obtained. The evolution of isobutane could not be confirmed unequivocally, since V is obtained at a high excess of TIBA which always contains isobutane and isobutene as impurities.

It is known that some HAIBu_2^1 (DIBAH) is always present in commercial TIBA samples, thus at high Al/Zr ratios DIBAH might be expected to affect the chemical reactions in the above system. The possible role of HAIBu_2^1 was tested in two experiments. In the first one, addition of $[\text{CPh}_3]\text{B}(\text{C}_6\text{F}_5)_4$ (Zr/B = 1:1) to a mixture of $(\text{SBI})\text{ZrCl}_2$ / TIBA / DIBAH (Zr:Al:Al = 1:3.5:1.5) resulted in the generation of IV along with unidentified minor species having broad

^1H NMR peaks. Further addition of TIBA ($\text{Al}/\text{Zr} = 20$) led to conversion to **V** (with minor by-products), as was the case without added DIBAH. In the second sample, species **IV** was generated in ordinary way ($(\text{SBI})\text{ZrCl}_2/\text{Al}^i\text{Bu}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Zr}:\text{Al}:\text{B} = 1:5:1$), excess TIBA was removed by washing with toluene, and 1,2-dichlorobenzene was added to obtain a homogeneous solution). Then, HAl^iBu_2 ($\text{Zr}/\text{Al} = 1:3.5$) was added. After this operation, according to the ^1H and ^{13}C NMR spectra, **IV** converted to an unidentified species different from **V**, whereas traces of **V** (already present in **IV** before the addition of DIBAH) remained unchanged. Based on these results, we concluded that DIBAH did not participate in the transformations of interest, either alone or in combination with TIBA.

2.2. The system $(\text{SBI})\text{ZrMe}_2/\text{Al}^i\text{Bu}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$

The situation regarding the zirconocene dimethyl system $(\text{SBI})\text{ZrMe}_2/\text{Al}^i\text{Bu}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ is somewhat different. First of all, low Al/Zr ratios could not be used here, because even at $\text{Al}/\text{Zr} = 10$ only 50% of Zr were converted to $(\text{SBI})\text{ZrMeBu}^i$. Thus, a high excess of TIBA was used for sample preparation. It was found that after stirring the mixture $(\text{SBI})\text{ZrMe}_2\text{AlBu}_3^i/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Zr}:\text{Al}:\text{B} = 1:40:1$) for 15 min at room temperature, ca. 70% of the zirconium complex was converted to species **V** (Scheme 4) along with minor unidentified by-products.

An experiment with $(\text{SBI})\text{ZrMe}_2/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Zr}:\text{B} = 1:1$) clearly indicated the formation of known [11] species $[(\text{SBI})\text{ZrMe}(\text{S})][\text{B}(\text{C}_6\text{F}_5)_4]$ **III** (see Section 4). Addition of AlBu_3^i ($\text{Al}:\text{Zr} = 3$) immediately converted **III** into species **V** as the only zirconium product.

Nevertheless, an experiment with $(\text{SBI})\text{ZrMe}_2\text{AlBu}_3^i/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Zr}:\text{Al}:\text{B} = 1:5:1$) was undertaken and showed the formation of a red-brown oil containing a mixture of at least three zirconium species, all of which had mostly broad NMR lines. One of them is species **V**, however, we failed to assign other signals due to their broad line widths and overlapping signals. The reaction mixture

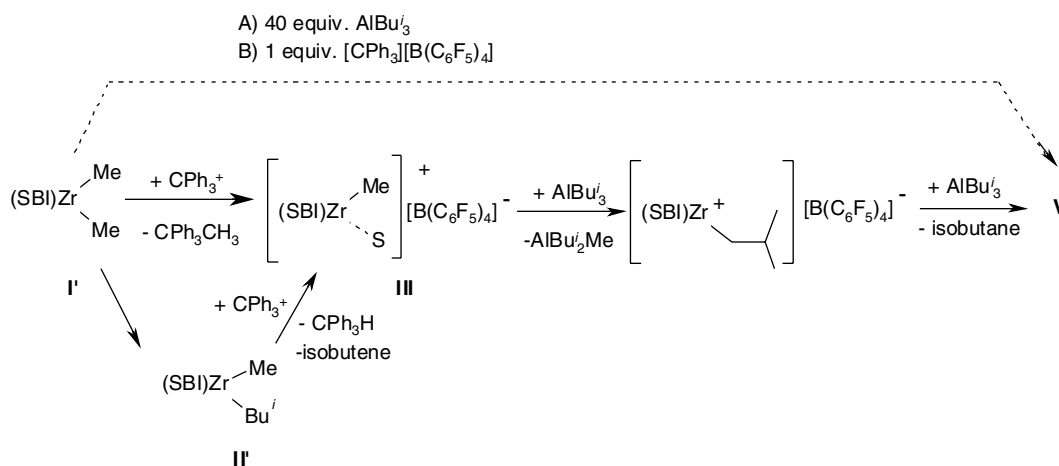
was unstable and converted to complexes of the type **V** (i.e. having ^1H peaks in the range of $\delta -1$ to -4) in the presence of a 2–3-fold excess of residual TIBA. After 12 h, mainly **V** was detected in the mixture.

Cationic hydride species are capable of initiating isobutene polymerization [22,31,32]. When different amounts of isobutene [(a) ca. 1 equiv.; (b) ca. 40 equiv.] were added to the NMR tube containing **V** and stirred for several minutes, the ^1H and ^{13}C NMR spectra showed dissolved polyisobutene (^{13}C , δ 60.0, CH_2 ; δ 38.6, C ; δ 31.7, CH_3), alongside unchanged species **V**.

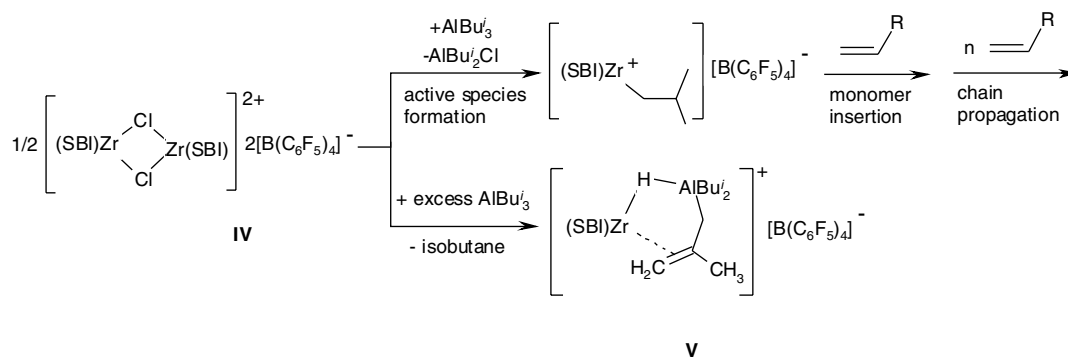
2.3. On the nature of the intermediates

Thus, at given concentrations ($[\text{Zr}] = 0.02\text{--}0.1\text{ M}$, $[\text{Al}] = 0.5\text{--}1.6\text{ M}$) species **IV** and **V** co-exist in solution, so that an excess of TIBA is required to convert **IV** into **V**. Once formed, **IV** could either transform into the active species (via replacement of the chloride ligand by isobutyl, as in the iron-based system reported by Babik and Fink [33]) with subsequent monomer insertion and chain propagation or react with TIBA to yield **V** (Scheme 5). Apparently, the latter reaction route is realized in the absence of the monomer. In practical polymerizations, the concentration of TIBA are 3–4 orders of magnitude lower than in this NMR study, so the formation of **V** should be much slower than monomer insertion and further polymerization. Besides, complex **IV** showed evident activity in propylene polymerization and is, therefore, the most likely precursor of the polymerizing species in the $(\text{SBI})\text{ZrX}_2/\text{AlBu}_3^i/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ catalysts.

The picture looks slightly different in the system $\text{rac}-(\text{SBI})\text{ZrMe}_2\text{AlBu}_3^i/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in this case, the ability of cationic species $[(\text{SBI})\text{ZrMe}(\text{S})][\text{B}(\text{C}_6\text{F}_5)_4]$ **III** itself to undergo monomer insertion and chain growth cannot be excluded [29]; otherwise, the methyl ligand in **III** can be likewise substituted by isobutyl to form the cationic active species presumed to be present in the $(\text{SBI})\text{ZrCl}_2/\text{AlBu}_3^i/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ system.



Scheme 4. Reaction routes proposed for $(\text{SBI})\text{ZrMe}_2$.



Scheme 5. Possible reactions of complex IV.

3. Conclusions

The cationic zirconium(IV) species formed in ternary systems $(\text{SBI})\text{ZrX}_2/\text{AlBu}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, where $\text{X} = \text{Cl}, \text{Me}$, were studied by multinuclear NMR spectroscopy. In the first system ($\text{X} = \text{Cl}$), the crystallographically characterized $[(\text{SBI})\text{Zr}(\mu\text{-Cl})_2\text{Zr}(\text{SBI})][\text{B}(\text{C}_6\text{F}_5)_4]_2$ ion pair **IV** predominates at low Al/Zr ratios ($\text{Al/Zr} < 10$), while at higher Al/Zr ratios (≥ 20) mainly $[(\text{SBI})\text{Zr}(\mu\text{-H})(\mu\text{-C}_4\text{H}_7)\text{-Al}^i\text{Bu}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**V**) is formed. In the presence of excess TIBA, species **IV** was shown to polymerize propylene and is the most likely precursor of the active sites of propylene polymerization. Species **V** is formed in both systems at high Al/Zr ratios in the absence of monomer and is probably the thermodynamic sink of the catalyst.

4. Experimental

4.1. General

Triisobutylaluminum (TIBA) was purchased from Tomskneftekhim as toluene solution ($\leq 2\%$ Al as DIBAH, total Al content 1.6 M, containing some dissolved isobutene and isobutane) and diluted to obtain a solution of $[\text{Al}] = 0.5 \text{ M}$ or used as received for experiments with high Al/Zr ratios. DIBAH was a commercial reagent (Aldrich) and used as 0.84 M solution in hexanes. Trimethylaluminum (TMA) was purchased from Aldrich. Toluene was purified by refluxing over sodium metal and distilled under dry nitrogen. 1,2-Difluorobenzene and 1,2-dichlorobenzene were dried over molecular sieves (4 Å). All operations were carried out under dry nitrogen (99.999%) by standard Schlenk techniques. Solids and toluene were transferred and stored in a glove box. $(\text{SBI})\text{ZrCl}_2$ [34], $(\text{SBI})\text{ZrMe}_2$ [35] and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ [36] were synthesized following the literature methods.

^1H , ^{13}C , ^{19}F NMR spectra were recorded in standard 5 mm NMR tubes on Bruker Avance DPX-300 or Avance DPX-250 spectrometers. Typical operating conditions for ^{13}C NMR measurements were the following: spectral width 20 kHz; spectrum accumulation frequency 0.2–0.1 Hz; 100–10,000 transients, 90° pulse at 6.7 μs . Correct integral values were obtained from inverse gated spectra. ^{13}C , ^1H -

correlations were established by using standard Bruker HXCBI (for direct C–H interactions) and COLOC (for long-range C–H interactions) pulse programs. Operating conditions for ^1H NMR measurements: spectral width 5 kHz; spectrum accumulation frequency 0.2–0.5 Hz; number of transients 32–64, ca. 30° pulse at 2 μs . Typical operating conditions for ^{19}F NMR measurements: spectral width 30 kHz; spectrum accumulation frequency 0.1–0.5 Hz; number of transients 32–64. For calculations of ^1H and ^{13}C chemical shifts, the resonance of the CH_3 -group of toluene solvent was taken as δ 2.09 and 21.40, respectively. ^{19}F chemical shifts were referenced externally to CFCl_3 . Sample temperature measurements uncertainty and temperature reproducibility were less than $\pm 1^\circ\text{C}$.

4.2. Preparation of NMR samples

The appropriate amounts of zirconium complex (typically, 0.02–0.15 mmol) and $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_3]$ were placed in 5 mm NMR tubes in a glove box and capped with rubber septa. Further addition of AlBu_3 solution ($\text{Al/Zr} = 1, 2, 3, 5, 10$) to the tube with the zirconium complex was performed outside the glove box with gas-tight microsyringes. After recording the NMR spectra of the resulting complex **II**, the solution was transferred into the tube with $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_3]$ upon slight cooling. The sample was shaken for several minutes while warming to room temperature. After phase separation, the organic (upper) phase was removed and, if necessary, the blue or green-blue oily phase was washed with toluene (1 \times 1 mL or 2 \times 1 mL). After that, NMR spectra of complex **IV** were recorded either directly in the oily phase, or 0.1–0.2 mL 1,2-dichlorobenzene (or 1,2-difluorobenzene) was added to the oily phase to obtain a homogeneous solution. Reactions with high excesses of TIBA ($\text{Al/Zr} = 20$ or 30) were performed in a 10 mL Schlenk flask, with magnetic stirring for 15–30 min. After that, the organic phase was removed, and the brown oily residue containing complex **V** was washed with toluene, diluted with 1,2-dichlorobenzene and injected in an NMR tube with nitrogen atmosphere.

Propylene and isobutene were injected in the NMR tubes via gas-tight syringes. An experiment with addition of high excess of isobutene was performed as follows: a

50 mL flask with a magnetic stirrer was charged with ca. 0.05 mmol of complex **V** in toluene/1,2-dichlorobenzene, cooled in the bottom part to freeze the solution, evacuated, filled with isobutene atmosphere and allowed to warm to room temperature at 500 rpm stirring for 15 min.

4.3. NMR data for zirconium complexes

Hereinafter, only clearly detected signals are presented. Some of the peaks in the aromatic region are overlapped with toluene and 1,2-difluorobenzene resonances.

4.3.1. (SBI)ZrCl₂

¹H NMR (toluene, 20 °C): δ 5.66 (d, 2H, Cp-*H*, *J*_{HH} = 3 Hz; the second Cp doublet is masked by toluene peaks), 0.55 (s, 6H, Si(CH₃)₂).

¹³C NMR (toluene, 50 °C): δ 118.0 (2C, Ind), 117.5 (2C, Ind), -1.88 (2C, Si(CH₃)₂). Few signals were found due to low solubility of (SBI)ZrCl₂.

4.3.2. (SBI)ZrMe₂

¹H NMR (toluene, 20 °C): δ 6.61 (d, 2H, Cp-*H*, *J*_{HH} = 3 Hz), 5.61 (d, 2H, Cp-*H*, *J*_{HH} = 3 Hz), 0.53 (s, 6H, Si(CH₃)₂), -1.10 (s, 6H, Zr(CH₃)₂).

¹³C NMR (toluene, 20 °C): δ 126.0 (2C, Ind), 125.0 (2C, Ind), 124.9 (2C, Ind), 124.5 (2C, Ind), 117.8 (2C, Ind), 111.4 (2C, Ind), 84.4 (2C, Si-C(Cp)), 37.1 (2C, Zr(CH₃)₂), -1.9 (2C, Si(CH₃)₂).

4.3.3. Reaction of (SBI)ZrCl₂ with AlBu₃ⁱ:

(SBI)ZrCl(Buⁱ) (II)

At TIBA/Zr = 5, [Zr] = 0.02 M, ~90% conversion of (SBI)ZrCl₂ into **II** was observed.

¹H NMR (toluene, 20 °C, TIBA/Zr = 5, [Zr] = 0.02 M): δ 5.85 (d, 1H, Cp-*H*, *J*_{HH} = 3 Hz), 5.45 (d, 1H, Cp-*H*, *J*_{HH} = 3 Hz), 0.84 (s, 3H, -CH₂CH(CH₃)₂), 0.82 (s, 3H, -CH₂CH(CH₃)₂), 0.55 (s, 3H, SiCH₃), 0.47 (s, 3H, SiCH₃), -0.56^(*) (dd, 1H, Zr-CHH-, *J*_{HH} = 12.7 Hz, *J*_{HZr} = 5.8 Hz), -0.93^(*) (dd, 1H, Zr-CHH-, *J*_{HH} = 12.7 Hz, *J*_{HZr} = 6.2 Hz).^(*) – peak positions are concentration dependent.

¹³C NMR (toluene, 20 °C, TIBA/Zr = 5, [Zr] = 0.02 M): δ 118.5 (1C, Ind), 116.9 (1C, Ind), 114.8 (1C, Ind), 112.2 (1C, Ind), 87.6 (1C, Si-C(Cp)), 86.9 (1C, Si-C(Cp)), 83.0 (1C, Zr-CH₂-)^(*), 33.2 (1C, Zr-CH₂-CH(CH₃)₂), -1.69 (1C, Si-CH₃), -2.47 (Si-CH₃).^(*) – peak position is concentration dependent; at TIBA/Zr = 10, [Zr] = 0.065 M, Zr-CH₂- peak was found at 88.3 ppm.

4.3.4. Independent preparation of (SBI)Zr(Cl)CH₂CHMe₂ (II)

(SBI)ZrCl₂ (0.20 g (0.45 mmol)) was suspended in 50 mL of toluene at 0 °C. To the suspension 1.0 mL of MgClCH₂CHMe₂ was added slowly. After the reaction mixture was stirred at 0 °C for 2 h, the temperature was raised to 10 °C and it was stirred 10 h with the temperature

maintained at 10 °C. Filtering off the solid residues and the removal of volatiles gave an orange solid, which was washed with 10 ml of light petroleum and dried to afford the orange product 0.20 g (96%).

¹H NMR (toluene-*d*₈, 20 °C): δ 7.59 (d, 1H, Ar-*H*, *J*_{HH} = 8.8 Hz), 7.24 (m, 2H, Ind-*H*), 7.1–6.8 (m, Cp-*H* and Ind-*H*), 6.93 (d, 1H, Cp-*H*, *J*_{HH} = 3 Hz), 5.82 (d, 1H, Cp-*H*, *J*_{HH} = 3 Hz), 5.60 (d, 1H, Cp-*H*, *J*_{HH} = 3 Hz), 1.99 (m, 1H, -CH₂CHMe), 0.91 (d, 3H, -CH₂CH(CH₃)₂, *J*_{HH} = 6.5 Hz), 0.84 (d, 3H, -CH₂CH(CH₃)₂, *J*_{HH} = 6.5 Hz), 0.57 (s, 3H, Si(CH₃)₂), 0.50 (s, 3H, Si(CH₃)₂), -0.78 (m, 1H, -CH₂CH(CH₃)₂), -0.96 (m, 1H, -CH₂CH(CH₃)₂). ¹³C NMR (toluene-*d*₈, 20 °C): δ 132.4, 131.5, (119–125 Ind-C overlapped with toluene-*d*₈) 118.3, 116.7, 115.3, 112.0, 88.0, 86.9, 78.0, 32.1, 29.1, 26.4, -1.7, -2.3.

4.3.5. Reaction of (SBI)ZrMe₂[CPh₃][B(C₆F₅)₄]: complex III

The starting reactants (SBI)ZrMe₂ (0.02 mmol) and [CPh₃][B(C₆F₅)₄] (0.02 mmol) were placed in a 5 mm NMR tube in a glove box and capped with septum stoppers. Then, 0.5 ml of toluene-*d*₈ and 0.2 ml of 1,2-difluorobenzene were added and the tube was shaken for several minutes. The ¹H spectrum recorded after 5 min indicated the initial formation of the homobinuclear Zr species [(SBI)ZrMe₂(μ-Me)][B(C₆F₅)₄] (both diastereomers). After storing the sample for several hours at room temperature, formation of [(SBI)ZrMe(S)][B(C₆F₅)₄] (**III**) was revealed by ¹H NMR. No coordination of anion to zirconium was observed by ¹⁹F NMR.

¹H NMR (complex [(SBI)ZrMe(S)][B(C₆F₅)₄], toluene/1,2-difluorobenzene, 2 °C): δ 5.30 (d, 1H, Cp-*H*, *J*_{HH} = 3 Hz), 5.04 (d, 1H, Cp-*H*), 0.60 (s, 3H, Si(CH₃)₂), 0.35 (s, 3H, Si(CH₃)₂), -0.67 (s, 3H, Zr-CH₃); 1.99 ppm (s, 3H, CPh₃CH₃).

¹³C NMR (complex [(SBI)ZrMe(S)][B(C₆F₅)₄], toluene/1,2-difluorobenzene, 2 °C): δ 58.3 (1C, Zr-CH₃), -2.74 (1C, Si(CH₃)₂), -4.16 (1C, Si(CH₃)₂); 52.6 (Ph₃CCH₃), 30.3 (Ph₃CCH₃).

¹⁹F NMR (complex [(SBI)ZrMe(S)][B(C₆F₅)₄], toluene/1,2-difluorobenzene, 2 °C): δ -132.5 (2F, *o*-F), -162.9 (t, 1F, *p*-F, *J*_{FF} = 20.7 Hz), -166.9 (t, 2F, *m*-F).

This complex displays a well-documented ion pair symmetrization [11b,37,38] leading to coalescence of the Cp-*H* and Si(Me)₂ NMR peaks at +20 °C. The ¹H NMR data at +22 °C are presented below. The estimated apparent Δ*G*_{ex}[‡] value of 14 kcal mol⁻¹ (at 20 °C) is close to those observed for similar exchange processes [11b,37].

¹H NMR (complex [(SBI)ZrMe(S)][B(C₆F₅)₄], toluene/1,2-difluorobenzene, -22 °C): δ 5.28 (br, 2H, Cp-*H*), 0.54 (br, 6H, Si(CH₃)₂), -0.65 (s, 3H, Zr-CH₃).

4.3.6. NMR reaction of (SBI)ZrCl₂/Al(Buⁱ)₃/[CPh₃][B(C₆F₅)₄]: complex IV

Complex **IV** was predominantly formed at Al/Zr ratios of 5–10 after 3–15 min shaking of the NMR tube with (SBI)ZrCl₂ + AlBu₃ⁱ + [CPh₃][B(C₆F₅)₄]. **IV** formed a

green or blue-green oil in the NMR tube. It is stable for days in a fridge and at least 2 days at room temperature. Surprisingly, washings with toluene did not remove all TIBA: even after 2×1 mL washings, ca. 1.5 molecules of TIBA per one Zr complex were found in the reaction mixture.

^1H NMR (toluene/1,2-dichlorobenzene, 20 °C): δ 6.42 (d, 2H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 5.39 (d, 2H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 0.84 (s, 6H, Si(CH₃)₂); 5.31 (s, 1H, CPh₃H).

^{13}C NMR (toluene/1,2-dichlorobenzene, 20 °C): δ 135.0 (2C, Ind), 127.1 (2C, Ind), 127.0 (2C, Ind), 124.0 (2C, Ind), 122.6 (2C, Ind), 121.6 (2C, Ind), 88.2 (2C, Si-C(Cp)), -2.9 (2C, Si(CH₃)₂); 57.5 (1C, CPh₃H).

^{19}F NMR (toluene/1,2-dichlorobenzene, 20 °C): δ -133.3 (2F, *o*-F), -163.9 (1F, *p*-F, $J_{\text{FF}} = 20.7$ Hz), -167.7 (2F, *m*-F).

Complex **IV** can equally be obtained by the reaction of the independently prepared (SBI)Zr(Cl)CH₂CHMe₂ (**II**) with 1 equiv. of [CPh₃][B(C₆F₅)₄].

4.3.7. NMR reaction of (SBI)ZrCl₂/Al(*Bu*^{*i*})₃/[CPh₃][B(C₆F₅)₄]: single crystals of complex [(SBI)Zr(μ-Cl)₂Zr(SBI)][B(C₆F₅)₄]₂ (**IV**)

Complex **IV** was generated at Al/Zr ratios of 5:1 after 5 min shaking of the NMR tube with (SBI)ZrCl₂+AlBu₃^{*i*}[CPh₃][B(C₆F₅)₄] in toluene at slight cooling (ca. 0 °C). After separation of the organic phase, the oily phase was washed with 0.5 mL of toluene to remove excess TIBA, and after the addition of 0.15 mL of 1,2-difluorobenzene a homogeneous blue-green solution resulted. The sample was exposed to ambient temperature and room light for ca. 1 week to yield green crystals that turned red after separation and washing with 1,2-difluorobenzene. X-ray diffraction revealed the dicationic dimeric structure of [(SBI)Zr(μ-Cl)₂Zr(SBI)][B(C₆F₅)₄]₂ with co-crystallized toluene molecules (for details see Supporting information).

4.3.8. NMR reaction of (SBI)ZrCl₂/Al(*Me*)₃/[CPh₃][B(C₆F₅)₄]: complex **IV**

Complex **I** (0.05 mmol) and [CPh₃][B(C₆F₅)₄] (0.05 mmol) were placed in 5 mm NMR tubes in a glove box and capped with septum stoppers. Then, 0.34 M AlMe₃ solution (Al/Zr = 7.5) was added to the tube with the (SBI)ZrCl₂ outside the glove box with a gastight microsyringe. After recording the NMR spectra of the resulting complex (SBI)ZrClMe, the solution was transferred into the tube with [CPh₃][B(C₆F₅)₄] upon slight cooling. The sample was shaken for several minutes while warming to room temperature. Complex **IV** was formed along with [(SBI)Zr(μ-Me)₂AlMe₂][B(C₆F₅)₄] after 3–5 min shaking of the NMR tube with ((SBI)ZrCl₂ + AlMe₃) + [CPh₃][B(C₆F₅)₄] (Al:Zr:B = 1:7.5:1). Both cationic Zr complexes are stable at room temperature for at least 6 h. After phase separation, the organic (upper) phase was removed and its NMR spectrum recorded separately. Washing the oily phase with toluene (2 × 0.5 mL washings) almost completely removed AlMe₃. After that, 0.1 mL 1,2-dichloro-

benzene (1,2-difluorobenzene) was added to the oily phase to obtain a homogeneous solution.

^1H NMR (complex [(SBI)Zr(μ-Me)₂AlMe₂][B(C₆F₅)₄], toluene/1,2-dichlorobenzene, 20 °C): δ 6.15 (d, 2H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 5.05 (d, 2H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 0.70 (s, 6H, Si(CH₃)₂), -0.74 (s, 6H, Al-CH₃), -1.35 (s, 6H, Al-CH₃-Zr); 2.00 (s, 3H, CPh₃CH₃).

^{13}C NMR (complex [(SBI)Zr(μ-Me)₂AlMe₂][B(C₆F₅)₄], toluene/1,2-dichlorobenzene, 20 °C): δ 124.7 (2C, Ind), 119.0 (2C, Ind), 116.1 (2C, Ind), 85.4 (2C, Si-C(Cp)), 34.4 (2C, Al-CH₃-Zr), -3.0 (2C, Si(CH₃)₂); -7.3 ppm (2C, $\Delta\nu_{1/2} = 8$ Hz, Al-CH₃).

^1H NMR (complex **IV**, toluene/1,2-dichlorobenzene, 20 °C): δ 6.30 (d, 2H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 5.29 (d, 2H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 0.76 (s, 6H, Si(CH₃)₂); 2.00 (s, 3H, CPh₃CH₃).

^{13}C NMR (complex **IV**, toluene/1,2-dichlorobenzene, 20 °C): δ 124.0 (2C, Ind), 122.5 (2C, Ind), 121.5 (2C, Ind), 88.1 (2C, Si-C(Cp)), -3.1 (2C, Si(CH₃)₂).

4.3.9. Independent preparation of **IV** from **III**

A solution of **III** and Ph₃CMe (0.02 mmol) in toluene/1,2-difluorobenzene was generated in an NMR tube as described above, and Me₃SiCl (0.022 mmol) was added with a gas-tight microsyringe. The tube was shaken, and ^1H NMR spectrum recorded after 10 min indicated the quantitative formation of **IV**.

^1H NMR (complex **IV**, toluene/1,2-difluorobenzene, 20 °C): δ 6.31 (d, 2H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 5.29 (d, 2H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 0.91 (s, 6H, Si(CH₃)₂); 2.01 (s, 3H, CPh₃CH₃), 0.23 (Me₃SiCl), 0.00 (SiMe₄).

^{13}C NMR (complex **IV**, toluene/1,2-difluorobenzene, 20 °C): δ 91.7 (2C, Si-C(Cp)), -2.8 (2C, Si(CH₃)₂).

4.3.10. NMR reaction of (SBI)ZrCl₂/AlBu₃^{*i*}/[CPh₃][B(C₆F₅)₄]: complex **V**

Complex **V** was the dominant product formed at Al/Zr ratios of 20–30 after 10–30 min magnetic stirring as described above. It is stable for at least 1 d at room temperature. Along with **V**, residual **IV** was detected in the reaction mixture (ca. 20% of **IV** at Al/Zr = 30).

^1H NMR (toluene/1,2-dichlorobenzene, 20 °C): δ 6.26 (d, 1H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 5.66 (d, 1H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 5.34 (d, 1H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 5.28 (d, 1H, Cp-*H*, $J_{\text{HH}} = 3$ Hz), 3.03 (s, 1H, Zr-CHH-*), 2.51 (s, 1H, Al-CHH-*), 0.22 (s, 1H, Al-CHH-*), 0.75 (s, 3H, Si-CH₃), 0.68 (s, 3H, Si-CH₃), -1.73 (s, 1H, Zr-CHH-*), -3.35 (s, 1H, Zr-H-Al).

^{13}C NMR (toluene/1,2-dichlorobenzene, 20 °C): δ 166.6 (1C, -CH₂CMeCH₂-), 121.9 (1C, Ind), 119.3 (1C, Ind), 113.0 (1C, Ind), 111.0 (1C, Ind), 108.7 (1C, Ind), 108.4 (1C, Ind), 93.0 (1C, Si-C(Cp)), 86.9 (1C, Zr-CH₂-), 82.7 (1C, Si-C(Cp)), 53.8 (1C, -CH₂-Al), -1.99 (1C, Si-CH₃), -3.82 (1C, Si-CH₃).

^{19}F NMR (toluene/1,2-dichlorobenzene, 20 °C): δ -133.0 (2F, *o*-F), -163.7 (1F, *p*-F, $J_{\text{FF}} = 20.7$ Hz), -167.5 (2F, *m*-F).

* The geminal $^2J_{\text{HH}}$ coupling constants within the Zr–CHH– and Al–CHH– fragments are very small, so that no correlations are observed in H,H-COSY spectra. However, all necessary cross peaks are present in C,H-heteronuclear correlation spectra (see Supporting information).

4.3.11. NMR reaction of (SBI)ZrMe₂/Al(*Bu*^{*i*})₃/[CPh₃][B(C₆F₅)₄]: complex V

Complex V was the major product formed at Al/Zr ratio 40 after 15 min magnetic stirring as described above. Along with complex V (ca. 70% of zirconium), two unidentified Zr species were detected in the reaction mixture (20% of a C₂-symmetric complex and 10% of a C₁-symmetric one). NMR data of thus obtained complex V were identical to those of complex V formed in (SBI)ZrCl₂/AlBu₃^{*i*}/[CPh₃]-[B(C₆F₅)₄] system.

4.4. Crystal structure analysis of [(SBI)Zr(μ-Cl)₂Zr(SBI)] [B(C₆F₅)₄]₂ (IV)

A crystal was mounted on a glass fibre coated in nujol and fixed in a cold nitrogen stream on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 153(2) K and processed with the HELENA program [39] and no absorption corrections were applied. The structure was determined by direct methods in SHELXS-97 [40]. Refinement was by full-matrix least-squares methods in SHELXS-97 [40]. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in idealised positions and their isotropic thermal parameters were set to ride on the U_{eq} values of the parent carbon atom. Scattering factors for neutral atoms were taken from [41].

Crystal data for IV: C₅₁H₂₆BClF₂₀SiZr, fw 1184.29; crystal size 0.3 × 0.3 × 0.3 mm; monoclinic, space group C2/c (No.15); $a = 24.021(7) \text{ \AA}$, $b = 15.486(2) \text{ \AA}$, $c = 24.816(7) \text{ \AA}$; $\beta = 90.97(1)^\circ$; $V = 9230(4) \text{ \AA}^3$; $Z = 4$; $D_{\text{calc}} = 1.704 \text{ g/cm}^3$; $\mu = 0.442 \text{ mm}^{-1}$; $F(000) = 4704$; $-29 \leq h \leq 29$; $0 \leq k \leq 19$; $0 \leq l \leq 30$; 9275 reflections collected, of which 9052 were independent ($R_{\text{int}} = 0.0889$) and 3580 with $I > 2\sigma(I)$ were observed. Final $R_1 [I > 2\sigma(I)] = 0.1107$, wR_2 (all data) = 0.3852, $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + (b \cdot P)]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The co-crystallized toluene molecule was found to be severely disordered around the sixfold axes of the benzene ring such that the methyl group was not detectable. It was treated in the refinement as a benzene molecule. The benzene ring was fitted with a rigid group constraint (regular hexagon $d_{\text{CC}} = 1.39 \text{ \AA}$). The temperature factors of the 6 C atoms were refined isotropically as a free variable. All H atoms are calculated. The coordinates, s.o.f. and $U = 0.05$ are fixed. The H atoms of the disordered cocrystallized toluene molecule were omitted.

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Appendix A. Supplementary data

CCDC 612556 contain the supplementary crystallographic data for IV. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.037.

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