

Ternary metallocene catalyst systems based on metallocene dichlorides and $\text{AlBu}_3^i/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ NMR investigations of the influence of Al/Zr ratios on alkylation and on formation of the precursor of the active metallocene species

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Received 2 November 2000; accepted 28 November 2001

Abstract

The formation of the precursors of the polymerization-active species of the metallocene dichlorides Cp_2ZrCl_2 and $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ by successive reaction with AlBu_3^i and $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ was investigated by means of NMR spectroscopy. More than two equivalents of AlBu_3^i are required for total conversion of the metallocene dichlorides in the first step. The reaction of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ with AlBu_3^i leads exclusively to the mono-*iso*-butyl complex $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$, independent of the surplus AlBu_3^i used, whereas in the case of Cp_2ZrCl_2 a series of metallocene products are observed, depending on the Al/Zr ratio used. When this ratio was increased to above 10, the reaction could be exclusively directed to form the dimer metallocene complex $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlBu}_3^i]_2$. The reaction of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ with metallocene/aluminium alkyl mixtures prepared with 10, 20, 50 and 100 equivalents of AlBu_3^i leads to the precipitation of an oily liquid, which contains resulting cationic metallocene complexes. These liquid phases can be purified by extraction and subsequently used for NMR measurements. With one exception, mixtures of two or three different cationic metallocene products are obtained, depending on the Al/Zr ratio and on the metallocene ligand used. An Al/Zr ratio of 100 the reaction of the $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2/\text{AlBu}_3^i$ mixture with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ exclusively leads to the cationic heterodinuclear metallocene complex $[\text{Ph}_2\text{C}(\text{CpFlu})\text{Zr}-\mu\text{-H}-\mu\text{-(C}_4\text{H}_7\text{)-AlBu}_2^i]^+$, a novel type of allyl-bridged cation, which was characterized by NMR data. None of the reactions of metallocene dichloride/aluminium alkyl mixtures with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ lead to the degradation of $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, whereas in the absence of metallocenes AlBu_3^i reacts with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ to give $\text{AlBu}_{3-x}^i(\text{C}_6\text{F}_5)_x$ compounds. Based on these results and with additional information from the literature a mechanism is proposed to explain the formation of $[\text{Ph}_2\text{C}(\text{CpFlu})\text{Zr}-\mu\text{-H}-\mu\text{-(C}_4\text{H}_7\text{)-AlBu}_2^i]^+$. © 2002 Published by Elsevier Science B.V.

Keywords: Metallocene catalysts; Triisobutyl aluminium; Preactivation; NMR investigation

1. Introduction

The fact that highly active olefin polymerization catalysts can be generated from metallocene dialkyls L_2MR_2 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{L} =$ cyclopentadienyl-based bridged or non-bridged ligands, $\text{R} =$ alkyl or benzyl) and cation-forming agents as $\text{B}(\text{C}_6\text{F}_5)_3$,

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$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ has been well investigated. The resulting active metallocene cation $[\text{L}_2\text{MR}]^+$ is highly electrophilic and usually stabilized by bulky, weakly coordinating counteranions like $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ or $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ [1–3].

For industrial applications these binary catalyst systems have the disadvantage that most of the active metallocene species are consumed by reaction with impurities. Ternary catalyst systems based on a zirconocene dichloride, an aluminium alkyl and a cation-forming agent are less sensitive to impurities and easier to handle [4–7]. Thus, use of these ternary systems is preferred in technical polymerization processes [8–10].

Little is known about the mechanism that leads to the formation of the precursor of the active species in ternary catalyst systems. Usually the precursor of the active species of the metallocene dichloride is formed by successive reactions with a large excess of aluminium alkyl and 1–2 equivalents of a cation-generating agent. This mechanism, thus, involves at least two steps, assumed to be an alkylation of the metallocene dichloride followed by the formation of the cationic metallocene species [5,6].

In the 1970s, Kaminsky and Sinn [11] showed that the reaction of Cp_2ZrCl_2 with AlEt_3 leads to a series of different zirconocene species, depending on the Al/Zr ratio used. More recently, Brintzinger and Beck [12] investigated the alkyl exchange between AlMe_3 and 15 different metallocene dichlorides LLZrCl_2 . They found that these reactions lead exclusively to zirconocene monomethyl monochloro complexes LLZrClMe . Even with a large excess of AlMe_3 no dimethyl complexes LLZrMe_2 were observed.

Bochmann and Sarsfield [13] discovered the facile degradation of $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ by reaction of the metallocene activator $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ with AlR_3 ($\text{R} = \text{Me}, \text{Bu}^i$) and assumed the formation of transient “[AlR_2] $^+$ ” cations to explain the mechanism.

We have already investigated the influence of the Al/Zr ratios used in $\text{LLZrCl}_2/\text{Al}(\text{Bu}^i)_3/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ catalyst systems on the activity in high-pressure and solution polymerizations [10]. We were, therefore, interested to now determine, whether the Al/Zr ratio has an influence on the preparation of this type of catalyst system. In this paper, we will describe the role of the excess $\text{Al}(\text{Bu}^i)_3$ on the alkylation step and on the formation of the precursor of the active

metallocene species, by means of NMR spectroscopy, using the *ansa*-metallocene $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ and the non-bridged metallocene Cp_2ZrCl_2 .

2. Experimental

2.1. General considerations

All experiments were carried out under argon, using Schlenk and vacuum line techniques. Prior to use, toluene, benzene, hexane and THF were distilled under nitrogen from sodium–potassium alloy. Ether was distilled under nitrogen from lithium aluminium hydride. Benzene- d_6 was dried over calcium hydride and deoxygenated via several freeze-thaw cycles, followed by vacuum transfer from the same. AlBu_3^i (96%, Aldrich) was used after analysis of the *iso*-butene content by NMR analysis. Bu^iMgCl and Cp_2ZrCl_2 (Aldrich) were used as purchased. The compounds $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ and $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ were donated by BASF AG. The ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker ARX 300 instrument. ^1H and ^{13}C chemical shifts are reported versus C_6D_6 and were determined by reference to the residual ^1H (7.20 ppm) or ^{13}C (128 ppm) solvent peaks. ^{19}F spectra were referenced externally to CFCl_3 .

2.2. Preparation of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ with Bu^iMgCl

A solution of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ (1.169 g, 2.1 mmol) in THF (10 ml) was cooled to 0°C and reacted with Bu^iMgCl (1.05 ml, 2.1 mmol). While the mixture was being warmed to room temperature the color changed from dark red to orange. Then the reaction mixture was stirred for 6 h. The solvent was removed under vacuum and the orange-yellow product was washed three times with 20 ml diethyl ether. The volatiles were removed under vacuum. The remaining product was dissolved in 50 ml *n*-hexane. After filtration and solvent removal a yellow precipitate was obtained. It was dried under vacuum to yield $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ (0.131 g, 226.5 μmol , 10.8%). ^1H NMR (C_6D_6 , 20°C): δ 8.04 (d, 1H, Flu), 7.84 (d, 1H, Flu), 7.72 (t, 2H, Ph), 6.86 (t, 1H, Flu), 6.68 (t, 1H, Flu), 6.49 (d, 1H, Flu), 6.45 (q, 1H, Cp), 6.26 (d, 1H, Flu), 6.08 (q, 1H, Cp), 5.73 (q, 1H, Cp),

5.33 (q, 1H, Cp), 1.82 (m, 1H, CH, *iso*-butyl), 0.95 (d, 3H, CH₃, *iso*-butyl), 0.86 (d, 3H, CH₃, *iso*-butyl), –0.80 (“A” part of an ABX system, 1H, ²J_{AB} = 13 Hz, CH₂, *iso*-butyl), –1.11 (“B” part of an ABX system, ²J_{AB} = 13 Hz, 1H, CH₂, *iso*-butyl). ¹³C NMR (C₆D₆, 20 °C): δ 145.8, 145.7 (C_q, Ph), 129.8, 129.7, 128.9, 126.9, 126.8, 126.7, 126.2, 124.9, 124.6, 124, 123.9 (CH, Flu/Ph), 123.7, 123.6 (C_q, Flu), 122.7, 122.6 (CH, Flu/Ph), 121.3, 120.9 (C_q, Flu), 119.5 (CH), 114.8, 114.5 (CH, Cp), 108.8 (C_q, Cp), 103.3, 103.8 (CH, Cp), 77.5 (C_q, Flu), 73.3 (CH₂, *iso*-butyl), 58.3 (C_q, methylene bridge), 32.8 (CH, *iso*-butyl), 28.9, 26.9 (CH₃, *iso*-butyl).

2.3. Reaction of Ph₂C(CpFlu)ZrCl₂ with AlBu₃ⁱ

An orange slurry of Ph₂C(CpFlu)ZrCl₂ in benzene-*d*₆ was treated with various amounts of AlBu₃ⁱ at 20 °C. With Al/Zr ratios up to 10 a red-orange solution was obtained after a few minutes. With higher Al/Zr ratios the color changed to yellow immediately. With Al/Zr ratios of 10 or 50 the NMR spectra showed only signals of Ph₂C(CpFlu)ZrClBuⁱ and aluminium alkyls. In no cases was evolution of gas detected. If the solution was heated to 80 °C at an Al/Zr ratio of 10 the color changed from red to dark brown, but no change in the NMR could be detected. Example: a solution of AlBu₃ⁱ (0.16 ml, 2.02 M, 323 μmol) in benzene-*d*₆ was added to a slurry of Ph₂C(CpFlu)ZrCl₂ (0.018 g, 32.3 μmol) in 1 ml benzene-*d*₆. ¹H NMR, Al alkyl signals have been omitted (C₆D₆, 20 °C): δ 7.98 (d, 1H, Flu), 7.75 (d, 1H, Flu), 7.64 (t, 2H, Ph), 7.42 (m, 2H, Ph), 7.36 (t, 1H, Flu), 7.11 (t, 2H, Ph), 6.98 (m, 4H, Ph), 6.86 (t, 1H, Flu), 6.61 (t, 1H, Flu), 6.53 (q, 1H, Cp), 6.33–6.30 (d/q, 2H, Flu/Cp), 6.19 (d, 1H, Flu), 5.70 (q, 1H, Cp), 5.30 (q, 1H, Cp), 1.80 (*n*, 1H, CH, *iso*-butyle), –0.81 (“A” part of an ABX system, 1H, ²J_{AB} = 13 Hz, CH₂, *iso*-butyle), –1.05 (“B” part of an ABX system, ²J_{AB} = 13 Hz, 1H, CH₂, *iso*-butyle). ¹³C NMR (C₆D₆, 20 °C): δ 145.2, 145.1 (C_q, Ph), 129.52, 129.47, 129.08, 129.03, 127.2, 127.1, 126.73, 126.66, 126.58, 125.5, 125.1, 125, 124.3, 124 (CH, Flu/Ph), 123.25, 123.18 (C_q, Flu), 122.7 (CH), 121.4, 121 (C_q, Flu), 115.5, 114.7 (CH, Cp), 108.2 (C_q, Cp), 104.5 (CH, Cp), 104.2 (CH, Cp), 85.4 (CH₂, *iso*-butyl), 75.9 (C_q, Flu), 58.3 (C_q, methylene bridge), 33.6 (CH, *iso*-butyl), Me signals overlapped by AlBu₃ⁱ.

2.4. Ph₂C(CpFlu)ZrCl₂/AlBu₃ⁱ/[PhNMe₂H][B(C₆F₅)₄] systems

A slurry of Ph₂C(CpFlu)ZrCl₂ in benzene-*d*₆ was treated with 10, 20, 50 and 100 equivalents of AlBu₃ⁱ. After stirring for 30 min the mixture was heated to 60 °C and added to one equivalent of [PhNMe₂H][B(C₆F₅)₄] in benzene-*d*₆ at 60 °C. Strong evolution of *iso*-butane and *iso*-butene occurred immediately. After 10 min the reaction was completed and the ionic compounds precipitated as a dark-green or brown-yellow oil. The upper phase contained mostly benzene-*d*₆, aluminium alkyls and PhNMe₂, but no metallocene compounds (note: before addition it was important to heat the [PhNMe₂H][B(C₆F₅)₄]/benzene-*d*₆ slurry to the boiling point of benzene to obtain a two-phase mixture containing a colorless oil of borate/benzene in the lower phase and a small amount of dissolved borate in benzene in the upper phase). Example: a slurry of Ph₂C(CpFlu)ZrCl₂ (0.357 g, 641 μmol) in 3 ml benzene-*d*₆ was treated with AlBu₃ⁱ (16.12 ml, 64.1 mmol). After 30 min the yellow solution was added to a solution of [PhNMe₂H][B(C₆F₅)₄] (0.514 g, 641 μmol) in 3 ml benzene-*d*₆ at 60 °C. After 10 min the reaction was completed and the mixture was cooled to room temperature. The precipitated brown oil (0.5–1 ml, 0.064–0.128 M) was washed three times with 2 ml of benzene-*d*₆ to remove traces of PhNMe₂ and excess AlBu₃ⁱ. The color of the obtained oil changed to dark green. It was directly used to record the NMR spectra. The resulting NMR data assigned to [Ph₂C(CpFlu)Zr-μ-H-μ-(C₄H₇) - AlBu₂ⁱ][B(C₆F₅)₄]^{*} AlBu₃ⁱ (A): ¹H NMR (C₆D₆, 20 °C): δ 7.75 (d, 1H), 7.63 (d, 2H), 7.50 (d, 1H), 6.70 (m, 2H), 6.51 (d, 1H), 6.23 (d, 1H), 5.62 (s, 1H, Cp), 5.40 (s, 1H, Cp), 5.24 (s, 1H, Cp), 4.81 (s, 1H, Cp), 2.87 (s, 1H, Zr-CH₂), 2.28 (d, 1H, CH₂-Al), 2 (*n*, 2H, CH, *iso*-butyl groups of AlBu₂ⁱ), 1.77 (t, 3H, CH, AlBu₃ⁱ), 1.22 (s, 3H, allyl CH₃), 1.06 (d, 12H, CH₃, *iso*-butyl groups of AlBu₂ⁱ), 0.97 (sb, 18H, CH₃, AlBu₃ⁱ), 0.32 (sb, 4H, CH₂, *iso*-butyl groups of AlBu₂ⁱ), 0.03 (sb, 6H, CH₂, AlBu₃ⁱ), –1.66 (s, 1H, Zr-CH₂), –2.78 (s, 1H, Zr-H-Al). ¹³C NMR (C₆D₆, 20 °C): δ 163.4 (C_q, allyl C), 149.1 (d, C_q, *o*-CF, J_{CF} = 241.4 Hz), 143.5 (C_q, Ph), 142.9 (C_q, Ph), 138.9 (d, C_q, *p*-CF, J_{CF} = 246.9 Hz), 137 (d, C_q, *m*-CF, J_{CF} = 244.1 Hz), 129.6, 129.43, 129.36, 129.2, 128.9, 127.3, 127.2, 126.4,

126.1, 125.8, 123.2, 121.5 (CH, Flu/Ph), 120, 119.4, 118.4, 117.7, (C_q, Flu), 115.3 (CH, $J_{\text{CH}} = 180.2$ Hz, Cp), 109.1 (CH, $J_{\text{CH}} = 180.2$ Hz, Cp), 107.8 (C_q, Cp), 102.1 (CH, $J_{\text{CH}} = 180.2$ Hz, Cp), 98 (CH, $J_{\text{CH}} = 180.2$ Hz, Cp), 90.5 (CH₂, $J_{\text{CH}} = 157.5$ Hz, Zr–CH₂), 74.4 (C_q, Flu), 58.3 (C_q, methylene bridge), 47.7 (CH₂, $J_{\text{CH}} = 129.4$ Hz, CH₂Al), 26.6 (CH₃, allyl), 26.4 (CH₃, *iso*-butyl groups of AlBu₃ⁱ), 26.2 (CH, methine, *iso*-butyl groups of AlBu₃ⁱ). ¹⁹F NMR (C₆D₆, 20 °C): δ –131.8 (sb, 8F, *o*-F), –162.4 (t, 4F, $J = 20.4$ Hz, *p*-F), –166.2 (sb, 8F, *m*-F).

2.5. Reaction of AlBu₃ⁱ with [PhNMe₂H][B(C₆F₅)₄]

A solution of [PhNMe₂H][B(C₆F₅)₄] in benzene-*d*₆ was treated with 2 and 4 equivalents of AlBu₃ⁱ at 60 °C. After 10 min the heating bath was removed and the resulting solution was stirred at room temperature until the evolution of gas ceased (note: before addition of AlBu₃ⁱ it was important to heat the [PhNMe₂H][B(C₆F₅)₄]/benzene-*d*₆ slurry to the boiling point of benzene to obtain a two-phase mixture containing a colorless oil of borate/benzene in the lower phase and a small amount of dissolved borate in benzene in the upper phase). On completion of reaction a one phase solution was obtained. Apart from the reaction products *iso*-butane and PhNMe₂, three main B and Al products were observed, BBU₃ⁱ [32], Al(C₆F₅)₃ [13] and AlBuⁱ(C₆F₅)₂. The product distribution depends only slightly on the Al/B ratio used. Example: according to the description above AlBu₃ⁱ (0.35 ml, 0.27 g, 1.37 mmol) was reacted with a solution of [PhNMe₂H][B(C₆F₅)₄] (0.275 g, 0.34 mmol) in 1 ml benzene-*d*₆. The resulting solution was used to record the NMR spectra. NMR (C₆D₆, 20 °C): BBU₃ⁱ [¹H NMR δ 2.02 (m, 1H, CH), 1.17 (d, 2H, CH₂, $J = 6.9$ Hz), 0.88 (d, 6H, CH₃, $J = 6.6$ Hz)]; AlBuⁱ(C₆F₅)₂ [¹H NMR δ 1.74 (m, 1H, CH), 0.92 (d, 6H, CH₃, partly obscured by signals of AlBu₃ⁱ), 0.54 (d, 2H, CH₂ $J = 7.2$ Hz); ¹⁹F δ –119.5 (m, 2F, *o*-F), –154.7 (t, 1F, $J = 19.9$ Hz, *p*-F), –162.6 (m, 2F, *m*-F)]; Al(C₆F₅)₃ [¹⁹F δ –122.1 (d, 2F, *o*-F), –152.4 (t, 1F, $J = 19.9$ Hz, *p*-F), –161.1 (m, 2F, *m*-F)]; HBUⁱ [¹H NMR δ 1.63 (m, 1H, CH), 0.84 (d, 9H, CH₃, $J = 6.6$ Hz)]; PhNMe₂ coordinated to Al or B compounds [¹H NMR δ 6.8–6.6 (m, 5H, Ar), 2.53 (s, 6H, CH₃)].

2.6. Reaction of Cp₂ZrCl₂ with AlBu₃ⁱ

A slurry of Cp₂ZrCl₂ in benzene-*d*₆ was treated with various amounts of AlBu₃ⁱ at 20 °C. With Al/Zr ratios up to 10, a yellow solution was obtained after a few minutes. With higher Al/Zr ratios, the color changed to pale yellow immediately. With Al/Zr ratios of 10 or 20, only signals of [Cp₂ZrH₂·AlBu₃ⁱ]₂ and aluminium alkyls remained. Example: a solution of AlBu₃ⁱ (0.24 ml, 958 μ mol) in benzene-*d*₆ was added to a slurry of Cp₂ZrCl₂ (0.028 g, 95.8 μ mol) in 1 ml benzene-*d*₆. ¹H NMR, Al alkyl signals have been omitted (C₆D₆, 20 °C): δ 5.66 (s, 10H), –0.88 (t, 2H, Zr–H–Al), –1.95 (bs, 2H, Zr–H–Zr). ¹³C NMR (C₆D₆, 20 °C): δ 104.4 (CH, Cp).

2.7. Cp₂ZrCl₂/AlBu₃ⁱ/[PhNMe₂H][B(C₆F₅)₄] systems

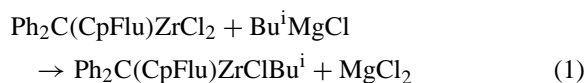
A slurry of Cp₂FluZrCl₂ in benzene-*d*₆ was treated with 10, 20, 50 and 100 equivalents of AlBu₃ⁱ. After stirring for 30 min the mixture was heated to 60 °C and added to one equivalent of [PhNMe₂H][B(C₆F₅)₄] in benzene-*d*₆ at 60 °C (note: before addition it was important to heat the [PhNMe₂H][B(C₆F₅)₄]/benzene-*d*₆ slurry to the boiling point of benzene to obtain a two-phase mixture containing a colorless oil of borate/benzene in the lower phase and a small amount of dissolved borate in benzene in the upper phase). Strong evolution of *iso*-butane and *iso*-butene occurred immediately. After 10 min the reaction was completed and the ionic compounds precipitated as a colorless oil. The upper phase contained mostly benzene-*d*₆, aluminium alkyls and PhNMe₂, but no metallocene products. Example: a slurry of Cp₂ZrCl₂ (83 mg, 285 μ mol) in 3 ml benzene-*d*₆ was treated with AlBu₃ⁱ (7.16 ml, 28.5 mmol). After 30 min the pale yellow solution was added to [PhNMe₂H][B(C₆F₅)₄] (0.228 g, 285 μ mol) in 3 ml benzene-*d*₆ at 60 °C. After 10 min the reaction was completed and the mixture was cooled to room temperature. The precipitated colorless oil (0.5–1 ml, 0.57–0.29 M) was washed three times with 2 ml of benzene-*d*₆ to remove excess AlBu₃ⁱ and some PhNMe₂. Subsequently, the colorless oil was used to record the NMR spectra. The ¹H NMR shows three metallocene products, which could not be further identified. The product ratio depended on the Al/Zr ratio used. The ¹⁹F NMR

showed exclusively $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (C_6D_6 , 20°C): δ -131.9 (sb, 8F, *o*-F), -162.4 (t, 4F, $J = 20.4$ Hz, *p*-F), -166.3 (sb, 8F, *m*-F).

3. Results and discussion

3.1. Reaction of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ with Bu^iMgCl and AlBu_3^i

Reaction of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ with one equivalent of Bu^iMgCl in THF leads to the highly air-sensitive $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$, which can be isolated as a yellow powder (reaction (1)).



In contrast to the C_s symmetric $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$, $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ has a chiral metal center due to four different ligands attached to the zirconium. Thus, the methylene group and the methyl groups are

diastereotopic. Consequently, the ^1H NMR spectrum shows two sets of resonances for the CH_3 groups and the signals of the CH_2 group appear as an ABX pattern at -0.80 and -1.11 ppm, with a coupling constant of $^2J_{\text{AB}}$ of 13 Hz (Fig. 1, middle).

No significant changes in the ^1H NMR spectra occurred after the addition of three equivalents of AlBu_3^i to a solution of freshly prepared $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ in benzene- d_6 (Fig. 1, top). The spectra show only the signals of the chiral metallocene and the resonances of AlBu_3^i .

The reaction of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ with various amounts of AlBu_3^i was investigated in a series of NMR experiments. The spectra show that only the mono-*iso*-butyl complex $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ is formed, as seen in Fig. 2.

Even when an Al/Zr ratio of 50 is used no other products are observed. The spectra recorded with Al/Zr ratios of 2 and 5 still show the resonances of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$, whereas with Al/Zr ratios higher than 10, total conversion of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ is observed. This can be attributed to an equilibrium of the

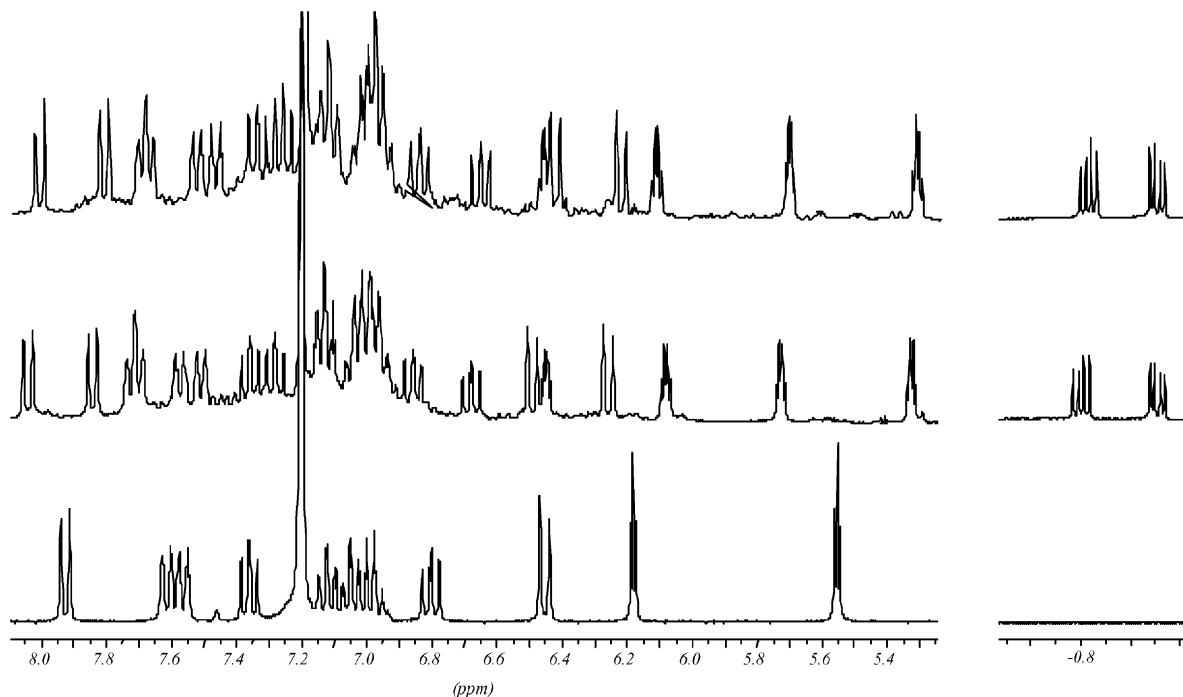


Fig. 1. Aromatic and methylene group ^1H NMR signals of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ (bottom), $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ (middle) and $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i + 3$ equivalents of AlBu_3^i (top). Al alkyl signals have been omitted.

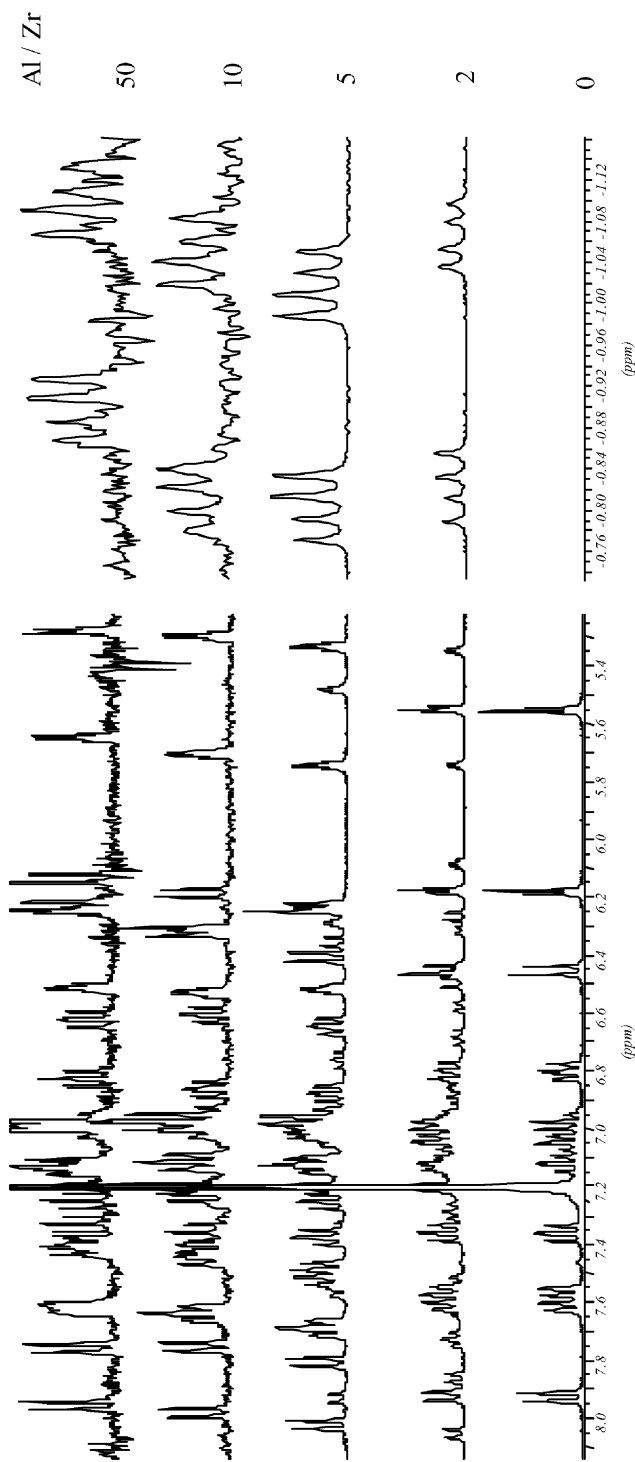
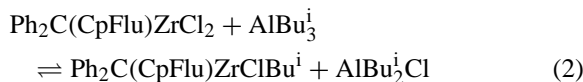


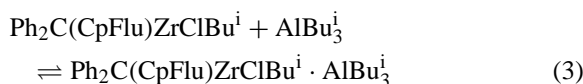
Fig. 2. Aromatic and methylene group ^1H NMR signals of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ reacted with 0, 2, 5, 10 and 50 equivalents of AlBu_3 (bottom to top). Al alkyl signals have been omitted.

isobutyl exchange reaction between $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ and AlBu_3^i (reaction (2)).



Brintzinger and Beck [12] have already described equilibria of methyl exchange reactions of zirconocene dichlorides with AlMe_3 leading to the monomethyl metallocene complexes exclusively. Varying the Al/Zr ratios, they observed a small shift of the NMR signals of Cp_2ZrCl_2 and Cp_2ZrMeCl , which they attributed to the formation of hetero dinuclear associates with aluminium alkyls.

In our series of experiments the ^{13}C spectra show a large stepwise shift of the CH_2 resonance of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ from 73.6 to 85.4 ppm, if the Al/Zr ratio is increased from 0 to 2 and 5 to 10. This can be due to an equilibrium involving the formation of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i \cdot \text{AlBu}_3^i$ or $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i \cdot \text{AlBu}_2^i\text{Cl}$, lowering the electron density of the metal center via Zr–Cl–Al bridges (reaction (3)).



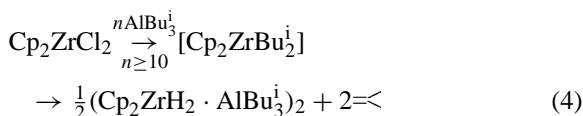
As can be seen in Fig. 2, the ^1H resonances of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ and of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ show only a slight change below Δ , 0.1 ppm, with an increasing Al/Zr ratio. Therefore, only the ^{13}C resonance of the CH_2 group bound to the zirconium atom seemed to be a reliable indicator of the formation of $\text{LLZrClBu}^i \cdot \text{AlR}_3$ associates.

3.2. Reaction of Cp_2ZrCl_2 with AlBu_3^i

Reactions of Cp_2ZrCl_2 with 2, 5, 10 and 20 equivalents of AlBu_3^i were performed in C_6D_6 and investigated by NMR spectroscopy. Similarly to the reaction of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ with AlBu_3^i , for total conversion of Cp_2ZrCl_2 more than two equivalents of AlBu_3^i are required and with Al/Zr ratios of 10 and 20 only one uniform metallocene product could be detected. Based on known spectroscopic data of $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlMe}_3]_2$ [14] the product was identified as $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlBu}_3^i]_2$, a dimeric metallocene complex containing Zr–H–Zr and Zr–H–Al bridges. Fig. 3 shows the significant parts of the ^1H NMR spectrum of a mixture resulting

from a reaction of Cp_2ZrCl_2 and 10 equivalents of AlBu_3^i .

In the ^1H NMR spectra the bridged hydrogens show resonances at -0.88 and -1.95 ppm. The signal at -0.88 ppm is a triplet, whereas the other is very broad. The latter can be due to exchange reactions. With regard to the signals of bridged hydrogens and the Cp ligand, the same ^1H NMR spectrum was found for the analogous complex $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlMe}_3]_2$, which was prepared by reacting $[\text{Cp}_2\text{ZrH}_2]_n$ with AlMe_3 [14]. The pure complex $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlMe}_3]_2$ was described as thermally unstable, decomposing even at room temperature. In contrast to this, $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlBu}_3^i]_2$ remained unchanged for days in the reaction mixture. This can be due to a stabilizing effect from the surplus AlBu_3^i present in the reaction mixture. It can be assumed that $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlBu}_3^i]_2$ is formed via $\text{Cp}_2\text{ZrBu}_2^i$ (reaction (4)).



In fact, the spectra show substantial amounts of isobutene and the spectrum obtained with two equivalents of AlBu_3^i shows three main Cp signals. Two of the main Cp signals can be assigned to Cp_2ZrCl_2 and $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlBu}_3^i]_2$, respectively but even using ^{13}C data none of the Cp signals could be positively assigned to an *iso*-butyl complex such as $\text{Cp}_2\text{ZrBu}_2^i$, $\text{Cp}_2\text{ZrClBu}^i$ or $\text{Cp}_2\text{ZrHBu}^i$. The origin of the observed isobutene is at least partly due to the equilibrium shown in reaction (5).



Therefore, the amount of isobutene observed gave no reliable mechanistic information. No assignments could be made for ClAlBu_2^i , HAlBu_2^i or complexed AlBu_3^i due to overlapping signals caused by the large excess of the aluminium alkyl, exchange reactions and possible aluminium alkyl dimers which can be formed.

3.3. NMR investigations of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2 / \text{AlBu}_3^i / [\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $\text{AlBu}_3^i / [\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ systems

NMR samples of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2 / \text{AlBu}_3^i / [\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ systems were prepared in a

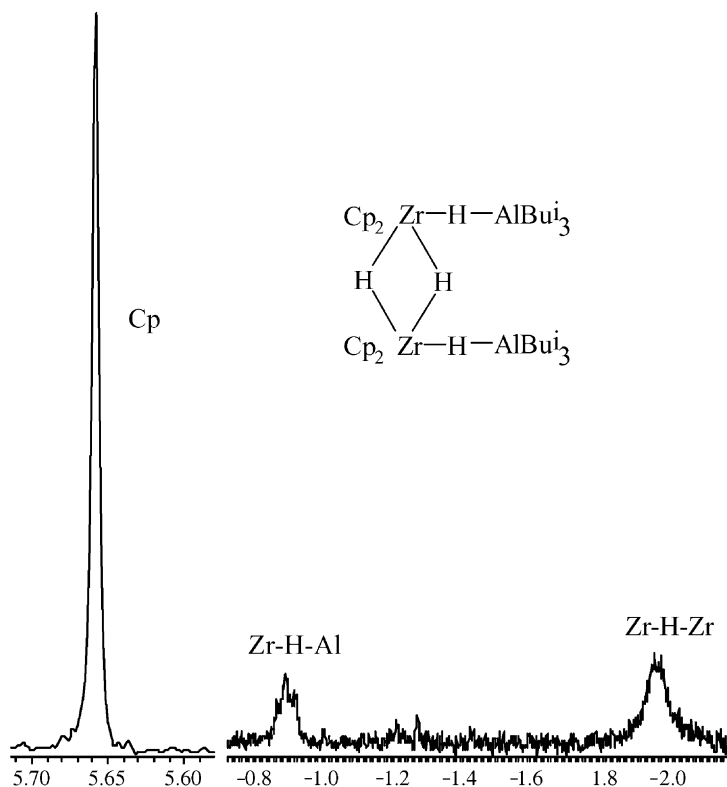


Fig. 3. ^1H NMR resonances assigned to $[\text{Cp}_2\text{ZrH}_2\cdot\text{AlBu}_3]_2$. Al alkyl signals have been omitted.

two-step procedure similar to the usual conversion of a metallocene dichloride to form a solution of the precursor of the active metallocene species used for polymerization. A slurry of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ in benzene- d_6 was treated with 10, 20, 50 and 100 equivalents of AlBu_3^i and the resulting mixtures were reacted with one equivalent of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, as described in Section 2. The second reaction step was accompanied by the evolution of gas. An analysis of the gas trapped in a gas mouse showed a mixture of *iso*-butene and *iso*-butane. An increase of the *iso*-butene/*iso*-butane ratio from 1.4 to 1.9 was observed with an increase of the Al/Zr ratio of the reaction mixture from 10 to 100. During the evolution of gas a dark green or brownish-yellow oil containing the resulting ionic metallocene species, precipitates. Three extractions of the oil with benzene- d_6 removed excess AlBu_3^i and PhNMe_2 which formed during the

reaction. One to two hours after this purification the oil was characterized by NMR spectroscopy.

The precipitation of oils during the formation of cationic metallocene complexes in benzene is described in [15–17]. We found that the two-phase solutions obtained show a behavior similar to systems that Atwood defined as “liquid clathrates” [18,19]. Atwood reported that these liquid inclusion compounds form upon interaction of aromatic molecules with certain species related to $\text{M}[\text{Al}_2\text{R}_6\text{X}]$. These liquid clathrates contain a certain ratio of aromatic and ionic molecules. Therefore, they are immiscible with excess aromatic solvents and show the appearance of two phases. The upper phase contains excess aromatic solvents and all neutral compounds, the bottom phase is the liquid clathrate. Accordingly, in our two-phase system, the NMR spectra show that the upper phase contains only the non-ionic compounds PhNMe_2 , aluminium

alkyls and most of the benzene- d_6 . The bottom phase contains the ionic compounds, some benzene- d_6 , but no free or complexed *N,N*-dimethylaniline.

If the reaction was performed with Al/Zr ratios of 10, 20 or 50, two cationic metallocene species were detected in the NMR spectra of the bottom phase (Fig. 4).

In the ^1H NMR spectra one of these metallocene species shows only two Cp resonances at 5.83 and 5.03 ppm, indicating a C_s symmetric metallocene complex. The signals of the C_s symmetric complex decrease with increasing Al/Zr ratios and disappeared when 100 equivalents of AlBu_3^1 are used. Further identification was not possible due to overlap with signals of the second species, which was identified as $[\text{Ph}_2\text{C}(\text{CpFlu})\text{Zr}-\mu\text{-H}-\mu\text{-(C}_4\text{H}_7)\text{-AlBu}_2^1][\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{AlBu}_3^1$ (**A**)—a novel type of allyl-bridged cation. The signals of this species are visible in all the spectra and increase with increasing Al/Zr ratios. When the reaction is performed with an excess of 100 equivalents of AlBu_3^1 the spectra show only the signals assigned to **A**.

An assignment of all the signals in the ^1H and ^{13}C NMR spectra (Fig. 5) was possible using 2D NMR experiments and led to a remarkable bridged structure [20].

As shown in Fig. 5, an AlBu_2^1 fragment is bound to the Zr center via a Zr–H–Al bridge and an allylic Zr– C_4H_7 –Al group, forming a six-membered ring. The resonance for the bridging hydride is found as a singlet at -2.78 ppm.

The allylic framework was unambiguously proved with C, H correlated and long range C, H correlated 2D NMR spectra, as shown in Figs. 6 and 7.

The C, H correlation spectra in Fig. 6 yield cross signals for all protons and ^{13}C nuclei which are connected by a ^{13}C , ^1H coupling over one bond ($^1J_{\text{C,H}}$). The connected lines (dotted) in Fig. 6 show the coupling of the allylic CH_2 proton signals with ^{13}C resonances, which are identified as methylene groups in the ^{13}C DEPT spectra. Fig. 7 shows the long range C, H correlation spectra of **A**. The cross signals describe ^{13}C , ^1H spin pairs connected by two- or three-bond couplings ($^2J_{\text{C,H}}$ and $^3J_{\text{C,H}}$). The cross signals of this spectra clearly show a $^2J_{\text{C,H}}$ coupling of protons of the CH_3 group with a quarternary ^{13}C atom (a) and two $^3J_{\text{C,H}}$ couplings of protons of the CH_3 group with the two methylene ^{13}C atoms (b and c). As expected, no cross signal is obtained for the bridged Zr–H–Al hydron.

The diastereotopic methylene group Zr– CH_2 of the allyl ligand shows characteristic signals for each proton, at 2.87 and -1.66 ppm in the ^1H NMR. Alt et al. [21] described a similar upfield shift of one proton of the analogue diastereotopic methylene group in bridged fluorenylidene–indenylidene complexes. They explained it as a shift to high field induced by one benzene ring of the fluorenyl ligand. Accordingly, the diastereotopic methylene group Al– CH_2 shows the same pattern of singlets at 2.28 ppm and around 1 ppm, but with a smaller upfield shift of the high field resonance. The corresponding resonances of the carbon atoms are found at 90.5 ppm, assigned to Zr– CH_2 with a $^1J_{\text{C,H}}$ coupling constant of 157.5 Hz and at 47.7 ppm assigned to Al– CH_2 with a $^1J_{\text{C,H}}$ coupling constant of 129.4 Hz. These data indicate the non-symmetric bonding of the bridging allyl ligand [22]. The chemical shifts and coupling constants are evidence for the sp^2 -hybridized nature of the Zr– CH_2 carbon atom, whereas the Al– CH_2 carbon has a strong sp^3 character. There is no evidence for α -agostic interactions with the metal centers, because in this case the coupling constants would be expected to be much lower [23]. A 2D NIOSY NMR experiment was performed in order to obtain more information about the stereochemistry, but no significant correlation signals appeared.

High-temperature NMR experiments up to 70°C showed no change of the resonances in the spectra. No coalescence was detected for the methylene resonances, i.e. there was no rotation or fluxional ligand exchange (π -allyl/ σ -allyl ligand exchange) of the allylic group. Characteristic for a methallylic structure is the resonance at 163.4 ppm of the quarternary allyl carbon atom. In the literature, shifts of 157 and 180 ppm are reported for the quarternary methallyl carbon atoms in cationic zirconocenes with η^3 -bound methallyl groups [17,24,25]. The allylic methyl group appears as a singlet at 1.22 ppm in the ^1H and at 26.6 ppm in the ^{13}C NMR spectra. Resonances for the two *iso*-butyl groups appear as a multiplet at 2 ppm for the methine, as a doublet at 1.06 ppm for the methyl and as a broad signal at 0.32 ppm for the methylene protons.

Interestingly, there is another AlBu_3^1 present in the bottom phase, as could be clearly seen from coupling patterns in the 2D NMR spectra and from integration of the ^1H NMR. Even after washing the precipitated oil several times with benzene- d_6 it was not possible

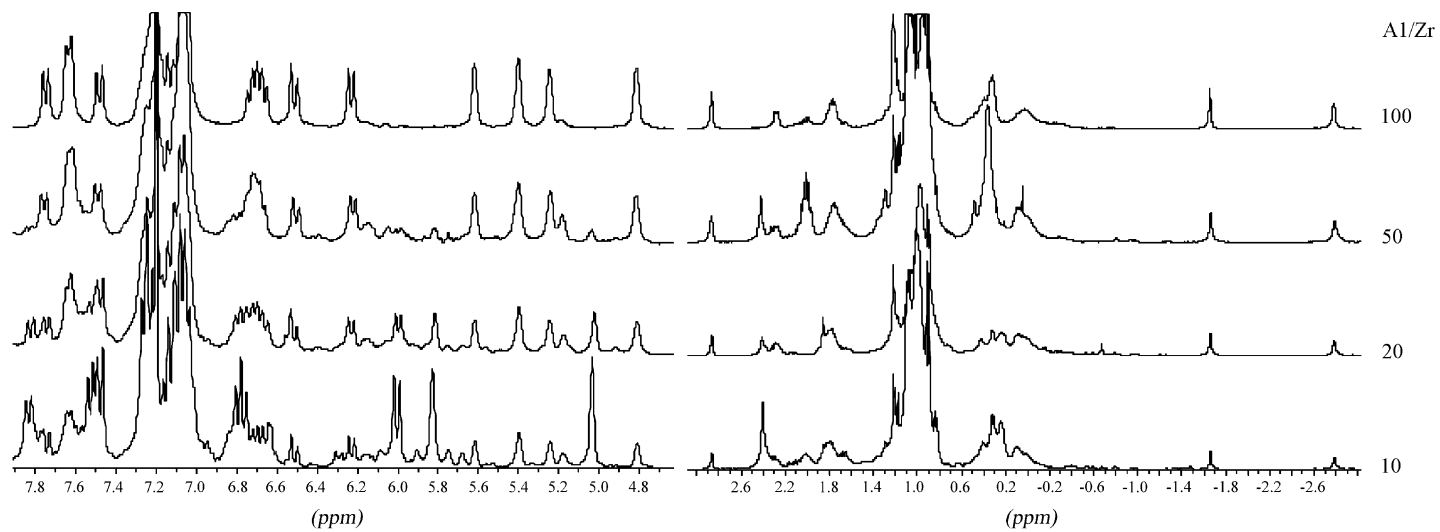


Fig. 4. ^1H NMR spectra of bottom phase resulting from mixtures of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2/\text{AlBu}_3^i/[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ prepared in C_6D_6 with various quantities of AlBu_3^i .

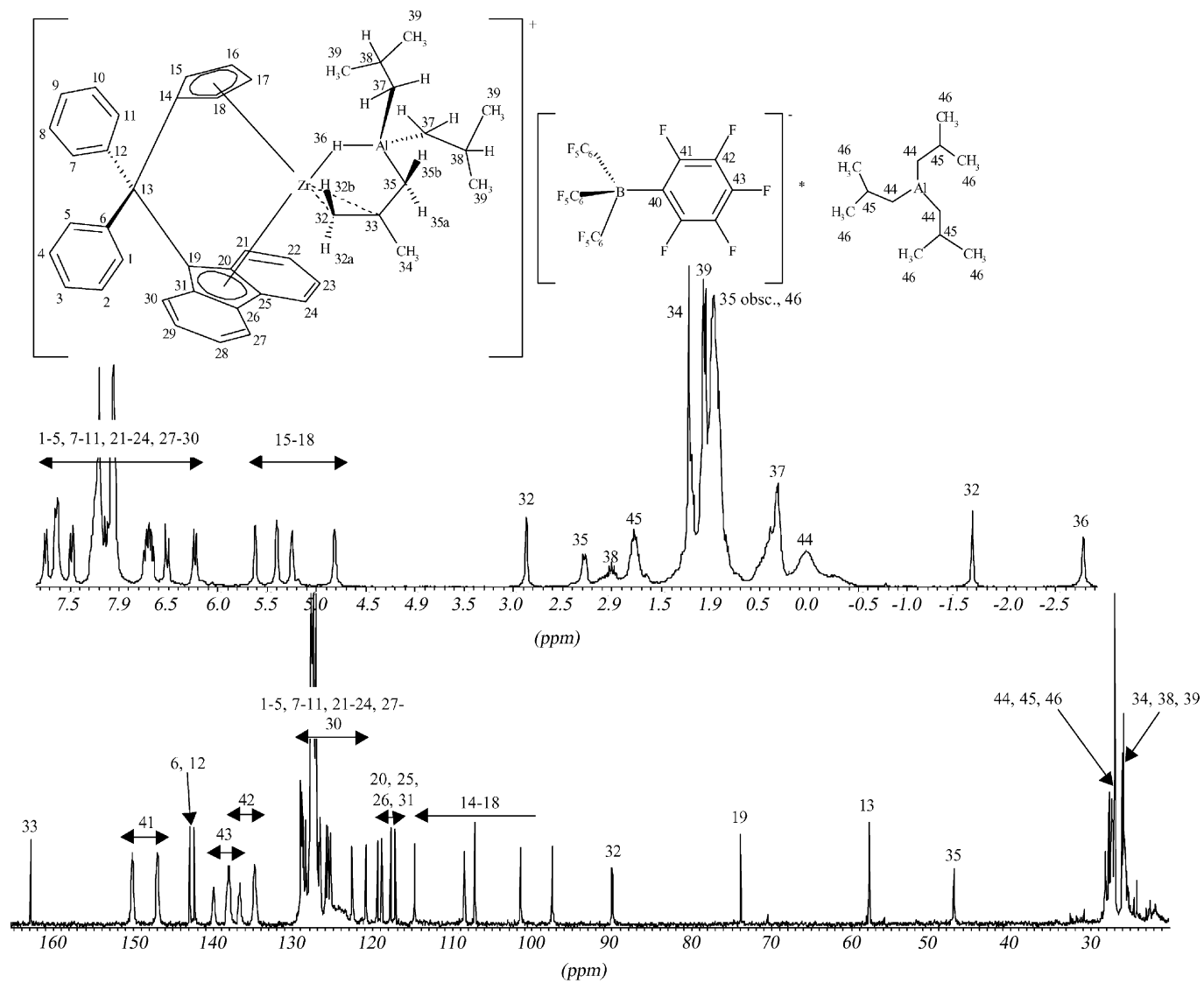


Fig. 5. ^1H and ^{13}C NMR spectra of $[\text{Ph}_2\text{C}(\text{CpFlu})\text{Zr-}\mu\text{-H-}\mu\text{-C}_4\text{H}_7\text{-AlBu}_2^i][\text{B}(\text{C}_6\text{F}_5)_4]\text{-AlBu}_3^i$ (A). Assignment of signals.

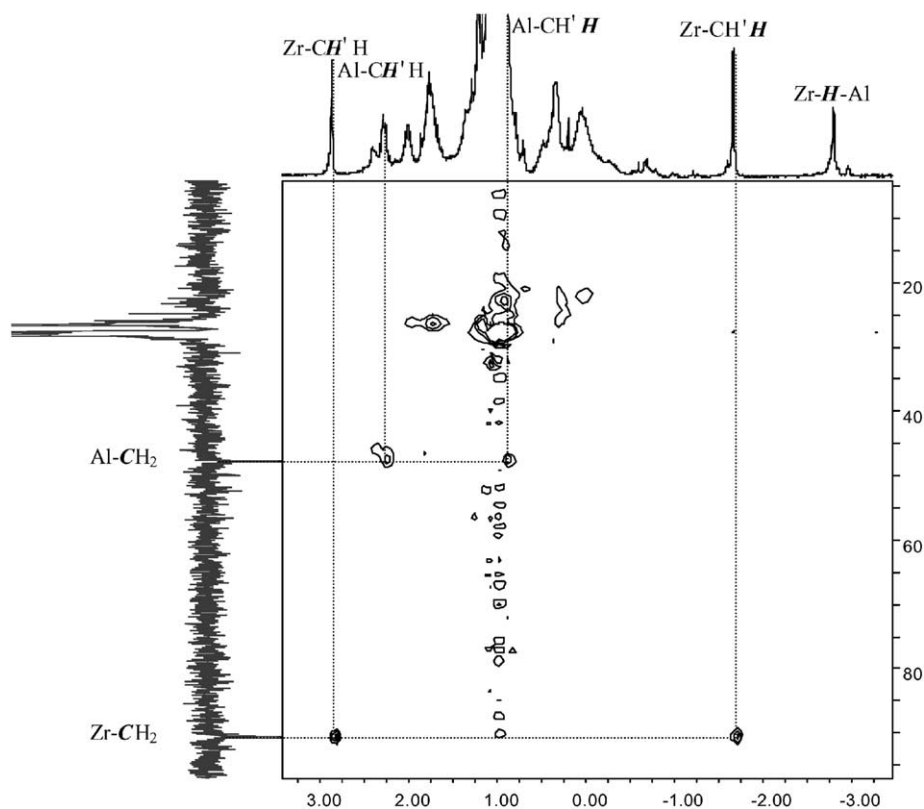


Fig. 6. C, H correlated spectra of **A** (^1H vs. ^{13}C DEPT spectra). Assignment of CH_2 -allylic resonances.

to extract all the AlBu_3^i . This observation is in good accord with the liquid clathrate theory of Atwood [18]. Zaworotko et al. [26] made an observation, similar to Atwood's, that liquid clathrates are best obtained if they have the exact composition of "MA Al_2 ". This is evidence for a stabilizing effect of this AlBu_3^i unit and could explain why we were not able to isolate the precursor of the active complex as a solid. All efforts to remove the solvent in vacuum led to the decomposition of **A**. The anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ does not coordinate to the metallocene cation. In any case, the ^{19}F NMR spectra show only the resonances of non-coordinated $[\text{B}(\text{C}_6\text{F}_5)_4]^-$.

No investigations have been carried out to determine how this allyl-bridged cation reacts under polymerization conditions. The solutions of samples used for the NMR experiments were much more concentrated than preactivated catalyst solutions used for polymerizations [10]. With the assumption that

the species **A** also exists in low concentrated, preactivated, ternary catalyst solutions it can be proposed that the bridged structure must open to allow the approach and insertion of monomer at the active site. Allylic activation of a coordinated propene, followed by chain propagation into the Zr(allyl) species were observed by Marks and co-workers [27], and Richardson and co-workers [28]. More recent studies of allylic activation in propene polymerizations were done by the groups of Brintzinger et al. [15], Ziegler and co-workers [29], and Resconi and co-workers [30]. Allylic complexes of metallocene cations and of *iso*-butene were described by Teuben et al. [31].

The generation of complex **A** from a mixture of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i/\text{AlBu}_3^i$ and $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ must be a multi-step reaction, and we assume that the initial step is the reaction of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ with AlBu_3^i , which is present in large excess in the mixture.

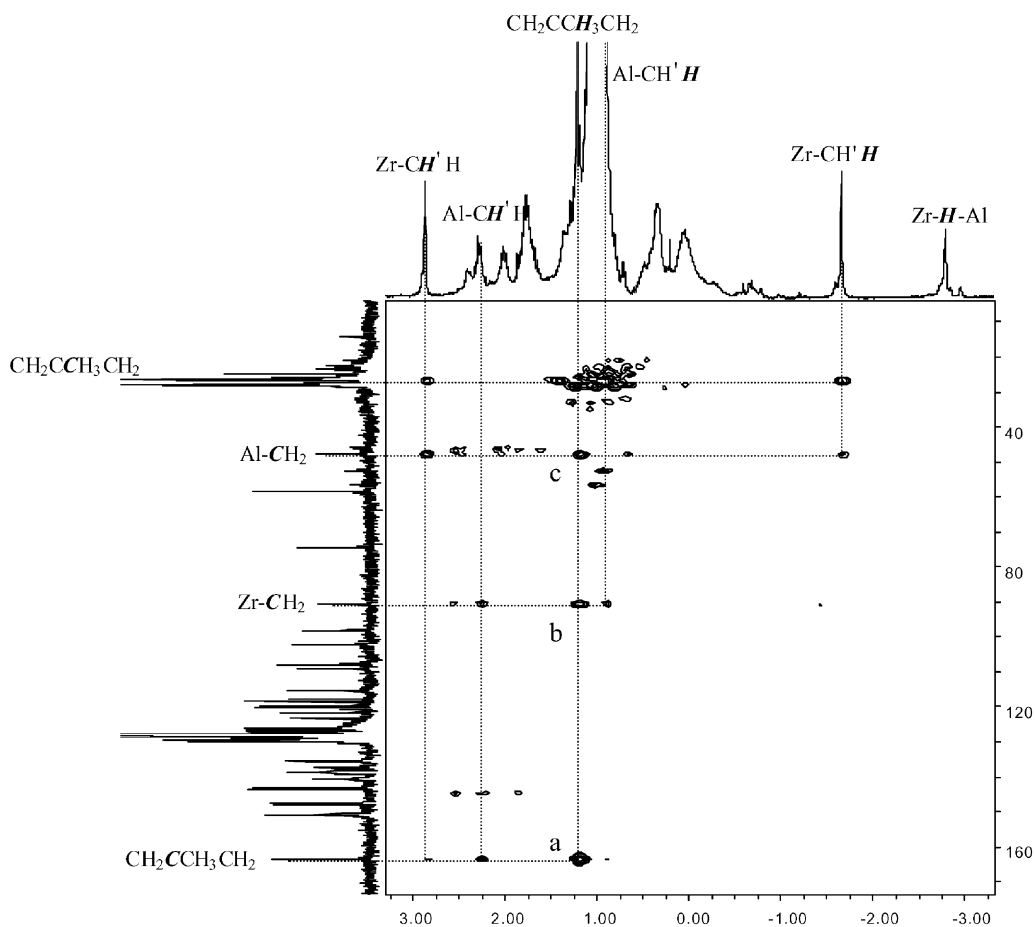
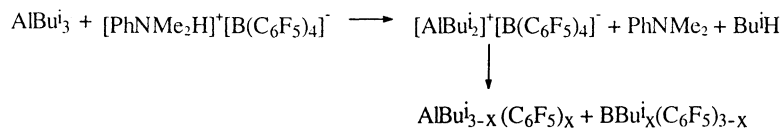


Fig. 7. Long range C, H correlated spectra of A (^1H vs. ^{13}C NMR). Assignment of allylic resonances.

A separate investigation carried out by us showed that reactions of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ with 2 and 4 equivalents AlBu_3^i lead to complete degradation of $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (reaction (6)).



The reaction is accompanied by the formation of *iso*-butane and PhNMe_2 and the reaction proceeds faster with a higher Al/B ratio. As shown in reaction (6) the formation of $\text{AlBu}_{3-x}^i(\text{C}_6\text{F}_5)_x$ compounds can be attributed to a transient $[\text{Bu}^i_2\text{Al}]^+$ cation.

Bochmann and Sarsfield [13] described a similar formation of transient $[\text{AlBu}_2^i]^+$ by reaction of AlBu_3^i with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. They observed the formation of Ph_3CH and *iso*-butene, whereas the resulting

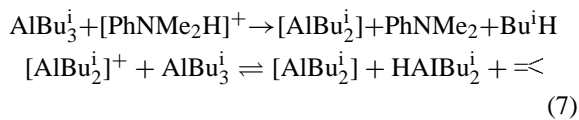
transient $[\text{AlBu}_2^i]^+$ reacts with $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ to give $\text{AlBu}_{3-x}^i(\text{C}_6\text{F}_5)_x$ compounds.

However, in the $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i/\text{AlBu}_3^i/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ system, we observed no degradation of the anion, which may be due to the

presence of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ and an high excess of AlBu_3^i .

Direct reaction of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ in toluene in the absence of AlBu_3^i led to a dark violet-colored solution and the formation of a violet precipitate. NMR spectra showed a number of species that could not be identified. None of these products were found in the presence of excess AlBu_3^i . It is assumed that the reaction of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ in the absence of AlBu_3^i is based on a different reaction mechanism compared to the reaction in the presence of excess AlBu_3^i .

We, therefore, propose a mechanism as outlined in reaction 7 and Scheme 1. We believe that the initial step of the reaction leading to the formation of complex **A** is the reaction of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ with AlBu_3^i , which is present in large excess in the mixture (reaction (7)).



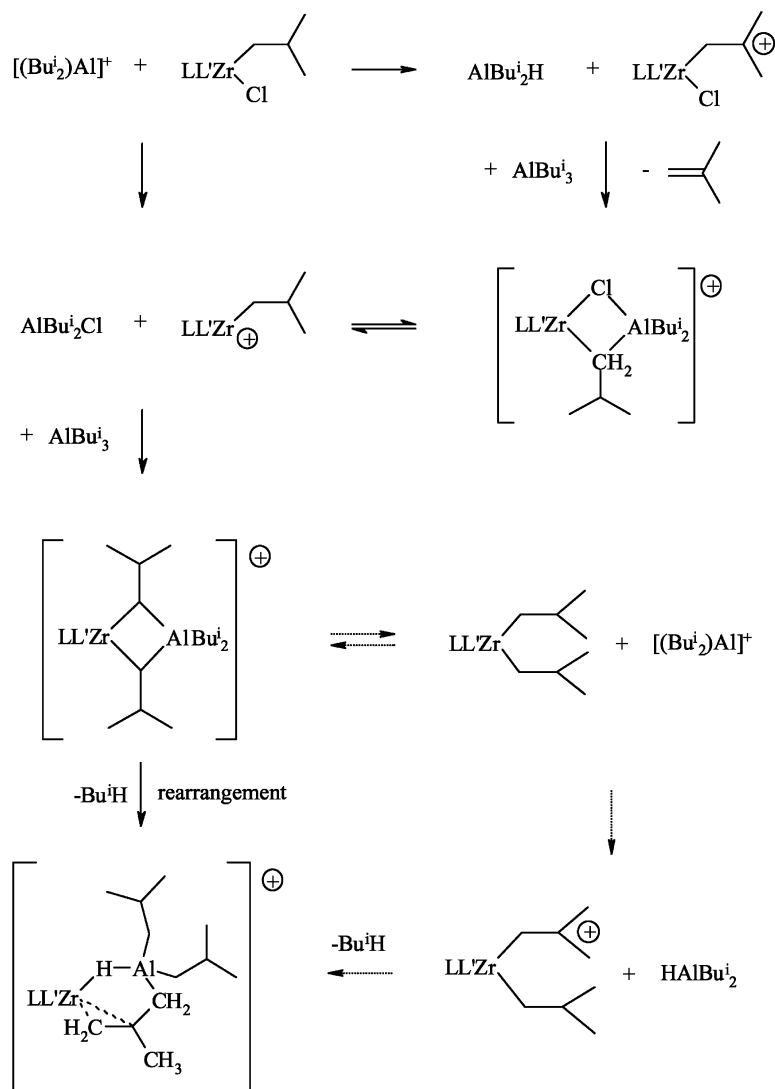
In the first step, protonation of AlBu_3^i leads to evolution of *iso*-butane and generates a transient $[\text{Bu}_2^i\text{Al}]^+$ cation. It can be assumed that $[\text{Bu}_2^i\text{Al}]^+$ easily reacts with more AlBu_3^i . β -Hydride abstraction results in the formation of AlBu_2^iH and $[\text{Bu}_2^i\text{AlCH}_2\text{CMe}_2]^+$ which, after the loss of *iso*-butene, regenerates $[\text{Bu}_2^i\text{Al}]^+$. This preliminary equilibrium also explains the formation of *iso*-butene and its dependency on the amount of AlBu_3^i . With increasing concentration of AlBu_3^i more *iso*-butene is formed, which is consistent with the results from the gas analysis. Transient $[\text{AlBu}_2^i]^+$ could abstract the chloride or a β -hydride from $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$, which is the only metallocene product of the alkylation step independent of the excess AlBu_3^i used. As shown in Scheme 1 both abstractions can lead to $[\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrBu}^i]^+$.

It is well known that metallocene cations form dinuclear complexes with aluminium alkyls [1]. Therefore, in the presence of excess AlBu_3^i the dinuclear complex $[\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrBu}^i \cdot \text{AlBu}_3^i]^+$ can be formed. With the loss of *iso*-butane, this complex can rearrange to form $[\text{Ph}_2\text{C}(\text{CpFlu})\text{Zr}-\mu\text{-H}-\mu\text{-(C}_4\text{H}_7\text{)-AlBu}_2^i]^+$, as determined by NMR. The rearrangement can be

illustrated as shown with dotted arrows in Scheme 1. A similar rearrangement was already been described by Bochmann and co-workers [25] for the reaction of $\text{Cp}_2\text{Zr}(\text{Bu}^i)_2$ with Ph_3C^+ . Under evolution of *iso*-butane this reaction leads to the allyl complex $[\text{Cp}_2\text{Zr}(\eta^3\text{-methallyl})]^+$. The cationic complex $[\text{Ph}_2\text{C}(\text{CpFlu})\text{Zr}-\mu\text{-H}-\mu\text{-(C}_4\text{H}_7\text{)-AlBu}_2^i]^+$ that we found can be seen as the allyl complex $[\text{Ph}_2\text{C}(\text{FluCp})\text{Zr}(\eta^3\text{-methallyl})]^+$ stabilized by HAiBu_2^i . This led us to assume that the C_s symmetric metallocene compound formed with low Al/Zr ratios was probably $[\text{Ph}_2\text{C}(\text{FluCp})\text{Zr}(\eta^3\text{-methallyl})]^+$, but this could subsequently be ruled out by the NMR spectra of the product mixtures that show only the allyl fragment of compound **A**. However, it is evident that the formation of both metallocene complexes depends strongly on the Al/Zr ratio used in the reaction procedure. An explanation for this phenomenon can be the different neutral Al and Zr complexes that can be protonated by reaction with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$. If the excess of AlBu_3^i is large, protonation of Al complexes is favored, leading to transient Al cations and further to **A**; whereas at low Al/Zr ratios protonation of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$ is possible, leading to the C_s symmetric metallocene species.

3.4. NMR investigations of the $\text{Cp}_2\text{ZrCl}_2/\text{AlBu}_3^i/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ system

For NMR investigations of the formation of the precursor of the active complex of Cp_2ZrCl_2 the NMR samples were prepared as described above for $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$, using the same Zr/Al/B ratios. Three different cationic metallocene species were detected as the main products of the activation reaction in the NMR spectra. The ratios of the resulting three metallocene species depend on the Al/Zr ratio used, but could not be shifted to the formation of one uniform metallocene species as was possible with $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$. In contrast to the findings with $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2/\text{Al}^i(\text{Bu})_3/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ systems, the amine PhNHMe_2 could only be partly removed from the bottom phase by extraction. This may be due to a coordination of the amine to some of the cationic metallocene species. The ^1H NMR spectra of $\text{Cp}_2\text{ZrCl}_2/\text{AlBu}_3^i/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ systems show 12 resonances of bridged hydrogens between -0.5 and -6.5 ppm and at least six broad



Scheme 1. Proposed formation of $[\text{Ph}_2\text{C}(\text{CpFlu})\text{Zr}-\mu\text{-H}-\mu\text{-(C}_4\text{H}_7\text{)-AlBu}_2^i]^+$. $\text{LL}' = \text{Ph}_2\text{C}(\text{CpFlu})$; and the anion, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, has been omitted.

singlets between 5 and 6.4 ppm, typical for unbridged Zr–H. As we observed in the case of the activation of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$, the ^{19}F NMR only shows the intact anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and no indication of a coordination to cationic species.

4. Conclusions

The results show that the Al/Zr ratio has a strong influence on the reaction of metallocene dichlorides

with AlBu_3^i . For a total conversion of both metallocene dichlorides used, more than two equivalents of AlBu_3^i are required. With a surplus of 10 equivalents of AlBu_3^i , or higher, one uniform metallocene species is formed. Furthermore, the type of products found depend on the ligand of the metallocenes. The bridged $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ is converted to the monoalkyl complex $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrClBu}^i$. Even with a 50-fold excess of AlBu_3^i no further reaction to the dialkyl complex is observed. With Cp_2ZrCl_2 the uptake of

more than one AlBu_3^i equivalent is observed, leading to $[\text{Cp}_2\text{ZrH}_2 \cdot \text{AlBu}_3^i]_2$ as the single metallocene product if 10 or more AlBu_3^i equivalents are used.

Independent of the excess aluminium alkyl used, the metallocenes are converted quantitatively to cationic species if the products of metallocene dichloride/ AlBu_3^i mixtures are reacted with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$. However, the type of cationic species formed depends strongly on the Al/Zr ratio used. In the case of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ two species were detected below an Al/Zr ratio of 50, whereas with Cp_2ZrCl_2 at least three species were found. Reaction of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$ with an Al/Zr ratio of 100 results exclusively in the formation of $[\text{Ph}_2\text{C}(\text{CpFlu})\text{Zr}-\mu\text{-H}-\mu\text{-(C}_4\text{H}_7\text{)-AlBu}_2^i][\text{B}(\text{C}_6\text{F}_5)_4]^-$. AlBu_3^i (A). In no case could degradation or complexation of $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ be detected.

In the absence of metallocenes the reaction of AlBu_3^i with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ leads to complete degradation of $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, which is due to the formation of transient $[\text{Al}^i\text{Bu}_2]^+$. In combination with results from literature these observations lead to a proposed mechanism for the formation of the precursor of the active complex of $\text{Ph}_2\text{C}(\text{CpFlu})\text{ZrCl}_2$. Most characteristic is the initial reaction of AlBu_3^i with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ resulting in the generation of transient aluminium cations. It should be noted that the metallocene concentrations that were used for the NMR experiments were much higher than metallocene concentrations of preactivated catalyst solutions used for polymerizations. Therefore, one should take care in drawing conclusions from our results and extrapolate them to catalyst solutions.

Acknowledgements

The authors wish to thank the Bundesministerium für Bildung und Forschung and BASF AG for financial support.

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