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Zirconium Allyl Complexes as Participants in Zirconocene-Catalyzed α-Olefin Polymerizations**

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Abstract: *In a search for the hitherto elusive catalyst resting state(s) of zirconocene-based olefin polymerization catalysts, a combination of UV/Vis and NMR spectrometric methods reveals that polymer-carrying cationic Zr allyl complexes make up about 90 % of the total catalyst concentration. Other catalyst species that take part in the polymerization process have to be generated from this allyl pool into which they appear to relapse rather frequently.*

Owing to their practical utility, *ansa*-zirconocene catalysts for α-olefin polymerizations have been thoroughly studied, such that the reaction mechanisms responsible for stereoselective chain growth and for competing isomerization and chain-release reactions are now understood in substantial detail.[1] Surprising uncertainty prevails however with regard to the nature of those complex species that actually predominate during ongoing polymerization catalysis.

Zirconocene cations carrying σ-bound,[2,3] agostic,[4] regioirregular,[5] or allylic polymer chain ends[6,7] at their Zr centers have been either directly observed or otherwise suspected to be present during zirconocene-catalyzed olefin polymerization. Zirconocene allyl cations, in particular, have been characterized rather thoroughly with regard to structural and reactivity details.[8] Neither these nor any of the other entities mentioned above have so far been shown however to constitute a major active catalyst participant under conditions approaching practically useful polymerization catalysis, that is, at ambient or higher temperatures and in the presence of excess olefin.

Herein we present experimental evidence that cationic complexes with Zr bound allylic chain ends do indeed constitute the predominant species during polymerization of 1-hexene by an *ansa*-zirconocene-based catalyst system activated by tritylium perfluorotetraphenylborate.[9]

While studying catalyst systems obtained from *rac*-[$Me_2Si(1\text{-indenyl})_2ZrMe_2$] ([(SBI)$ZrMe_2$]) by activation with tritylium perfluorotetraphenyl borate in the presence of trimethylaluminum, we noticed that the bright red color of the heterobinuclear cation [(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ (**1**),[10] the main zirconocene species present in such a reaction system,[11] changes to an intense purple upon addition of excess 1-hexene at room temperature. In the UV/Vis spectra of a 0.4 mM solution of cation **1**,[12] the initial absorbance of cation **1** at 498 nm disappears immediately after addition of 800 equiv of 1-hexene, while a new absorbance appears at $\lambda_{max} = 560$ nm,[13] which culminates after 4–6 min and then partly disappears again (Figure 1).

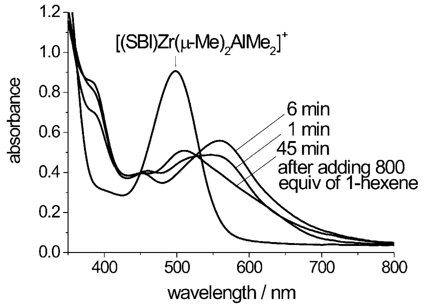

Figure 1. UV/Vis spectra of a 0.4 mM toluene solution of [(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ (**1**) at 25 °C, before and at various times after addition of 100 μL of 1-hexene.[12]

A first indication that the absorbance at 560 nm might be associated with the formation of Zr allyl complexes comes from the observation that an analogous reaction with 1-^{13}C-labeled 1-hexene gives rise to a ^{13}C signal at $\delta = 84.6$ ppm with $J_{C,H} = 149$ Hz,[12] which is very similar to signals previously shown to be associated with the presence of Zr allyl complexes.[3,7,8i] The time resolution of such ^{13}C NMR experiments is not sufficient however to follow the rather fast appearance of the complex species with $\lambda_{max} = 560$ nm. ^{1}H NMR signals of these species on the other hand are not easily discernable among those of the monomer and the polymer products. In two relatively unobstructed spectral regions, between $\delta = 2.5$ and 6.5 ppm, we were able to detect several ^{1}H NMR signals, which appeared within the first few minutes after 1-hexene addition, synchronously to the absorbance at 560 nm.[12] These signals are thus most likely due to the complex species with $\lambda_{max} = 560$ nm. A clarification of the nature of these species by NMR methods is thwarted, however, by the limited number,

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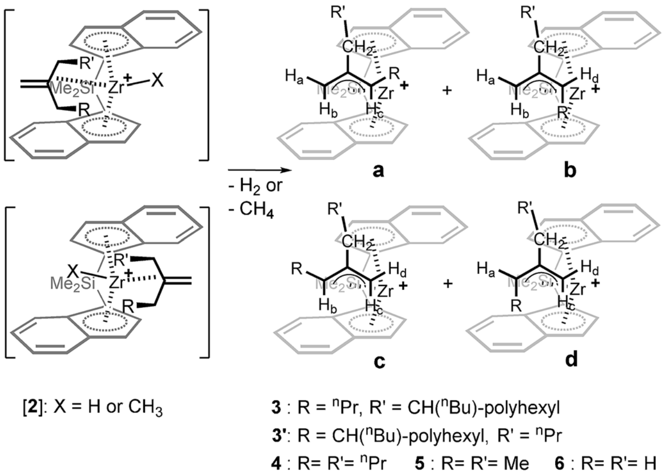
incomplete resolution, and temporal instability of these rather broad signals.[12]

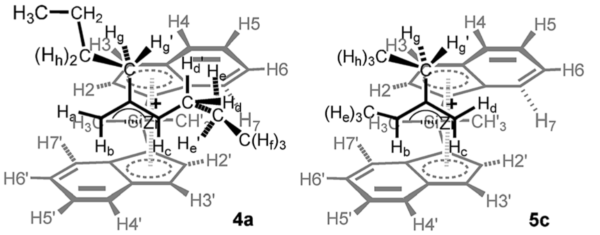
Along with this paucity of NMR data, formation of multiple Zr allyl isomers will encumber the structural assignment of Zr allyl complexes that arise in these catalyst systems. Zr allyl formation, for example from an intermediary (SBI)Zr hydride polyolefin cation **2** (Scheme 1), can give rise to four diastereomers and, furthermore, to positional isomers, where the central allyl position is occupied either by the polymer main chain (**3a–d**) or by an alkyl side chain (**3′a–d**).[7] Even if steric restraints were to disfavor formation of some of these isomers, structural characterization of these product mixtures by NMR spectroscopic methods would undoubtedly meet with great difficulties.



Scheme 1. Cationic (SBI)Zr allyl complexes expected to form from unsaturated polyhexene chain ends (**3a–d**, **3′a–d**) and from symmetrically substituted dialkyl-olefins (**4a–d**, **5a–d**, and **6**). Diastereomeric Zr allyl products are shown with *si*-coordinated indenyl ligands.

To circumvent these difficulties, we sought to clarify the nature of the species with $\lambda_{max} = 560$ nm by comparing their UV/Vis spectra with those of Zr allyl model complexes, the structures of which are more readily characterized by NMR spectroscopic methods. Suitable (SBI)Zr allyl model cations can be expected to form when cation **1** reacts, under release of CH_4, with a symmetric alkene, such as 2-butyl-1-hexene or 2-ethyl-1-butene (Scheme 1).[8a,i] The resulting cations **4a–d** and **5a–d** would then closely mimic the geometry of polymer-carrying Zr allyl intermediates, but cannot give rise to positional isomers owing to the symmetry of their olefin precursors.

When a 1 mM C_6D_6 solution of cation **1** is allowed to react with 260 equiv of 2-butyl-1-hexene for 72 h at room temperature, the resulting product mixture does give rise to three sets of ^{1}H NMR signals with intensity ratios of about 4:2:1, each of which is assignable to one (SBI)Zr allyl isomer.[14] The most abundant product was identified by two-dimensional NMR methods as isomer **4a**. With intra-ligand connectivities ascertained by NOESY and double-quantum filtered COSY relations, the mutual orientation of allyl and bis-indenyl ligands was determined by observation of NOESY cross peaks between allyl proton H_c and indenyl proton H3′ and between 2-^{n}butyl proton H_g and indenyl proton H3 and of significant aromatic high-field shifts of allyl proton H_b and 1-^{n}propyl proton H_e due to their positions above or below indenyl C_6 rings (Scheme 2).[12]



Scheme 2. Structures of the most abundant isomers of the model Zr allyl cations **4** and **5**, determined by two-dimensional NMR spectroscopic methods.[12]

For the more abundant one of the two minor diastereomers, interconversion with **4a**, presumably by way of η^3-η^1-η^3-allyl rearrangement,[8i] is indicated by the observation of spin-polarization transfer between corresponding ^{1}H NMR signals. The signals of both of the minor diastereomers were not of sufficient size, however, for a structure determination by two-dimensional NMR methods. As diastereomer **4d** appears to be most disfavored by steric effects, the ^{1}H NMR signals of the two minor isomers are most likely to be assigned to structures **4b** and **4c**. Signals of cation **1** are no longer observable in these reaction systems. Its reaction with excess 2-butyl-1-hexene to the Zr allyl cations **4a–c**, even though rather slow, can thus be assumed to have gone to completion.

An analogous reaction of cation **1** with excess 2-ethyl-1-butene gave a product mixture, which showed again several sets of ^{1}H NMR signals, each assignable to one Zr allyl isomer. The most abundant of the allyl complex isomers, which constitutes about 40 % of the total Zr content, is complex **5c** (Scheme 2).[12] Here, the smaller allyl substituents are apparently most favorably placed on the same side of the (SBI) ligand framework. Complex **5a**, a homologue of **4a**, accounts for about 30 % of the total Zr content. The third isomer **5e**, with about 25 % of the total Zr concentration, contains a tri-substituted allyl ligand. It appears to arise by an isomerization of the olefin before its conversion to the Zr allyl product.[12] As in the previous case, cation **1** is not detectable any more in such a reaction mixture; reaction with 2-ethyl-1-butene thus appears to convert it completely into Zr allyl cations of type **5**.

UV/Vis spectra of a toluene solution containing the Zr allyl cations of type **4** (shown in Figure 2 together with that of cation **1**, from which it was obtained by reaction with 2-butyl-1-hexene) are characterized by a main absorption band at 550 nm, a minor band at 452 nm, and a shoulder on its UV slope at 385 nm. A solution containing Zr allyl cations **5**, obtained from cation **1** by an analogous reaction with 2-ethyl-1-butene, gives a UV/Vis spectrum closely similar to that of cations **4**, as expected for these closely related complexes (Figure 2).[15,16]

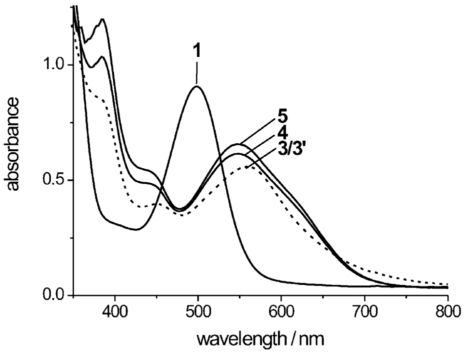


Figure 2. UV/Vis spectra of a 0.4 mM toluene solution of $[(\mathrm{SBI})\mathrm{Zr}(\mu\text{-}\mathrm{Me})_2\mathrm{AlMe}_2]^+$ (**1**) at 25 °C, before and after conversion to the Zr allyl cations **4** and **5** by reactions with excess of 2-butyl-1-hexene and of 2-ethyl-1-butene, respectively (solid lines) and of an identical solution of **1** after conversion to polymer-carrying Zr allyl species **3**/**3′** by reaction with 100 μL of 1-hexene for 6 min (broken line, see Figure 1).[12]

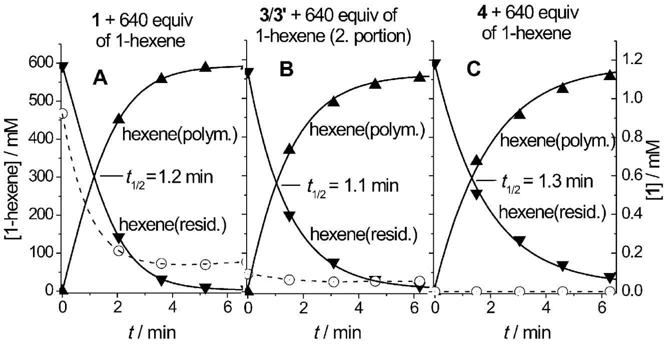


Figure 3. Consumption of 0.48 mmol of 1-hexene (black triangles, left scale) in 0.75 mL of a 1 mM solution of complex **1** (A, left), consumption of a second portion of 0.48 mmol of 1-hexene in the same solution (B, middle); consumption of 0.48 mmol of 1-hexene in 0.75 mL of a 1 mM solution of the Zr allyl complexes of type **4** (C, right). Residual concentrations of complex **1** in each reaction mixture are indicated by open circles (broken lines, right scale). All reactions conducted at 22 °C; concentrations determined by ^{1}H NMR spectroscopy.[12]

Comparison of the UV/Vis spectra of the model Zr allyl cations **4** and **5** with those observed during the polymerization of 1-hexene (Figure 2) clearly shows that the latter must likewise be due to the presence of Zr allyl cations. The striking similarity of the respective spectra (with regard to their main bands at 550-560 nm as well as with regard to their minor bands at about 450 nm and their short-wavelength shoulders at 385 nm) leaves no reasonable doubt that (SBI)Zr allyl cations of type **3**/**3′** are indeed formed in these catalyst systems. Slight differences with respect to $\lambda_{\max}$ values are most likely related to differences in the respective substituents of the allyl ligand,[15] in particular to the presence of a tertiary C atom in the polyhexyl chain, in close vicinity to the allyl group.

The UV/Vis spectra of cations **3**/**3′** are similar to those of cations **4** and **5** also with regard to the intensity of their absorbance at 550–560 nm. If we assume that the molar absorptivity of these Zr allyl cations are close to each other, we can estimate that cations of type **3**/**3′** constitute about 90 % of the total zirconocene content of these catalyst systems after reaction times of 4–6 min.[18] The spectra shown in Figure 1 indicate, furthermore, that already one minute after addition of 800 equiv of 1-hexene about 80 % of cation **1** has been converted into polymer-carrying Zr allyl cations.

The appearance of (SBI)Zr allyl cations **3**/**3′** already during the earliest phase of 1-hexene polymerization raises the question as to whether these species are active participants in the catalytic polymerization process or merely deactivation products. Active roles of Zr allyl species in catalytic polymerization and some of its side reactions had been proposed in earlier studies.[1a,6] More recently, Landis and Christianson have investigated catalyst systems obtained by activating $[(\mathrm{SBI})\mathrm{ZrMe}_2]$ with tritylium perfluorotetraphenyl borate in the absence of any aluminum alkyls in toluene solution at −40 °C.[7] Zr allyl complexes, shown to be present after depletion of the monomer, were found to be inert under these conditions against further hexene additions and were thus proposed to be deactivated species rather than active participants in polymerization catalysis.[7] To assess the catalytic activity of Zr allyl species under our present reaction conditions, we have measured the rates of 1-hexene polymerization in a 1 mM $\mathrm{C_6D_6}$ solution of cation **1** in the presence of 2.7 equiv of $\mathrm{AlMe_3}$,[19] and, for comparison, in an otherwise identical solution containing the Zr allyl cations **3**/**3′** (Figure 3).

When 1-hexene (640 equiv) is added to the solution of cation **1**, the monomer is converted to polyhexene with a half-life time of about 1.2 min (Figure 3, left). At the same time, cation **1** is strongly diminished; only about 15 % of its initial concentration is found to be left after 4–6 min, in accord with our UV/Vis data. When an equally large second portion of 1-hexene is added to this solution about 20 min later, polymerization proceeds at practically the same rate as before, as shown by an estimated half-life time of about 1.1 min (Figure 3, center). This indicates that the polymer-carrying Zr allyl cations of type **3**/**3′**, which now predominate in this solution according to the NMR and UV/Vis data presented above, furnish catalyst systems with similar activity as those initiated by cation **1**.

To eliminate any doubts concerning possible contributions of residual cation **1** or other complex species to the observed polymerization rate, we have conducted additional experiments, where cation **1** is first allowed to react with excess 2-butyl-1-hexene, so as to be completely converted into the Zr allyl model complexes of type **4**. Addition of 1-hexene to such a solution leads, again, to polymerization with a rate practically indistinguishable from those of the two previous experiments (Figure 3, right). As expected, the NMR signals of the initial cationic Zr allyl complexes of type **4** are completely replaced, within a few minutes, by those ascribed above to the polymer-carrying Zr allyl species of type **3**/**3′**.[12,17]

These data provide conclusive evidence that catalyst systems containing predominantly or exclusively (SBI)Zr allyl cations, either of the polymer-carrying or of the model type, give rise to catalytic activities, which are clearly on a par with those associated with cation **1** under comparable conditions.[18] These cationic Zr allyl species, which make up

90% or more of the total catalyst content, can thus be viewed as a resting-state reservoir, from which other species involved in the polymerization process are continuously regenerated. Cationic Zr polymeryl species capable of further chain growth have been shown to be accessible from Zr allyl cations by uptake of H_2, by allyl versus methyl exchange with Al−Me units of a co-catalyst or by direct monomer insertion into the Zr allyl unit to form polymer chains containing internal C=C double bonds.[1a,6c,8d]

To determine which mechanism of exiting from the resting state dominates in a given catalyst system, further data, such as polymer microstructures and molar mass distributions as well as end-group quantification by isotope labeling experiments, will be required in parallel to the respective degrees of Zr allyl complex formation. When such data become available for different catalysts, activators, and monomers, the relevance of Zr allyl resting states under other (for example, industrial) reaction conditions can be assessed and rational explanations for the unusual kinetics of these catalyst systems[20] and for the still enigmatic dependence of their activities on the structure of the respective zirconocene precatalysts might finally be achieved.

Experimental Section

All of the operations were carried out in an argon-filled glovebox or in vacuo by break-seal techniques. Solvents and liquid reagents (toluene, [D$_6$]benzene, 1-hexene, 2-ethyl-1-butene, 2-butyl-1-hexene) were degassed and dried over molecular sieves (4 Å) or distilled from sodium. [(SBI)ZrMe$_2$] was obtained from MCAT Co. Konstanz, and trimethylaluminum from Aldrich Chemical Co. All glassware (NMR tubes, UV/Vis cells, sample vials) were cleaned with chromic sulfuric acid, rinsed with ion-free water, and dried, first at 110°C and then in vacuo.

Solutions of [(SBI)Zr(μ-Me)$_2$AlMe$_2$][B(C$_6$F$_5$)$_4$] for NMR experiments were prepared in the glove box by transferring 0.5–1 mg amounts of [(SBI)ZrMe$_2$] directly into 5 mm OD glass NMR tubes, dissolving them in 0.4 mL of a stock solution of AlMe$_3$ in C$_6$D$_6$, and then slowly dissolving the appropriate amounts of [Ph$_3$C][B(C$_6$F$_5$)$_4$], deposited on the glass wall of the NMR tube, in the reaction mixture. The NMR tube, closed with a PTFE-lined rubber septum, was taken from the glovebox, inside an argon-filled Schlenk vessel, from which it was transferred immediately to the dinitrogen-swept cavity of the NMR spectrometer. 1-Hexene was added to the NMR tube through the septum closure from a PE syringe, which had also been kept inside an argon-filled Schlenk vessel. Reactions of C$_6$D$_6$ solutions of [(SBI)Zr(μ-Me)$_2$AlMe$_2$][B(C$_6$F$_5$)$_4$] with 2-ethyl-1-butene or 2-butyl-1-hexene were conducted in a sample vial and the reaction mixture then transferred to an NMR tube inside the Ar-filled glovebox. ^{1}H NMR spectra were recorded on a Bruker AV 400 spectrometer, using 90° pulses (24 μs) with 2.7 s acquisition time and 1 s delay time. Chemical shifts are referenced to 7.16 ppm for the residual ^{1}H NMR signal of [D$_6$]benzene.

Solutions for UV/Vis experiments were similarly prepared in small (4 mL) sample vials, using a stock solution of AlMe$_3$ in toluene, and then transferred to 1 cm UV/Vis cuvettes equipped with a double-septum closure. UV/Vis spectra were recorded with a Shimadzu UV-2501 PC spectrometer, after which the UV/Vis cuvettes were immediately transferred back to the glovebox for storage.

Further experimental details of individual NMR and UV/Vis experiments, data analysis, NMR spectra, and signal assignments are described in the Supporting Information.

Caution! Trimethylaluminum is pyrophoric and must be handled with special precautions.[21]

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Keywords: allyl complexes · *ansa*-zirconocenes · olefin polymerization · polymerization catalysis · resting states

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[11] Along with cation **1**, small amounts (ca. 2–25%) of a methylidene- and methyl-bridged binuclear cation, [{(SBI)Zr}$_2$(μ-CH$_3$)(μ-CH$_2$)]$^+$, can arise in these reaction systems, particularly when AlMe$_3$ is absent (see the Supporting Information). This species appears to be quite unreactive toward 1-hexene and toward 2-butyl-2-hexene and 2-ethyl-2-butene.

[12] For details, see the Supporting Information.

[13] A minor absorbance band at 452 nm and a shoulder at 385 nm are likewise associated with the formation of this catalyst species.

[14] Along with these signal sets that are due to Zr allyl products, small signal sets that are due to dimerization products of 2-butyl-1-hexene are detectable in these reaction systems (see the Supporting Information).

[15] The cation [(SBI)Zr(methallyl)]$^+$ (**6**, Scheme 1) has a UV/Vis maximum at 530 nm with a shoulder at 600 nm (see the Supporting Information). This deviation from the spectra of species **4** and **5** shows that the UV/Vis spectra are sensitive to substituents at the Zr-bound allyl group.

[16] Zr allyl complexes of type **4** and **5** are light-sensitive. Exposure of their solutions to light from a fluorescence lamp gives rise to an EPR signal at $g = 1.984$, which was previously shown to be due to Zr^{III} ion pairs of type $[(SBI)Zr^{III}]^+ BR_4^-$; T. N. Lenton, J. E. Bercaw, V. N. Panchenko, V. A. Zakharov, D. E. Babushkin, I. E. Soshnikov, E. P. Talsi, H. H. Brintzinger, *J. Am. Chem. Soc.* **2013**, *135*, 10710.

[17] The ^{1}H NMR signals assigned to cations **3/3′** differ in their chemical shifts from those of cations **4** (see the Supporting Information).

[18] This result is supported by a UV/Vis experiment, where complex **4** is first generated by reaction of cation **1** with excess 2-butyl-1-hexene and then used to polymerize 1-hexene (see the Supporting Information).

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