Metallocene Catalysts for the Polymerization and Copolymerization of α-Olefins:

A Research Collaboration Project Report

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SUMMARY: Results obtained during the tenure of a BMBF-supported collaborative research project, comprising the parts "Exploration of new *ansa*-metallocene complexes", "Commercially applicable metallocene syntheses", "Metallocene catalysts on solid supports" and "Improved control of the polymerization process", are reported in condensed form.

Introduction: Origins and Aims of the Project

After several years of bilateral collaboration with the Division of Dr. Schweier at the Kunststofflaboratorium of BASF AG and after a first 3-year period of BMBF-sponsored collaborative research involving also the research group of Prof. Mülhaupt at the University of Freiburg, the research group of Prof. Brintzinger at the University of Konstanz participated in a second collaborative research project with these two research partners. This project, which was established through the initiative and under the guidance of the Kunststofflaboratorium of BASF AG in November 1996 and supported until March 2000 by the Bundesminister für Bildung und Forschung, was aimed at "the development of novel, environmentally friendly and easily recyclable polyolefin materials with broad applicability and of energy-efficient catalytic processes for their production." Mechanical and thermal properties of polyolefin materials and polyolefin blends were to be controlled, by way of the microstructural architecture of α-olefin copolymers, through the use of tailor-made metallocene catalysts

To contribute toward this goal, the research group of Prof. Brintzinger had proposed the project parts A-D, described in subsequent sections of the following report. Since it is meant to give a condensed overview of the results originating from this collaborative project, results reported by other research groups, even though valuable contributions to the questions addressed, will thus not be referred to in this research report.

Part A: Exploration of New *ansa*-Metallocene Complexes

This project part was aimed at the synthesis of novel metallocene complexes and at their characterization with regard to their suitability as catalysts for the production of copolymers which incorporate otherwise incompatible comonomers. One approach toward this goal consisted in the synthesis of a series of new *ansa*-zirconocene complexes with hitherto unattained ligand structures. Among these are the complexes represented in Figure 1.[1] These complexes extend the spectrum of metallocene catalysts previously characterized with regard to their copolymerization properties.[2]
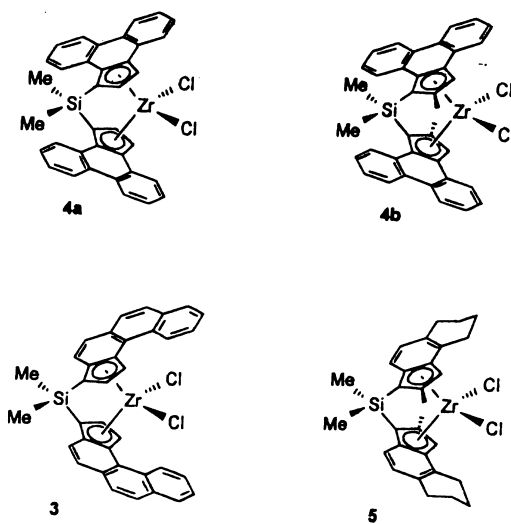

Fig. 1: New Me₂Si-bridged zirconocene complexes.

Unbridged zirconocene complexes with similarly modified ligand structures (Figure 2) were synthesized with the intention to gain access to stereoblock polymers with elastomeric properties.[3] In a recent extension of this study, the relations between the dynamics of ligand rotation and the polymer microstructure were investigated by means of dynamic NMR methods and of molecular mechanics calculations.[4]
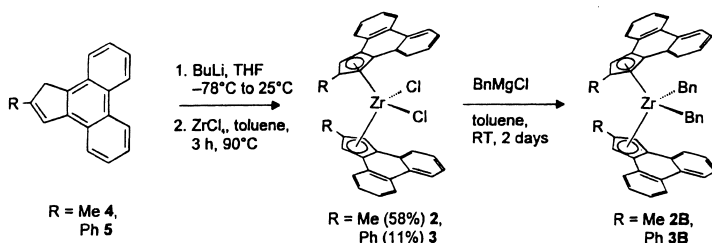
Fig. 2: New unbridged zirconocene complexes.

Related complexes with titanium as central metal (Figure 3) were synthesized and gave, when investigated with regard to their properties as catalysts for the syndiotactic polymerization of styrene, hitherto unattainable activity values.[5]
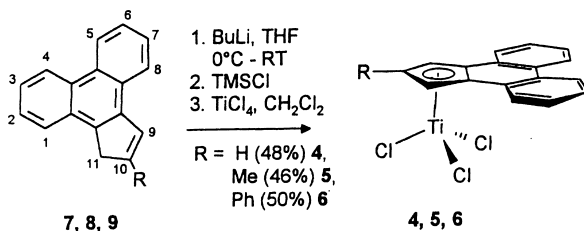

Fig. 3: New titanium complexes for the syndiospecific polymerization of styrene.

Titanium-containing metallocene compounds, with structures analogous to those of the mostly used zirconocene compounds, have so far hardly been synthesized and investigated with regard to their properties as olefin polymerization or copolymerization catalysts. First advances toward this goal were recently achieved by a new synthesis route which starts from titanium phenolate complexes[6].

Besides these studies on group IV metal complexes, attempts were also made to obtain novel complexes with other central metals. Dimethylphosphonium-bridged yttrocene complexes, which would be isoelectronic to the "classic" dimethylsilyl-bridged zirconocene complexes, were not amenable by the normally successful methods for metallocene synthesis .[7] Instead, we discovered an interesting new access to novel barium-containing metallocenes, which are of more interest for the anionic polymerization of dienes and of styrene, however, than for the

tasks defined for this project.[7,8)]

Vanadium-containing *ansa*-metallocenes with a variety of substituent patterns (Figure 4) were obtained by way of several synthetic routes. [9,10)] As yet we were not able, however, to obtain catalyst systems active for olefin polymerizations from these vanadocene complexes. Presumably, the great tendency of these complexes to change their oxidation states is detrimental for their catalytic activity.
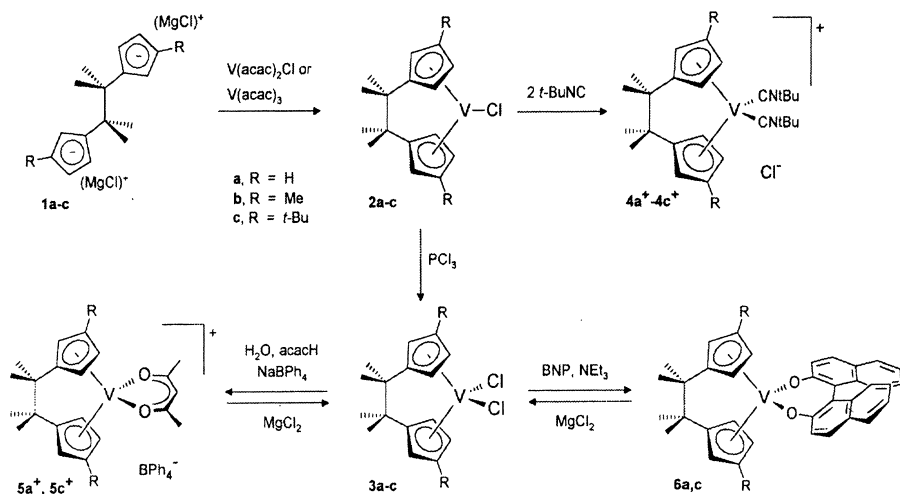

Fig. 4: Syntheses of *ansa*-vanadocene complexes.

Based on our investigations on *ansa*-chromocene complexes,[11)] we have recently begun to synthesize chiral complexes with Cr(II) and Cr(III) centers and to test these with regard to their properties as polymerization catalysts. Our studies on these complexes – as well as on related complexes with Fe(II) centers – are still in progress.[12)]

While the majority of the new complex structures resulting from this project part did not significantly advance the state of the art of polymerization catalysis so far, we still regard the prospects of our ongoing attempts to make new titanium- and chromium-containing complexes available for polymerization studies as promising and we intend to bring these investigations to a successful conclusion.

Part B: Commercially Applicable *ansa*-Metallocene Syntheses

The main goal of this project part was the development of new methods for metallocene syntheses which would allow the preparation of the *ansa*-zirconocene complexes of foremost interest for the production of new copolymers with commercially viable yields and, above all, under avoidance of the *meso* byproducts, which had always been obtained in comparable amounts so far. With regard to this task, a number of different approaches were pursued:

As a first possibility, the lability of zirconocene compounds against photoisomerization, known from earlier studies in our laboratory, was to be utilized in such a manner that the racemic product formed by a photo-induced *meso-rac* interconversion reaction was captured by the lithium salt of binaphthol as a chiral auxiliary reagent (Figure 5).
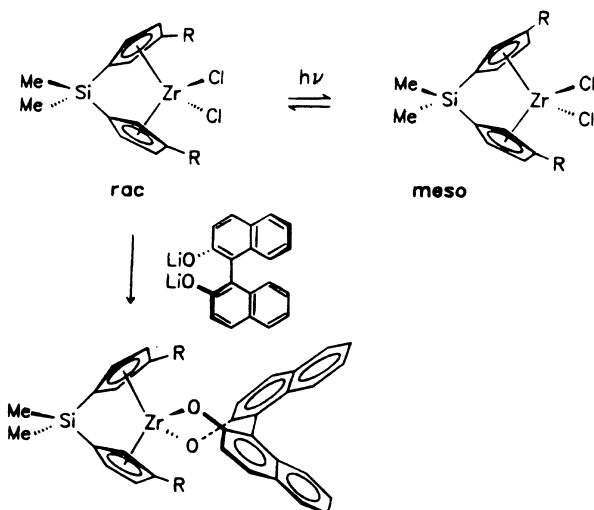
Fig. 5: Photochemical interconversion of meso and racemo zirconocene isomers.

This procedure did indeed allow the complete conversion of *rac*- and *meso*-product mixtures to the pure racemic binaphtholate complexes, especially with *ansa*-zirconocenes carrying a methyl substituent in 2-position ,[13] but it appears doubtful whether such a photoconversion reaction would be amenable to scale-up for large-scale metallocene syntheses.

Unexpectedly, *ansa*-zircconocene binaptholate complexes were soon afterwards found to be amenable also to a thermal conversion of the *meso*-isomer to the racemic product, with the latter being the sole product. In the meantime, this procedure was further developed to yield also enantiomerically pure *ansa*-zircconocene complexes (Figure 6), which find application as catalysts for asymmetric hydrogenations.[14]
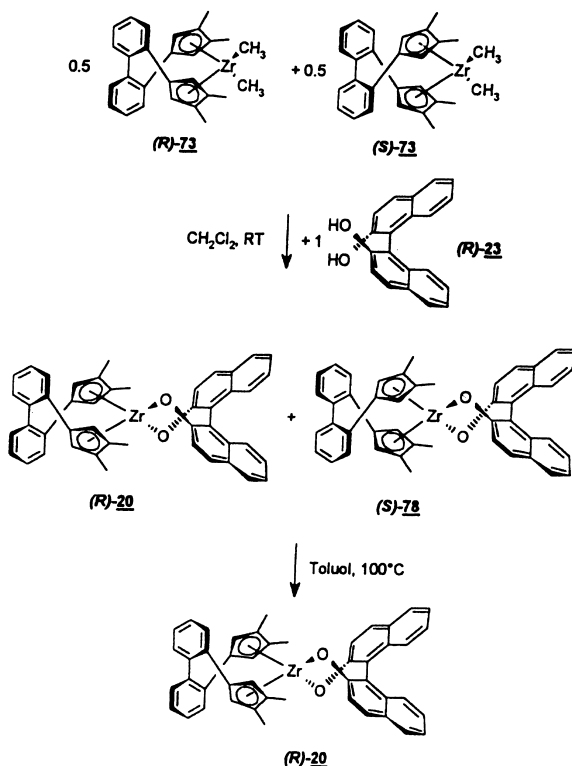

Fig. 6: Thermal conversion of zircconocene enantiomers.

Another procedure, likewise developed at the University of Konstanz, starts from a different point of venue: Me_2Si-bridged ligand compounds are converted, by reaction with tin amides, to polycylic spiro-tin compounds, which adopt – for steric reasons – exclusively an axially symmetric rac configuration. The latter give, upon complex formation with $ZrCl_4$, the racemic zircconocene complexes in high yields, completely free of any *meso* diastereomers (Figure 7).

This procedure is limited to cyclopentadienyl complexes, however; so far, it was not possible to develop an analogous protocol for the technically more interesting indenyl derivatives.[15]
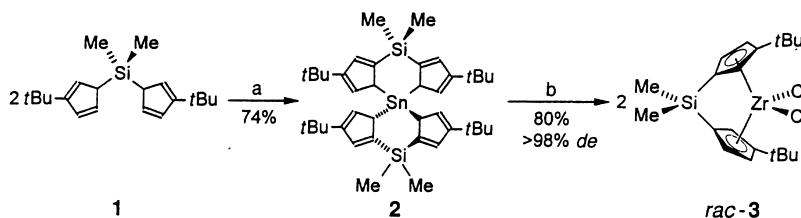

Fig. 7: Stereospecific *ansa*-zirconocene synthesis *via* a spiro-tin compound
(a: Sn(NMe$_2$)$_4$, b: ZrCl$_4$).

In order to develop practically applicable syntheses also for the technically more important indenyl-type complexes, the Me$_2$Si-bridged ligand compounds were converted – instead of tin derivatives – into the corresponding magnesocene complexes.[16] While reaction of these magnesium complexes with ZrCl$_4$ did not give a *rac*-selective complex formation, reaction with Zr-biphenolate complexes yielded the racemic complexes with excellent stereoselectivity and high yield (Figure 8). This procedure is presently being optimized for large-scale application and is likely to become the most favorable technical synthesis for zirconocene precatalysts of practical interest for the production of copolymers.[16]
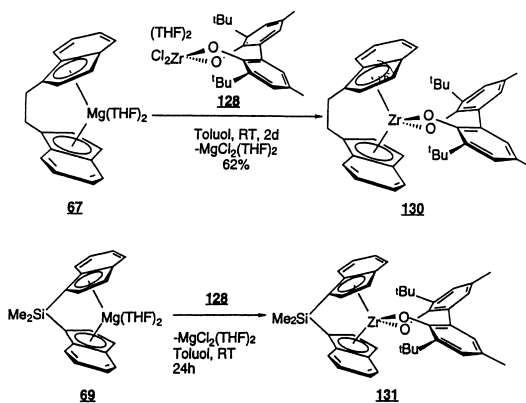

Fig. 8: Stereospecific *ansa*-zirconocene synthesis via a Zr-biphenolate.

Part C: Metallocene Catalysts on Solid Supports

In this project part, it was to be clarified whether the presently favored – presumably mostly physical – mode of adsorption of active zirconocene catalysts at the surface of SiO_2 and other support materials might be replaced by covalent fixation by way of Si-O-Si-alkyl linkers and whether this might remedy some of the problems associated with physisorbed catalysts – especially their tendency to leak from the support into the reaction medium.

In a rather intensive investigation, which concerned among other questions the development of adequate protection strategies for the reactive Zr center, *ansa*-zirconocene complexes with suitable linker functions were finally synthesized and covalently attached to SiO_2 surfaces, where the ensuing catalyst species were characterized by solid-state NMR and by UV/VIS spectroscopy (Figure 9).[17] The activities achievable with these supported catalysts were far from satisfactory, however. For this reason, and because of the publication of a parallel study by a Japanese research group, this approach, which appeared too involved for technical applications anyhow, was not pursued any further.
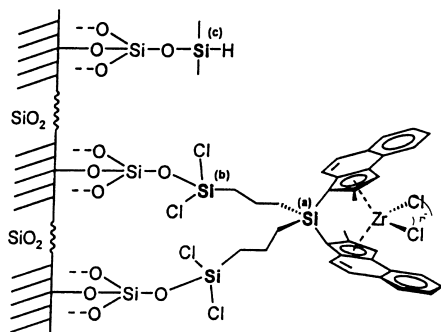

Fig. 9: Zirconocene complex covalently linked to an SiO_2 surface, with residual surface OH groups blocked by dimethyl silane groups.

UV/VIS spectroscopy, however, which was initially used for the characterization of these covalently supported zirconocene catalysts,[17] has been developed in the meantime into a quality control method excellently suited also for physisorbed catalyst systems (see project part D).

Part D: Improved Control of the Polymerization Process

In this project part, basic information concerning essential reaction paths in metallocene-catalyzed polymerization reactions was to be elaborated, which might contribute to the control and optimization of catalyst systems under practically useful reaction conditions.

Motivated by observations on various modes of action of different activator reagents in zirconocene-catalyzed propene polymerizations,[18] more detailed studies were undertaken on interactions between zirconocene precatalysts and their activators. A first result concerned the primary step of catalyst activation: The extent of methyl transfer from trimethyl aluminum to a zirconocene dichloride is sensitively dependent on the degree of electron deficiency at the
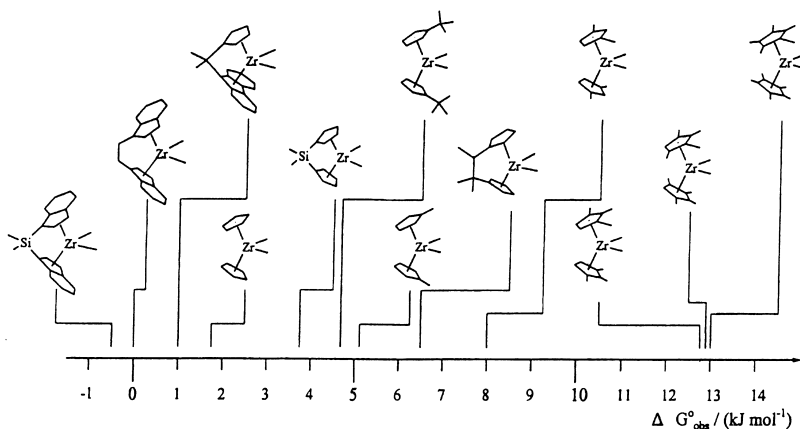

Fig. 10: Free enthalpy changes $\Delta G^{\circ}_{OBS} = -RT \ln K_{OBS}$ for methyl transfer from Al_2Me_6 to different zirconocene dichloride complexes.

Zr Center (Figure 10)[19]. To yield catalytically active species, the olefin substrate must displace the anion from a contact ion pair with weakly coordinating anion, formed by reaction with the Lewis-acidic activator. As models for this – not directly observable – equilibrium reaction, analogous reactions with phosphines instead of an olefin substrate were investigated.[20] These investigations and recent related studies on reactions with amines and ethers instead of an olefin substrate lead uniformly to the notion that displacement of the anion occurs by an associated (bimolecular) attack of the entering ligand at the Zr center

rather than by a unimolecular dissociation of the contact ion pair (Figure 11).[21]

No indications are obtained for the frequently invoked formation of "free" zirconocene alkyl cations. Based on these kinetic and mechanistic results, rational relations between substituent patterns of zirconocene complexes and important characteristics of the polymerization process – such as activities and polymer chain lengths – are presently being developed.
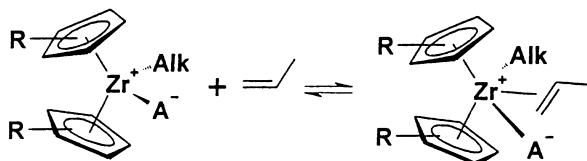

Fig. 11: Associative complex formation with an olefin substrate.

Another task in this regard concerns the reaction steps which lead to the isomerization of Zr-bound polymer chains and – simultaneously therewith – to the termination of chain growth. By use of density-functional calculations, the reaction steps involved in this process were identified and investigated with regard to their steric and electronic boundary conditions.[22]

A detailed experimental investigation on the reactivity of zirconocene-allyl complexes, which arise as inhibiting intermediates in polymerization catalyst systems, yielded kinetically relevant information concerning the rates of allyl transfer to the alkyl aluminum cocatalyst and of propene insertions into Zr-allyl bonds (Figure 12). Density-functional calculations support these estimates and identify reactions with H_2 gas as the fastest way to remove these inhibiting Zr-allyl complexes (Dissertation Susanna Lieber).[23]
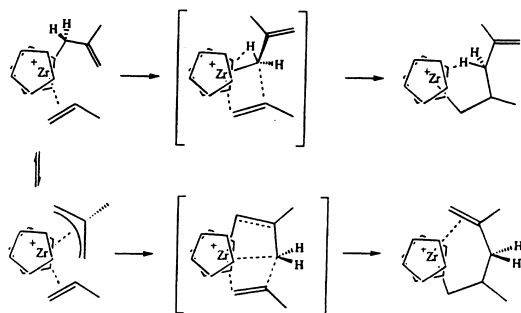

Fig. 12: Alternative reaction paths for the insertion of propene into Zr-allyl bonds.

Based on kinetic data obtained in the group of Professor Fink (Max-Planck Institute Mülheim)

a general scheme for the course of zirconocene-catalyzed olefin polymerizations, comprising all essential elementary reactions, was established and its parameters statistically evaluated for different catalysts.[24] From the resulting reaction profiles (Figure 13), it becomes apparent which reaction steps are rate determining for the overall process and thus predestined for further optimization efforts.
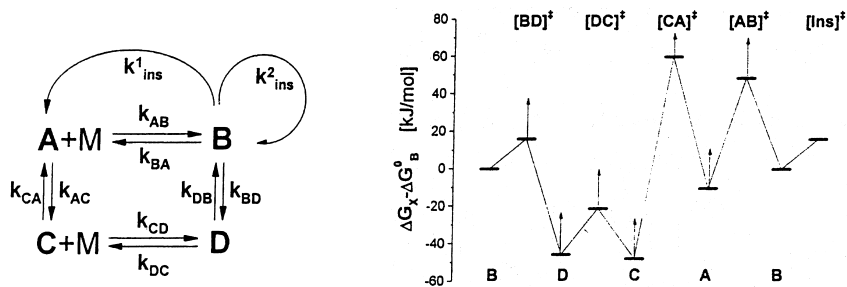

Fig. 13: Generalized reaction scheme (left) and free-energy reaction profile for a particular zirconocene catalyst (right), statistically evaluated from experimental kinetic data.

Further investigations into the reaction dynamics of active catalyst systems, based on NMR measurements of diffusion coefficients,[25] and of the rates of anion exchange reactions,[26] have provided first insights with regard to concentration-dependent formation of ion quadruples and higher-order ion aggregates in these catalyst solutions (Figure 14).
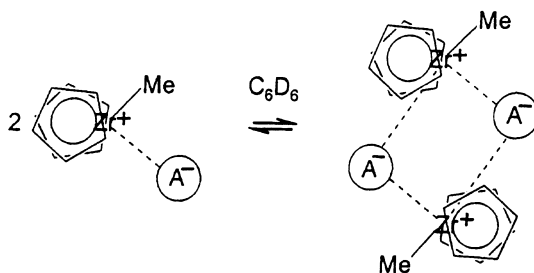

Fig. 14 : Ion quadruples in zirconocene catalyst solutions.

A further, essential goal of this project part was the spectroscopic observation of active catalysts *in situ*, i. e. directly in the "working" reaction mixture. A first attempt in this regard was undertaken by means of IR-spectroscopic methods. All essential bands of the zirconocene dihalide precatalysts and of their neutral and cationic alkyl activation products were assigned by means of comparison measurements and force-field calculations (Figure 15).[27] For supported catalysts, however, this method proved unsuitable, due to extensive band overlap with the SiO_2 support material.
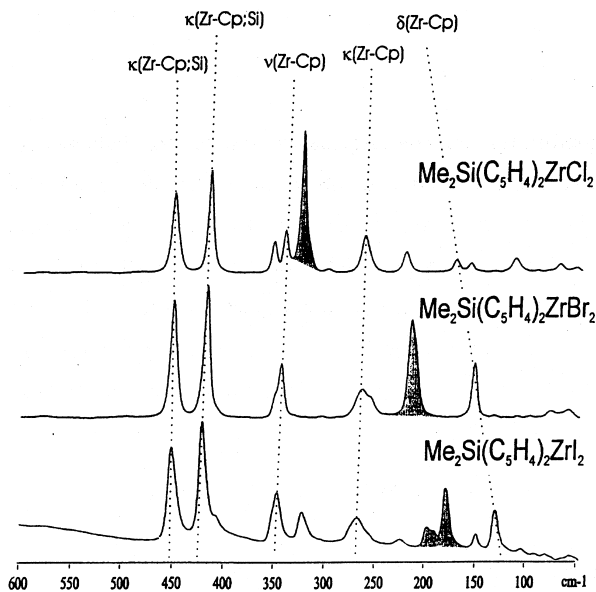

Fig. 15: IR-bands of bridged zirconocene dihalide complexes (shaded bands are Zr-halide stretching modes).

The UV/VIS techniques described already in Part C, however, could be developed to a highly useful characterization method. Application of these methods to homogeneously dissolved catalyst systems lead to the conclusion that the frequently discussed active species formed by reaction with a large excess of methyl alumoxane (MAO) are not – as hitherto assumed – "free" zirconocene alkyl cations, but rather their $AlMe_3$ adducts (Figure 16).[28] Extended investigations of this kind to modified MAO activators and to zirconocene and other catalysts on solid supports are presently under way in our laboratories.
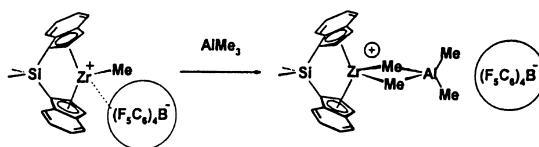
Reaction of $Me_2Si(Ind)_2ZrMe^+$ $(F_5C_6)_4 B^-$ with TMA.
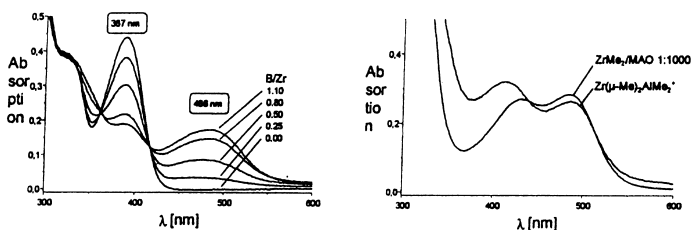
Fig. 16: UV/VIS-spectra for the formation of the cation $Me_2Si(Ind)_2Zr(\mu\text{-}Me)_2AlMe_2^+$ from $Me_2Si(Ind)_2ZrMe+TMA+PhNMe_2H^+(F_5C_6)_4B^-$ (left) and of $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$-MAO ([Al]:[Zr]=4000:1) and $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2Zr(\mu\text{-}Me)_2AlMe_2^+$ (right).

The formation of trialkyl aluminum adducts of this kind is essential also for another theme of great practical interest, the alkyl-aluminum mediated transfer of growing polymer chains from one type of catalyst to another. A first investigation on the underlying processes gave evidence that these transfer reactions proceed in a predictable manner, which is dictated by the steric requirements of the Zr centers donating and accepting the polymer chains and by those of the polymer chains themselves (Dissertation Susanna Lieber).[29]

This research direction is to be further extended toward inclusion of catalysts containing also group-8 transition metals (Fe, Ni, Pd) with the aim to obtain fundamentally new copolymers with chain segments of entirely different comonomer contents and microstructures.[30] For block copolymers of this novel type, useful practical applications in heterophase compatibilization – i. e. in the amalgamation of otherwise immiscible polymers – are to be expected.

Conclusion

While results of project parts A and C have been of limited applicability, parts B and D have lead to commercially viable metallocene syntheses and to potentially useful possibilities to modify the polymerization process. These areas are still being extended by further studies.

Acknowledgements

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