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The heterogenization of homogeneous metallocene catalysts for olefin polymerization

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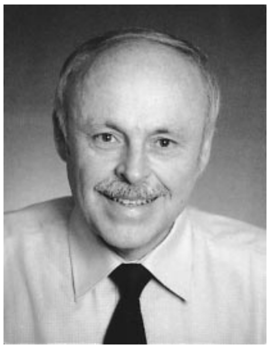
Metallocene complexes of titanium, zirconium and hafnium are very active and versatile catalysts for olefin polymerization and are already contributing to commercial production. Owing to a variety of catalyst parameters a wide range of polymers with various properties are accessible. Since metallocene complexes are homogeneous in solution they can easily be studied by spectroscopic methods. However, for industrial application they must be heterogenized.

1 Introduction

Metallocene complexes have revolutionized the world of polyolefins[1–3] and they are going to contribute polymers with new properties and applications. They represent a new generation of olefin polymerization catalysts and they offer many advantages compared with the Ziegler–Natta and Phillips catalysts. Owing to their homogeneous nature every molecule has an active site and thus metallocene catalysts can be many more times as active as established Ziegler–Natta catalysts. One of the record holders in terms of activity for ethylene polymerization is the bridged bis(fluorenyl) complex [Zr($C_{13}H_8C_2H_4$-$C_{13}H_8$)Cl_2] that can produce 300 tons of polyethylene (g Zr)$^{-1}$ h^{-1}.[4] The variation of the aromatic ligands, the bridge and the metal provides an enormous amount of parameters to control the polymerization reactions in terms of stereospecificity (when prochiral olefins such as propylene are applied), long chain and short chain branching and the generation of block copolymers (oscillating catalysts). In other words, metallocene catalysts can produce tailored polyolefins for nearly every purpose and with these "new materials" they generate new markets, like LLDPE (linear low density polyethylene).

Helmut G. Alt was born in 1944. He received his chemical education at the Technische Universität München. After his postdoctoral period with M. D. Rausch at the University of Massachusetts in 1973/1974 he returned to Munich. In 1978 he joined his "Doktorvater", Professor M. Herberhold, at the newly founded University of Bayreuth and finished his Habilitationsarbeit in 1980. There he is an extraordinary professor in chemistry. He has published more than 200 papers and is the inventor/coinventor of numerous patents. His research interests include transition metal complexes and their application in catalysis and synthesis.



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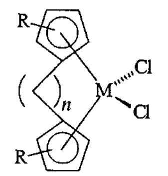
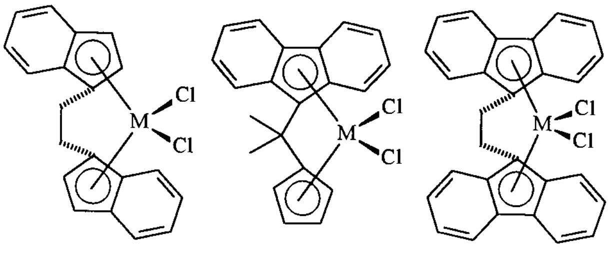


M = Ti, Zr, Hf
n = bridging unit, consisting of 1-3 atoms in the backbone
R = hydrocarbyl substituents or fused ring systems
(indenyl, fluorenyl and substituted derivatives)

The first application of a metallocene catalyst goes back to the '50s when the Breslow[5] and Natta[6] groups independently found that [$TiCp_2Cl_2$] (Cp = cyclopentadienyl) can be activated with mixed aluminium alkyl halides to polymerize ethylene in homogeneous solution but with poor activity. The next breakthrough came in the late '70s when Sinn and Kaminsky[7–9] applied methylalumoxane [$(MeAlO)_n$] (MAO) as a much better cocatalyst for activation than $AlXR_2$. In the '80s Brintzinger and co-workers[10] contributed the first ansa-bis(indenyl) complexes with fixed symmetry (*rac* form) to produce isotactic polypropylene. In 1988 Razavi and co-workers synthesized the mixed ansa-metallocene complex [$ZrC_5H_4CMe_2C_{13}H_8Cl_2$] that opened the door to syndiotactic polypropylene.[11] My group succeeded with the synthesis of the first bridged bis(fluorenyl) complexes like [M($C_{13}H_8C_2H_4C_{13}H_8$)Cl_2] (M = Zr or Hf)[4] that proved excellent catalyst precursors for the polymerization of ethylene.

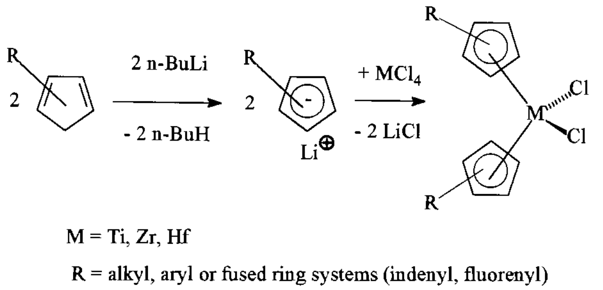


M = Zr, Hf

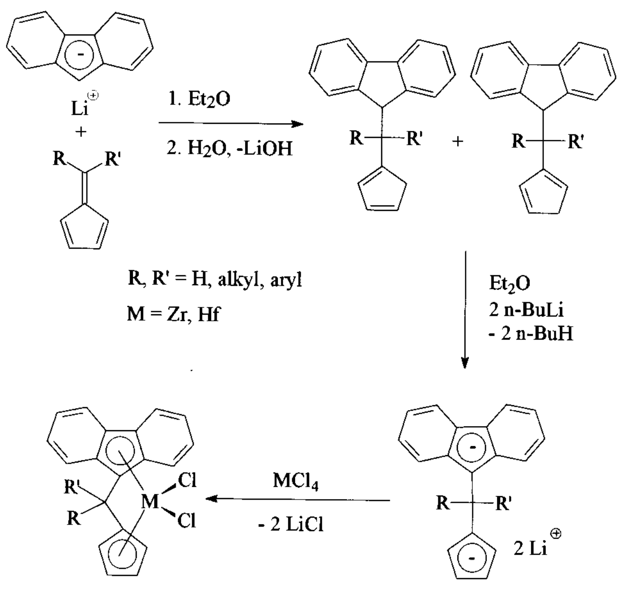
Today numerous reviews are available dealing with the application of various metallocene catalysts.[12–19] In the past ten years the Alt research group at the University of Bayreuth have synthesized more than 600 different metallocene and half-sandwich catalysts and tested them for olefin polymerization. From the very beginning it was our goal to cover all possible applications for olefin polymerization and not only concentrate on specialities like isotactic polypropylene, syndiotactic polypropylene or block copolymers deriving from the stereospecific polymerization of propylene. It turned out that metallocene complexes can also be used as attractive catalysts for the polymerization of ethylene generating short or long chain branching and thus providing materials with superior mechanical and optical properties. Some of these new resins are already in the market like the linear low density polyethylenes (LLDPE) "mPact" (Phillips Petroleum Company) or "Elite" (Dow).

2 Preparation and activation of metallocene catalyst precursors

The most common catalyst precursors are metallocene dichloride complexes. This class of compounds is air-stable but very sensitive to moisture due to the high oxophilicity of zirconium or hafnium. Depending on the nature of the aromatic ligands several methods for the preparation of unbridged and bridged metallocene complexes are available (Schemes 1–4). A special route allows the preparation of an ansa-metallocene complex with an Si–N–Si backbone in the bridge.[23]



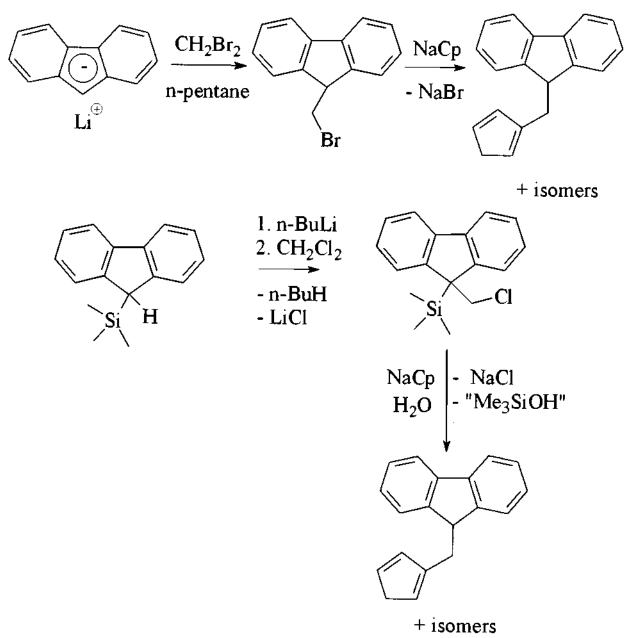
Scheme 1 Preparation of unbridged metallocene dichloride complexes.



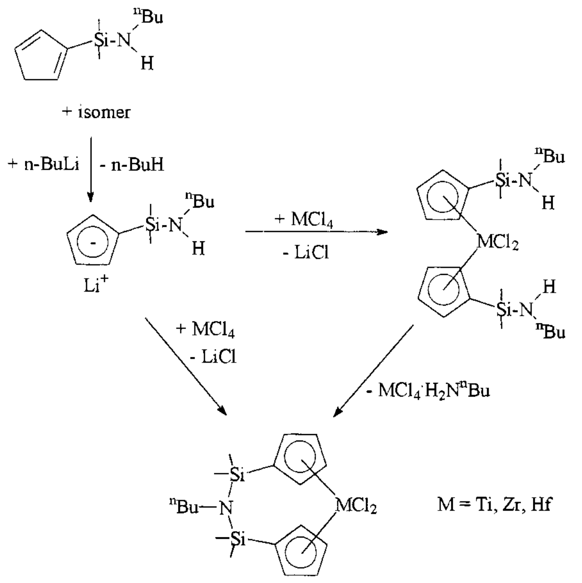
Scheme 2 Preparation of ansa-metallocene dichloride complexes *via* the "fulvene method".[20,21]

3 Activation of the catalyst precursors and mechanism of the polymerization

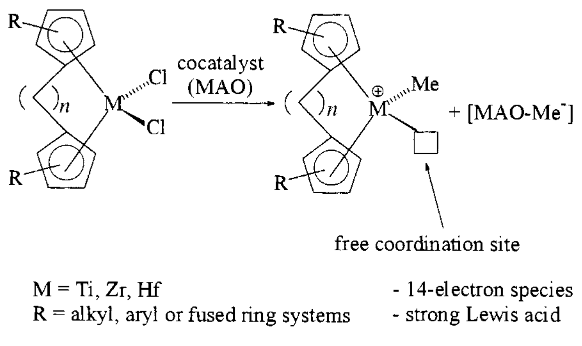
In order to obtain active metallocene catalysts it is necessary to activate the catalyst precursor (Scheme 5). For this purpose methylalumoxane is the most commonly used reagent to generate a cationic metallocene monomethyl cation that is supposed to be the actual catalyst. Other potential cocatalyst anions can be various borates, especially $[B(C_6F_5)_4]^-$.[24] The chemical nature of MAO is still not quite clear. The partially hydrolysed trimethylaluminium seems to consist of linear $-[MeAlO]_n-$



Scheme 3 C,C Coupling reactions for the preparation of ligand precursors.[22]



Scheme 4 Preparation of a metallocene complex with a bridging Si–N–Si unit.[23]



Scheme 5 Activation of a metallocene dichloride complex.

units, *n* ranging from 5 to 20. However, cyclic species can also exist that aggregate to cages. Such a cage could accommodate a monomeric $AlMe_3$ molecule which accomplishes the necessary activation steps:[25,26] methylation of the metallocene dichloride complex, and the subsequent carbanion abstraction to generate the catalytically active metallocene monomethyl cation. The resulting ion pair is the active catalyst. Indeed, it is possible to increase the activity of such catalysts by magnitudes when the cation and the anion can be separated as in the case of substituted bis(fluorenyl) complexes. This can be achieved by substituting the 4 and 5 positions of the fluorenyl ligands of the ansa-complex $[Zr(C_{13}H_8C_2H_4C_{13}H_8)Cl_2]$.[27] After activation with MAO the activity for ethylene polymerization increases by a factor of five.

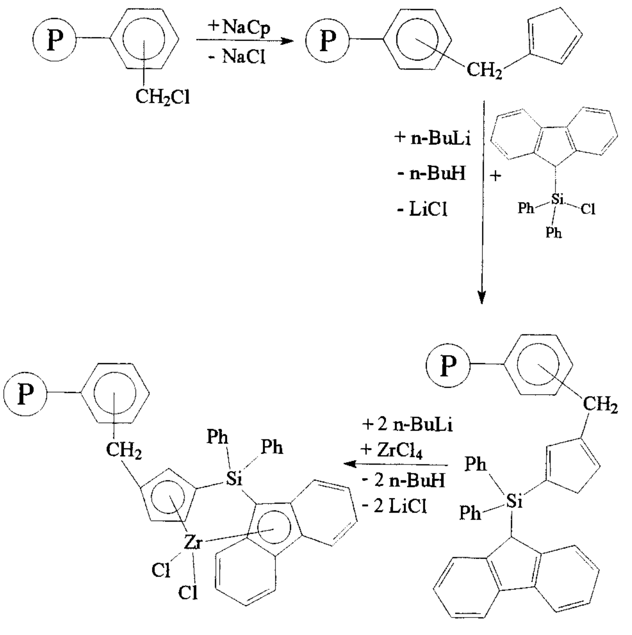
The reaction mechanism of these "single-site" catalysts comprises three essential steps: co-ordination of the olefin, olefin insertion, *i.e.* alkyl migration, to generate the polymer chain and generation of a new co-ordination site by inversion. Each step can be influenced by changing parameters like the nature of the ligand, the metal, the cocatalyst and the solvent.

4 The heterogenization of metallocene catalysts

Though metallocene complexes possess excellent activities and stereospecificities for the polymerization of prochiral olefins as well as narrow molecular weight distributions of the generated polymers they are not suitable for technical application. Since metallocene catalysts are of homogeneous nature they cannot be applied in the conventional gas phase or slurry reactors because they would cause "fouling". This means the formed polyolefin is deposited at the reactor walls and causes all the problems that are known from the "boiler scale effect"; a continuous process is not possible. Since the established Ziegler–Natta and Phillips catalysts are all heterogeneous it is necessary to support metallocene catalysts for industrial application.

4.1 Organic support materials

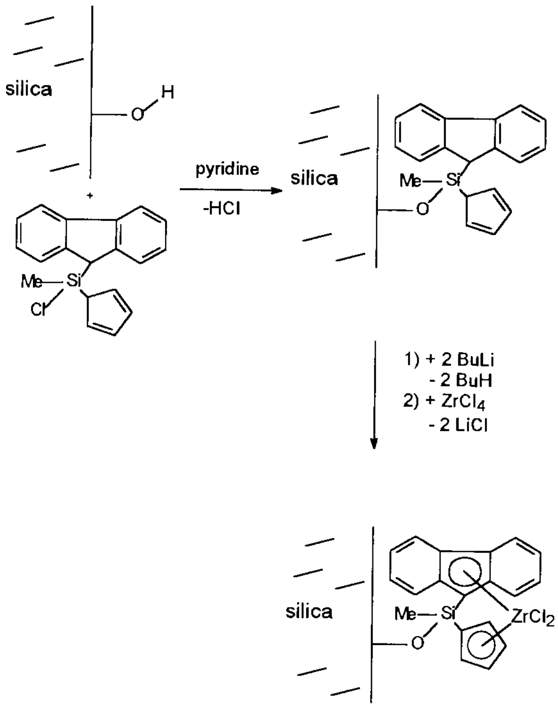
One approach is the use of organic support materials like cross-linked polystyrene.[28–30] It is also possible to fix a ligand precursor on a polymeric support and then build up the catalyst[31] (Scheme 6). This approach avoids polar components on the support surface that could decrease the catalyst activity.



Scheme 6 Fixation of a catalyst on polystyrene.

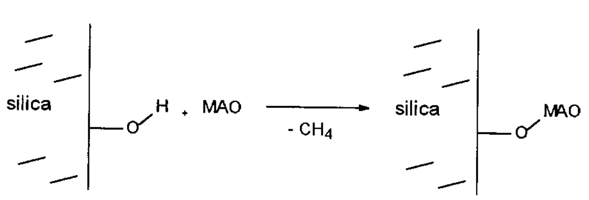
4.2 Inorganic support materials

Inorganic support materials are widely used for Ziegler–Natta and Phillips catalysts: silica, alumina, magnesium dichloride and mixtures thereof are representative examples.[32,33] The fixation of the catalyst can either be performed by an absorption process at the surface of the solid particles or by a chemical bond, for instance with silica (Scheme 7). It is interesting that a stereospecific catalyst for the polymerization of syndiotactic polypropylene, such as $[Zr(C_5H_4CMe_2C_{13}H_8)Cl_2]$/MAO, can change its stereospecificity from syndiotactic to isotactic because the bulky support no longer allows the inversion step in the process (change of the active sites of the catalyst molecules).[35] These inorganic support materials can also be used to control the morphology of the resulting polymer particles so that free flowing powders are obtained and reactor fouling is prevented.



Scheme 7 Fixation of a catalyst on silica.[34]

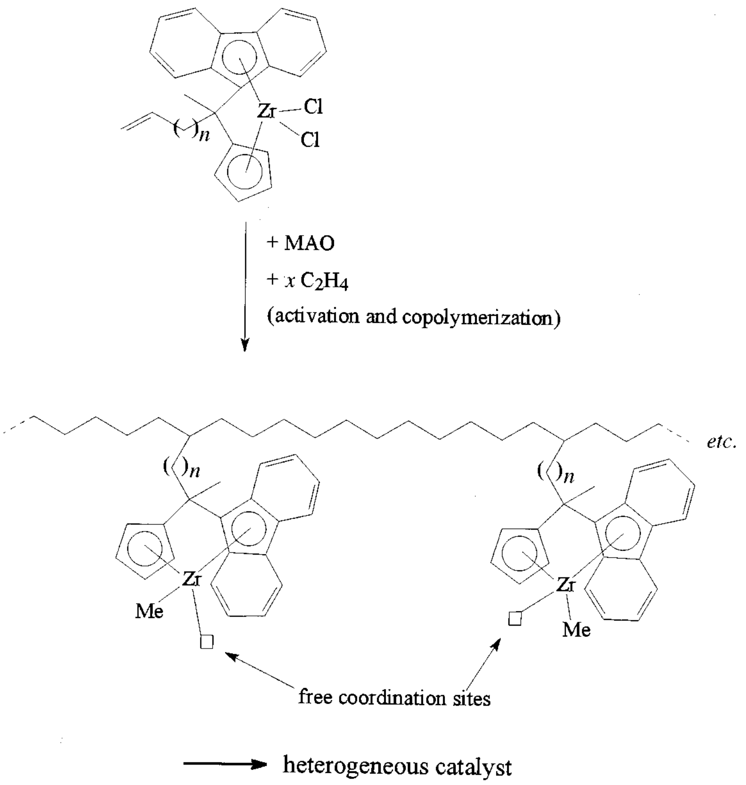
Another method is to immobilize the cocatalyst methylalumoxane. This can be accomplished by the reaction of MAO and wet silica and provides a universal heterogeneous cocatalyst.[36]



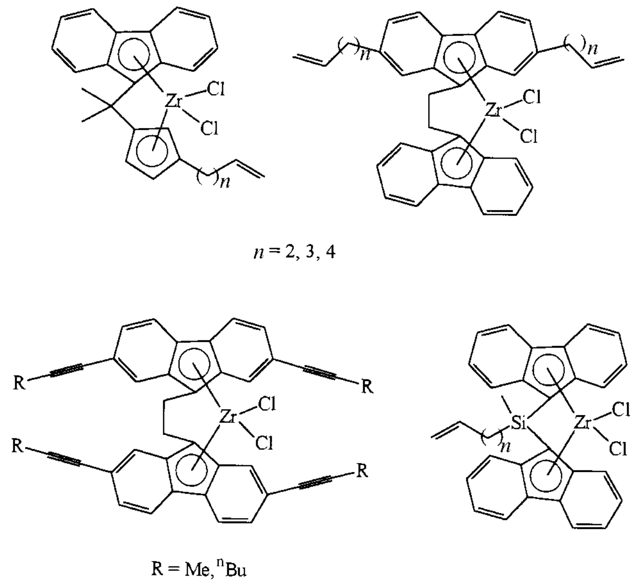
4.3 The self-immobilization of metallocene catalysts

All these methods have the disadvantage that the catalysts can lose magnitudes of their activities[17] because their metal centres (Lewis acids) are not accessible at the surface or they can be blocked by oxygen functions (Lewis bases). Thus we tried a completely different approach that would avoid all these problems. The idea was to synthesize metallocene catalysts with an olefin or alkyne function that can be used as a comonomer in the polymerization process. The following complexes are typical examples for this approach.[37]

Such a metallocene dichloride complex can be activated in solution with MAO to give a homogeneous catalyst (Scheme 8).

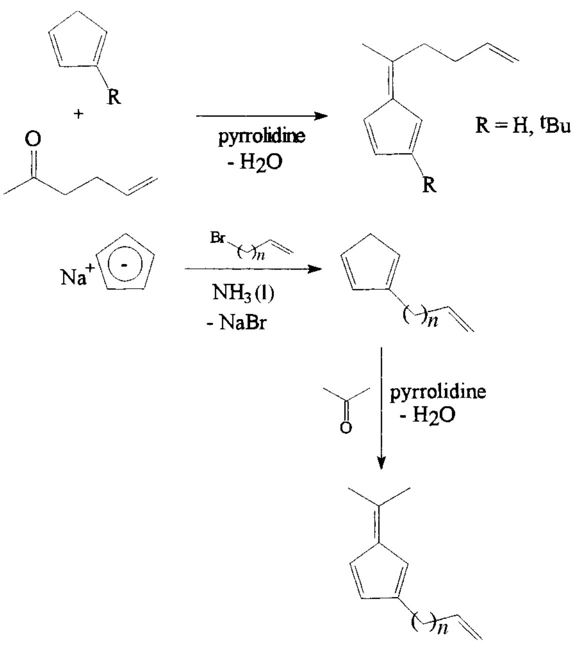


Scheme 8 Proposed mechanism for the "self-immobilization" of a homogeneous ansa-metallocene complex.[37]



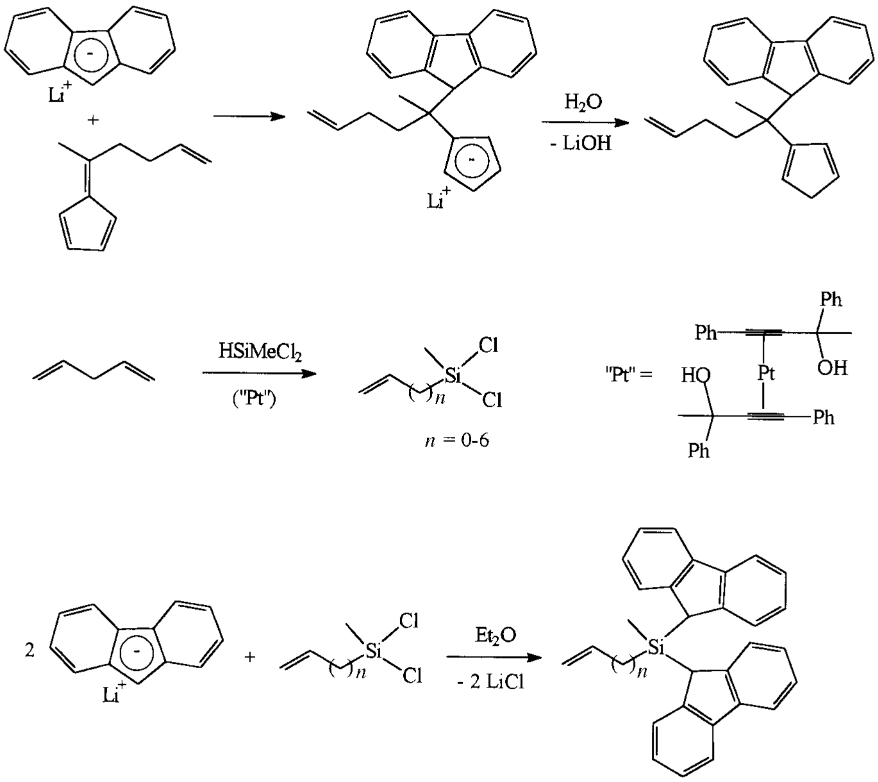
As soon as an olefin like ethylene is applied the olefin is polymerized and simultaneously catalyst molecules are incorporated into the growing polymer chain due to their olefin function. As a consequence a precipitate is formed that consists of polyethylene and incorporated active catalyst. When the homogeneous catalyst solution is coloured the formed precipitate adopts the same colour and when the suspension is allowed to stand for a while the supernatant solvent becomes colourless (Fig. 1). In other words the homogeneous catalyst is transferred to a heterogeneous system without using any support. This catalyst system can provide its own support. As a very pleasant side effect the excess of MAO in the washing liquid can be used again for activation processes and can be recycled. In this way the enormous excess of MAO can be reduced from 10000 to *ca.* 500. Schemes 9–11 describe the synthesis of some typical catalyst precursors.[38–40]

The structure of $[Zr\{C_{13}H_8C(Me)(C_4H_7)C_5H_3{}^tBu\}Cl_2]$ is shown in Fig. 2.[37]

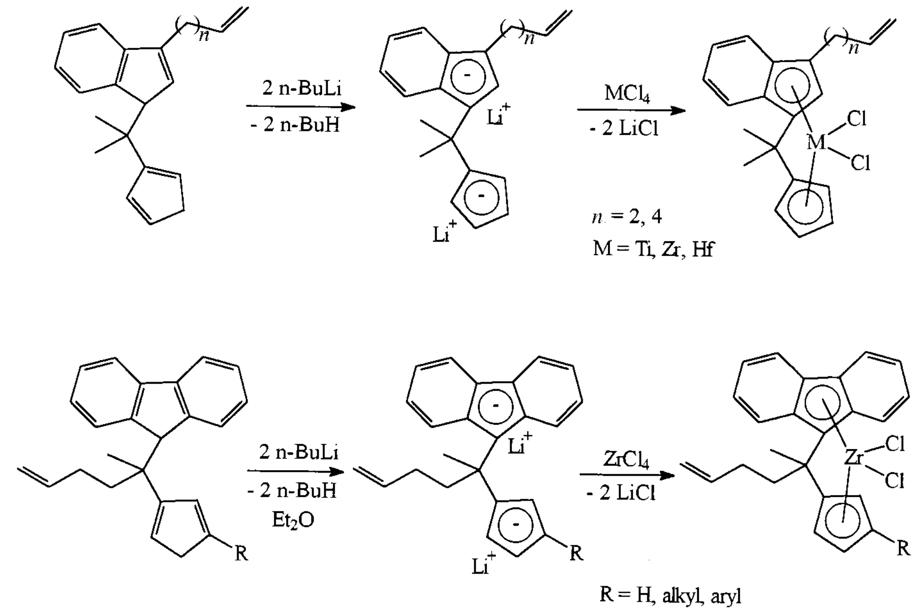


Scheme 9 Preparation of fulvenes with ω-alkenyl substituents as ligand precursors.

The mechanism of this self-immobilization is still not quite clear. It is possible that several different intramolecular and intermolecular mechanisms take place, *e.g.* as in Scheme 12. Another alternative is an intermolecular hydrozirconation reaction to form dinuclear species (Scheme 13). The necessary hydrido complexes could be provided by β-H-elimination termination steps during the polymerization process. The formation of a metallacyclic system could also be responsible for the catalytic process. We have an experimental indication for this step: in a ^1H NMR experiment we have demonstrated that the olefin protons of an alkenyl substituent disappear as soon as only one equivalent of C_2H_4 is applied.



Scheme 10 Synthesis of various ligand precursors *via* C,C coupling reactions.



Scheme 11 Synthesis of various ω-alkenyl substituted ansa-metallocene complexes.

4.4 Ethylene polymerization and effect of substituents

The length of the alkenyl substituent determines the activity of the catalyst and the molecular weight of the formed polymer. We studied this with a whole variety of catalysts in order to optimize the parameters (Figs. 3 and 4).[38] It turned out that an alkenyl substituent with five carbon atoms gave the highest activity. The catalyst molecule is fixed in a polymer chain and it needs a certain amount of freedom to become available to the monomers. This behaviour can also be explained with the "dog on a leash" phenomenon.

The different molecular weights of the polymers can be explained in a similar way: the length of the alkenyl substituent must have some steric influence on the rate of the β-hydrogen elimination reaction that terminates the growth of the polymer chain. The length of the alkenyl substituent could influence this process due to various steric requirements.

This method of self-immobilization offers another very interesting aspect: since the active catalyst is a cationic species we need an anion for compensation. In the preparation process we can isolate the heterogeneous ion pair. This means from the aluminium content of the catalyst we can figure out how many aluminium atoms contribute to the hitherto unknown MAO anion. We found the number 80 by atomic absorption methods. Now we can speculate what such an MAO anion could look like.

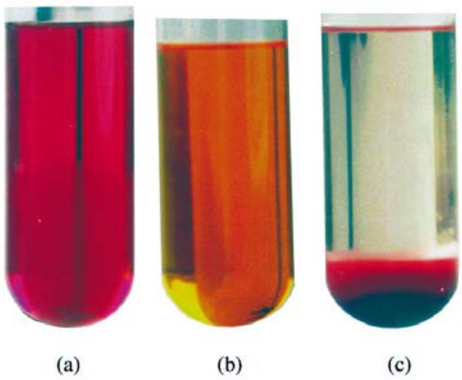
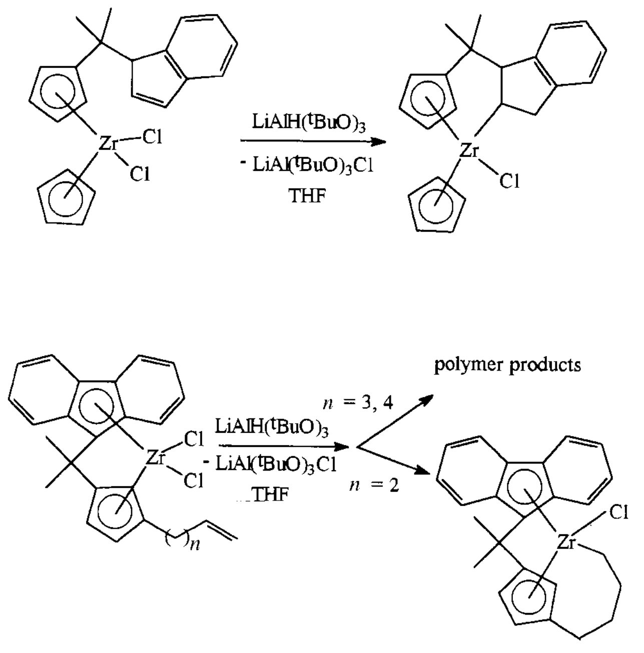
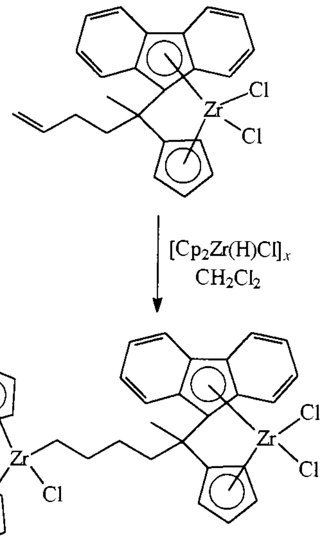


Fig. 1 (a) Metallocene dichloride complex in toluene solution. (b) Metallocene dichloride complex activated with MAO in toluene solution. (c) Generated heterogeneous catalyst in toluene suspension after prepolymerization with ethylene.



Scheme 12 Intramolecular cyclization reactions.[37–39]



Scheme 13 Formation of a dinuclear metallocene complex by a “hydrozirconation” reaction.

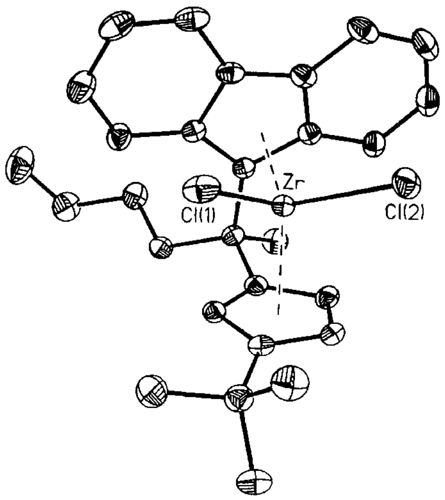


Fig. 2 Molecular structure of $[Zr\{C_{13}H_8C(Me)(C_4H_7)C_5H_3{}^tBu\}Cl_2]$.

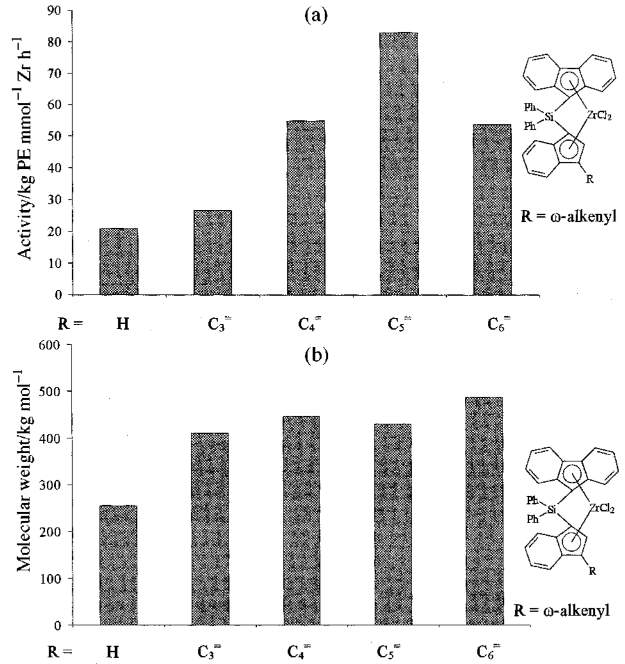


Fig. 3 Influence of the ω-alkenyl substituent chain length R on the catalyst activity and the molecular weight of the produced polyethylene ($C_3{}^= $ = 3-propenyl *etc.*). Conditions: 1 mg catalyst precursor, 7 ml MAO in toluene solution (30%), 500 ml pentane solvent in a 1 l reactor, 10 bar ethylene pressure, 60 °C, 1 h reaction time.

5 Conclusion

The self-immobilization of metallocene complexes provides an elegant tool to heterogenize homogeneous metallocene catalysts in order to apply them for industrial processes. In addition the position and the chain length of the ω-alkenyl substituents that are needed for this process determine the activity of the catalysts and the molecular weight of the formed polyethylenes in a wide range.

6 Acknowledgements

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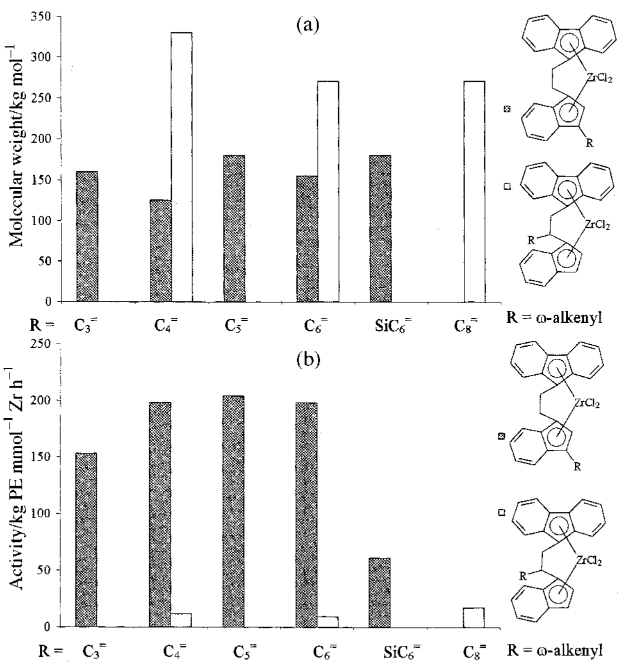

Fig. 4 Influence of the position and the chain length of the ω-alkenyl substituent on the activity of a catalyst and the molecular weight of the produced polyethylene. Conditions as in Fig. 3.

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