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Review

Metallacyclic metallocene complexes as catalysts for olefin polymerization

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Contents

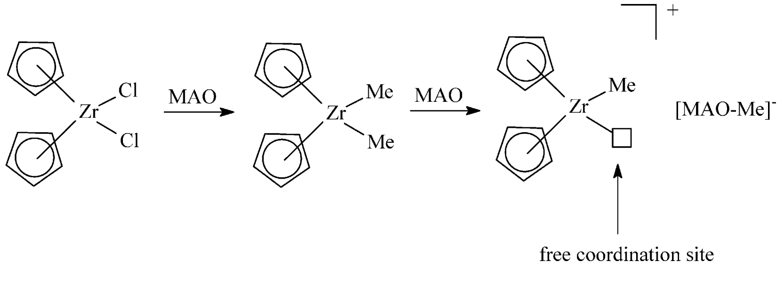
Abstract

Metallacyclic metallocene complexes of titanium, zirconium and hafnium can be prepared by hydrogen elimination processes of suitable substituents such as ω-phenylalkyl or ω-alkenyl at the aromatic ligands. In some cases, the intermediates containing agostic hydride ligands can be isolated and characterized. The synthesized metallacyclic metallocene complexes can be activated with methyl aluminoxane (MAO) and are then able to polymerize 1-olefins catalytically. The advantages of such catalysts are their high thermal stability and their potential of self-immobilization combining the advantages of homogeneous and heterogeneous catalysis and their high activities. In some cases these catalysts show activities that are three to four times higher than the activities of the parent dichloride complexes. The fact that these catalysts do not contain any halides and that they remain in the produced polymer makes them very friendly to the environment when they are thermally decomposed.

Keywords: Metallacyclic metallocene; MAO; Ligand

1. Introduction

In the past 20 years metallocene complexes have established as versatile catalysts in olefin polymerization [1–20]. In most cases the catalyst precursors are applied as the dichloride species. In the activation step, for instance in the reaction with methyl aluminoxane (MAO), they are transferred into the catalytically active metallocene methyl cations.



These cations are strong Lewis acids. Therefore, it is advantageous to avoid any Lewis basic components in the

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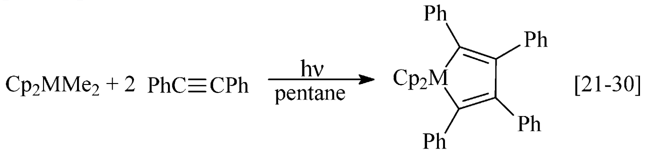
catalysis process. In this respect the halide ligands are counter productive because they do not disappear in the activation process but are incorporated in the cocatalyst. One approach to avoid halide components in the catalyst is the application of the corresponding metallocene dialkyl or dicarbyl complexes. However, these complexes can decompose easily at elevated temperatures and the yield in the synthesis is not always satisfying. Therefore, another approach looked very attractive: the application of metallacyclic metallocene complexes. This type of complex provides the essential metal carbon sigma bond for the catalytic olefin insertion in the polymerization process.

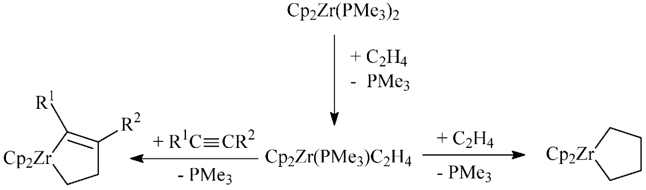
2. Known metallacyclic metallocene complexes

Metallacyclic metallocene complexes are accessible from metallocene synthons and suitable components. For instance [21–30]:



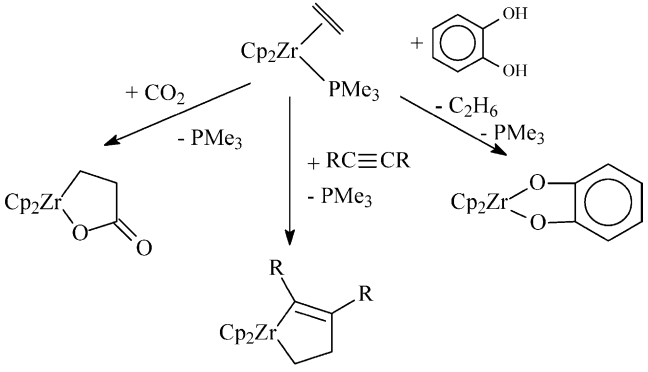
M = Ti, Zr, Hf

The unsaturated parent titanium metallacycle $Cp_2TiC_4H_4$ [31,32] is more temperature labile than the unsaturated phenyl derivative. The saturated titanacyclopentane decomposes at even lower temperatures [33,34]. The corresponding zirconium derivative can be prepared from trimethylphosphane stabilized precursors [35,36]:



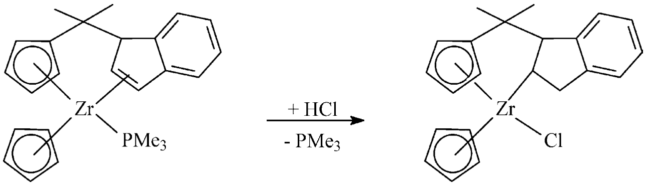
R = alkyl, aryl

A very versatile starting compound is the ethylene complex $Cp_2Zr(C_2H_4)PMe_3$ [35–38] that can be used as a synthon for the synthesis of a variety of metallacycles [39]:

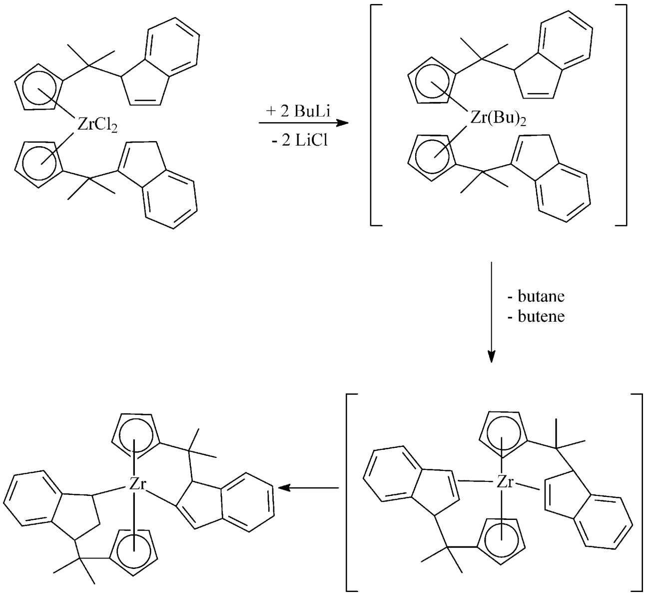


R = H, Me

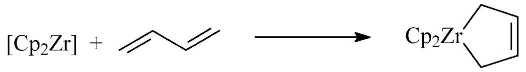
In a similar manner π-olefin complexes can be transferred into metallacycles upon protonation [40].



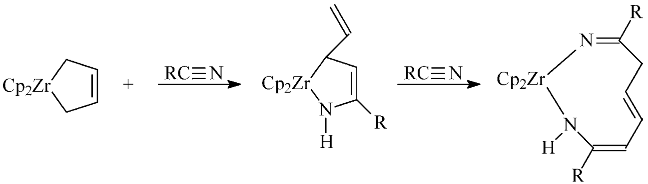
The reaction of metallocene dichloride complexes with alkyl substituents containing terminal indenyl groups and butyl lithium results in the formation of a “double metallacycle” that has been characterized by an X-ray structure [41].



Another approach to metallacycles is the reaction of in situ generated zirconocene and butadiene [42–45]. The research group of G. Erker has explored this chemistry to perfection.



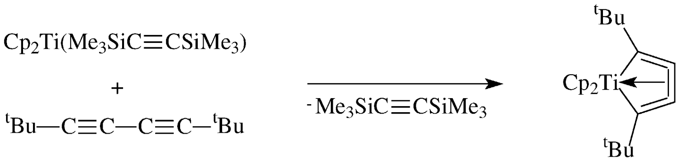
The metallacyclic product can react with substrates like RCN to give larger ring systems [46,47].



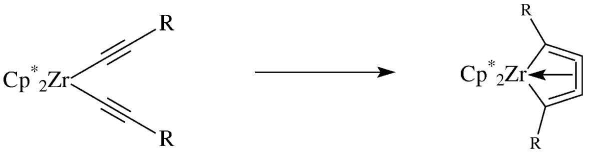
R = CMe$_3$, CH$_2$Ph

Boron and aluminum reagents give similar products [48–50].

Another broad and comprehensive approach to metallacyclic metallocene complexes has been elaborated by Rosenthal and co-workers [51–63] in the past decade. In most cases a highly reactive metallocene complex of titanium or zirconium with a bis(trimethylsilyl)acetylene ligand is the starting complex providing the metallocene synthon. In the following typical examples are presented:



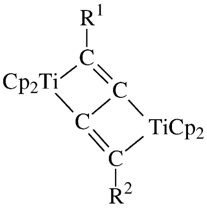
[51]



[56]

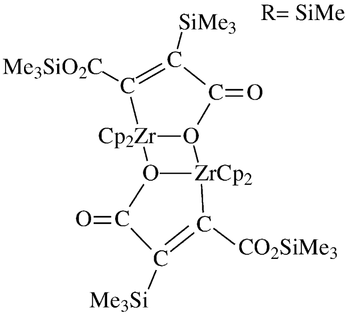
R = Ph
R = SiMe3

R = Ph
R= SiMe3

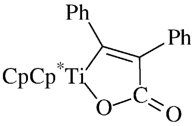


$R^1 = R^2 = {}^tBu$
$R^1 = SiMe_3, R^2 = {}^tBu$

[51]

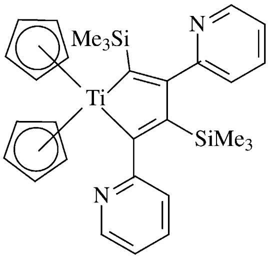


[52]

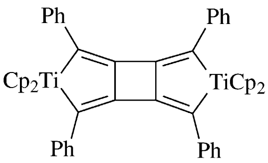


$Cp^* = C_5Me_5$

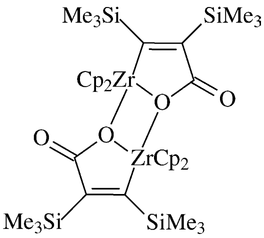
[53]



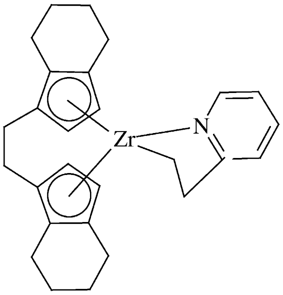
[54]



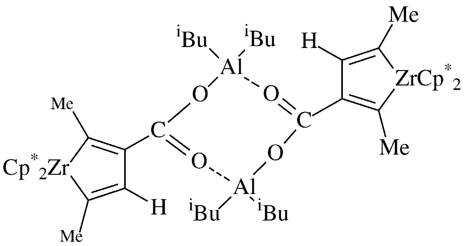
[57]



[58]

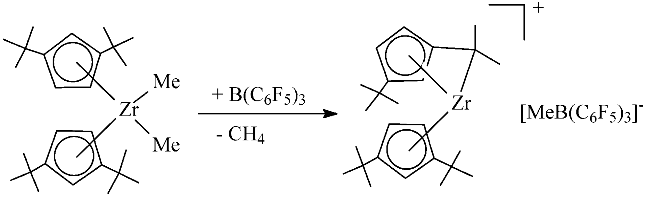


[60]



[63]

An approach to cationic metallacyclic metallocene complexes has been demonstrated with the following reaction [64]:



Obviously the strong Lewis acid $B(C_6F_5)_3$ abstracts a methyl anion from the metal and the in situ generated fragment $[(C_5H_3{}^tBu_2)_2ZrMe]^+$ is stabilized via an intramolecular CH-activation step to give the cationic metallacycle and methane.

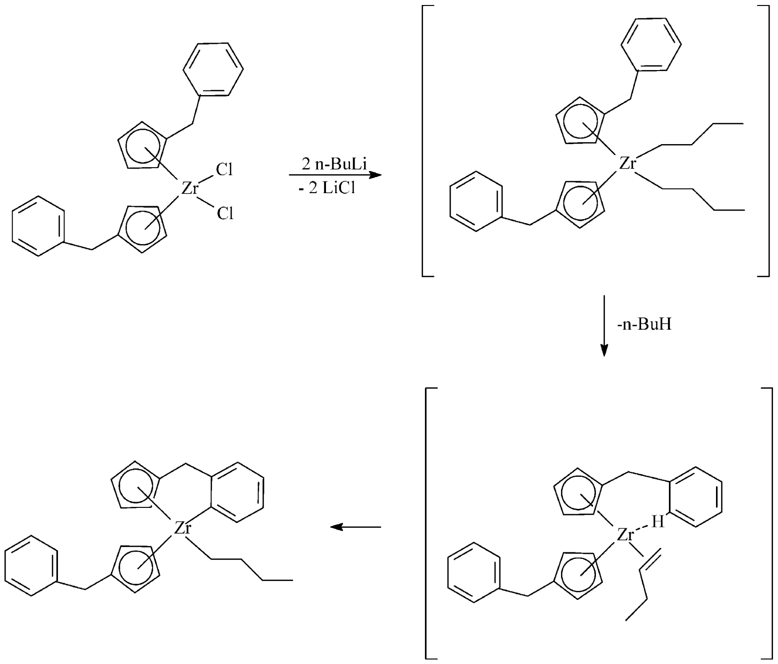
3. Synthesis and characterization of metallacyclic metallocene complexes

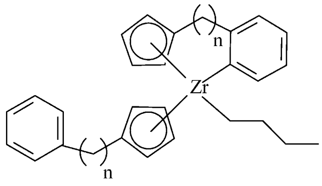
ansa Metallocene dihalide complexes and ansa dihalide half-sandwich complexes are not considered as metallacyclic complexes. Since these complexes do not contain a metal carbon sigma bond they cannot be applied as catalysts without activation. Therefore, it was our intention to find a general route for the synthesis of metallacyclic metallocene complexes that already have at least one metal carbon sigma bond and no halide ligands.

(a) ω-Aryl groups at the substituent

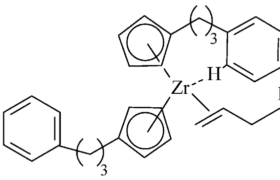
An excellent approach is the reaction of ω-phenylalkyl substituted zirconocene dichloride complexes with two equivalents of *n*-butyl lithium leading to cyclometallation [65].

During this reaction a zirconocene dibutyl complex [66] is formed as an intermediate. The unsubstituted parent complex has been characterized [67]. In the next step the dibutyl complex eliminates *n*-butane via β-hydrogen transfer [68,69] and a butene complex is formed. Then an ortho-metallation process takes place yielding the final metallacyclic metallocene butyl complex. In some cases the butene complex precursor with an agostic hydrogen can be isolated and characterized [70]. Such a coordination mode, the phenyl substituent being fixed at the metal via an agostic hydrogen in the ortho position, has also been observed by Green and co-workers [71]. Catalysts with short spacers ($n = 1$, 2) produce only metallacycles, spacers with three carbon atoms lead to butene complexes and spacers with four or five carbon atoms give mostly dinuclear complexes with η^6—bonded phenyl ligands [72]. This concept can be expanded to a whole variety of metallocene dichloride complexes with ω-aryl substituents. Some representative metallacycles are given below (see [73]).





1 (n = 1)
2 (n = 2)



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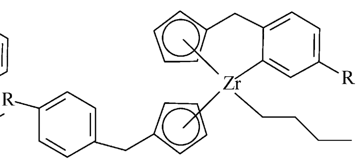
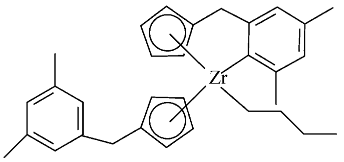


4 (R = Me)
5 (R = F)



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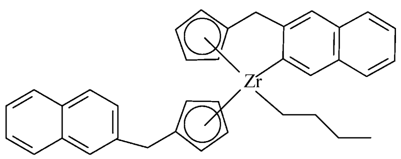

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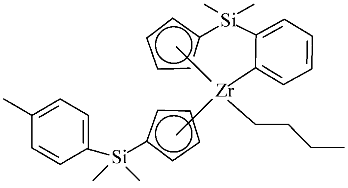

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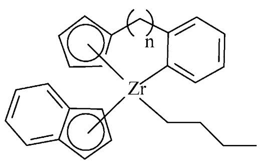
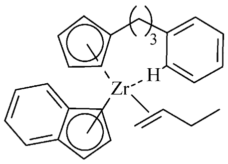
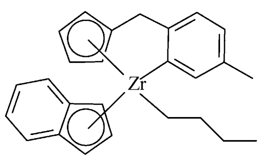


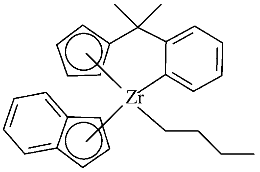
9 (n = 1)
10 (n = 2)



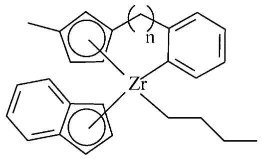
11



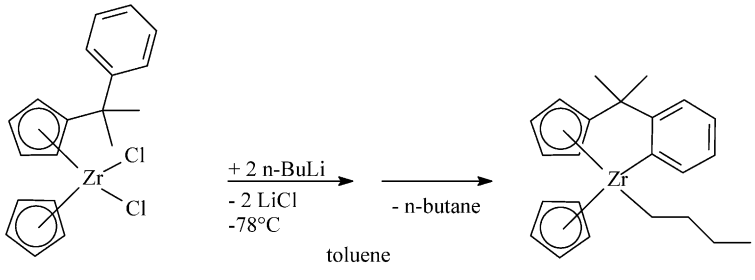
12



13

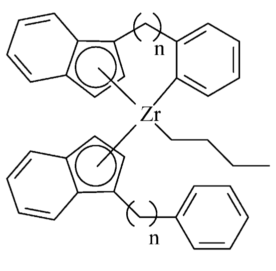


14a,b (n = 1)
15a,b (n = 2)

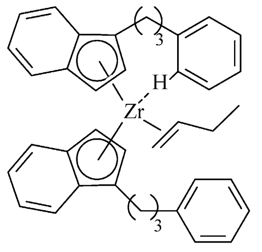


16c

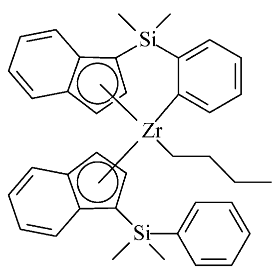
16



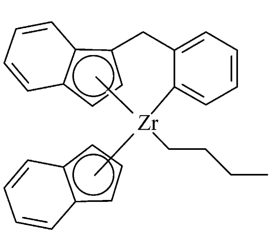
17a,b (n = 1)
18a,b (n = 2)



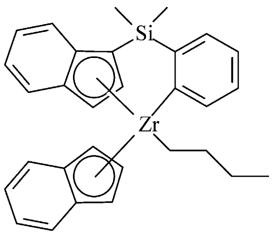
19a,b



20a,b

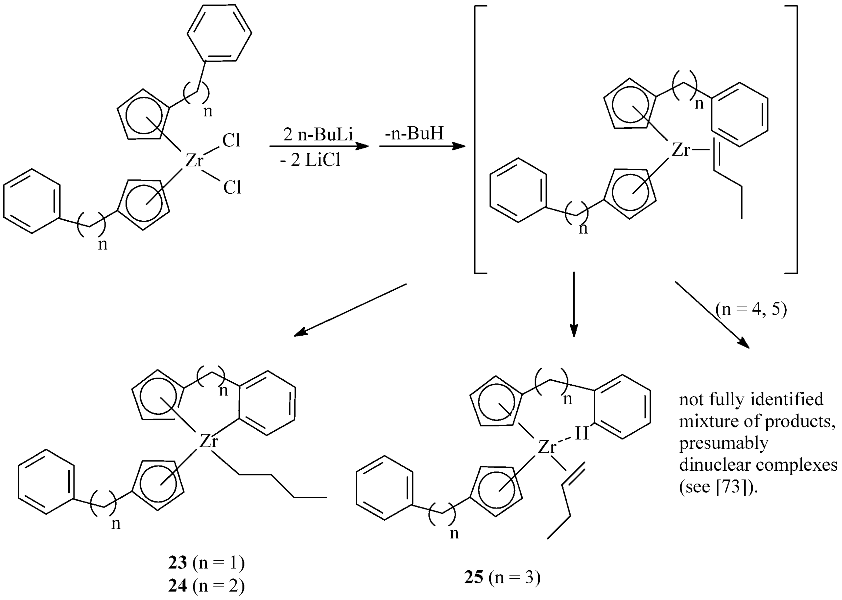


21a,b



22a,b

The length of the CH_2 spacer units connecting the ω-aryl groups and the cyclopentadieny ligand decides the pattern of the products [73].

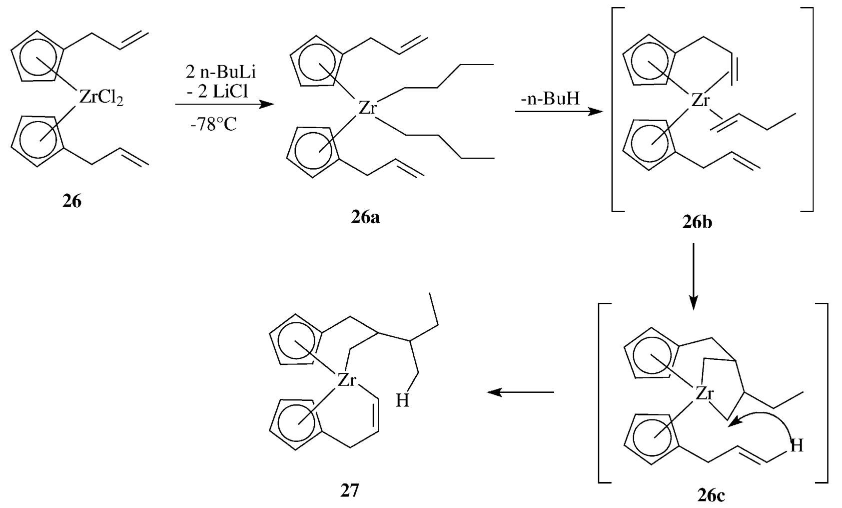


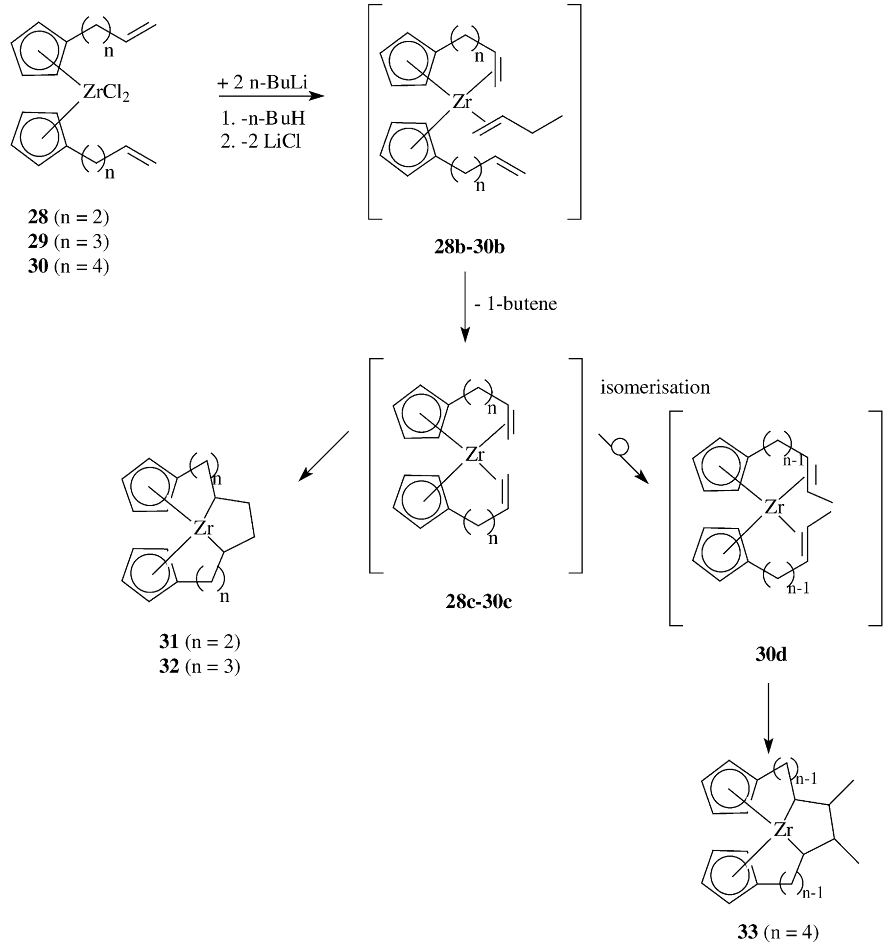
not fully identified mixture of products, presumably dinuclear complexes (see [73]).

The reason for the formation of three different types of products seems to depend on the extent of overlap of the π-electrons of the phenyl ring and the hybride orbitals of zirconium [74]. In the case of a C3-spacer, the interaction of an agostic hydrogen in the ortho position of the phenyl group and a free orbital of zirconium is favored. The thermal stability of the butene complexes in solution is amazing [64] and obviously the consequence of such a strong interaction. A similar situation is known from $Cp_2Zr(PMe_3)$(butene) [75]. For this type of reaction, spacers with hetero atoms like silicon can also be successfully applied.

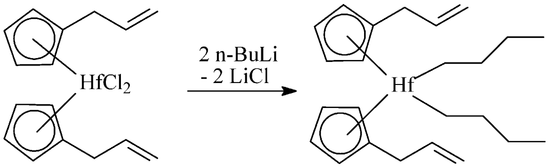
b) Reactions with ω-alkenyl functions

Metallocene complexes with ω-alkenyl substituents in the ligand framework can form metallacyclic compounds via an intramolecular hydrozirconation process [76–81] or by an oxidative addition reaction of an in situ formed zirconocene [82]. A broad access to metallacyclic metallocene complexes is the reaction of ω-alkenyl substituted metallocene dichloride complexes and two equivalents of *n*-butyl lithium. For instance:


ZrCl$_2$
26
2 n-BuLi
- 2 LiCl
-78°C
Zr
26a
-n-BuH
Zr
26b
Zr
H
26c
Zr
H
27


n
ZrCl$_2$
n
28 (n = 2)
29 (n = 3)
30 (n = 4)
+ 2 n-BuLi
1. -n-BuH
2. -2 LiCl
n
Zr
n
28b-30b
- 1-butene
n
Zr
n
28c-30c
isomerisation
n-1
Zr
n-1
30d
n
Zr
n
31 (n = 2)
32 (n = 3)
n-1
Zr
n-1
33 (n = 4)

The course of the reaction is very similar in the case of the ω-phenyl derivatives. The zirconium derivatives are reactive enough for the complex reaction cascade. The titanium compounds are very labile. The corresponding hafnocene complexes are not reactive enough and the reaction stops after the first sequence [83,84].



In the case of the zirconium derivative the dibutyl complexes are stable at lower temperatures (−40 °C) for several minutes and can be characterized by NMR spectroscopy. Also the unsubstituted parent metallocene complex is accessible for characterization [67].

The decisive reaction step in the formation of a metallacycle is probably a 2 + 2 + 2 cycloaddition [85,86] leading to a zirconacyclopentane moiety. With bis(allylcyclopentadienyl)zirconium dichloride the zirconacyclopentane structure is most likely formed by the integration of the 1-butene ligand into the ring structure. Obviously because of the close proximity of the allyl group to the second cyclopentadienyl ligand, the reaction does not stop at this stage but it seems to proceed with a CH-activation reaction in which a hydrogen atom of the allyl group is transferred to a methylene group in an α-position to the central metal. The metallacycle **26** is obtained in quantitative yield; its structure could be confirmed by one and two dimensional NMR spectroscopy. Only one stereo isomer is formed in this multi-step reaction despite the presence of several centers of asymmetry.

In the reaction of the bis(alkenylcyclopentadienyl)zirconium dichloride complexes **27–29** having a longer spacer unit between the double bond and the cyclopentadienyl ligand (C2–C4), the metastable η^2-butene-η^2-alkenylzirconium moiety (**27b–29b**) is most likely formed in an analogous manner to **26**.

However, presumably for steric reasons, the reactions of the metallocene complexes with C2–C4 spacers then seem to proceed through a 1-butene elimination and the double bond of the alkenyl group on the second cyclopentadienyl ligand coordinates to the now free coordination site (**28c–30c**). This coordination of the alkenyl group with elimination of 1-butene can also be interpreted as a displacement reaction. Such displacement reactions of 1-butene from the coordination sphere of zirconium by various donors (e.g. ethylene, alkynes, trimethylphosphine) have been described a number of times for unsubstituted zirconocene complexes [83,84].

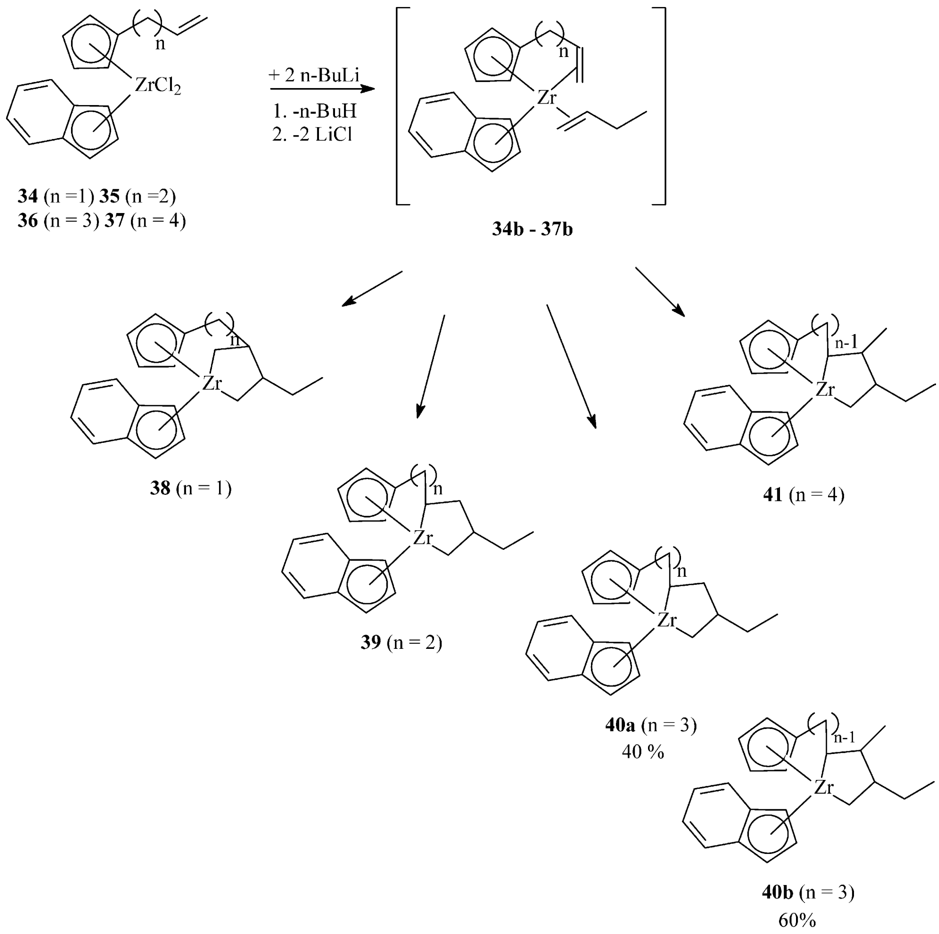
The proposed metallocene intermediates **28c** and **29c** with C2 and C3 spacers react with the formation of a Cs symmetrical zirconacyclopentane structure to the metallacycles **31** and **32**.

In contrast to metallacycle **26c**, with its bridge from the metallacyclopentane structure to the π-ligand on the β-carbon to zirconium, the metallacycles **31–33** have bridges on the α-carbon atom. It can be assumed that the differing bridge positions are due to steric requirements, in particular to avoid excessive ring strain. Unbridged metallacyclopentane complexes, for example $Cp_2ZrC_4H_4Me_2$, with their non-existent steric effects, always form mixtures of isomers with branching methyl groups in the α- and β-positions [36,39].

With the proposed metallocene intermediate **30c** having a C4 spacer, an isomerization of the terminal double bond in hex-5-enyl groups to hex-4-enyl groups with the formation of the proposed **30d** seems to occur prior to the reaction of the zirconacyclopentane structure to the metallacycle **33**. This type of double bond isomerization is facilitated in the coordination sphere of transition metals and found in a number of reactions catalyzed by transition metals [87]. The isomerization presumably proceeds via the π-allyl hydride mechanism, involving a metal-induced intramolecular 1,3-hydrogen shift [88,89].

Because of the proposed isomerization, the zirconacyclopentane structure of metallacycle **33** has two methyl groups in positions 3 and 4 of the zirconacyclopentane structure. An analogous structure was shown in a substituted titanocene complex, prepared by reduction of the associated titanium dichloride complex with magnesium in tetrahydrofuran [90].

Besides the symmetrical bis(cyclopentadienyl)zirconium dichloride complexes, other complexes of the type (alkenylcyclopentadienyl)(indenyl)zirconium dichloride were reacted with two equivalents of *n*-butyl lithium. The (alkenylcyclopentadienyl)(indenyl)zirconium dichloride complexes **34–37** with mixed substituents and C1–C4 spacers were prepared in a known fashion by reacting the respective alkenylcyclopentadienyl lithium derivatives with indenyl zirconium trichloride in diethyl ether [81].



When the metallocene dichloride complexes **34–37** with mixed substituents are treated with two equivalents of n-butyl lithium, the reaction is likely to proceed in the formation of a metastable η^2-1-butene-η^2-alkenyl zirconium moiety (**34b–37b**), as with the symmetrical bis(alkenylcyclopentadienyl)zirconium dichlorides **26** and **28–30**.

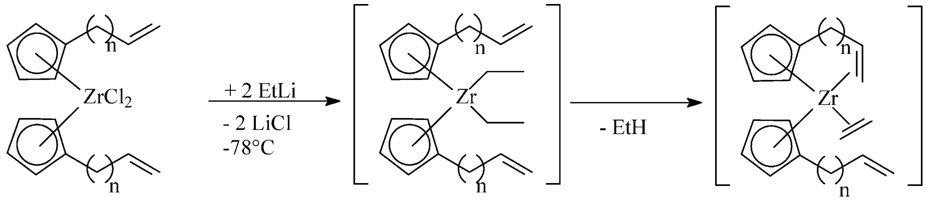
Since the second π-ligand has no alkenyl group, in contrast to the bis(alkenylcyclo-pentadienyl)zirconium dichloride complexes **28–30** with C2 and C4 spacers, no displacement of 1-butene by the alkenyl group can occur. Furthermore, because of the missing second allyl group, the reaction of (allylcyclopentadienyl)(indenyl)zirconium dichloride (**34**) with *n*-butyl lithium does not go further in comparison with bis(allylcyclopentadienyl)zirconium dichloride (**26**) where a hydrogen atom is probably transferred in a CH activation reaction to the zirconacyclopentane structure. Therefore, most likely, in the (allylcyclopentadienyl)(indenyl)zirconium dichloride (**34**) with mixed substituents, a completely different metallacyclic structure as compared with the symmetrical bis(alkenylcyclopentadienyl)zirconium dichloride (**26**) is obtained.

As with metallacycle **27**, the metallacycle **38** (both C3-alkenyl groups) is bridged from the metallacyclopentane structure to the π-ligand on the β-carbon atom to zirconium. The metallacycles **39–41** (C4–C6-alkenyl precursor) have, as do their symmetrical metallacyclic analogs **31–33**, the bridges at the α-carbon atoms.

As with metallacycle **33**, in intermediate **36b** an isomerization of the terminal double bond (pent-4-enyl group) to a pent-3-enyl group and thus the formation of metallacycle **40b** seem to occur to the extent of 60%, prior to the formation of the zirconacyclopentane structure. The structural isomer **40a**, where no double bond formation occurs, is formed to the extent of 40%.

In intermediate **37b**, presumably because of the different steric situation, the proposed isomerization of the terminal double bond (hex-5-enyl) to form the zirconacyclopentane structure (**41**) proceeds with 100%.

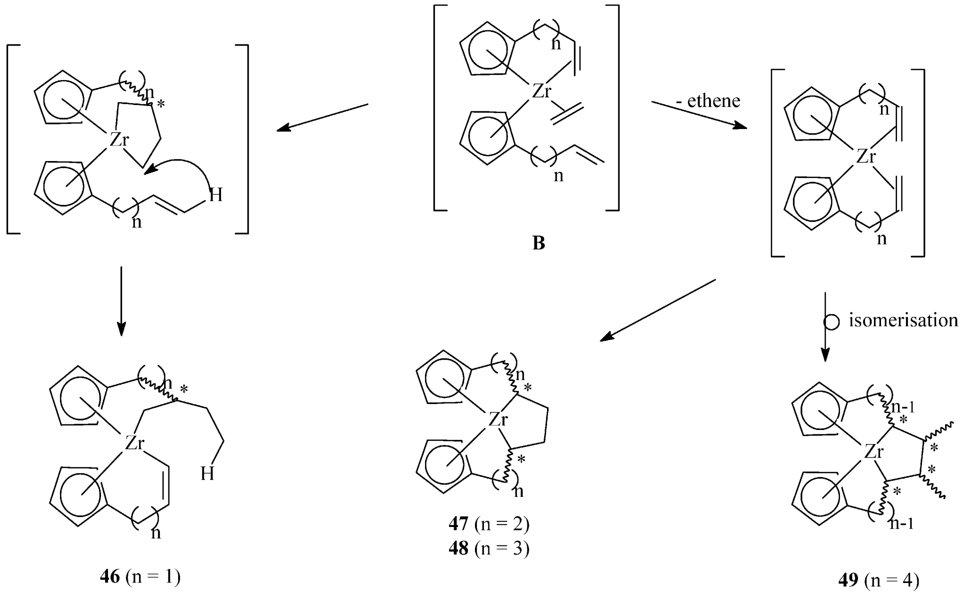
The reaction methods are very versatile to synthesize various types of the unbridged and bridged metallocene complexes, symmetrical or asymmetrical: for instance [91]:



42 (n = 1)
43 (n = 2)
44 (n = 3)
45 (n = 4)

In order to find out whether or not the in situ from the butyl lithium reagent generated butene can participate in the reaction, other lithium organyls were applied and/or different free olefins or acetylenes were added to the reacting components.

Symmetric, bisalkenyl substituted metallocene complexes eliminate the generated alkene except in the case of a C1 spacer and a metallacycle is formed by a cycloaddition reaction of the two alkenyl substituents.



B

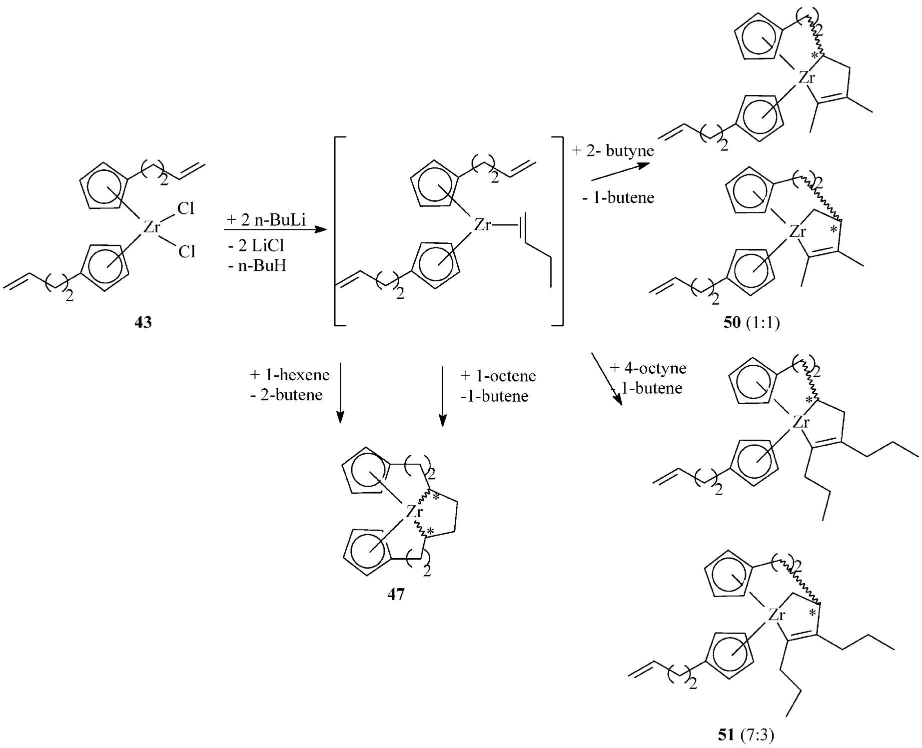
46 (n = 1)

47 (n = 2)
48 (n = 3)

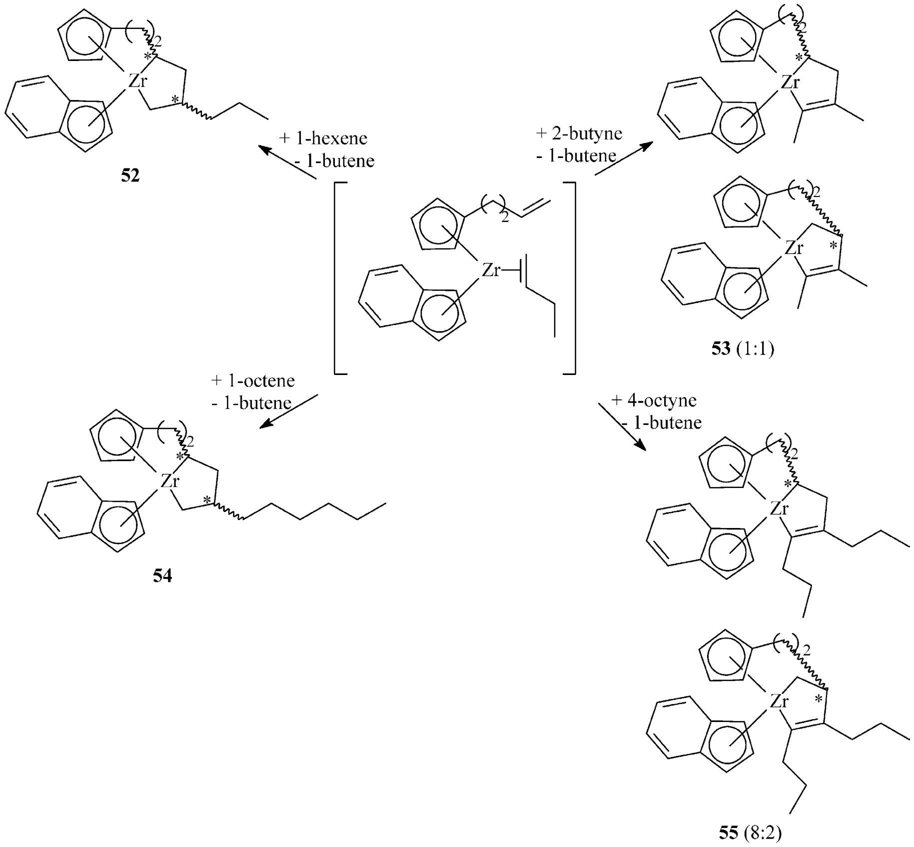
49 (n = 4)

In a different manner asymmetric, mono alkenyl substituted metallocene complexes incorporate the olefin intermediate into the metallacyclic structure in all investigated cases.

When the reaction of symmetric di ω-alkenyl substituted metallocene dichloride complexes and alkyl lithium is performed in the presence of free olefins or acetylenes, no incorporation of the free olefin into the metallacyclic structure could be observed. However, alkynes are incorporated via a cycloaddition reaction.

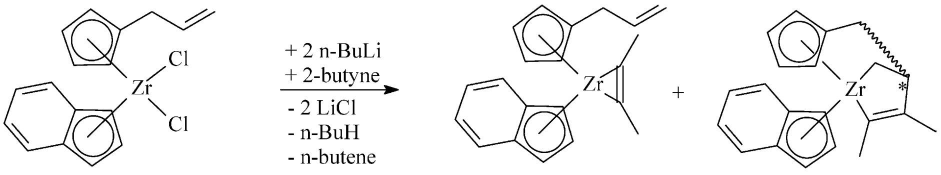


In the reaction of the symmetric bisalkenyl substituted metallocene complexes **42** and **43** with two equivalents of *n*-butyl lithium no additional alkene is incorporated. Added alkynes change the reaction pathway. The intermediate butene complex eliminates 1-butene and incorporates 2-butyne and 4-octyne to give the unsaturated metallacycles **50a**,**b** and **51a**,**b** as isomeric mixtures.



In a similar manner the indenyl derivative 1 reacts with 2-butyne and 4-octyne to give the metallacycles **53a**,**b** and **55a**,**b** as isomeric mixtures.

In addition to **56b**, a 2-butyne complex **56a** is formed in this reaction:

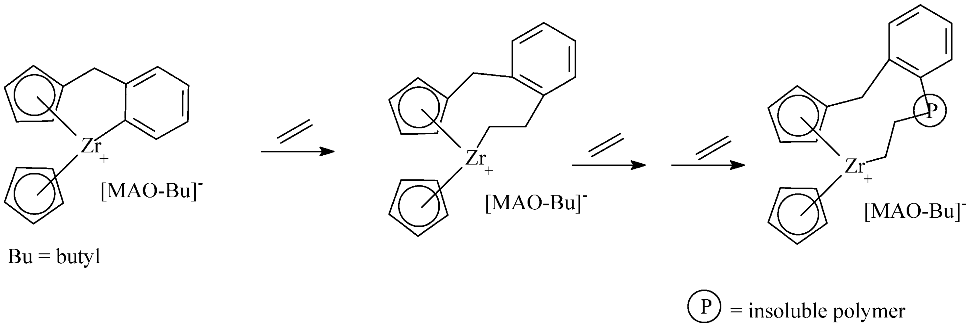


34 **56a** **56b**

We consider **56a** as an intermediate in this reaction sequence. It is stable because of steric and electronic reasons. A very similar metallocene complex with a bis(trimethylsilyl)ethyne ligand has been obtained by reduction of the parent metallocene dichloride with magnesium [59].

4. Application as catalysts for olefin polymerization

All synthesized metallacyclic metallocene complexes can be activated with MAO and then be applied as catalysts for olefin polymerization. A comparison with the parent metallocene dichloride complexes [70,73,92,93] shows that they have a higher activity in most cases and they are self-immobilizing in solution [77]. Another very important aspect is the fact that these catalysts do not contain any halides and as a consequence the polymers so produced cannot release any hydrogen halides upon thermal decomposition or combustion. Such resins are very friendly to the environment.



After activation of the metallacycle with MAO, the ring expands during polymerization through repeated ethylene insertion into the metal carbon sigma bond of the metallacycle. Finally, an insoluble polymer is formed that is directly attached to one π-ligand of the active catalyst cation.

In this manner, the catalyst is immobilized and further ethylene insertion occurs by heterogeneous catalysis. During the polymerization, the metallacycle opens due to a chain termination reaction. Further formation of polymer results from heterogeneously catalyzed olefin insertions into the cationic metallocene mono alkyl complex.

As an alternative, a different metallocene cation can be discussed as potential catalyst: the butyl ligand is still coordinated to the metal, the metallacyle has opened and the ortho position of the terminal phenyl group and MAO form an anion.

We do not favor this possibility because the Zr-phenyl bond is thermodynomically a much stronger bond than the Zr-butyl bond and therefore harder to break. Another argument is the fact that the colored activated metallacycles can undergo “self-immobilization” reactions [76] with ethylene in toluene solution to give colored prepolymerized heterogeneous catalysts. Such a behavior is not known from the reaction of “conventional” metallocene catalysts and MAO.

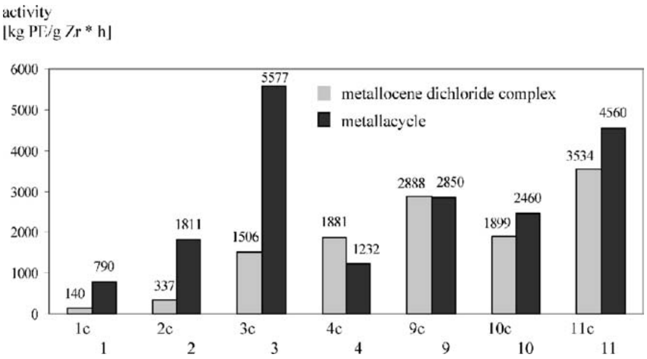
The activities of metallacycles **1**–**3** significantly increase as the length of the spacer chain increases. The three metallacycles produce polyethylenes with molecular weights in a narrow range (290–350 kg/mol). The DSC data for these resins are given in Table 1.

The activities of the mixed substituted metallocene dichloride complexes **9c**–**12c** and of the corresponding metallacycles **9**–**11** increase as the chain length of the ω-phenylalkyl group increases [73].

Table 1
Overview of the polymerization experiments[a] and polymer analytic results

Complex (catalyst precursor)	Activity[b] (kg PE/g Zr h)	$\bar{M}_n$[c] (kg mol^{-1})	DSC	
			T_m (°C)	ΔH_m (J g^{-1})
1	790.4	360	133.1	188
2	1810.7	290	142.2	212
3	5577.0	350	137.2	138
4	1231.6	330	135.7	148
5	1040.0	510	136.4	154
6	1413.7	520	124.8	170
8	164.5	650	142.0	132
9	2850.0	450	141.1	145
10	2460.0	610	134.0	156
11	4560.0	450	136.1	153
13	100.7	590	138.9	137
14a,**b**	1325.0	770	139.6	138
19a,**b**	1509.0	360	138.2	143
20a,**b**	131.6	500	136.0	154
21a,**b**	2222.9	620	135.3	149
22a,**b**	878.0	580	131.4	148

[a] T_p = 60 °C; solvent: 500 ml pentane; 10 bar ethylene pressure.
[b] [M]/[Al] = 1:3000.
[c] Intrinsic viscosity.



A comparison of the activities of metallacycles **1**–**3**/MAO shows an analogous behavior (Table 2).

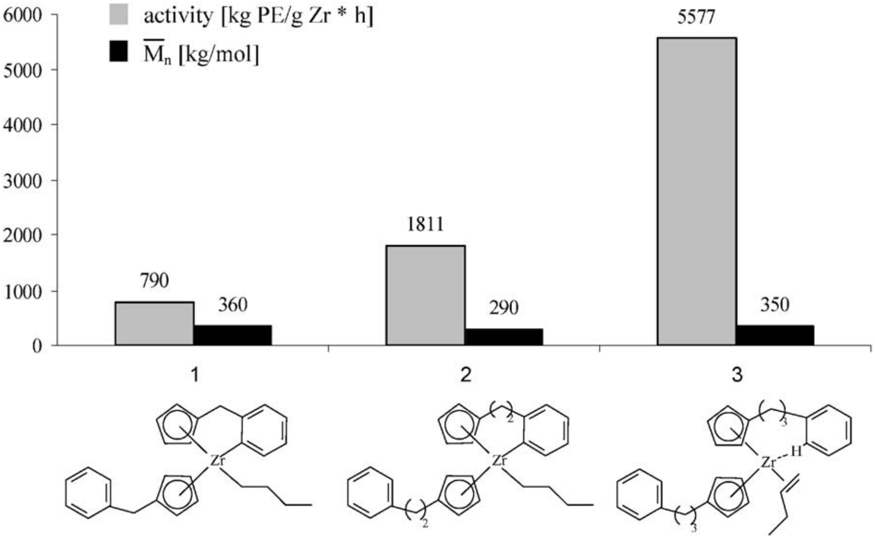
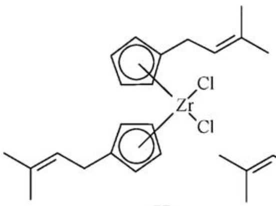


Table 2
DSC data[a] for polyethylenes obtained from the homogeneous polymerisations with **1**–**3**/MAO

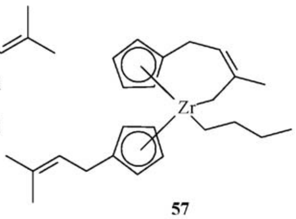
Metallocene complex	T_m (°C)	ΔH_m (J/mol)	α (%)
1	133.1	188	64.9
2	142.2	212	73.2
3	137.7	138	47.6

[a] The values are taken from the second heating course of the DSC.

In the case of the dimethylallyl substituted metallocene dichloride complexes **57c** and **58c** and the corresponding metallacycles **58** and **57** and the trimethylsilyl substituted analogs **59c** and **60c** and **59** and **60**, the metallacycles show higher activities in catalytic ethylene polymerization reactions than the parent dichloride complexes [92].



57c



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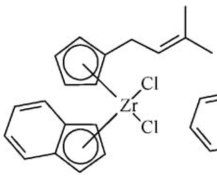
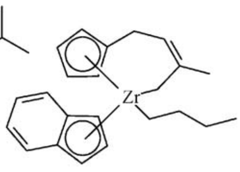


58c



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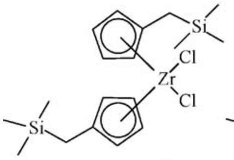
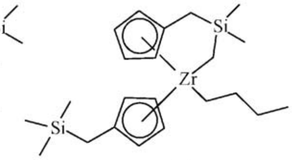


59c



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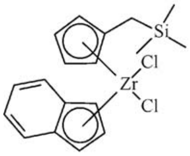
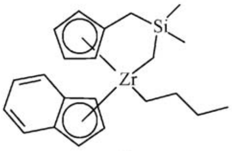


60c



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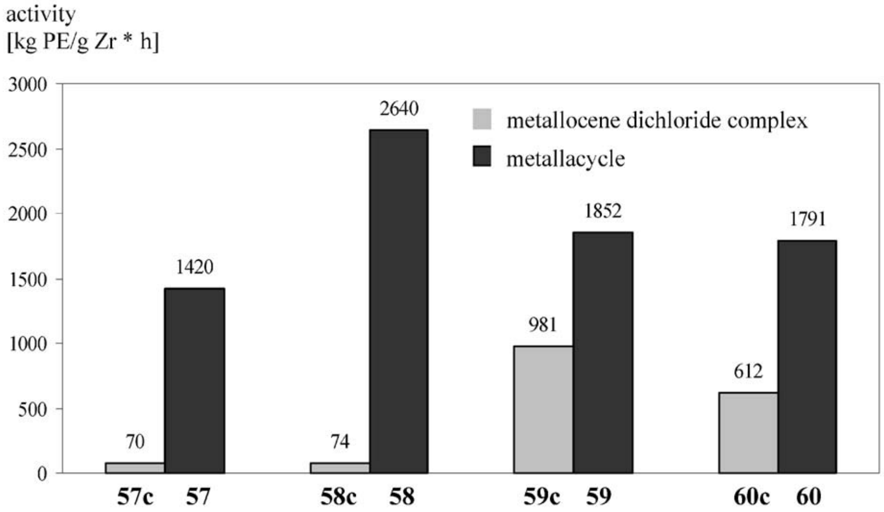
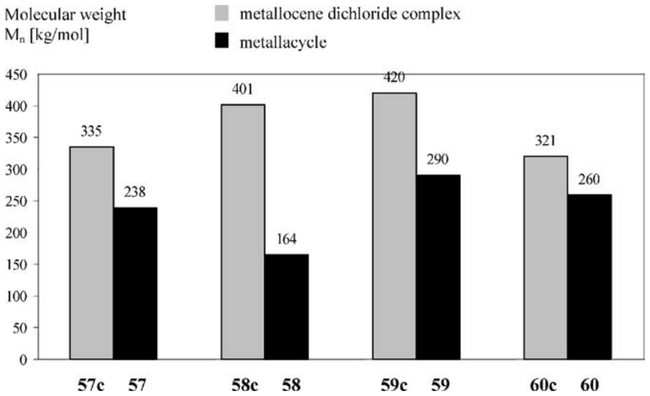


The reason for this behavior could be that the former chloro ligands from the metallocene complexes are substituents on the MAO cages after the activation step [94]. As Lewis bases they are able to block the coordination sites of the Lewis acidic metal and thus they reduce the activities of the catalysts. Another argument for the higher activites of the metallacycles could be the rigid structure of the metallacycles. Finally the “ring slippage” phenomenon, the bonding change from η^5 to η^1 in the series Cp, Ind, Flu, meets the expectations in terms of higher activities [95].

The molecular weights M_n of the polyethylenes produced show a different trend:



The metallocene dichloride complexes produce considerably higher molecular weights than the metallacyclic counterparts. This is indicative for an easier chain termination reaction presumably by β-hydrogen elimination in the case of the metallacycles.

5. Conclusion

A variety of metallacyclic metallocene complexes is accessible by a simple synthetic route: metallocene dichloride complexes with aryl or terminal alkenyl substituents react with two equivalents of butyl lithium to give the corresponding metallacycles via CH activation reactions. Metallacyclic metallocene complexes in combination with MAO have proven as excellent olefin polymerisation catalysts. In most cases they are superior to the parent metallocene dichloride complexes because they do not contain any halide components that could be counter productive for the activities of such catalysts. In addition, these catalysts are very friendly to the environment. Since they remain in the generated polyolefin resin they do not produce any halogen containing products upon thermal degradation.

Acknowledgement

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