Russian Chemical Bulletin, Vol. 44, No. 1, January, 1995 1

Reviews

Metallocene complexes as homogeneous catalysts in olefin polymerization*

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Ansa metallocene dichloride complexes of titanium, zirconium, and hafnium can be activated by methyl aluminoxane (MAO) to give excellent catalysts for the homogeneous polymerization of ethylene and propylene. The symmetry of the corresponding metallocene dichloride complexes is essential for the stereospecific polymerization of propylene (isotactic, syndiotactic or atactic). The application of fluorenyl groups instead of cyclopentadienyl groups greatly increases the activity of the catalysts. The first ansa bis(fluorenyl) complexes of zirconium and hafnium, $(C_{13}H_8{-}C_2H_4{-}C_{13}H_8)MCl_2$ (M = Zr, Hf), have been prepared. It was found that after the activation by MAO the zirconium derivative demonstrates a very high activity. Several model complexes are presented in order to discuss the mechanism of the polymerization.

Key words: zirconium, hafnium, ansa metallocene complexes, ansa bis(fluorenyl) complexes; homogeneous polymerization of ethylene, model complexes.

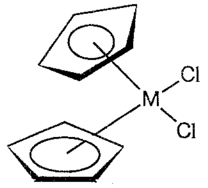
Forty years after the discovery of Ziegler Natta catalysts this research field is as interesting and as original as ever.[1]

Many research groups from all over the world, in industry and academia, are working on the newest generation of catalysts for olefin polymerization. There is a good reason for this: currently, 55 million tons of polyethylene and polypropylene alone are produced every year; a market that is worth hundreds of billions of dollars. The main tasks in this research area are:

— better and cheaper catalysts for the already known polymers;

— catalysts for new materials and new applications. This means: new markets.

A renaissance in olefin polymerization has been initiated in the past 10 years: a new generation of homogeneous catalysts has appeared on the scene, *viz.*, metallocene complexes of titanium, zirconium, and hafnium. In this paper a few aspects of this fascinating research area will be discussed.



M = Ti, Zr, H

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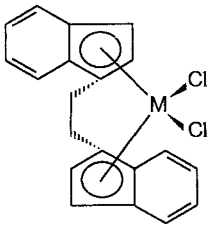
* This paper was presented at the INEOS-94 Workshop "The Modern Problems of Organometallic Chemistry" (Moscow, May 21—27, 1994).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 7—14, January, 1995.

As early as 1957 Breslow *et al.*[2] demonstrated that metallocene dichloride complexes can be activated with mixed aluminum alkyl halides to polymerize ethylene in homogenous solutions. However, the activity of the AlR_xCl_{3-x} ($x = 1$ to 3) type catalysts thus prepared was insufficient and they could not compete with the heterogeneous Ziegler and "Philips" catalysts. In the early 80's Kaminsky *et al.*[3,4] found that the efficiency of these catalysts could be improved with different methylaluminoxane (MAO = $\left[\overset{\text{Me}}{\overset{|}{\text{Al}}}-\text{O}\right]_x$, where $x = 7$ to 20) type cocatalysts (*vide infra*).

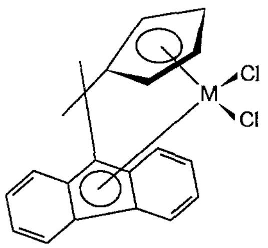
The next breakthrough was the discovery that metallocene complexes with special symmetry may be used as efficient catalyst precursors for the stereo-selective polymerization of substituted 1-olefins like propylene.[5,6] The activation of these complexes with MAO leads to very active catalysts for the production of isotactic polypropylene.

Brintzinger and Kaminsky[7] were among the first pioneers to realize the necessity of the application of so-called ansa metallocene complexes in order to maintain the symmetry of the catalyst during polymerization. The bridge between the two aromatic ligands prevents their rotation. To be more precise, in order to produce isotactic polypropylene, C_2 symmetry of the catalyst precursor is necessary. In the meantime, many other research groups use these ansa bis(indenyl) complexes of zirconium and hafnium for the production of isotactic polypropylene. Certain substituents at certain positions in the molecules of these catalysts may have a drastic influence not only on the activity and the stereoselectivity of the catalyst but also on the molecular weight of the generated polymer.



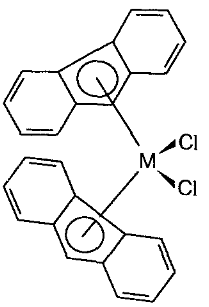
M = Zr, Hf
C_2 Symmetry

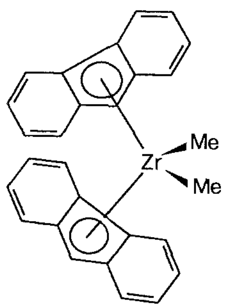
The next milestone in homogeneous olefin polymerization was Razavi's synthesis of a "mixed" ansa metallocene complex, that is, one with cyclopentadienyl and fluorenyl ligands connected with an isopropylidene bridge.[8] This complex possesses C_s symmetry and is a catalyst precursor of excellent activity and stereospecifity. Obviously, all of these positive effects have something to do with the fluorenyl ligand. Activation of the ansa (cyclopentadienyl)fluorenyl complexes with MAO makes it possible to obtain very active catalysts for the production of syndiotactic polypropylene.



M = Zr, Hf
C_s Symmetry

Five years ago we started to study ansa bis(fluorenyl) complexes, which had not been investigated at that time. We were interested in studying their catalytic potential. The two bis(fluorenyl) complexes that had been prepared before, both without a bridge, are shown below. Samuel and Setton synthesized bis(fluorenyl) zirconium dichloride[9] as early as 1965. The preparation of this compound was very complicated, and it was not stable in solution.



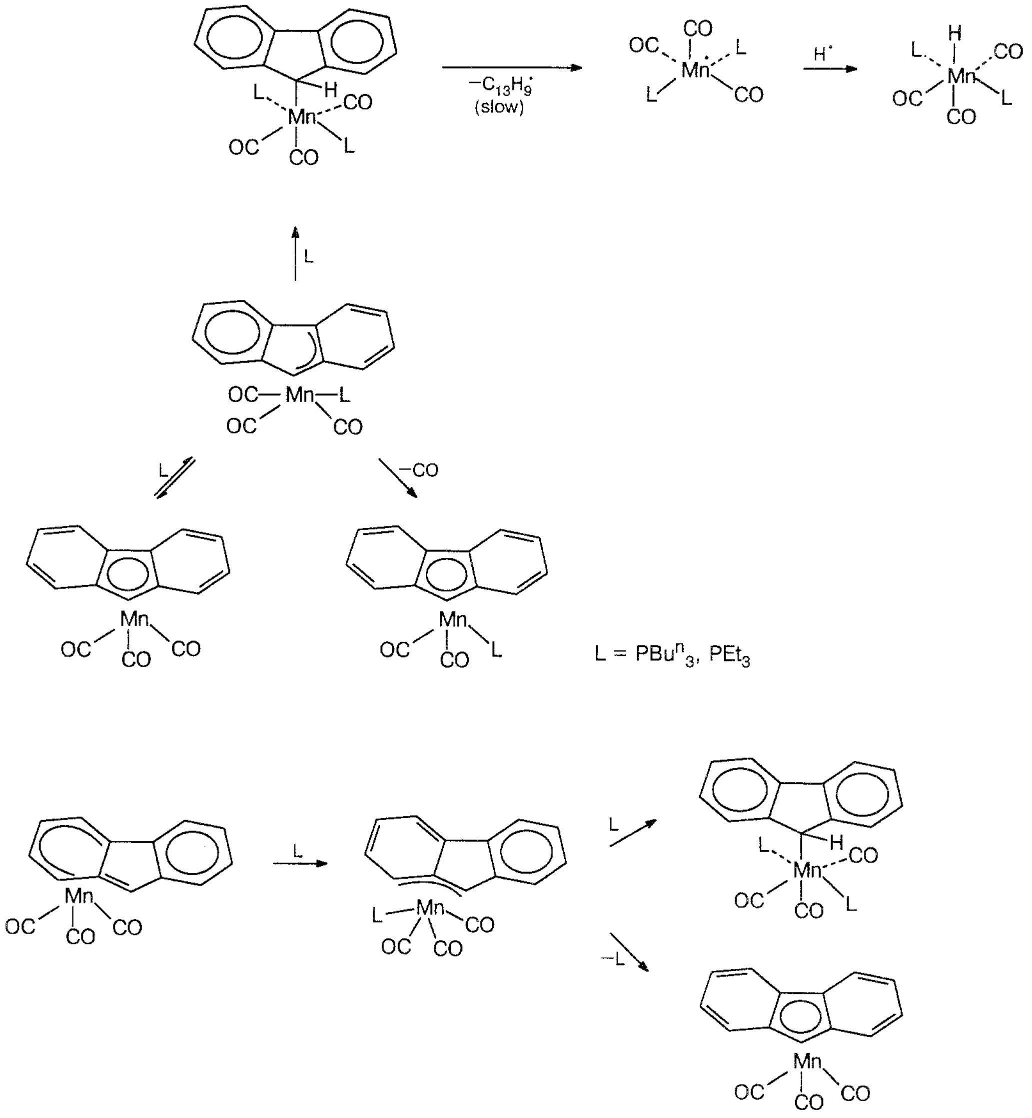


In 1974, as a postdoc with Prof. Rausch at the University of Massachusetts, the author developed a one-pot synthesis of the corresponding bis(fluorenyl)dimethyl complex.[10] In those days it was not obvious that these compounds would be promising candidates for the catalytic polymerization of olefins, and so we did not give them proper attention.

It was clear, however, that bis(fluorenyl) complexes behave differently from the corresponding cyclopentadienyl and indenyl derivatives. As just one example: everybody knows ferrocene and bis(indenyl) iron, but the corresponding bis(fluorenyl) iron remains unknown. The same is true for the corresponding ruthenium and osmium analogs. First, fluorenyl ligands are bulky and they may cause steric hindrance in the coordination sphere of a metal. Second, fluorenyl ligands are not cyclopentadienyl analogs, since the 5-membered ring of the fluorenyl anion can act as a η^5-bonded ligand only because it "steals" π-electrons from the neighboring aromatic 6-membered rings.

Indeed, one very characteristic feature of the fluorenyl ligand is its tendency to undergo ring slippage reactions of the type $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$. The reaction of $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ with alkylphosphines (Scheme 1) is an example of such a transformation.

Scheme 1



Biagioni *et al.*[11] showed that η^5-fluMn(CO)$_3$ readily reacts with the ligands L (L = PR$_3$, P(OR)$_3$) to give a 1:1 adduct in which the fluorenyl ligand is η^3-bonded. In this 1:1 adduct, the fluorenyl ligand is able to undergo further ring slippage to yield a 1:2 adduct in which the fluorenyl ligand is η^1-bonded; the η^1-bonded fluorenyl ligands can easily be eliminated, and it is obvious that such a "decomposition pathway" is the reason for the instability of many fluorenyl complexes.

Biagioni[11] failed to isolate the η^3-fluMn(CO)$_3$L complex, but he suggested two different versions of the η^3-bonding mode, *i.e.*, internal and external. In the meantime, both versions have been realized and confirmed by X-ray structural analysis.[12] The preparation and the structure of an ansa metallocene complex with an η^3-bonded fluorenyl ligand are presented in Scheme 2.

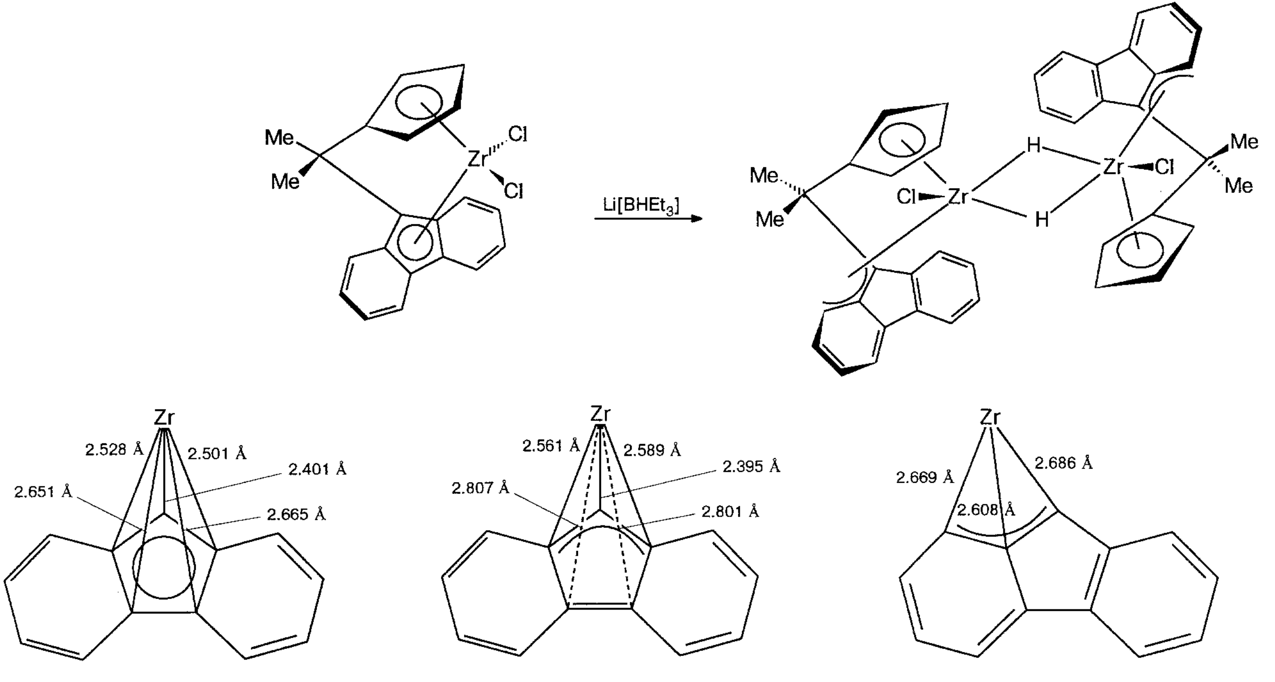
We developed a very simple method for the preparation of ansa bis(fluorenyl) complexes of zirconium and hafnium of the (η^5 : η^5-C$_{13}$H$_8$C$_2$H$_4$C$_{13}$H$_8$)MCl$_2$ type, where M = Zr or Hf[13] (Scheme 3).

We started with fluorene reacting with BuLi to form the corresponding anion. This anion was reacted stepwise with 1,2-dibromoethane to obtain the desired coupling product (see Scheme 3). The next step was the reaction with MeLi, which yielded the corresponding dianion. The subsequent reaction of the dianion with MCl$_4$ gave the ansa bis(fluorenyl) complexes of zirconium or hafnium. By the way, the analogous titanium complex could not be prepared by this method.

We were able to grow crystals from the free bis(fluorenyl)ethane and the corresponding ansa bis(fluorenyl) zirconium complex and to carry out the X-ray analysis of them (Figs. 1 and 2).

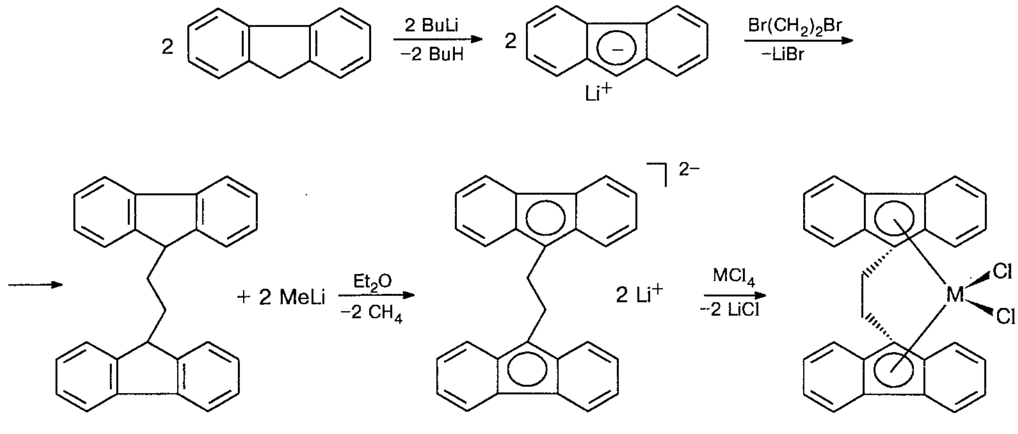
One can see from Fig. 1 that the two fluorenyl groups are at the maximum distance from each other. In the Zr complex (see Fig. 2) both fluorenyl moieties are

Scheme 2



$(\eta^5{:}\eta^5\text{-}C_{13}H_8CMe_2C_5H_4)ZrCl_2$ $(\eta^5{:}\eta^3\text{-}C_{13}H_9)_2ZrCl_2$

Scheme 3



coordinated to the metal in a η^5-manner. The metal—carbon distances vary considerably between 2.417(5) and 2.698(5) Å due to the fact that the organic ligand is a rigid system.

The C—C axis of the 1,2-ethanediyl bridge (see Fig. 1) does not lie in a plane that can bisect the molecule into two symmetric moieties.

The ansa bis(fluorenyl) zirconium complex is an excellent catalyst for the polymerization of ethylene: after the activation with MAO, its activity is $54 \cdot 10^6$ (g/g$_M$) h^{-1} (Table 1). This means that 1 g of zirconium produces ~300 million grams (300 tons) of polyethylene. The analogous hafnium complex has a lower activity and produces a material with a lower molecular weight. The latter feature is quite unusual, since in most of the other cases hafnium complexes produce polymers of higher molecular weight than do their zirconium analogs due to the stronger Hf—C bond in the intermediates.

The comparatively narrow molecular weight distribution of the polymers is typical of metallocene catalysts.

Ansa bis(fluorenyl) complexes have high thermal stability. They survive heating to 120 °C for several hours without losing their activity. This is a significant difference from the labile unbridged bis(fluorenyl) complexes which had been presented before.

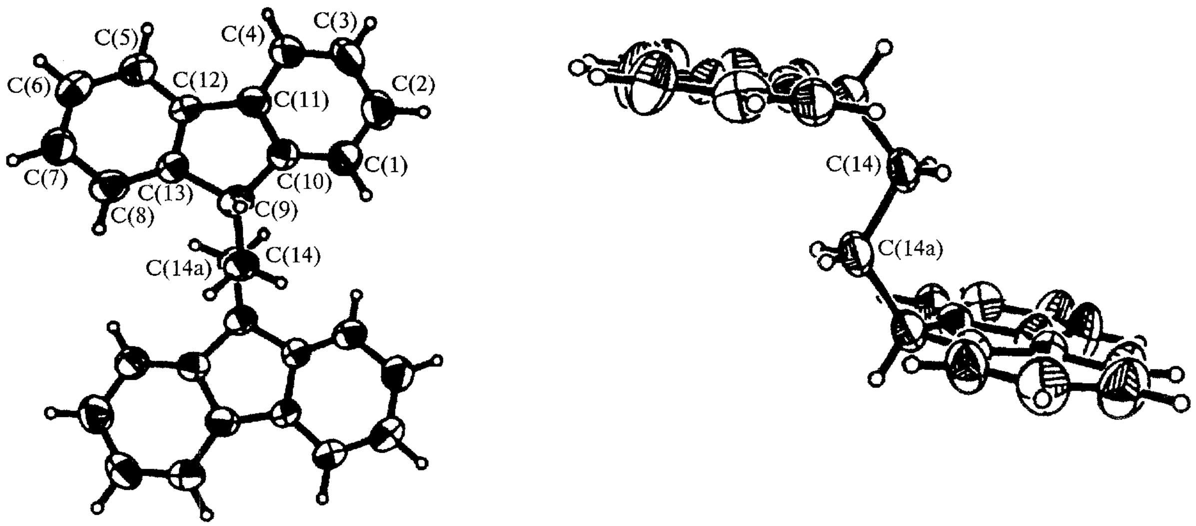


Fig. 1. Molecular structure of $C_{13}H_8—C_2H_4—C_{13}H_9$.

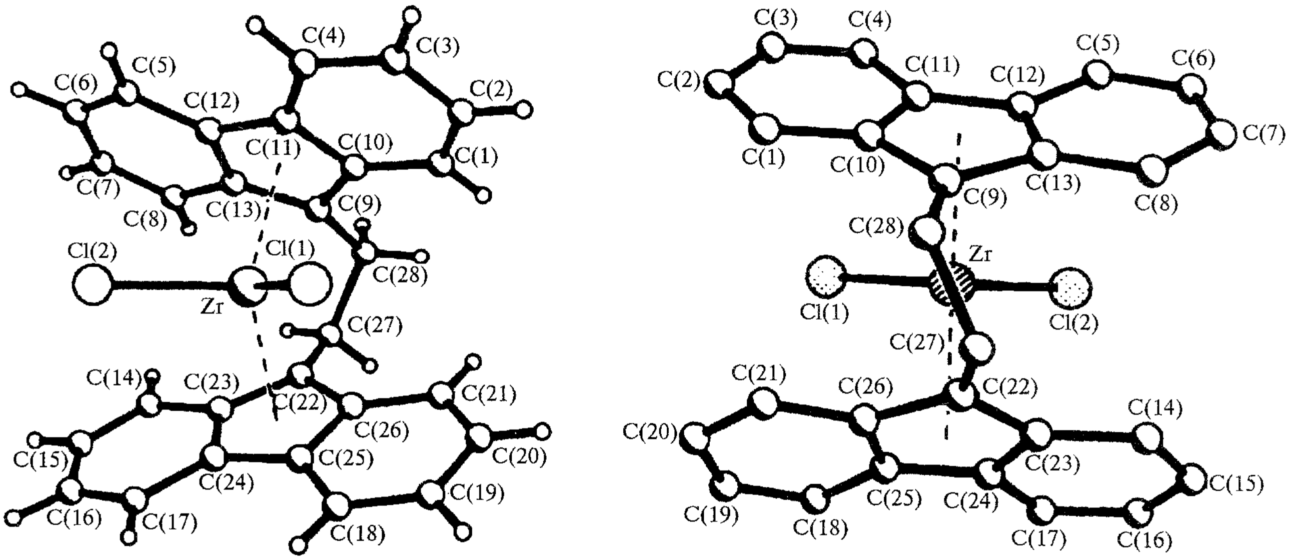


Fig. 2. Molecular structure of the $(\eta^5{:}\eta^5\text{-}C_{13}H_8C_2H_4C_{13}H_8)ZrCl_2$ complex.

Table 1. Polymerization data of $(\eta^5{:}\eta^5\text{-}C_{13}H_8C_2H_4C_{13}H_8)MCl_2$ complexes [M = Zr (**1**), Hf (**2**)]

Complex	Concentration of M* (in toluene) $/10^{-6}$ mol L^{-1}	Activity $/10^6$ (g/g_M) h^{-1}	M_w	M_w/M_n
1	0.49	54	400000	2.12
2	0.42	1.5	248000	2.69

* MAO (Al : M = 500 : 1).

Propylene can also be actively polymerized by ansa bis(fluorenyl) complexes. The product, however, is atactic polypropylene. In contrast, the unbridged racemic bis(1-methylfluorenyl) zirconium dichloride, because of its C_s symmetry, is a stereospecific catalyst for the production of isotactic polypropylene. This catalyst was recently described, its structure (Fig. 3) having been proved by X-ray analysis.[14]

The activity of ansa bis(fluorenyl) complexes greatly depends on the solvent. In order to explain this behavior, it is necessary to discuss the mechanism of the polymerization process in general.

The various metallocene dichloride complexes are catalyst precursors and they can be activated by a cocatalyst like MAO (Scheme 4).

Other counterions like $[B(C_6F_5)_4]^-$ or $[B(C_6F_5)_3Me]^-$ *etc.* can also be used to stabilize the metallocenium methyl cation formed. This cation represents a 14-electron species and is coordinatively unsaturated.

The stabilization of such a metallocene cation can be achieved with a weak coordinating anion. In solution,

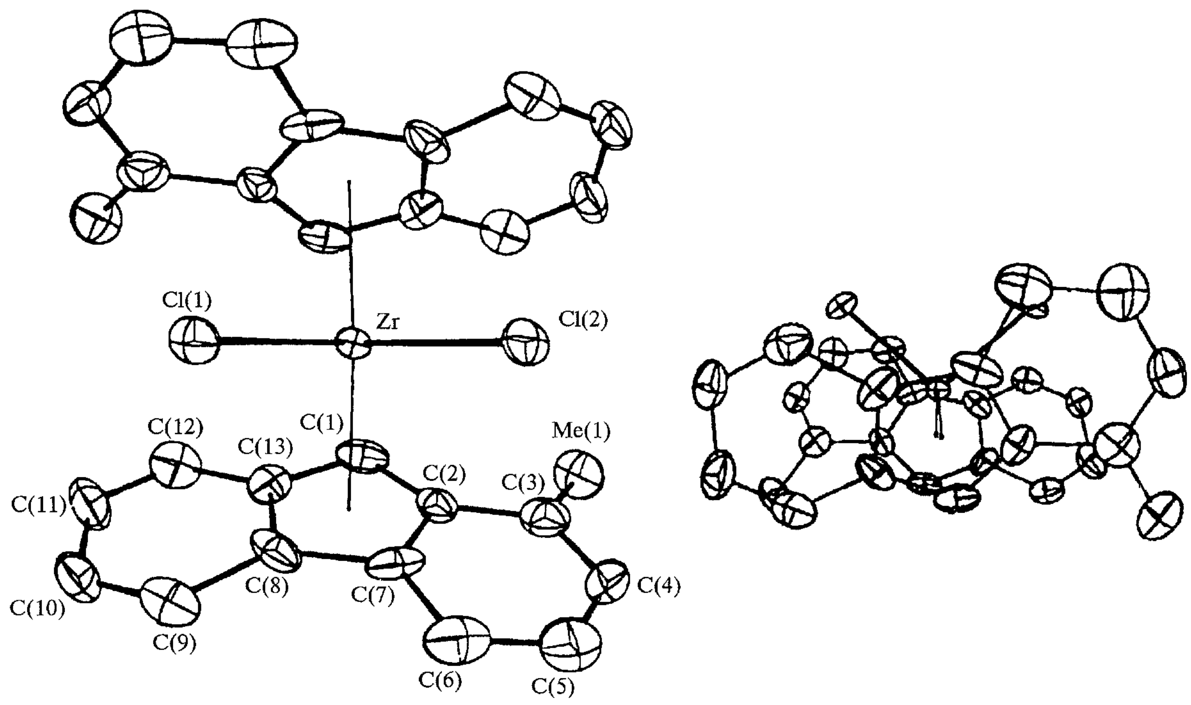
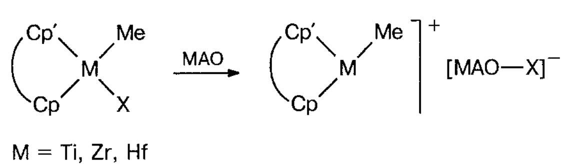


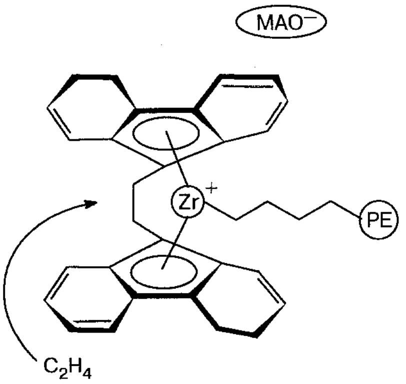
Fig. 3. Bis(1-methylfluorenyl) zirconium dichloride as a catalyst precursor for isotactic polypropylene.

Scheme 4



ion-paired metallocenium methyl cations can undergo ion pair reorganization processes (Scheme 5), and this might be the reason for the strong influence of the solvent on the activity of metallocene catalysts.

Scheme 5



(PE is polyethylene)

The next step of the catalytic process is the coordination of the monomeric olefin to the metal with the formation of an olefin complex. This step is not crucial in ethylene polymerization but is extremely important in the case of stereospecific propylene polymerization. For a better understanding of these various steps in homogenous polymerization we became interested in various model complexes.

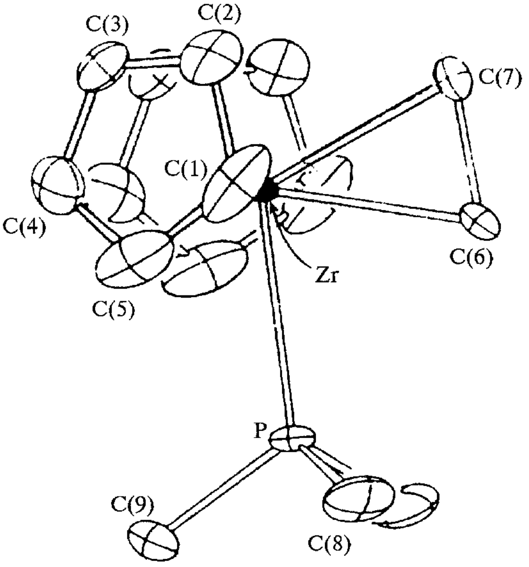


Fig. 4. Molecular structure of the $Cp_2Zr(C_2H_4)PMe_3$ complex.

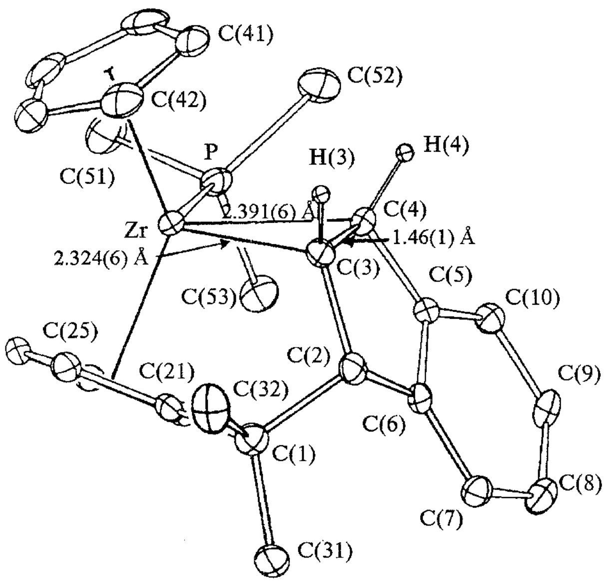
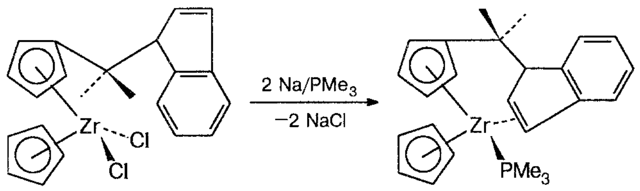


Fig. 5. Molecular structure of the functionalized zirconocene complex.

In this regard, the ethylene complex $Cp_2Zr(C_2H_4)PMe_3$ (see Ref. 15) is one of the key complexes. The X-ray structure of this complex (Fig. 4) reveals that the C—C axis of the ethylene ligand lies in the plane of Cp_2ZrPMe_3 fragment. Even when the olefin moiety is linked with a Cp ligand the C—C axis takes the same orientation.[16] Scheme 6 represents the preparation of such a functionalized zirconocene complex. Its molecular structure is shown in Fig. 5.

Scheme 6

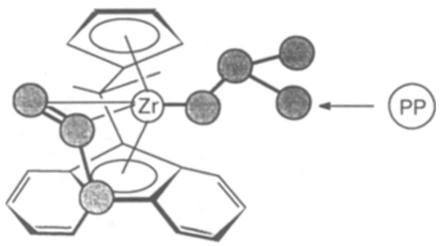


As soon as one Cp ligand is replaced with fluorenyl, four different possibilities emerge for the coordination of a prochiral olefin such as propylene. Molecular modeling calculations indicate that only one orientation has an energy minimum. Corradini and coworkers[17] claim the following orientation of the propylene ligand in the Razavi—Even complex (Scheme 7):

— the C—C axis lies in the plane that is formed by the bridging C atoms and the two methyl substituents of the cation fragment;

— the methyl substituents of the alkyl ligand point away from the metal.

Scheme 7



(PP is polypropylene)

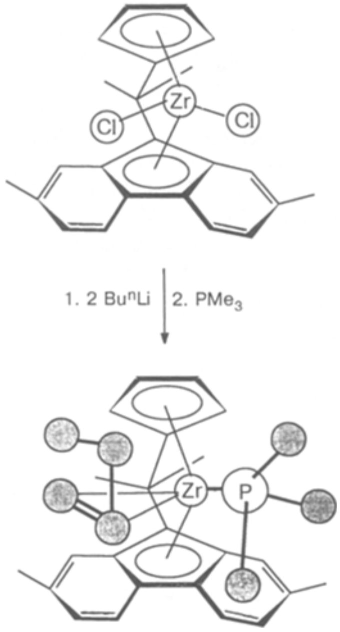
In order to confirm Corradini's calculations, we prepared the corresponding butene complex (Scheme 8), since the butene and 2,7-(dimethyl)fluorenyl ligands should impose the same steric requirements as the propene and fluorenyl ligands, correspondingly.

The author's coworker, R. Zenk, found by NOE difference NMR spectroscopy (Fig. 6) that the butene ligand in this PMe_3 complex must have a different orientation from that which one would expect based on Corradini's predictions, at least in solution.

This does not mean that Corradini is wrong. Both versions could be possible due to the fact that the electronic and steric requirements imposed by the PMe_3 ligand are different from those of the growing polypropylene chain. In other words, "little changes can make a big difference", which is very typical of metallocene chemistry.

In conclusion the author would like to express his thanks to his former coworker S. Palackal and R. Zenk who were involved in these investigations.

Scheme 8



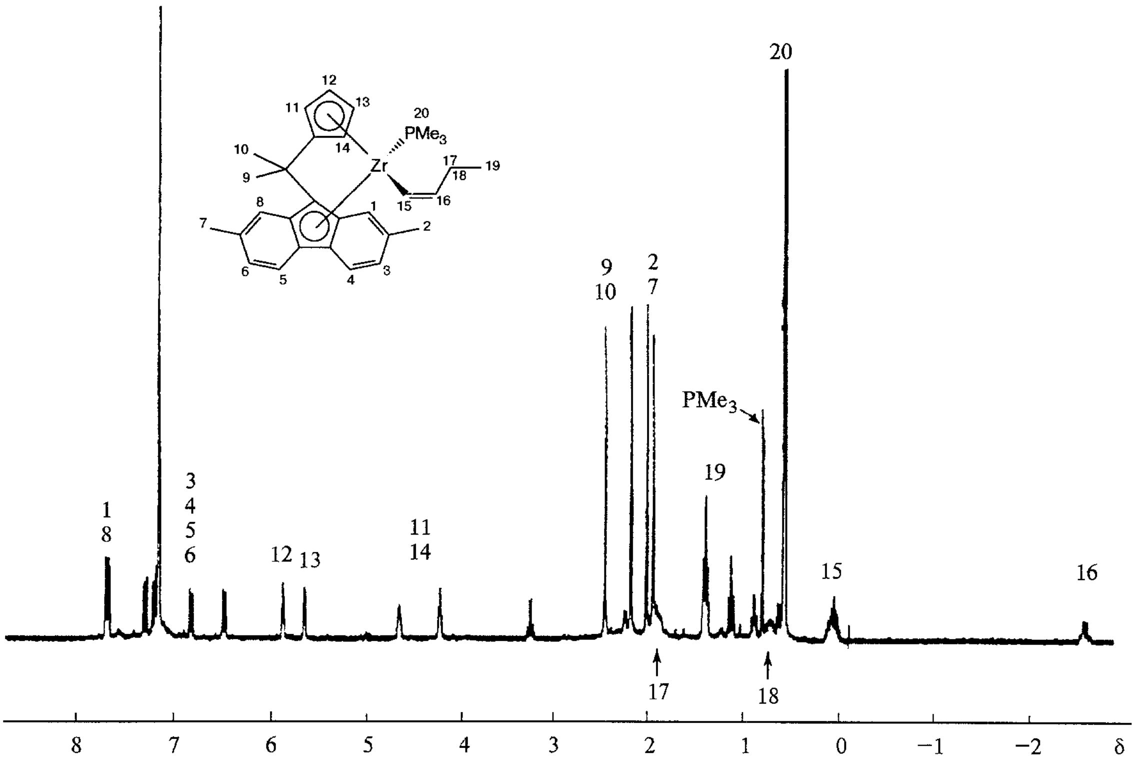


Fig. 6. ^{1}H MNR NOE-difference spectra of the ansa metallocene trimethyl phosphine complex. The numbers indicate signal assignments.

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Received July 28, 1994