Available online at www.sciencedirect.com

SCIENCE DIRECT®

Coordination Chemistry Reviews 250 (2006) 242–258

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Ansa-metallocene polymerization catalysts: Effects of the bridges on the catalytic activities

Baiquan Wang *

State Key Laboratory of Elemento-Organic Chemistry, Department of Chemistry, Nankai University, Tianjin 300071, PR China

Received 22 December 2004; accepted 5 May 2005
Available online 23 June 2005

Contents

Abstract

Ansa-metallocene complexes have been extensively studied as the precatalysts for olefin polymerization. The bridges have important effects on the activities of the catalysts and polymer properties such as molecular weight and tacticity, mainly by altering the framework of the catalysts. Here, we review the effects of the structures of *ansa*-metallocene complexes on the catalytic activities, especially the effects of the bridges on the catalytic activities.

Keywords: *Ansa*-metallocene; Metallocene catalyst; Olefin polymerization; Bridged ligand; Isotactic polypropylene; Syndiotactic polypropylene

1. Introduction

Metallocene catalysts have been one of the most actively investigated research topics for more than 20 years [1,2]. Studies of various ring-bridged cyclopentadienyl and indenyl metallocene complexes have demonstrated that the activity

---

Abbreviations: Cp, C_5H_5; Cp′, generic cyclopentadienyl ligand; Flu, fluorenyl ($C_{13}H_9$); Ind, indenyl (C_9H_7); $IndH_4$, tetrahydroindenyl; *i*-PP, isotactic polypropylene; PE, polyethylene; PP, polypropylene; MAO, methyl aluminoxane

* Fax: +86 22 23502458.
E-mail address: bqwang@nankai.edu.cn.

0010-8545/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2005.05.012

and the stereoselectivity of olefin polymerization reactions can be significantly affected by slight structural variations of the bridging groups and ring substituents in metallocene catalysts. The latin term *ansa* (meaning bent handle, attached at both ends) was first introduced by Lüttringhaus and Kullick for bridged ferrocenes [3a–c], and Brintzinger and co-workers pioneered the design and synthesis of these complexes in 1979 [3d–e]. Since the C_2-symmetric ethylidene bridged metallocene complexes, racemic $(C_2H_4)(IndH_4)_2MCl_2$ (M = Ti, Zr, Hf), activated with MAO produced highly isotactic PP [4], plenty of Group 4 *ansa*-metallocene complexes have been developed and applied as olefin polymerization catalysts [2,5]. Numerous books and review articles on the *ansa*-metallocene catalysts have been written [2], but few of them on the structure–activity relationship of *ansa*-metallocene polymerization catalysts [2b]. The influence of the ligand framework on the activity includes mainly steric and electronic effect. On the basis of steric parameters, the activity is improved by enlarging the reaction space of the metal center, mainly by increasing the M–Cen (Cen = centroid of the five-ring for any η^5-based ligand) distance and the dihedral angle between two π-ligand planes, and by decreasing the ∠Cen–M–Cen angle. For the *ansa*-metallocene catalyst, the bridge is an important factor (*ansa*-effect [5i]) to affect the activity and stereoselectivity mainly by steric effect and also by electronic effect. So in this review, the focus is on the effects of the bridges on the activities of *ansa*-metallocene catalysts. This not only can help us to design more active olefin polymerization catalysts but can also promote their further application in organic synthesis.

2. Single atom bridged metallocene catalysts

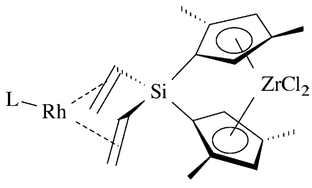
2.1. Single silicon bridged metallocene catalysts

Dimethylsilylene bridged metallocene catalysts comprise one of the most commonly studied types of *ansa*-metallocene catalyst. Similar to the unbridged metallocene catalysts, Me_2Si bridged zirconocene catalysts in general are much more active than the corresponding titanocene and hafnocene catalysts in olefin polymerization [1,2,6,7]. The low activity of Ti complexes are generally attributed to the poor thermal stability of Ti(IV) oxidation state [2c,4a], while the low activity of Hf complexes has been attributed to the higher strength of the Hf–C bond compared to the Zr–C bond [2c,8] or to kinetic reasons (slow olefin co-ordination and insertion step) [2b]. A stereorigid bridged metallocene cation usually has closely equivalent metal–centroid bond lengths and angles, as does its neutral precursor [9], and thus the latter structure may be relied on as a model for the former, and for interpretation of the polymerization results. Thus, the high activities of Me_2Si bridged zirconocene catalysts can be easily explained by comparing their geometric parameters shown in Table 1 with the unbridged metallocene complexes.

For zirconocene dichlorides, introduction of a Me_2Si bridge decreases the ∠Cen–Zr–Cen angle and increases the dihedral angle between two cyclopentadienyl planes. This increases the reaction space of the metal center and increases the catalytic activity for olefin polymerization [5,13]. The large reaction space of the metal center is also responsible for their higher activity than other zirconocene catalysts with two atoms or longer bridges [1d,e,2a,5,6b,14,15]. For titanocene dichlorides, introduction of a Me_2Si bridge decreases the ∠Cen–Ti–Cen angle and the dihedral angle. The Ti–Cen distance increases evidently than Cp_2TiCl_2, indicating the decrease of the stability. This means that not only is the reaction space of the metal center not increased, but the stability of the titanocene complex is also decreased after being bridged with a Me_2Si group. So the Me_2Si bridged titanocene catalyst shows lower activity for olefin polymerization [1,2]. However, at a low temperature, the Me_2Si bridged and unbridged titanocene catalysts usually show higher activities than the corresponding zirconocene catalysts for polymerization of ethylene and even of propylene [16,17]. But when polymerization temperature increases, the activities of the titanocene catalysts decrease sharply, in contrast to the higher activities of the zirconocene catalysts at higher temperature. This means that the poor thermal stability is a main reason for the low activities of the Me_2Si bridged and unbridged titanocene catalysts.

Replacement of a methyl group of the Me_2Si bridge with hydrogen, alkyl, vinyl, allyl or phenyl group gives similar structures and polymerization activities [18a–e]. For the divinylsilylene bridged metallocene catalysts, when a rhodium unit is introduced to co-ordinate with the two vinyl groups at the bridging silicon atom (Scheme 1), significantly enhanced activities and molecular weights are observed for α-olefin polymerization, due to the electron-donating effect of the rhodium units [18fg].

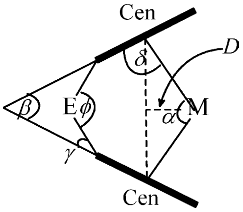
The silacycloalkylidene bridged cyclopentadienyl titanocene catalysts $(CH_2)_nSi(C_5H_4)_2TiCl_2$ (n = 1–3) (Scheme 2) show remarkably higher activities for ethylene polymerization than the corresponding zirconocene analogues and $Me_2Si(C_5H_4)_2TiCl_2$, and produce PE with high molecular weights ($M_w = 1.3–2.6 \times 10^6$) [17]. The activity increases with the increasing of the size of bridge ring. By comparing the structural parameters, it can be found that replacement of a Me_2Si bridge with a silacyclopentylidene bridge makes the Ti–Cen distances, the D values, and the Cen–Cen distances decrease



L = Ind, Cp, C_5Me_5

Scheme 1. Heterobimetallic *ansa*-metallocene complexes.

Table 1
Relevant geometrical parameters of selected bis(cyclopentadienyl) metallocene complexes[a]

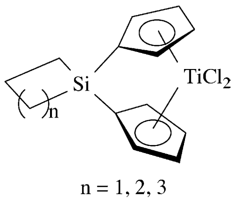


Complex	ϕ (°)	Cen–Cen (Å)	D (Å)	α (°)	γ (°)	δ (°)	β (°)	M–Cen (Å)	References
Cp_2TiCl_2		3.747	0.853	131.0		85.3	58.5	2.059	[12]
$Me_2Si(C_5H_4)_2TiCl_2$	89.5(1)	3.741	0.898	128.7	19.2	90.1	51.2	2.075	[11]
$(CH_2)_4Si(C_5H_4)_2TiCl_2$[b]	90.7(3)	3.736	0.889	129.1	18.6	87.6	55.7	2.069	[17]
$(CH_2)_5Si(C_5H_4)_2TiCl_2$[b]	90.1(6)	3.747	0.885	129.4	18.2	87.6	55.4	2.072	[17]
$Me_2C(C_5H_4)_2TiCl_2$	96.7(1)	3.588	1.005	121.5	14.9	85.8	66.9	2.056	[21]
$(CH_2)_4C(C_5H_4)_2TiCl_2$	96.9(2)	3.571	1.008	121.1	15.1	86.1	65.6	2.061	[19b]
					15.0	86.9		2.040	
$(CH_2)_5C(C_5H_4)_2TiCl_2$	96.6(2)	3.573	1.009	121.1	14.5	85.9	65.7	2.061	[19b]
					15.2	87.0		2.042	
$(CH_2)_6C(C_5H_4)_2TiCl_2$	96.6(3)	3.563	1.000	121.4	14.6	86.2	65.6	2.049	[19b]
					15.1	86.8		2.037	
Cp_2ZrCl_2		3.982	0.933	129.3		88.8	53.5	2.203	[10]
$Me_2Si(C_5H_4)_2ZrCl_2$	93.2(2)	3.905	1.008	125.4	18.2	88.9	56.8	2.197	[11]
$(CH_2)_3Si(C_5H_4)_2ZrCl_2$	94.7(1)	3.934	0.998	126.2	18.2	87.0	59.7	2.206	[20]
$(CH_2)_4Si(C_5H_4)_2ZrCl_2$	94.3(3)	3.915	1.006	125.6	18.5	87.7	59.1	2.201	[17]
$(CH_2)_5Si(C_5H_4)_2ZrCl_2$	94.0(2)	3.921	1.010	125.5	17.9	87.6	59.3	2.205	[17]
$Me_2C(C_5H_4)_2ZrCl_2$	99.8(2)	3.730	1.152	116.6	14.2	86.0	71.4	2.192	[21]
$(CH_2)_4C(C_5H_4)_2ZrCl_2$	99.8(5)	3.728	1.151	116.6	13.5	85.2	71.2	2.197	[19b]
					14.2	87.4		2.185	
$(CH_2)_5C(C_5H_4)_2ZrCl_2$	99.7(5)	3.725	1.155	116.4	14.6	86.5	69.9	2.199	[19b]
					14.5	87.1		2.184	
$(CH_2)_6C(C_5H_4)_2ZrCl_2$	99.1(2)	3.699	1.149	116.3	14.2	87.4	69.5	2.171	[19b]
					14.3	86.9		2.184	

[a] In the schematic representation of an *ansa*-metallocene molecule above [22], Cen is the center of the cyclopentadienyl ring; ϕ is the angle C(bridgehead)-E-C(bridgehead); δ is the angle between the M–Cen vector and the cyclopentadienyl plane; γ is the angle between the E-C (bridgehead) vector and the cyclopentadienyl plane; β is the dihedral angle between the two cyclopentadienyl planes; α is the angle Cen–M–Cen.

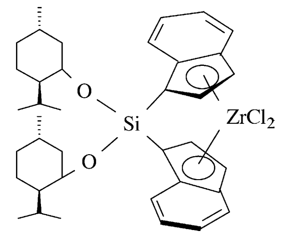
[b] The average values are given, due to the exiting of two independent molecules in the unit.

slightly, while the dihedral angles increased largely for the titanocene complexes (55.4–55.7° versus 51.2°) than for the zirconocene complexes (59.1–59.3° versus 56.8°). The increased stabilities and enlarged reaction space of the metal centers are responsible for their high activities for ethylene polymerization. However, it seems that the dimension of the large silicon atom bridge and the small titanium atom are not matched very well. The sharp decrease of the activities with increase of temperature indicates the thermal stabilities of the silacycloalkylidene bridged titanocene catalysts are still low. At a higher temperature (70 °C), the activity of $(CH_2)_4Si(C_5H_4)_2TiCl_2$ is nearly comparable with that of the corresponding zirconocene analogue [19b]. The silacyclobutylidene bridged zirconocene complex is found to undergo ring opening polymerization (ROP) with Karstedt's catalyst. But the ROP product shows much lower activity for ethylene polymerization than the silacyclobutylidene bridged zirconocene catalyst, which shows activity comparable to those found for Cp_2ZrCl_2 [20].



Scheme 2. Silacycloalkylidene bridged metallocene complexes.

The Me_2Si bridged cyclopentadienyl and indenyl zirconocene catalyst $Me_2Si(C_5H_4)(Ind)ZrCl_2$ shows low activity for propylene polymerization and produces PP with very low molecular weight [23]. The Me_2Si bridged cyclopentadienyl and fluorenyl zirconocene catalyst shows strong decrease in activity and stereoregularity for propylene polymerization compared with $Me_2C(C_5H_4)(Flu)ZrCl_2$ and $PhP(C_5H_4)(Flu)ZrCl_2$ [24b]. Introduction of two phenyl groups instead of two methyl groups at the bridging silicon atom results in the increase in activity and decrease in

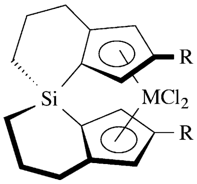


Scheme 3. Optically active dimenthoxysilylene bridged metallocene.

molecular weight [25]. When a *tert*-butyl group is introduced to the 3-position of the cyclopentadienyl ring, it can produce highly isotactic PP with high activity [1b].

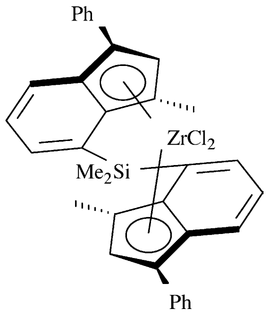
The C_2-symmetric Me_2Si bridged metallocene catalysts polymerize propylene with higher activity, higher molecular weight and isotacticity than the ethylidene bridged analogues, due to the higher stereorigidity and favorable electronic characteristics [5]. The Me_2Si bridged bis(tetrahydroindenyl) zirconocene catalyst shows lower activity but affords higher isotactic PP than the bis(indenyl) analogue [5h]. Introduction of two phenyl groups into the bridging silicon atom, both the activity for propylene polymerization and the isotacticity of PP produced decrease [1b]. Substitution on appropriate positions of the indenyl ligands gives much higher activity, stereospecificity and molecular weight of PP. The Me_2Si bridged bis(2-methyl-4-arylindenyl) zirconocene catalysts are the best metallocene catalysts for isotactic propylene polymerization [1d,6b]. The optically active dimenthoxysilylene bridged bis(indenyl) zirconocene catalyst (Scheme 3) shows extremely high activities for ethylene, propylene and ethylene–hexene polymerizations with $Al(iPr)_3/[Ph_3C]^+[B(C_6F_5)_4]^-$. The three strongly electron-donating atoms (one Si and two O) plus two other big alkyl groups in the bridging moiety could be a contributing factor [26].

The silacyclopentylidene bridged bis(indenyl) zirconocene catalyst shows lower activity with MAO, but slightly higher activity with $AlR_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ for ethylene polymerization than $Me_2Si(Ind)_2ZrCl_2$. The activities for propylene polymerization both with MAO and with $AlR_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ are much lower than that of $Me_2Si(Ind)_2ZrCl_2$ [27a]. The silacyclobutylidene bridged bis(indenyl) zirconocene catalyst shows very high activity for ethylene polymerization, but slightly low activity for propylene polymerization [27b]. The spirosilane bridged zirconocene catalysts (Scheme 4) show lower activity for propylene polymerization than the Me_2Si bridged analogues but produce highly isotacitic PP (*mmmm* = 97–99%) [28]. The Me_2Si bridged bis(fluorenyl) zirconocene catalyst $Me_2Si(Flu)_2ZrCl_2$ shows much higher activity for propylene polymerization than the ethylidene bridged analogue and other bridged and unbridged metallocene catalysts at low Al/Zr molar ratio (Al/Zr = 2000), and produces atactic PP with very high molecular weight [13b]. Bridging the two 4,4′-positions of indenyl groups and with appropriate substitution (Scheme 5) also lead to high isospecific system: for example, *rac*-$Me_2Si(4,4'\text{-}(3\text{-Me-1-Ph-indenyl})_2)ZrCl_2$ produces *i*PP with good activity, acceptable molecular weight and good melting point (*mmmm* = 98.2%) [1c].



R = *i*Pr, *t*Bu

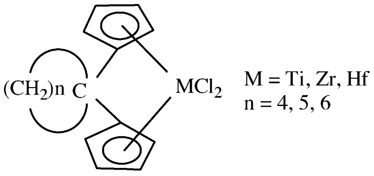
Scheme 4. Spirosilane bridged metallocene complexes.



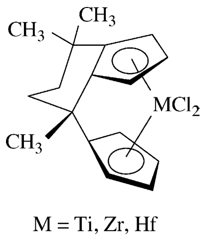
Scheme 5. 4,4′-Dimethylsilylene bridged metallocene complexes.

2.2. Single carbon bridged metallocene catalysts

The isopropylene bridged metallocene catalysts are another kind of commonly studied *ansa*-metallocene catalyst due to their high performance in stereoregular propylene polymerization [2,29,30]. The isopropylene bridged titanocene catalyst $Me_2C(C_5H_4)_2TiCl_2$ shows much higher activity for ethylene polymerization than the zirconocene analogue, especially at a lower temperature [19b]. This is very different from the general recognition that zirconocene catalysts exhibit higher activities than titanocene catalysts in olefin polymerization [2,31]. For zirconocene dichlorides, introduction of a short Me_2C bridge increases the dihedral angle between two cyclopentadienyl planes and the D value, decreases the ∠Cen–Zr–Cen angle and the Cen–Cen distance (Table 1). The metal atom moves out much further than that in the unbridged and Me_2Si bridged analogues. Although the reaction space of the metal center is further increased, but this makes the stability of the Me_2C bridged zirconocene catalyst decreased significantly. This has been further confirmed by the broader MWD values (14–17) and the bimodal or trimodal GPC curves of the PE produced by $Me_2C(C_5H_4)_2ZrCl_2$ [19b]. This is consistent with a theoretical study by an ab initio Hartree–Fock method [32]. The view that the dimension of the short single carbon atom bridge does not match the co-ordination requirement of the large zirconium atom can also explain why the catalytic activities of many single carbon atom bridged zirconocene catalysts are lower than those of single silicon atom bridged



Scheme 6. Cycloalkylidene bridged metallocene complexes.



Scheme 7. Fused-ring C_1-bridged metallocene complexes.

analogues for ethylene polymerization [1e,6]. For titanocene dichlorides, after introduction of a Me_2C bridge, the Ti–Cen distances are nearly equal to those in Cp_2TiCl_2 (2.056 Å versus 2.059 Å), but much shorter than those of $Me_2Si(C_5H_4)_2TiCl_2$. This indicates that the small bridging carbon atom and small titanium atom are matchable. Introduction of a Me_2C bridge decreases the ∠Cen–Zr–Cen angle and increases the dihedral angle between two cyclopentadienyl planes. The reaction space of the metal centers increased significantly, but the stability of the Me_2C bridged titanocene catalyst hardly decreases due to the similar Ti–Cen distances, small differences in the dihedral angle between two cyclopentadienyl planes and ∠Cen–M–Cen angle in comparison with Cp_2TiCl_2. So $Me_2C(C_5H_4)_2TiCl_2$ shows higher activity for ethylene polymerization even than the corresponding zirconocene analogue.

Introduction of a cycloalkylidene bridge instead of the Me_2C bridge (Scheme 6) affords a highly active and thermally stable *ansa*-titanocene catalyst system, which exhibits much higher activity than the zirconocene and hafnocene analogues for ethylene polymerization, and shows the highest activity at a higher temperature [19]. The cycloalkylidene bridged titanocene catalyst has similar geometrical parameters to $Me_2C(C_5H_4)_2TiCl_2$. The dihedral angle between two cyclopentadienyl planes decreases slightly, but still much larger than that of Cp_2TiCl_2. The Cen–Cen distance and the average M–Cen distance decrease due to the nonbonded interaction between the cycloalkylidene bridge and two cyclopentadienyl groups. This greatly improves the stability of the cycloalkylidene bridged titanocene catalyst while retaining the large reaction space of the metal center. The higher activity of the single carbon bridged titanocene catalyst than that of the zirconium analogue is observed mainly for ethylene polymerization [6,19,33] and in a few cases for propylene polymerization [33]. The activity for propylene polymerization is strongly affected by the molecular symmetry of catalysts and steric effects, due to the larger steric effect of propylene monomer than that of ethylene. So, *ansa*-zirconocene catalysts usually show higher activities for propylene polymerization than titanocene and hafnocene analogues due to the larger atom radius of zirconium than titanium and hafnium. With the metallocene catalysts bridged by a fused-ring unit (Scheme 7), partly isotactic high molecular weight PP is formed using the titanocene catalyst with activity of 300 g PE/(g Ti h) at low temperature, while much low molecular weight PP is obtained from the zirconocene catalyst with similar activity [16b,34].

The C_s-symmetric Me_2C bridged cyclopentadienyl and fluorenyl metallocene catalysts $Me_2C(C_5H_4)(Flu)MCl_2$ (M = Zr, Hf) show much high activities for propylene polymerization than for ethylene polymerization and produce highly syndiotactic PP [2,8,29,35]. The hafnium complex shows lower activity but produces higher molecular weight PP than the zirconium analogue. When a *tert*-butyl or a trimethylsilyl group is introduced to the 3-position of the cyclopentadienyl ring, it can produce isotactic propylene with much improved activities than the parent complex $Me_2C(C_5H_4)(Flu)ZrCl_2$, but the activities are still lower than $(C_2H_4)(Ind)_2ZrCl_2$ and $Me_2Si(Ind)_2ZrCl_2$ [1b,2b,36,37]. The methylidene bridged cyclopentadienyl and fluorenyl zirconocene catalysts $(CH_2)(C_5H_4)(Flu)MCl_2$ (M = Zr, Hf) show higher activities for propylene polymerization than the Me_2C bridged analogues and produce higher syndiotactic PP [38]. Introduction of bulky phenyl groups at the bridging carbon generally increases the activity for ethylene homo- and co-polymerization [39], but decreases the activity for propylene polymerization [2c,8b,40a]. However, in some cases, bulky phenyl or cyclohexyl groups at the bridging carbon increase the catalyst performance [2b,40b]. For the series of unsubstituted *ansa*-(C_5H_4)(Flu) zirconocene catalysts, the single carbon bridged zirconocene catalysts give the best performance. Syndiotacticity decreases in the order $Me_2C > Ph_2C > PhP \sim CH_2CH_2 > Ph_2Si > Me_2Si$, while molecular weights decrease in the order $Ph_2C > PhP > CH_2CH_2 > Me_2C \sim Me_2Si > Ph_2Si$ [2c].

The unsymmetrical single carbon bridged cyclopentadienyl and indenyl metallocene catalysts usually show low activities for ethylene and propylene polymerization [4d,6,23,41]. The cyclohexylidene bridged cyclopentadienyl and indenyl zirconocene catalyst is more active for ethylene polymerization than the Me_2C bridged analogue [42]. However, introduction of bulky *tert*-butyl groups to both the cyclopentadienyl and indenyl rings leads to very active and highly isospecific catalysts (% mm >99) [16a]. When a Me_2C bridge links cyclopentadienyl and indenyl groups at 2-position, the zirconocene catalyst is shown to be active to produce PE with low molecular weight and propylene oligomers [43].

The C_2-symmetric single carbon bridged bis(indenyl) zirconocene catalysts usually show low activities for ethylene and propylene polymerization and produce PE and PP with low molecular weight. The Me_2C bridged bis(tetrahydroindenyl) zirconocene catalyst shows lower activity but affords higher isotactic PP than the bis(indenyl) analogue [5h]. But after introduction of a *tert*-butyl group on the 3-position of the indenyl ring, the activity and isotacticity for propylene polymerization are much improved [22,30]. The *rac*-$(Me_2C)(3\text{-}t\text{Bu-indenyl})_2ZrCl_2$ produces *i*-PP with high isotacticity (*mmmm* ca. 95% at 50 °C). Interestingly, the *meso*-$(Me_2C)(3\text{-}t\text{Bu-indenyl})_2ZrCl_2$ is inactive for propylene polymerization. *Rac*-$(CH_2)(3\text{-}t\text{Bu-indenyl})_2ZrCl_2$/MAO produces *i*-PP with melting point and molecular weight similar to those of *i*-PP from *rac*-$(Me_2Si)(2,3,5\text{-}Me_3C_5H)_2ZrCl_2$ and *rac*-$(Me_2Si)(2\text{–}Me\text{-}4\text{-}Ph\text{-indenyl})_2ZrCl_2$, remains the chiral zirconocene catalyst with the highest performance, in terms of activity and *i*-PP stereoregularity and molecular weight, but has lower regiospecificity. The high performance of this kind of catalysts is not only a feature related to the bulky *tert*-butyl group on the 3-position but is also due to the short single carbon bridge, which imparts to the molecule a high rigidity and a much larger bite angle than other *ansa*-zirconocene catalysts (Table 2). If any of these features are missing, a silicon or ethylidene bridge instead of single carbon bridge, or a trimethylsilyl group instead of the *tert*-butyl group, a decrease in catalyst performance is observed. The single carbon bridged bis(fluorenyl) metallocene catalysts $(n\text{BuCH})(\text{Flu})_2MCl_2$ (M = Zr, Hf) show lower activities for ethylene polymerization and ethylene/1-hexene co-polymerization than the two carbons bridged analogues [2b,44,45].

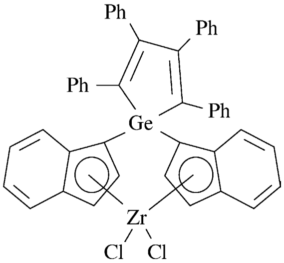
Table 2
Selected geometrical parameters (°) of single carbon and silicon bridged indenyl or fluorenyl *ansa*-metallocene complexes

Complex	ϕ	α	β	Ref.
Rac-$(CH_2)(Ind)_2ZrCl_2$	101.4(2)	117.4	72.4	[30,46]
Rac-$(CH_2)(3\text{-}t\text{Bu-indenyl})_2ZrCl_2$	102.2(2)	117.6	76.4	[22b]
Rac-$(MeCH)(C_5Me_4)(Ind)ZrCl_2$		118.2	71.5	[33d]
$Me_2C(C_5H_4)(Ind)ZrCl_2$	99.2(2)	117.1	71.6	[41]
$Me_2C(C_5H_4)(Flu)ZrCl_2$	99.4	118.6	72.0	[8a]
$Me_2C(3\text{-}t\text{BuC}_5H_3)(Flu)ZrCl_2$	99.4	118.4	74.0	[37]
$Me_2C(3\text{-}Me_3SiC_5H_3)(Flu)ZrCl_2$	98.3(3)	118.0	73.5	[36b]
Rac-$Me_2C(Ind)_2ZrCl_2$	100.3(3)	118.2	70.9	[47]
meso-$Me_2C(Ind)_2ZrCl_2$	100.1(3)	118.1	71.6	[47]
Rac-$Me_2C(3\text{-}t\text{Bu-indenyl})_2ZrCl_2$	100.1(5)	118.3	75.2	[22a]
Rac-$Me_2C(3\text{-}Me_3Si\text{-indenyl})_2ZrCl_2$	99.4(2)	117.4	72.6	[22a]
$Ph_2C(C_5H_4)(Flu)ZrCl_2$	99.1	117.6	72.8	[40a]
$Me_2Si(C_5H_4)(Ind)ZrCl_2$	93.8(2)	126.9		[41]
$Me_2Si(C_5H_4)(Flu)ZrCl_2$	93.4	127.9		[25]
Rac-$Me_2Si(Ind)_2ZrCl_2$	94.6(1)	127.8	61.9	[5a,30]
Rac-$Me_2Si(IndH_4)_2ZrCl_2$	94.3 (2)	126.4		[48]
Rac-$(CH_2)_4Si(Ind)_2ZrCl_2$	95.2(2)	127.6		[27c]
meso-$(CH_2)_4Si(Ind)_2ZrCl_2$	95.4(1)	127.7		[27c]
Rac-$(CH_2)_4Si(IndH_4)_2ZrCl_2$	94.2(2)	126.5		[27c]
$Ph_2Si(C_5H_4)(Flu)ZrCl_2$	95.5	129.3		[25]
Rac-$(CH_2)(Ind)_2HfCl_2$	101.8(6)	118.0	71.2	[46]
Rac-$(CH_2)(3\text{-}t\text{Bu-indenyl})_2HfCl_2$	102.5(6)	118.4	74.2	[22b]
$Me_2C(C_5H_4)(Flu)HfCl_2$	101.0	119.4	70.0	[8a,29a]
$Me_2C(3\text{-}Me_3SiC_5H_3)(Flu)HfCl_2$	98.9(3)	118.7	72.1	[36b]
$Ph_2C(C_5H_4)(Flu)HfCl_2$	99.6	118.2	72.8	[40a]
$Ph_2Si(C_5H_4)(Flu)HfCl_2$	96.3(6)	129.8		[18e]

The racemic ethylidene bridged tetramethylcyclopentadienyl and indenyl titanocene catalyst $(MeCH)(C_5Me_4)(Ind)TiCl_2$ catalyzes propylene polymerization to crystalline–amorphous block thermoplastic elastomer with activity of 2.5×10^5 g PP/(mol Ti h atm). In contrast, the zirconium analogue shows unusual lower activity for ethylene and propylene polymerization. The PE produced has bimodal distributions, indicating two or more active species [33]. This can also be attributed to the unmatchable dimension of the small carbon atom bridge with the co-ordination requirement of the large zirconium atom.

2.3. Single germanium, tin and phosphorus bridged metallocene catalysts

There are only a few of examples for the germanium bridged metallocene catalysts [15,31,49]. The dimethylgermylene bridged zirconocene catalysts show higher activities for ethylene and propylene polymerization than their titanocene and hafnocene analogues. The activities for ethylene polymerization are comparable with the Me_2Si bridged analogues and Cp_2ZrCl_2, but the activities for propylene polymerization are markedly lower than those recorded for Cp_2ZrCl_2. One feature of the dimethylgermylene bridged zirconocene catalysts is their high thermal stability. Most of them show the highest activity at higher temperature. With racemic dimethylgermylene bridged indenyl and 2-methylindenyl zirconocene catalysts *i*-PPs with [*mmmm*] = 81 and 84% are obtained [49b]. Racemic $Me_2Ge(2,3,5\text{-}MeC_5H)_2ZrCl_2$ shows slightly higher activity for 1-hexene polymerization than the corresponding Me_2Si bridged analogue both under high pressure and atmospheric pressure, and produces highly isotactic polyhexene [49d]. Highly isotactic polyhexene ([*mmmm*] = 91.6%) with very high molecular weight ($M_w = 2360{,}000$) is achieved by the hafnocene analogue [49d]. $Me_2Ge(C_5Me_4)_2HfCl_2$ shows four times higher activity for 1-hexene polymerization than the corresponding Me_2Si bridged analogue under high pressure [49f]. The diphenylgermylene bridged zirconocene catalyst $Ph_2Ge(C_5H_4)(Flu)ZrCl_2$ shows much low activity for propylene polymerization than the silicon or carbon bridged analogues [25]. The zirconocenium ion of *rac*-(1,2,3,4-tetraphenyl-1,3-butadiene-1,4-diyl) germylene bridged bis(1-indenyl) zirconium dichlorides (Scheme 8) shows a propylene polymerization activity of about 10^7 g PP/(mol Zr h), which is independent of polymerization temperature over a broad temperature range (−60 to 25 °C) [49f]. The structures of the germanium bridged metallocene complexes are similar to those of the silicon bridged analogues but with slightly decreased dihedral angles due to the larger atom radius of germanium than silicon. This, in general, slightly decreases the activity and stereoselectivity. The tin bridged metallocene $Me_2Sn(C_5H_4)_2Zr(NMe_2)_2$ and the binuclear complex $(Me_2N)_2Zr(C_5H_4)_2Sn(C_5H_4)_2Zr(NMe_2)_2$ have been prepared by reaction of Me_2SnCp_2 or Cp_4Sn with $Zr(NMe_2)_4$



Scheme 8. Germanium bridged metallocene complexes.

[50a]. The mononuclear tin bridged metallocene catalyst is considerably more active than its Me_2Si bridged counterpart in ethylene polymerization. The R_2Sn bridged (R = Me, Ph) bis(4-methylfluorenyl) zirconium complexes have also been prepared and applied for propylene polymerisation [50b]. The larger the bridging atom the less the stereospecifity of the formed polypropylene is observed.

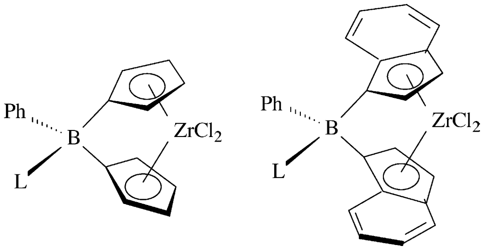
The examples of phosphorus bridged metallocene catalysts are also not very much [24]. *Rac*-PhP(Ind)$_2$ZrCl$_2$ shows activity of 24 kg/g Zr h at 67 °C for propylene polymerization and produces low molecular weight, weakly *i*-PP, while PhP(2-Me-4-Ph-indenyl)$_2$ZrCl$_2$ (R = Ph, *i*Pr) produces highly isotactic PP with higher activity (111–576 kg/g Zr h). When the PhP bridge is replaced by *i*PrP, the activity is ca. three to five times higher. Highly syndiotactic PP can be obtained with PhP(Flu)(C$_5$H$_4$)ZrCl$_2$. Its activity is lower than the Me_2C bridged analogue, but much higher than the Me_2Si bridged analogue. However, PhP(Flu)$_2$ZrCl$_2$ shows much lower activity for ethylene and propylene polymerization than the Me_2Si bridged analogue. The activity for ethylene polymerization of PhP(C$_5$Me$_4$)$_2$ZrCl$_2$ is comparable to that for Me$_2$Si(C$_5$Me$_4$)$_2$ZrCl$_2$, but less than that for (C$_5$Me$_5$)$_2$ZrCl$_2$. The chalcogenido derivatives Ph(E)P(C$_5$Me$_4$)$_2$ZrCl$_2$ (E = O, S, Se) exhibit similar activities. The phosphorus atom has a covalent radius of 1.06 Å and is slightly smaller than the silicon atom (1.11 Å). So, the phosphorus bridged metallocene complexes have larger dihedral angles than the corresponding Me_2Si bridged metallocene complexes (Table 3), and should have larger reaction space for the metal center. However, the electron-donating capability of the –PR-moiety may impact the effect of the bridge.

2.4. Boron bridged metallocene catalysts

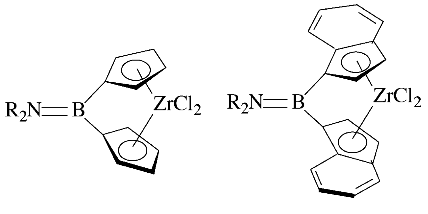
Boron bridged metallocene catalysts have recently attracted significant interest due to the Lewis-acidic character of the boron bridge [51]. Examples of boron bridged metallocene catalyst include the donor-co-ordinated *ansa*-metallocene catalysts Ph(L)BCp$'_2$ZrCl$_2$ (Cp$'$ = C$_5$H$_4$, Ind; L = SMe$_2$, OEt$_2$, PMe$_3$) (Scheme 9) [51cd]. The nature of the donor ligand L determines the activity and stereoselectivity of the catalytic system. The strong donor ligand PMe$_3$ provides high activity, and high stereoselectivity for propylene polymerization. For example, the PMe$_3$ adduct Ph(PMe$_3$)BInd$_2$ZrCl$_2$ displays high activity and stereoselectivity, which competes well with other *ansa*-metallocene catalysts, especially with respect to isotacticity and molecular weight. In contrast, the weak donor SMe$_2$ adduct is completely inactive under the same reaction conditions. The second kind of boron bridged metallocene catalysts is the aminoboranediyl bridged metallocene catalysts R$_2$NBCp$'_2$MCl$_2$ (Cp$'$ = C$_5$H$_4$, Ind, Flu; R = Me, *i*Pr, SiMe$_3$) (Scheme 10) [51e–h].

Table 3
Selected geometrical parameters (°) of germanium, phosphorus and boron bridged metallocene complexes

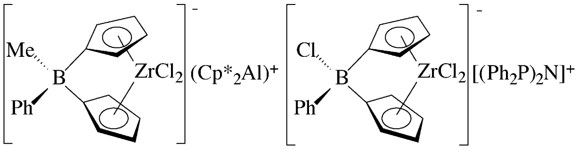
Complex	ϕ	α	β	Ref.
Me$_2$Ge(C$_5$Me$_4$)$_2$TiCl$_2$	89.7(2)		57.9	[49a]
PhP(C$_5$Me$_4$)$_2$TiCl$_2$	90.07(11)	129.4	61.6	[24c]
(Me$_3$Si)$_2$NB(C$_5$H$_4$)$_2$TiCl$_2$	98.3(6)	118.0	61.8	[51g]
MeP(C$_5$H$_4$)$_2$ZrCl$_2$	89.77(11)	122.2		[24d]
Me$_2$Ge(C$_5$H$_4$)(C$_5$Me$_4$)ZrCl$_2$	92.0(3)		57.8	[31]
	90.9(5)	129.9		[49c]
Me$_2$Ge(C$_5$Me$_4$)$_2$ZrCl$_2$	93.0(3)		59.3	[49a]
	92.7(3)	129.4		[49c]
MeP(C$_5$Me$_4$)$_2$ZrCl$_2$	93.43(13)	125.8	64.0	[24c]
PhP(C$_5$Me$_4$)$_2$ZrCl$_2$	93.6(3)	125.9	63.5	[24c]
Ph(S)P(C$_5$Me$_4$)$_2$ZrCl$_2$	96.1(3)	126.3	64.0	[24c]
Ph(Se)P(C$_5$Me$_4$)$_2$ZrCl$_2$	95.81(10)	126.3	64.5	[24c]
Ph(SMe$_2$)B(C$_5$H$_4$)$_2$ZrCl$_2$	101.1(2)	121.3	65.9	[51c]
Ph(PMe$_3$)B(C$_5$H$_4$)$_2$ZrCl$_2$	100.1(3)	121.1	68.5	[51c]
Me$_2$NB(C$_5$H$_4$)$_2$ZrCl$_2$	105.9(3)	120.8		[51f]
(*i*Pr)$_2$NB(C$_5$H$_4$)$_2$ZrCl$_2$	103.9(3)	119.6	65.5	[51e]
Ph(THF)B(Ind)$_2$ZrCl$_2$	101.5(2)	122.3	67.2	[51d]
Ph(PMe$_3$)B(Ind)$_2$ZrCl$_2$	99.4(2)	121.5	66.7	[51d]
(*i*Pr)$_2$NB(Ind)$_2$ZrCl$_2$	104.9(1)	121.6	66.8	[51e]
[Ph(Me)B(C$_5$H$_4$)$_2$ZrCl$_2$]$^-$	97.2(4)	120.5	65.2	[51i]
[Ph(Cl)B(C$_5$H$_4$)$_2$ZrCl$_2$]$^-$	99.4(4)	120.9	65.9	[51i]
(*i*Pr)$_2$NB(C$_5$H$_4$)(Flu)ZrCl$_2$	104.7(2)	122.2	68.1	[51h]
[Ph(Ph$_3$P$^+$CH$_2$)B$^-$]-(C$_5$H$_4$)$_2$ZrCl$_2$	97.1(4)	120.2	66.0	[51j]
Rac-[Ph(Ph$_3$P$^+$CH$_2$)B$^-$]-(2-Me-4-Ph-indenyl)$_2$ZrCl$_2$	97.6(3)	123.2	65.7	[51j]
meso-[Ph(Ph$_3$P$^+$CH$_2$)B$^-$]-(2-Me-4-Ph-indenyl)$_2$ZrCl$_2$	98.2(4)	123.2	68.3	[51j]



Scheme 9. Donor-co-ordinated boron bridged metallocene complexes.



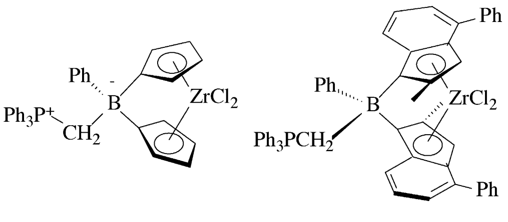
Scheme 10. Aminoboranediyl bridged metallocene complexes.



Scheme 11. Ionic boron bridged metallocene complexes.

The indenyl complex $(iPr)_2NB(Ind)_2ZrCl_2$ shows much higher activity both for ethylene and propylene polymerization than the cyclopentadienyl analogue, which is in the range shown by $Me_2Si(Ind)_2ZrCl_2$. The titanium complex $(Me_3Si)_2NB(Ind)_2TiCl_2$ also shows comparable activity with the zirconocene analogue for ethylene polymerization. The ethylene polymerization activity of $(iPr)_2NB(C_5H_4)(Flu)ZrCl_2$ is comparable with the Me_2Si bridged analogue. It also shows high activity for the co-polymerization of ethylene and 1-octene with the incorporation of 5.7 mol% of 1-octene and moderate activity for propylene polymerization. Modest isotactic PP (82–86 mm%) and syndiotactic PP (81 rr%) are obtained with this kind of C_2 symmetrical bis(indenyl) zirconocene and C_s symmetrical cyclopentadienyl and fluorenyl zirconocene catalysts, respectively. The third kind of boron bridged metallocene catalyst is the ionic or zwitterionic boron bridged metallocene catalyst (Schemes 11 and 12) [51i,j]. The ionic complexes $[Ph(Me)B(C_5H_4)_2ZrCl_2]^-[(C_5Me_5)_2Al]^+$ and $[Ph(Cl)B(C_5H_4)_2ZrCl_2]^-[(Ph_2P)_2N]^+$ show lower activity for ethylene polymerization than $Ph(PMe_3)B(C_5H_4)_2ZrCl_2$. However, the zwitterionic complex $[Ph(Ph_3P^+CH_2)B^-](C_5H_4)_2ZrCl_2$ exhibits remarkable ethylene (in the presence of 1-octene) polymerization activity (6836 kg PE/gZr), which is more than an order of magnitude greater than that of a related aminoborane-bridged system, Cp_2ZrCl_2 and the commercially successful metallocene catalyst $[(C_5Me_4)SiMe_2N(tBu)]TiCl_2$. Its propylene polymerization efficiency is also comparable with other boron and silicon bridged metallocene catalysts. The propylene polymerization activity of the mixture of racemic and *meso*-$[Ph(Ph_3P^+CH_2)B^-](2\text{-Me-4-Ph-indenyl})_2ZrCl_2$ is greater than that of a related Me_2Si bridged system at 70 and 85 °C, but decreased with further increase in temperature.

The structural parameters in Table 3 show that the boron bridged metallocene complexes are more distorted from a relaxed metallocene geometry than the silicon bridged metallocene complexes but less distorted than the carbon bridged metallocene complexes. The advantages of a boron bridge are its small size and the consequential high rigidity of the ligand framework, as well as its Lewis-acidic character. The enlarged reaction space than that of silicon bridged metallocene catalysts, higher stability than the carbon bridged zirconocene catalysts and the high stereoselectivity in propylene polymerization make the boron bridged metallocene catalysts became a new potential *ansa*-metallocene polymerization catalysts.

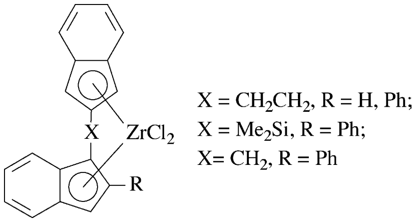


Scheme 12. Zwitterionic boron bridged metallocene complexes.

3. Two atoms bridged metallocene catalysts

3.1. Ethylidene bridged metallocene catalysts

Ethylidene bridged metallocene catalysts, the first *ansa*-metallocene catalysts to produce *i*-PP [4], is also one of the most studied *ansa*-metallocene catalysts. The smaller rigidity of the ethylidene bridge than Me_2Si or Me_2C bridge generally results in less isotacticity than the Me_2Si bridged analogues and less syndiotacticity than the Me_2C bridged analogues for propylene polymerization. However, the better co-polymerization ability than other metallocene catalysts makes the ethylidene bridged metallocene catalysts extensively studied [2,52]. *Rac*-$(C_2H_4)(Ind)_2ZrCl_2$ and *rac*-$(C_2H_4)(IndH_4)_2ZrCl_2$ afford not only *i*PP, but also has a polymerization activity two to three times greater than the unbridged catalysts that form only atactic PP [4b]. They also exhibit high activities for ethylene/propylene co-polymerization and produce co-polymer having co-monomer compositions about the same as the feed composition, due to the lower rates (ca. 10:1) of polymerization of ethylene:propylene than that with Cp_2ZrCl_2 [53]. The *meso* isomers show lower activities for propylene polymerization and produce only atactic polymer [54]. The racemic ethylidene bridged bis(3-alkylcyclopentadienyl) zirconocene catalysts exhibit somewhat lower activities, but the isotacticity of the PP produced is higher than those with the indenyl and tetrahydroindenyl analogues [54]. The racemic ethylidene bridged bis(indenyl) and bis(tetrahydroindenyl) hafnocene catalysts show similar activities for propylene polymerization but produce much higher molecular weight *i*-PP [4c]. It is remarkable that *rac*-$(C_2H_4)(Ind)_2HfCl_2$ is much more able to incorporate the co-monomer than the zirconium analogue [55]. The ethylidene bridged bis(fluorenyl) zirconocene catalyst $(C_2H_4)(Flu)_2ZrCl_2$ shows very high activity for ethylene and propylene polymerization and produces high molecular weight amorphous PP [13a,56], probably due to the enlarged dihedral angle (64.3°). The activity for ethylene polymerization is higher than that of the single carbon bridged analogue [44] but is still lower than that of the Me_2Si bridged analogue at lower Al/Zr molar ratio (Al/Zr = 2000) [13b]. With huge excess of MAO (Al/Zr = 20,000) the activity is much improved and much higher than that of the Me_2Si bridged analogue and other bridged zirconocene catalysts [2b,45]. A methyl substituent

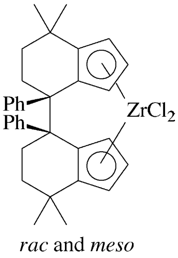


Scheme 13. 1,2′-Bridged bis(indenyl) *ansa*-metallocene complexes.

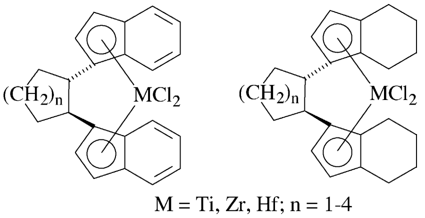
at position 4 or 5 of the fluorenyl fragment dramatically increases the catalytic activity of these *ansa*-metallocene catalysts [2b] by an order of magnitude. The unsymmetrical ethylidene bridged fluorenyl and indenyl metallocene catalysts, with proper substitution at the indenyl ligand, can produce high *i*-PP or ultrahigh molecular weight PP elastomer with high activities [57].

Bridging the 1,2′-positions of indenyl groups (Scheme 13), the isotacticities of the PP decrease significantly. The 1,2′-ethylidene bridged zirconocene catalyst shows lower activity for propylene polymerization than the Me_2Si and Me_2C bridged analogues, but produces PP with higher isotacticity and molecular weight than the latters [58]. When the ethylidene bridge is between the 2,2′-positions or 4,4′-positions of indenyl groups (Scheme 14), the catalysts show very high activities for ethylene polymerization, ethylene/α-olefin co-polymerization with highly preferential sequential ethylene incorporation, but low activities for propylene polymerization with producing low molecular weight, atactic or low isotactic PP [59].

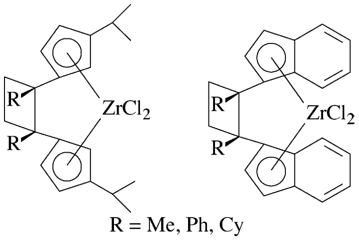
3.2. Other two carbons bridged metallocene catalysts



Scheme 15. Ligand joining bridged metallocene complex.

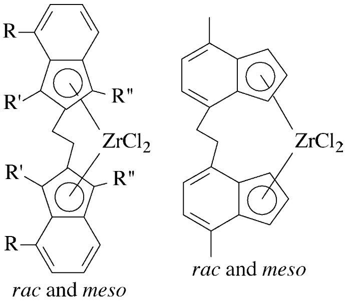


Scheme 16. *Trans*-1,2-cycloalkylene bridged metallocene complexes.

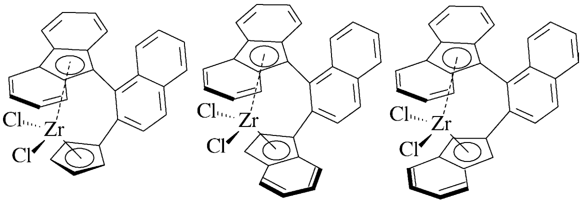


Scheme 17. Cyclobutylidene bridged metallocene complexes.

Substitution on the ethylidene bridge generally results the decrease of activity [14b,60]. The CH(Ph)CH_2 bridged bis(fluorenyl) zirconocene catalyst gives *i*PP with low isotacticity, low molecular weight and low activity, in contrast to $(C_2H_4)(Flu)_2ZrCl_2$, which produces high molecular weight atactic PP with very high activity [60b]. The bridged zirconocene catalyst in which the bridge is part of an η-fused bis(tetrahydroindenyl) ligand (Scheme 15) shows only a modest activity and a moderate isotacticity [61]. The *rac-trans*-1,2-cycloalkylene bridged bis(indenyl) and bis(tetrahydroindenyl) metallocene catalysts (Scheme 16) show lower activities for isospecific propylene polymerization than the acyclic two carbon atoms bridged analogues, but the *meso* isomers are virtually inactive, attributed to steric crowding of the active sites [62]. The novel *cis*-cyclobutylidene bridged zirconocene catalysts (Scheme 17), synthesized by intramolecular photochemical [2 + 2] cycloaddition of bis(2-alkenylcyclopentadienyl and indenyl) zirconium complexes [63], catalyze ethylene/1-octene co-polymerization with high activity and high 1-octene incorporation, which are comparable with those of “constrained geometry” catalysts. The 1,2-naphthylidene bridged indenyl zirconocene catalysts (Scheme 18) show higher activities for ethylene polymerization than the catalyst containing the cyclopentadienyl ligand, but the latter shows much higher activities for propylene polymerization than the previous one [64].



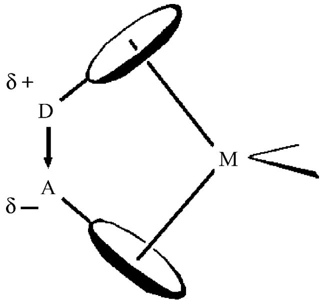
Scheme 14. 2,2′ or 4,4′-Ethylidene bridged metallocene complexes.



Scheme 18. 1,2-Naphthylidene bridged metallocene complexes.

3.3. Other two atoms bridged metallocene catalysts

The tetramethyldisilylene bridged metallocene catalysts show high activity for ethylene polymerization [65]. However, both the activity for propylene polymerization and the isotacticity of PP produced with racemic tetramethyldisilylene bridged bis(indenyl) and bis(tetrahydroindenyl) zirconocene catalysts, are much lower than that of the Me_2Si bridged analogue [1b,15,65,66], due to the bulky steric effect of the tetramethyldisilylene bridge. The co-polymerization of ethylene and 1-hexene is also achieved with this kind of catalysts with low activities [67]. The tetramethyldisilylene bridged bis(fluorenyl) zirconocene catalyst shows much lower activity for ethylene polymerization than the ethylidene bridged analogue [2b,45]. The Me_2SiCH_2 bridged bis(cyclopentadienyl) zirconocene catalyst shows comparable activity for ethylene polymerization with the Me_2Si bridged analogue [68]. At high Al/Zr molar ratio (Al/Zr = 2000) the activity of the Me_2SiCH_2 bridged bis(fluorenyl) zirconocene catalyst is much higher than the tetramethyldisilylene, single silicon and carbon bridged analogues, but still lower than the ethylidene bridged analogue [2b,45]. The Me_2SiCH_2 bridged bis(octahydrofluorenyl) zirconocene catalyst shows low activity for ethylene polymerization due to the bulky steric effect [69]. A kind of very important two atom bridged metallocene catalysts is the donor/acceptor (D/A) metallocene catalyst (Scheme 19) [70]. The characteristic feature is the incorporation of donor (e.g. O, N, P) and acceptor (e.g. B, Al) atoms into sandwich structures, resulting in highly polarized bonding interactions, which specifically restrict the rotation of the π-ligands and widen the aperture angle. The reverse process, which eliminates the dipolar interaction, shrinks the aperture angle and favors ring rotation. The actual state the system is in is temperature dependent and can be selected. The temperature dependant existence and co-existence of two stable forms (bridged/unbridged) of the same compound establishes a new dimension in catalyst design. Due to the high activity and the excellent capability of D/A-bridged metallocene catalyst to incorporate co-monomers, linear high melting high density polyethylene and PE with any desired amount of short chain branches along the main chain can be produced. Isotactic PP with high to very high molecular weights, high molecular weight essentially atactic PP with enhanced isotactic or syndiotactic contents can also be synthesized using the D/A approach.



Scheme 19. Donor/acceptor *ansa*-metallocene complexes [70b].

4. Three atoms or long bridged metallocene catalysts

4.1. Disiloxane bridged metallocene catalysts

Disiloxane bridged metallocene catalysts are among the most studied long bridged metallocene catalysts. The disiloxane bridged bis(cyclopentadienyl) zirconocene catalyst $(Me_2SiOSiMe_2)(C_5H_4)_2ZrCl_2$ shows higher activity for ethylene polymerization than the ethylidene or Me_2Si bridged analogues [68,77]. The disiloxane bridged bis(indenyl) and bis(tetrahydroindenyl) zirconocene catalysts $(Me_2SiOSiMe_2)(Ind)_2ZrCl_2$ and $(Me_2SiOSiMe_2)(IndH_4)_2ZrCl_2$, both racemic and *meso* isomers, show much higher activity for ethylene polymerization even than many single atom bridged metallocene catalysts [1d,6b]. The molecular weight of PE produced with *rac*-$(Me_2SiOSiMe_2)(Ind)_2ZrCl_2$ is much higher than those with the *meso* isomer and the tetrahydroindenyl analogues, and also significantly dependent on polymerization temperature [78,79]. Interestingly, the racemic isomers of the disiloxane bridged bis(indenyl) and bis(tetrahydroindenyl) zirconocene catalysts are completely inactive toward propylene [79,80], similar to another long bridged metallocene catalyst *rac*-$(Me_2SiCH_2CH_2SiMe_2)(Ind)_2ZrCl_2$ [5a], due to shielding of the metal center by the bulky bridge and by the indenyl or tetrahydroindenyl ligands. However, *meso*-$(Me_2SiOSiMe_2)(Ind)_2ZrCl_2$, which used to assign wrongly as racemic isomer, is reported to exhibit moderate activity for propylene polymerization and produce atactic polymer [81]. The unsymmetrical disiloxane bridged metallocene catalysts show slightly lower activities for ethylene polymerization due to the poor thermal stability [82]. From the structural parameters listed in Table 4 it can be seen that the dihedral angles between the two cyclopentadienyl planes in the disiloxane bridged metallocene complexes are much smaller than the single or two atoms bridged and unbridged metallocene analogues, especially for titanium complexes. Introduction of indenyl groups instead of cyclopentadienyl groups usually results the enlargement of the dihedral angles, but does not for *rac*-$(Me_2SiOSiMe_2)(Ind)_2ZrCl_2$. In the structure of *rac*-$(Me_2SiOSiMe_2)(Ind)_2ZrCl_2$ (Fig. 1)the line connecting the Zr atom with the gravity center of its two Cl atoms is no longer a C_2 axis. The $ZrCl_2$ fragment is oriented in *cis* configuration with the six-member ring of an indenyl group. The non-bonding interactions between them make the corresponding Zr–Cen distance much longer than the other one. The long disiloxane bridge also increases significantly the Zr–Cen distances than that of Cp_2ZrCl_2, and increases the reaction space and reactivity of the metal center. However, the long twisted siloxane bridge and two *trans* indenyl groups surround the metal center to

Table 4
Selected geometrical parameters (Å or °) of two atoms or long bridged metallocene complexes

Complex	M–Cen	α	β	Ref.
$(CH_2CH_2)(C_5H_4)_2TiCl_2$	2.053	128.2	53.2	[3d]
Rac-$(CH_2CH_2)(IndH_4)_2TiCl_2$	2.096	128.5		[3e,71]
$(CH_2CH_2)(2\text{-}Ind)_2TiCl_2$		128.6	43.9	[72]
$(CH_2CH_2)(2\text{-}IndH_4)_2TiCl_2$	2.097	129.5		[73]
$(CH_2)_3(C_5H_4)_2TiCl_2$	2.061	132.6	46.4	[90]
$(Me_2SiSiMe_2)(C_5H_4)_2TiCl_2$	2.066	132.6	48.3	[91]
$(Me_2SiOSiMe_2)(C_5H_4)_2TiCl_2$	2.067	132.5	48.8	[92]
Rac-$(Me_2SiOSiMe_2)(Ind)_2TiCl_2$	2.104 2.159	131.6	52.3	[93]
Rac-$(Me_2SiOSiMe_2)(IndH_4)_2TiCl_2$	2.077 2.125	133.7	51.7	[93]
$(CH_2CH_2)(C_5H_4)_2ZrCl_2$		125.8	56.4	[3a]
Rac-$(CH_2CH_2)(IndH_4)_2ZrCl_2$	2.214	125.2		[3f,71]
meso-$(CH_2CH_2)(IndH_4)_2ZrCl_2$	2.213 2.220	125.2		[54]
Rac-$(CH_2CH_2)(Ind)_2ZrCl_2$		125.3	60.4	[74]
		126.9	62.1	[30]
meso-$(CH_2CH_2)(Ind)_2ZrCl_2$		126.2		[74]
$(CH_2CH_2)(Flu)_2ZrCl_2$	2.269	129.0	64.3	[13b,56a]
$(CH_2)_3(C_5H_4)_2ZrCl_2$	2.193	129.5	50.2	[75]
$(Me_2SiSiMe_2)(C_5H_4)_2ZrCl_2$		130.9	51.2	[76]
$(Me_2SiOSiMe_2)(C_5H_4)_2ZrCl_2$	2.202 2.208	130.9	51.1	[94]
Rac-$(Me_2SiOSiMe_2)(Ind)_2ZrCl_2$	2.251 2.215	130.1	52.8	[83,95]
meso-$(Me_2SiOSiMe_2)(IndH_4)_2ZrCl_2$	2.232 2.239	131.5	57.3	[83]
Rac-$(Me_2SiOSiMe_2)(IndH_4)_2ZrBr_2$	2.247 2.220	132.2		[80]
Rac-$(CH_2CH_2)(Me_2SiInd)_2ZrCl_2$			54.0	[5a]
$(CH_2CH{=}CHCH_2)(C_5H_4)_2ZrCl_2$		130.0		[89a]
$[(CH_2)_4CH{=}CH(CH_2)_4](C_5H_4)_2ZrCl_2$	2.193 2.216	129.4		[89a]
$(CH_2)_9(C_5H_4)_2ZrCl_2$	2.194	130.6		[89b]
Rac-$(CH_2)_{12}(Ind)_2ZrCl_2$	2.245 2.241	133.7		[96]
$(Me_2SiOSiMe_2)(C_5H_4)_2HfCl_2$	2.192 2.183	131.1		[97]
$[Me_2SiN(n\text{Bu})SiMe_2](C_5H_4)_2HfCl_2$		130.8		[84]

resist the approach of a large monomer such as propylene. The surrounding is more close for the titanium analogue *rac*-$(Me_2SiOSiMe_2)(Ind)_2TiCl_2$ due to the small atom radius and short Ti–Cen distances and responsible for its poor activity even for ethylene polymerization. In contrast, the surrounding in *meso*-$(Me_2SiOSiMe_2)(Ind)_2ZrCl_2$ with the disiloxane bridge and two *cis* indenyl groups is not completed and it is still active for propylene polymerization. It is found that bridge with a single atom linker, for example, Me_2C or Me_2Si bridge, exerts a net electron-withdrawing effect, but with a three-carbon linker, the $CH_2CH_2CH_2$ bridge becomes electron-donating [3a]. The electronic effect of the disiloxane bridge, though is not clear, may also be an important factor for the high performance of the disiloxane bridged metallocene catalysts.

4.2. Other long bridged metallocene catalysts

Similar to the disiloxane bridged metallocene catalysts, the Si–N–Si bridged zirconocene catalysts $[Me_2SiN(R)SiMe_2]Cp'_2ZrCl_2$ ($Cp' = C_5H_4$, R = Me, *n*Bu, $PhCH_2CH_2CH_2$, $CH_2{=}CHCH_2$; Cp′ = Ind, R = *n*Bu) also show higher activities for ethylene polymerization than Cp_2ZrCl_2 and produce PE with high molecular weight [2b,84]. The Lewis-basic nitrogen atom is deactivated by two neighboring dimethylsilyl groups and therefore

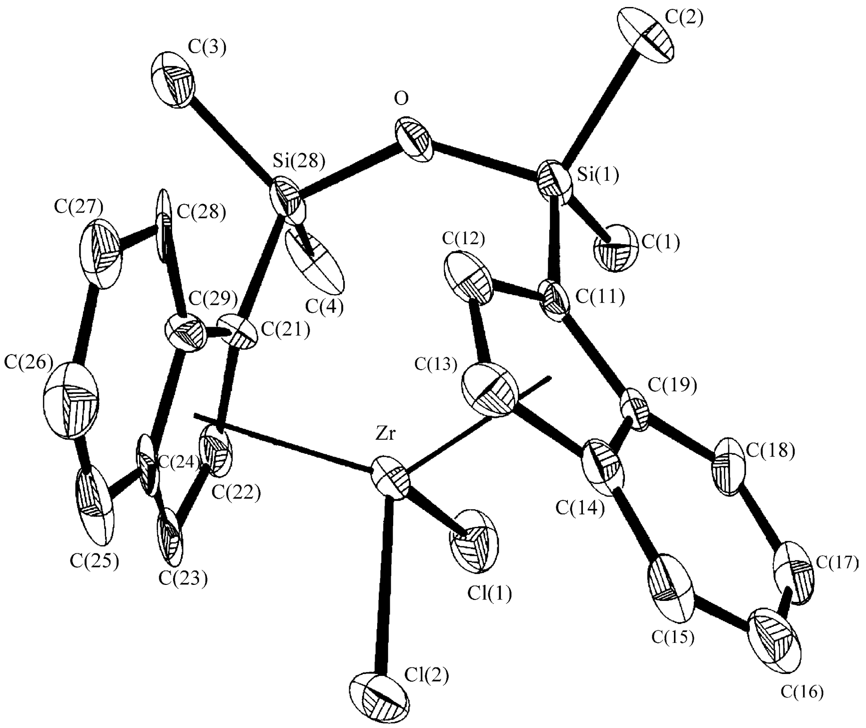
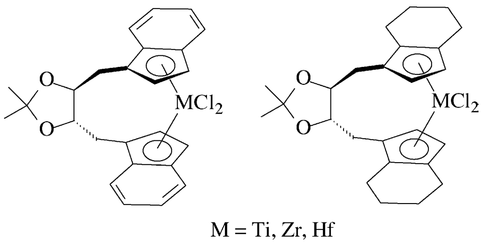
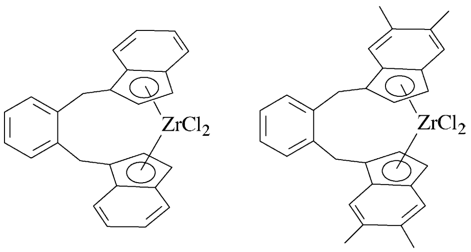


Fig. 1. The molecular structure of *rac*-($Me_2SiOSiMe_2$)$(Ind)_2ZrCl_2$ [83].

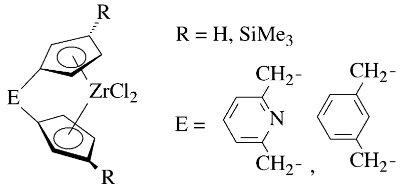
cannot interact with the cationic Lewis-acidic center of another catalyst molecule. However, introduction of a polar group $MeOCH_2CH_2$ to the nitrogen atom significantly decreases the activity. The Si–C–C–Si bridged zirconocene complex *rac*-($Me_2SiCH_2CH_2SiMe_2$)$(Ind)_2ZrCl_2$, the first ethylene-selective metallocene catalyst, shows high activity for ethylene polymerization, but is completely inactive toward propylene polymerization, due to shielding of the reaction center of the catalyst by the bulky bridge and by the indenyl ligand directed toward the $ZrCl_2$ moiety [5a]. The chiral long bridged metallocene catalysts based on the (4*S*, 5*S*)-*trans*-4, 5-bis(1H-inden-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane ligand (Scheme 20) have been synthesized and applied for olefin polymerization [85]. The indenyl and tetrahydroindenyl zirconium complexes show very high activities for ethylene polymerization and can polymerize propylene under high pressure with activities less than their ethylidene bridged counterparts to produce polymers with low stereoselectivity and optical activity. For the *o*-xylylene bridged bis(indenyl) zirconocene catalyst $[C_6H_4(CH_2\text{-}1\text{-}Ind)_2\text{-}1,2]ZrCl_2$ (Scheme 21), the *meso* isomer is more active than the racemic isomer in ethylene polymerization, but only the racemic isomer polymerizes propylene without stereoregularity due to the distortion of catalyst from the C_2 symmetry and the fluxionality of the long *o*-xylylene bridged ligand. The activities both for ethylene and propylene polymerization are lower than the ethylidene bridged analogue [86]. The long $CH_2CH_2N(Me)CH_2CH_2$, 2,6-pyridylenedimethylidene and *m*-xylylene bridged zirconocene catalysts (Scheme 22)



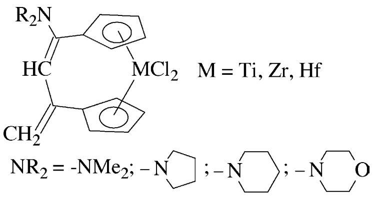
Scheme 20. Chiral long bridged metallocene complexes.



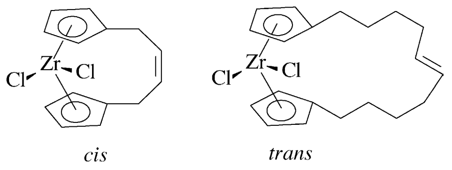
Scheme 21. *o*-Xylylene bridged metallocene complexes.



Scheme 22. 2,6-Pyridylenedimethylidene and *m*-xylylene bridged metallocene complexes.



Scheme 23. Novel rigid bridged metallocene complexes.



Scheme 24. Long unsaturated bridged metallocene complexes.

show slightly lower activities than Cp_2ZrCl_2 [87]. A kind of novel rigid *ansa*-metallocene catalysts (Scheme 23) has been synthesized by Mannich-type carbon–carbon coupling, and exhibits high activity for ethylene homo- and co-polymerization [88], with characteristics similar to those typically shown by the “constrained-geometry” catalysts. However, the activities for propylene polymerization are low and atactic PP is obtained. The long unsaturated C_4- and C_{10}-bridged zirconocene catalysts (Scheme 24) and $(CH_2)_9$ and $(CH_2)_{12}$ bridged zirconocene catalysts have similar structures and high activities for ethylene polymerization. The activities for propylene polymerization are lower and atactic PPs or propylene oligomers are obtained. The X-ray crystal structure analysis reveals the metallocene conformations where the long bridges are oriented toward the lateral sector of the bent metallocene wedge conformations in a largely unstrained fashion [89]. Complexes with chain lengths of C_{12} or longer seem to be similar to non-bridged complexes with rather open metal centers.

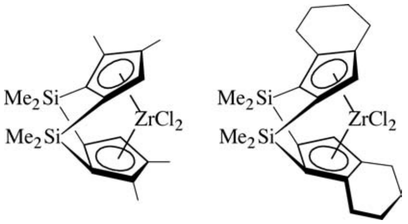
5. Doubly bridged metallocene catalysts

The doubly bridged metallocene catalysts have attracted interest due to their increased stereorigidity. However, only limited kinds of doubly bridged metallocene complexes have been prepared and only a few have been applied for olefin polymerization [1e,2a,98]. From the structural parameters listed in Table 5 it can be seen that after introduction of a second bridge, the opening of the metallocene wedge usually further increases, and is larger than the Me_2Si bridged metallocene complexes but smaller than the Me_2C bridged metallocene complexes. When substituents are introduced to the cyclopentadienyl rings, the dihedral angles between two cyclopentadienyl planes further increase and are even larger than that of the Me_2C bridged metallocene complexes. Similar to the poor stability of $Me_2C(C_5H_4)_2ZrCl_2$ [19b], decomposition of catalysts during the polymerization is observed for the doubly dimethylsilylene bridged bis(3,4-dimethylcyclopentadienyl) and bis(tetrahydroindenyl) zirconocene systems (Scheme 25), which give very low polymer yields, presumably after degradation to a single bridged species [98e]. The doubly dimethylsilylene bridged metallocene catalysts $(Me_2Si)_2(C_5H_2R)_2MCl_2$ (R = H, $SiMe_3$; M = Ti, Zr) show high activities for ethylene polymerization, but display very low activities for propylene polymerization and afford almost completely atactic PP [98h]. The exciting work concerning the doubly bridged metallocene catalysts is the new class of zirconocene catalysts for syndiospecific polymerization of propylene, developed by Bercaw and coworkers [98i–k]. The series of C_s- and C_1-symmetric doubly bridged metallocene complexes $(Me_2Si)_2(4\text{-}RC_5H_2)(3,5\text{-}i Pr_2C_5H)ZrCl_2$ (Scheme 26), when activated with MAO

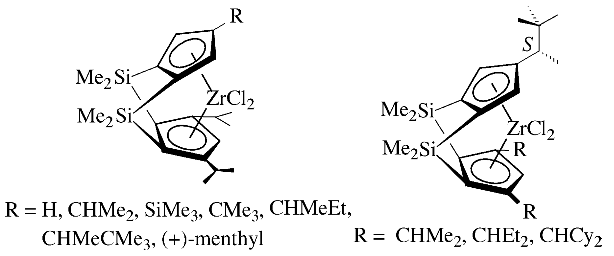
Table 5
Selected geometrical parameters (°) of doubly bridged metallocene complexes

Complex	M–Cen	α	β	Ref.
$(CH_2CH_2)_2(C_5H_3)_2TiCl_2$	2.055 2.056	124.5	57.8	[98a]
$(Me_2Si)_2(C_5H_3)_2TiCl_2$	2.068 2.072	126.0	64.4	[98d]
Rac-$(Me_2Si)_2(3\text{-}i\text{Pr-5-MeC}_5H)_2TiCl_2$	2.120	128.1	69.7	[98f]
$(CH_2CH_2)_2(C_5H_3)_2ZrCl_2$	2.187 2.192	120.0	62.5	[98ab]
$(CH_2CH_2)_2(Ind)_2ZrCl_2$[a]	2.219 2.218	120.2 120.4	24.8 28.0	[98c]
$(Me_2Si)_2(C_5H_3)_2ZrCl_2$	2.205 2.192	120.6	69.6	[98d]
Rac-$(Me_2Si)_2(3,4\text{-}Me_2C_5H)_2ZrCl_2$		121.8	72.1	[98e]
Rac-$(Me_2Si)_2(IndH_4)_2ZrCl_2$		122.5	72.9	[983]
$(Me_2SiOSiMe_2)_2(C_5H_3)_2ZrCl_2$	2.225	137.3	44.1	[98g]

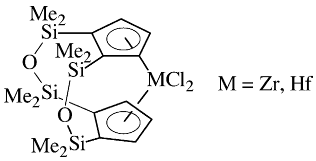
[a] Two independent molecules in a unit cell.



Scheme 25. Substituted doubly dimethylsilylene bridged metallocene complexes.



Scheme 26. Substituted doubly dimethylsilylene bridged metallocene complexes.



Scheme 27. Doubly disiloxane bridged metallocene complexes.

or borate co-catalysts, serve as high active, stereospecific catalysts for the polymerization of propylene. The activities are higher and the polymer polydispersities are general lower than those of $Ph_2C(C_5H_4)(Flu)ZrCl_2$. The C_s-symmetric catalysts (R = H, *i*Pr, $SiMe_3$, CMe_3) display high activity and syndiospecificity (>99.5%) in liquid propylene when activated with MAO. The C_1-symmetric catalysts (R = *rac*-CHMeEt, *rac*-CHMeCMe$_3$, (1*R*, 2*S*, 5*R*)-menthyl) display markedly different polymerization behavior, switching from moderately syndiospecific to isospecific when propylene concentration is decreased. By contrast, the C_{2v}-symmetric zirconocene catalyst $(Me_2Si)_2(3,5\text{-}i\text{Pr}_2C_5H)_2ZrCl_2$ displays a low activity for propylene polymerization and affords an atactic polymer [98k]. The reactivity ratios for ethylene–propylene co-polymerization are also strongly influenced by both the transition metal and the ancillary ligands [98l]. When an enantiopure methylneopentyl substituent is introduced on the “upper” cyclopentadienyl ring, the resulting optically active *ansa*-zirconocene catalysts (Scheme 26) show unprecedented activity for the polymerization of bulky racemic monomers bearing substitution at the 3- and/or 4-positions, and effect kinetic resolution of racemic monomers: the polymeric product is enriched with the faster reacting enantiomer, while recovered monomer is enriched with the slower reacting enantiomer [98m].

Introduction of two long disiloxane (Scheme 27) results in decrease rather than the additional expansion of the dihedral angle between the two cyclopentadienyl planes as shown with two short bridges [98g]. However, the increase of M–Cen distance may redeem the decrease of the dihedral angle and makes it still keep larger reaction space for the metal center. So, the doubly disiloxane bridged zirconocene catalyst shows higher activity for ethylene polymerization even than Cp_2ZrCl_2, but slightly lower than the monodisiloxane bridged zirconocene analogue.

6. Conclusions

There are so many structural and other factors affecting the catalytic activities and polymer properties such as molecular weight and tacticity. We have to confess that we still do not understand all the details in order to be able to predict the exact properties of a newly designed metallocene catalyst. However, the trend can be confirmed. This work provides a summarized, comparative overview of the structure–activity relationship of *ansa*-metallocene catalysts, especially the effects of the bridges on the catalytic activities. The bridge has a very large influence on the reaction space of the metal centers and the stability of the catalysts by altering the molecular framework and the electronic density of the metal centers with the bridges as special substituents. Short single atom bridges open up the dihedral angle between the two π-ligand planes and decrease the ∠Cen–M–Cen angle, resulting in decreased steric hindrance of the ligand and increased activities for olefin polymerization. The electronic nature and atom radius of the bridging atom have significant effects on the geometry parameters and catalytic activities of the *ansa*-metallocene catalysts. For the bridged bis(cyclopentadienyl) metallocene catalysts, the dimension of the small carbon bridge matches up well to the co-ordination requirement of the small titanium atom, while the dimension of the large silicon bridge matches up well to the co-ordination requirement of the large zirconium atom. Both of these bridged complexes achieve the largest reaction space of the metal center while retaining the stability of the metallocene complexes, and show higher activities than the unbridged and other bridged metallocene complexes. The substituents at the bridging atom have effects on the catalytic activities, but mainly on the stability of catalysts and polymer properties. The long bridged metallocene catalysts show high activities for ethylene polymerization in many cases but are practically inactive in propylene polymerization. Introduction of a doubly bridge efficiently increases the reaction space of the metal center by increasing the dihedral angle, but is accompanied by reduced stability of the catalyst, which in turn reduces the activity. However, the doubly bridged metallocene catalysts provide a more rigid molecular framework and have been applied successfully for stereospecific propylene polymerization.

Acknowledgments

This work was supported financially by the National Natural Science Foundation of China (20202004, 20421202, and 20474031), Natural Science Foundation of Tianjin (033603411), PetroChina, SRFDP (20030055001) and Program for New Century Excellent Talents in University.

References

[1] (a) W. Kaminsky, H. Sinn (Eds.), Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Springer, Berlin, 1988;
(b) G. Fink, R. Mülhaupt, H.-H. Brintzinger (Eds.), Ziegler Catalysts, Springer–Verlag, Berlin, 1995;
(c) W. Kaminsky (Ed.), Metalorganic Catalysts for Synthesis and Polymerization, Springer–Verlag, Berlin, 1999;
(d) K. Soga, T. Shiono, Prog. Polym. Sci. 22 (1997) 1503;
(e) A. Togni, R.L. Halterman (Eds.), Metallocenes: Synthesis, Reactivity, Applications, Wiley–VCH, Weinheim, 1998;
(f) W. Kaminsky, A. Laban, Appl. Catal. A: Gen. 222 (2001) 47;
(g) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.
[2] (a) H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143;

(b) H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205;
(c) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253;
(d) G.W. Coates, Chem. Rev. 100 (2000) 1223.

[3] (a) C.E. Zachmanoglou, A. Docrat, B.M. Bridgewater, G. Parkin, C.G. Brandow, J.E. Bercaw, C.N. Jardine, M. Lyall, J.C. Green, J.B. Keister, J. Am. Chem. Soc. 124 (2002) 9525;
(b) A. Lüttringhaus, W. Kullick, Angew. Chem. 70 (1958) 438;
(c) A. Lüttringhaus, W. Kullick, Macromol. Chem. 44–46 (1961) 669;
(d) J.A. Smith, J.V. Seyerl, G. Huttner, H.-H. Brintzinger, J. Organomet. Chem. 173 (1979) 175;
(e) F. Wild, L. Zsolnai, G. Huttner, H.-H. Brintzinger, J. Organomet. Chem. 232 (1982) 233;
(f) F. Wild, M. Wasiucionek, G. Huttner, H.-H. Brintzinger, J. Organomet. Chem. 288 (1985) 63.

[4] (a) J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355;
(b) W. Kaminsky, K. Külper, H.-H. Brintzinger, F.R.W.P. Wild, Angew. Chem. Int. Ed. Engl. 204 (1985) 507;
(c) J.A. Ewen, L. Haspeslagh, J. Am. Chem. Soc. 109 (1987) 6544;
(d) M.L.H. Green, N. Ishihara, J. Chem. Soc., Dalton Trans. (1994) 657.

[5] (a) W. Hermann, J. Rohrmann, E. Herdtweck, W. Spaleck, A. Winter, Angew. Chem. Int. Ed. Engl. 28 (1989) 1511;
(b) T. Mise, S. Miya, H. Yamazaki, Chem. Lett. (1989) 1853;
(c) W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm, W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 31 (1992) 1347;
(d) W. Spaleck, F. Kuber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E.F. Paulus, Organometallics 13 (1994) 954;
(e) U. Stehling, J. Diebold, R. Kirsten, W. Röll, H.-H. Brintzinger, S. Jüngling, R. Mülhaupt, F. Langhauser, Organometallics 13 (1994) 964;
(f) M.A. Giardello, M.S. Eisen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 115 (1993) 3326;
(g) M.A. Giardello, M.S. Eisen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 12114;
(h) L. Resconi, I. Camurati, O. Sudmeijer, Top. Catal. 7 (1999) 145;
(i) P.J. Shapiro, Coord. Chem. Rev. 231 (2002) 67.

[6] (a) W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck, J. Rohrmann, Makromol. Chem. 193 (1992) 1643;
(b) W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907.

[7] (a) E. Giannetti, G. Nicoletti, R. Mazzochi, J. Polym. Sci. Polym. Chem. 23 (1985) 2117;
(b) W. Kaminsky, K. Kuiper, S. Niedoba, Makromol. Chem. Macromol. Symp. 3 (1986) 377;
(c) J.C.W. Chien, B.-P. Wang, J. Polym, J. Polym. Sci., Part A: Polym. Chem. 28 (1990) 15;
(d) A. Yano, S. Yamada, A. Akimoto, Macromol. Chem. Phys. 200 (1999) 1356.

[8] (a) A. Razavi, J. Ferrara, J. Organomet. Chem. 435 (1992) 299;
(b) A. Razavi, L. Peters, L. Nafpliotis, J. Mol. Catal. A: Chem. 115 (1997) 129.

[9] R.F. Jordan, R.E. Lapointe, N. Baenziger, G.D. Hinch, Organometallics 9 (1990) 1539.

[10] (a) K. Prout, T.S. Cameron, R.A. Forder, Acta Cryst. B30 (1974) 2290;
(b) J.Y. Corey, X.-H. Zhu, L. Brammer, N.P. Rath, Acta Cryst. C51 (1995) 565.

[11] C.S. Bajgur, W.R. Tikkanen, J.L. Petersen, Inorg. Chem. 24 (1985) 2539.

[12] A. Clearfield, D.K. Warner, C.H. Saldarriaga-Molina, R. Ropal, I. Bernal, Can. J. Chem. 53 (1975) 1622.

[13] (a) L. Resconi, R.L. Jones, E. Albizzati, I. Camurati, F. Piemontesi, F. Guglielmi, G. Balbontin, Polym. Preprint 35 (1994) 663;
(b) L. Resconi, R.L. Jones, A.L. Rheingold, G.P.A. Yap, Organometallics 15 (1996) 998.

[14] (a) H. Wiesenfeldt, A. Reinmuth, E. Barsties, K. Evertz, H.-H. Brintzinger, J. Organomet. Chem. 369 (1989) 359;
(b) W. Röll, H.-H. Brintzinger, B. Rieger, R. Zolk, Angew. Chem. Int. Ed. Engl. 29 (1990) 279.

[15] W. Spaleck, M. Antberg, V. Dolle, R. Klein, J. Rohrmann, A. Winter, New J. Chem. 14 (1990) 499.

[16] (a) S. Miyake, Y. Okumura, S. Inazawa, Macromolecules 28 (1995) 3074;
(b) G. Erker, C. Psiorz, R. Fröhlich, M. Grehl, C. Krüger, R. Noe, M. Noite, Tetrahedron 51 (1995) 4347;
(c) J.A. Ewen, A. Zambelli, P. Longo, J.M. Sullivan, Macromol. Rapid Commun. 19 (1998) 71;
(d) M.H. Lee, Y. Han, D.-H. Kim, J.-W. Hwang, Y. Do, Organometallics 22 (2003) 2790;
(e) E. Polo, S. Losio, F. Fortini, P. Locatelli, M.C. Sacchi, Macromol. Symp. 213 (2004) 89.

[17] S.-J. Kim, Y.-J. Lee, E. Kang, S.H. Kim, J. Ko, B. Lee, M. Cheong, I.-H. Suh, S.O. Kang, Organometallics 22 (2003) 3958.

[18] (a) T. Huhn, N. Suzuki, Y. Yamaguchi, T. Mise, T. Chihara, Y. Wakatsuki, Chem. Lett. (1997) 1201;
(b) H. Zhu, G.-X. Jin, N. Hu, J. Organomet. Chem. 655 (2002) 167;
(c) A. Antiñolo, M. Fajardo, S. Gómez-Ruiz, I. López-Solera, A. Otero, S. Prashar, A.M. Rodríguez, J. Organomet. Chem. 683 (2003) 11;
(d) A. Antiñolo, M. Fajardo, S. Gómez-Ruiz, I. López-Solera, A. Otero, S. Prashar, Organometallics 23 (2004) 4062;
(e) V.V. Izmer, A.Y. Agatkov, V.M. Nosova, L.G. Kuz'mina, J.A.K. Howard, I.P. Beletskaya, A.Z. Voskoboynikov, J. Chem. Soc., Dalton Trans. (2001) 1131;
(f) Y. Yamaguchi, N. Suzuki, T. Mise, Y. Wakatsuki, Organometallics 18 (1999) 996;
(g) C. Takayama, Y. Yamaguchi, T. Mise, N. Suzuki, J. Chem. Dalton Trans. Soc. (2001) 948.

[19] (a) S. Xu, X. Deng, B. Wang, X. Zhou, L. Yang, Y. Li, Y. Hu, F. Zou, Y. Li, Macromol. Rapid Commun. 22 (2001) 708;
(b) B. Wang, B. Mu, X. Deng, H. Cui, S. Xu, X. Zhou, F. Zhou, Y. Li, L. Yang, Y. Li, Y. Hu, Chem. Eur. J. 11 (2005) 669.

[20] T.J. Peckham, P. Nguyen, S.C. Bourke, Q. Wang, D.G. Harrison, P. Zoricak, C. Russell, L.M. Liable-Sands, A.L. Rheingold, A.J. Lough, I. Manners, Organometallics 20 (2001) 3035.

[21] R.M. Shaltout, J.Y. Corey, N.P. Rath, J. Organomet. Chem. 503 (1995) 205.

[22] (a) L. Resconi, F. Piemontesi, I. Camurati, O. Sudmeijer, I.E. Nifant'ev, P.V. Ivchenko, L.G. Kuz'mina, J. Am. Chem. Soc. 120 (1998) 2308;
(b) L. Resconi, D. Balboni, G. Baruzzi, C. Fiori, S. Guidotti, Organometallics 19 (2000) 420.

[23] S.C. Yoon, T.K. Han, B.W. Woo, H. Song, S.I. Woo, J.T. Park, J. Organomet. Chem. 534 (1997) 81.

[24] (a) H.G. Alt, M. Jung, J. Organomet. Chem. 568 (1998) 127;
(b) C.J. Schaverien, R. Ernst, W. Terlouw, P. Schut, O. Sudmeijer, P.H.M. Budzelaar, J. Mol. Catal. A: Chem. 128 (1998) 245;
(c) J.H. Shin, T. Hascall, G. Parkin, Organometallics 18 (1999) 6;
(d) M. Hap, T. Gilles, T. Kruck, K.-F. Tebbe, Z. Naturforsch. B54 (1999) 482.

[25] K. Patsidis, H.G. Alt, W. Milius, S.J. Palackal, J. Organomet. Chem. 509 (1996) 63.

[26] Y.-X. Chen, M.D. Rausch, J.C.W. Chien, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 2093.

[27] (a) W.-M. Tsai, J.C.W. Chien, J. Polym. Sci. Part A: Polym. Chem. 32 (1994) 149;
(b) Y.-X. Chen, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 487 (1995) 29;
(c) H.J.G. Luttikhedde, R.P. Leino, J.H. Näsman, M. Ahlgrén, T. Pakkanen, J. Organomet. Chem. 486 (1995) 193.

[28] S. Mansel, U. Rief, M.-H. Prosenc, R. Kirsten, H.-H. Brintzinger, J. Organomet. Chem. 512 (1996) 225.

[29] (a) J.A. Ewen, R.L. Jones, A. Razavi, J.D. Ferrara, J. Am. Chem. Soc. 110 (1988) 6255;
(b) T. Keii, K. Soga (Eds.), Catalytic Olefin Polymerization, Studies in Surface Science and Catalysis, Elsevier, New York, 1990.
[30] V.A. Dang, L.-C. Yu, D. Balboni, T. Dall'Occo, L. Resconi, P. Mercandelli, M. Moret, A. Sironi, Organometallics 18 (1999) 3781.
[31] G. Tian, B. Wang, X. Dai, S. Xu, X. Zhou, J. Sun, J. Organomet. Chem. 634 (2001) 145.
[32] M. Linnolahti, T.A. Pakkanen, Macromolecules 33 (2000) 9205.
[33] (a) D.T. Mallin, M.D. Rausch, G.-Y. Lin, S. Dong, J.C.W. Chien, J. Am. Chem. Soc. 112 (1990) 2030;
(b) J.C.W. Chien, G.H. Llinas, M.D. Rausch, G.-Y. Lin, H.H. Winter, J. Am. Chem. Soc. 113 (1991) 8569;
(c) J.C.W. Chien, G.H. Llinas, M.D. Rausch, G.-Y. Lin, H.H. Winter, J. Polym. Sci. Part A: Polym. Chem. 30 (1992) 2601;
(d) G.H. Llinas, R.O. Day, M.D. Rausch, J.C.W. Chien, Organometallics 12 (1993) 1283.
[34] (a) G. Erker, C. Psiorz, C. Kruger, M. Nolte, Chem. Ber. 127 (1994) 1551;
(b) C. Psiorz, G. Erker, R. Frohlich, M. Grehl, Chem. Ber. 128 (1995) 357.
[35] (a) H.G. Alt, E. Samuel, Chem. Soc. Rev. 27 (1998) 323;
(b) H.G. Alt, M. Jung, J. Organomet. Chem. 568 (1998) 87;
(c) N. Herfert, G. Fink, Makromol. Chem. 193 (1992) 1359.
[36] (a) W. Kaminsky, O. Rabe, A.-M. Schauwienold, G.U. Schupfner, J. Hanss, J. Kopf, J. Organomet. Chem. 497 (1995) 181;
(b) A. Razavi, U. Thewalt, J. Organomet. Chem. 621 (2001) 267.
[37] A. Razavi, J.L. Atwood, J. Organomet. Chem. 520 (1996) 115.
[38] H.G. Alt, R. Zenk, J. Organomet. Chem. 526 (1996) 295.
[39] (a) A. Yano, M. Sone, S. Hasegawa, M. Sato, A. Akimoto, Macromol. Chem. Phys. 200 (1999) 933;
(b) A. Yano, S. Hasegawa, T. Kaneko, M. Sone, M. Sato, A. Akimoto, Macromol. Chem. Phys. 200 (1999) 1542;
(c) A. Yano, T. Kaneko, M. Sato, A. Akimoto, Macromol. Chem. Phys. 200 (1999) 2127.
[40] (a) A. Razavi, J.L. Atwood, J. Organomet. Chem. 459 (1993) 117;
(b) H.G. Alt, R. Zenk, J. Organomet. Chem. 518 (1996) 7.
[41] W.J. Gauthier, J.F. Corrigan, N.J. Taylor, S. Collins, Macromolecules 28 (1995) 3771.
[42] L. Wang, Y. Yuan, L. Feng, Y. Wang, J. Pan, C. Ge, B. Ji, Eur. Polym. J. 36 (2000) 851.
[43] M.N. Herzog, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 654 (2002) 29.
[44] B. Peifer, M.B. Welch, H.G. Alt, J. Organomet. Chem. 544 (1997) 115.
[45] P. Schertl, H.G. Alt, J. Organomet. Chem. 545–546 (1997) 553.
[46] A.Y. Agarkov, V.V. Izmer, A.N. Riabov, L.G. Kuz'mina, J.A.K. Howard, I.P. Beletskaya, A.Z. Voskoboynikov, J. Organomet. Chem. 619 (2001) 280.
[47] A.Z. Voskoboynikov, A.Y. Agarkov, E.A. Chernyshev, I.P. Beletskaya, A.V. Churakov, L.G. Kuz'mina, J. Organomet. Chem. 530 (1997) 75.
[48] H.J.G. Luttikhedde, R.P. Leino, J.H. Näsman, M. Ahlgrén, T. Pakkanen, Acta Cryst. C51 (1995) 1488.
[49] (a) S. Xu, X. Dai, B. Wang, X. Zhou, J. Organomet. Chem. 645 (2002) 262;
(b) S. Xu, G. Tian, B. Wang, X. Zhou, B. Liang, L. Zhao, Chem. J. Chin. Univ. 23 (2002) 595;
(c) C. Alonso-Moreno, A. Antiñolo, I. López-Solera, A. Otero, S. Prashar, A.M. Rodríguez, E. Villaseñor, J. Organomet. Chem. 656 (2002) 129;
(d) Y. Yamaguchi, N. Suzuki, A. Fries, T. Mise, H. Koshino, Y. Ikegami, H. Ohmori, A. Matsumoto, J. Polym. Sci. Part A: Polym. Chem. 37 (1999) 283;
(e) Y.-X. Chen, M.D. Rausch, J.C.W. Chien, Organometallics 13 (1994) 748;
(f) N. Suzuki, Y. Masubuchi, Y. Yamaguchi, T. Kase, T.K. Miyamoto, A. Horiuchi, T. Mise, Macromolecules 33 (2000) 754.
[50] (a) W.A. Herrmann, M.J.A. Morawietz, H.-F. Herrmann, F. Küber, J. Organomet. Chem. 509 (1996) 115;
(b) K. Patsidis, H.G. Alt, S.J. Palackal, G.R. Hawley, Russ. Chem. Bull. 45 (1996) 2216.
[51] (a) P.J. Shapiro, Eur. J. Inorg. Chem. (2001) 321;
(b) H. Braunschweig, F.M. Breitling, E. Gullo, M. Kraft, J. Organomet. Chem. 680 (2003) 31;
(c) D.S. Stelck, P.J. Shapiro, N. Basickes, A.L. Rheingold, Organometallics 16 (1997) 4546;
(d) M.T. Reetz, M. Willuhn, C. Psiorz, R. Goddard, Chem. Commun. (1999) 1105;
(e) A.J. Ashe III, X. Fang, J.W. Kampf, Organometallics 18 (1999) 2288;
(f) H. Braunschweig, C. von Koblinski, M. Mamuti, U. Englert, R. Wang, Eur. J. Inorg. Chem. (1999) 1899;
(g) H. Braunschweig, C. von Koblinski, R. Wang, Eur. J. Inorg. Chem. (1999) 69;
(h) A.J. Ashe III, X. Fang, A. Hokky, J.W. Kampf, Organometallics 23 (2004) 2197;
(i) C.T. Burns, D.S. Stelck, P.J. Shapiro, A. Vij, K. Kunz, G. Kehr, T. Concolino, A.L. Rheingold, Organometallics 18 (1999) 5432;
(j) P.J. Shapiro, F. Jiang, X. Jin, B. Twamley, J.T. Patton, A.L. Rheingold, Eur. J. Inorg. Chem. (2004) 3370.
[52] (a) B.Y. Lee, Y.H. Kim, Y.C. Won, C.B. Shim, D.M. Shin, Y.K. Chung, J. Organomet. Chem. 660 (2002) 161;
(b) M.H. Lee, J.-W. Park, C.S. Hong, S.I. Woo, Y. Do, J. Organomet. Chem. 561 (1998) 37;
(c) J. Jin, T. Uozumi, T. Sano, T. Teranishi, K. Soga, T. Shiono, Macromol. Rapid Commun. 19 (1998) 337.
[53] J.C.W. Chien, D. He, J. Polym, J. Polym. Sci. Part A: Chem. 29 (1991) 1585.
[54] S. Collins, W.J. Gauthler, D.A. Holden, B.A. Kuntz, N.J. Taylor, D.G. Ward, Organometallics 10 (1991) 2061.
[55] K. Heiland, W. Kaminsky, Makromol. Chem. 193 (1992) 601.
[56] (a) H.G. Alt, W. Milius, S.J. Palackal, J. Organomet. Chem. 472 (1994) 113;
(b) Y.-X. Chen, M.D. Rausch, J.C.W. Chien, Macromolecules 28 (1995) 5399.
[57] (a) E.J. Thomas, J.C.W. Chien, M.D. Rausch, Organometallics 18 (1999) 1439;
(b) E.J. Thomas, M.D. Rausch, J.C.W. Chien, Organometallics 19 (2000) 4077;
(c) U. Dietrich, M. Hackmann, B. Rieger, M. Klinga, M. Leskelä, J. Am. Chem. Soc. 121 (1999) 4348;
(d) B. Rieger, C. Troll, J. Preuschen, Macromolecules 35 (2002) 5742;
(e) S. Deisenhofer, T. Feifel, J. Kukral, M. Klinga, M. Leskelä, B. Rieger, Organometallics 22 (2003) 3495.
[58] M. Fineze, S.E. Reybuck, R.M. Waymouth, Macromolecules 36 (2003) 9325.
[59] (a) C.J. Schaverien, R. Ernst, P. Schut, W.M. Skiff, J. Am. Chem. Soc. 120 (1998) 9945;
(b) C.J. Schaverien, R. Ernst, P. Schut, T. Dall'Occo, Organometallics 20 (2001) 3436.
[60] (a) B. Rieger, G. Jany, R. Fawzi, M. Steimann, Organometallics 13 (1994) 647;
(b) B. Rieger, Polym. Bull. 32 (1994) 41;
(c) B. Rieger, T. Repo, G. Jany, Polym. Bull. 35 (1995) 87;
(d) G. Jany, T. Repo, M. Gustafsson, M. Leskelä, M. Polamo, M. Klinga, U. Dietrich, B. Rieger, Chem. Ber. 130 (1997) 747;
(e) T. Repo, G. Jany, K. hakala, M. Klinga, M. Polamo, M. Leskelä, B. Rieger, J. Organomet. Chem. 549 (1997) 177;
(f) H.G. Alt, M. Jung, J. Organomet. Chem. 580 (1999) 1.
[61] M. Könemann, G. Erker, R. Fröhlich, S. Kotila, Organometallics 16 (1997) 2900.

[62] (a) B. Rieger, J. Organomet. Chem. 428 (1992) 33;
(b) A. Steinhorst, G. Erker, M. Grehl, R. Frohlich, J. Organomet. Chem. 542 (1997) 191.
[63] (a) G. Erker, S. Wilker, C. Krüger, R. Goddard, J. Am. Chem. Soc. 114 (1992) 10983;
(b) G. Erker, S. Wilker, C. Krüger, M. Nolte, Organometallics 12 (1993) 2140;
(c) W.-L. Nie, G. Erker, G. Kehr, R. Fröhlich, Angew. Chem. Int. Ed. 43 (2004) 310;
(d) G. Erker, G. Kehr, R. Fröhlich, J. Organomet. Chem. 689 (2004) 1402;
(e) N. Iwama, T. Kato, T. Sugano, Organometallics 23 (2004) 5813.
[64] H.G. Alt, R.W. Baker, M. Dakkak, M.A. Foulkes, M.O. Schilling, P. Turner, J. Organomet. Chem. 689 (2004) 1965.
[65] (a) G. Tian, B. Wang, S. Xu, Y. Zhang, X. Zhou, J. Organomet. Chem. 579 (1999) 24;
(b) X. Sun, B. Wang, S. Xu, X. Zhou, J. Zhao, Y. Hu, Chem. J. Chin. Univ. 21 (2000) 222;
(c) B. Wang, S. Xu, X. Zhou, L. Su, R. Feng, D. He, Chem. J. Chin. Univ. 20 (1999) 77.
[66] O. Pérez-Camacho, S.Ya. Knjazhanski, G. Cadenas, M.J. Rosales-Hoz, M.A. Leyva, J. Organomet. Chem. 585 (1999) 18.
[67] H. Wigum, K.-A. Solli, J.A. Støvneng, E. Rytter, J. Polym. Sci. Part A: Polym. Chem. 41 (2003) 1622.
[68] V.C.J. Ramos, A. Munoz-Escalona, P. Lafuente, B. Pena, J. Martinez-Salazar, Polymer 45 (2004) 2061.
[69] R. Leino, H.J.G. Luttikhedde, A. Lehtonen, C.-E. Wilen, J.H. Nasman, J. Organomet. Chem. 545–546 (1997) 219.
[70] (a) K.A. Ostoja Starzewski, W.M. Kelly, A. Stumpf, D. Freitag, Angew. Chem. Int. Ed. 38 (1999) 2439;
(b) A. Ostoja Starzewski, Macromol. Symp. 213 (2004) 47.
[71] S. Collins, B.A. Kuntz, N.J. Taylor, D.G. Ward, J. Organomet. Chem. 342 (1988) 21.
[72] S. Parkin, S.R. Hitchcock, H. Hope, M.H. Nantz, Acta Cryst. C50 (1994) 169.
[73] S.R. Hitchcock, J.J. Situ, J.A. Covel, M.M. Olmstead, M.H. Nantz, Organometallics 14 (1995) 3732.
[74] F. Piemontesi, I. Camurati, L. Resconi, D. Balboni, A. Sironi, M. Moret, R. Zeigler, N. Piccolrovazzi, Organometallics 14 (1995) 1256.
[75] C.H. Soldarriaga-Molina, A. Clearfield, I. Bernal, J. Organomet. Chem. 80 (1974) 79.
[76] K.-H. Thiele, C. Schliessburg, K. Baumeister, K. Hassler, Z. Anorg. Allg. Chem. 622 (1996) 1806.
[77] D.-H. Lee, K.-B. Yoon, E.-H. Lee, S.-K. Noh, C.-S. Lee, W.-S. Huh, Macromol. Rapid Commun. 17 (1996) 325.
[78] B. Wang, L. Su, S. Xu, R. Feng, X. Zhou, D. He, Macromol. Chem. Phys. 198 (1997) 3197.
[79] B. Liang, Y. Li, G. Xie, Macromol. Rapid Commun. 17 (1996) 193.
[80] O.W. Lofthus, C. Slebodnick, P.A. Deck, Organometallics 18 (1999) 3702.
[81] W. Song, K. Shackett, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 501 (1995) 375.
[82] S. Xu, T. Wu, H. Cui, X. Dai, B. Wang, X. Zhou, F. Zou, Y. Li, Chem. J. Chin. Univ. 23 (2002) 1891.
[83] B. Wang, S. Xu, X. Zhou, N. Hu, Chem. J. Chin. Univ. 17 (1996) 231.
[84] H.G. Alt, K. Föttinger, W. Milius, J. Organomet. Chem. 564 (1998) 109.
[85] J.A. Bandy, M.L.H. Green, I.M. Gardiner, K. Prout, J. Chem. Soc., Dalton Trans. (1991) 2207.
[86] T.K. Han, B.W. Woo, J.T. Park, Y. Do, Y.S. Ko, S.I. Woo, Macromolecules 28 (1995) 4801.
[87] K. Peng, S. Xiao, Macromol. Rapid Commun. 14 (1993) 633.
[88] S. Knüppel, G. Erker, R. Fröhlich, Angew. Chem. Int. Ed. 38 (1999) 1923.
[89] (a) D. Hüerländer, N. Kleigrewe, G. Kehr, G. Erker, R. Fröhlich, Eur. J. Inorg. Chem. (2002) 2633;
(b) T. Jödicke, F. Menges, G. Kehr, G. Erker, U. Höweler, R. Fröhlich, Eur. J. Inorg. Chem. (2001) 2097.
[90] B.R. Davis, I. Bernal, J. Organomet. Chem. 30 (1971) 75.
[91] Y. Wang, S. Xu, X. Zhou, R. Wang, X. Yao, Acta Chim. Sinica 46 (1988) 674.
[92] M.D. Curtis, J.J. D'Errico, D.N. Duffy, P.S. Epstein, L.G. Bell, Organometallics 2 (1983) 1808.
[93] X. Zhou, B. Wang, S. Xu, Chem. J. Chin. Univ. 16 (1995) 887.
[94] (a) Y. Wang, X. Zhou, H. Wang, X. Yao, Acta Chim. Sinica 49 (1991) 1107;
(b) S. Ciruelos, T. Cuenca, P. Gómez-Sal, A. Manzanero, P. Royo, Organometallics 14 (1995) 177.
[95] H. Naderer, E. Siebel, R.D. Fischer, J. Organomet. Chem. 518 (1996) 181.
[96] G. Erker, C. Mollenkopf, M. Grehl, R. Fröhlich, C. Krüger, R. Noe, M. Riedel, Organometallics 13 (1994) 1950.
[97] S. Ciruelos, A. Sebastián, T. Cuenca, P. Gómez-Sal, A. Manzanero, P. Royo, J. Organomet. Chem. 604 (2000) 103.
[98] (a) B. Dorer, M.-H. Prosenc, U. Rief, H.H. Brintzinger, Organometallics 13 (1994) 3868;
(b) K. Hafner, C. Mink, H.J. Lindner, Angew. Chem. Int. Ed. Engl. 33 (1994) 1479;
(c) R.L. Halterman, A. Tretyakov, D. Combs, J. Chang, M.A. Khan, Organometallics 16 (1997) 3333;
(d) A. Cano, T. Cuenca, P. Gómez-Sal, B. Royo, P. Royo, Organometallics 13 (1994) 1688;
(e) W. Mengele, J. Diebold, C. Troll, W. Röll, H.-H. Brintzinger, Organometallics 12 (1993) 1931;
(f) S. Miyake, L.M. Henling, J.E. Bercaw, Organometallics 17 (1998) 5528;
(g) J. Jung, S.K. Noh, D.-H. Lee, S.K. Park, H. Kim, J. Organomet. Chem. 595 (2000) 147;
(h) K. Weiss, U. Neugebauer, S. Blau, H. Lang, J. Organomet. Chem. 520 (1996) 171;
(i) T.A. Herzog, D.L. Zubris, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11988;
(j) D. Veghini, L.M. Henling, T.J. Burkhardt, J.E. Bercaw, J. Am. Chem. Soc. 121 (1999) 564;
(k) S. Miyake, J.E. Bercaw, J. Mol. Catal. A: Chem. 128 (1998) 29;
(l) P. Longo, E. Siani, S. Pragliola, G. Monaco, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 3249;
(m) C.R. Baar, C.J. Levy, E.Y.-J. Min, L.M. Henling, M.W. Day, J.E. Bercaw, J. Am. Chem. Soc. 126 (2004) 8216.