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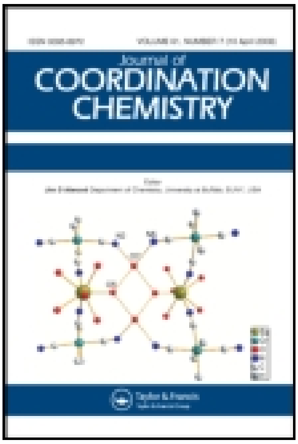

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Zirconium complexes in homogeneous ethylene polymerization

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REVIEW

Zirconium complexes in homogeneous ethylene polymerization

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This article reviews the recent progress of zirconium complexes for ethylene polymerization. Zirconium complexes are one of the most important types of catalysts for homogeneous ethylene polymerization. Polymerization behavior and polymer structure can be adjusted through the balancing of ligand structure. We surveyed the zirconium complexes synthesized from 2006 to early 2009 and summarize their comparative catalytic activities. Generally, the main factor observed is the steric bulk which on increasing reduces the catalytic activity. Electron count, electronic cloud, and inductive effect also influence the catalytic activity.

Keywords: Zirconium complexes; Homogeneous catalysis; Ethylene polymerization

1. Introduction

Olefins form polymers by addition/chain polymerization to give elastomers, fibers, and plastics. Polyolefins are huge-volume industrial materials and have varying physical and mechanical properties [1–3].

Olefins can be polymerized through three mechanisms [1]: (i) in free radical polymerization, free radical initiators are used which are thermally unstable molecules that decompose on heating or UV irradiation and produce free radicals to react with olefins to generate active centers which propagate the polymerization; (ii) in ionic polymerization, cationic or anionic reagents are used as chain initiators to produce carbonium ion or carbanion from olefins. They start propagation and form polyolefins, in some cases living polymers; (iii) in coordination polymerization, transition-metal complexes of IV-B–VIII-B are used as catalysts with alkyls of main group metals as co-catalyst for the activation of the catalyst.

Free radical mechanism gives random polymerization and produces highly branched and atactic polymers. By using coordination polymerization the tacticity of the polymer can be controlled. The polymers produced by coordination mechanism are generally isotactic and/or syndiotactic due to the regio-selectivity of the metal complexes [4]; steric bulk also plays an important role [5–10].

Coordination polymerization can be heterogeneous or homogeneous, and known as Ziegler Natta catalysis when metal chlorides are used as catalysts in

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heterogeneous phase. Soluble metal complexes are used in homogeneous olefin polymerization [11–16]. The homogeneous systems show 7–40 times more catalytic activity for polymerization as compared to heterogeneous systems [17–28]. Among the transition metals, the group IV-B metals show highest catalytic activities for olefin polymerization [29–35]. Among the group IV-B metals zirconium (Zr) is second to titanium (Ti) in catalytic activity, at temperatures of less than 50°C, for olefin polymerization [36, 37]. In some cases Zr shows better activity [38, 39]. Kaminsky *et al.* [40] have shown that for ethylene polymerization, zirconium catalyst is more active than titanium or hafnium catalysts, especially at temperatures over 50°C. This difference may be attributed to the greater number of active centers present in the Zr catalyst. Zr-based metallocenes have assumed importance. Electrodialysis, chemical trapping, XPS, surface chemical, NMR spectroscopic and theoretical studies argue indirectly that the role of the Lewis acid (AlR_3 or aluminoxane) is to promote (e.g., by alkide abstraction) the formation of unsaturated "cation-like" active centers (e.g., $[Cp_2MR]^+$). The primary reaction step for the formation of active centers is methylation of the transition metal compound by methylaluminoxane (MAO) (scheme 1). The active sites and mechanism proposed for ethylene polymerization are discussed in a review [41].

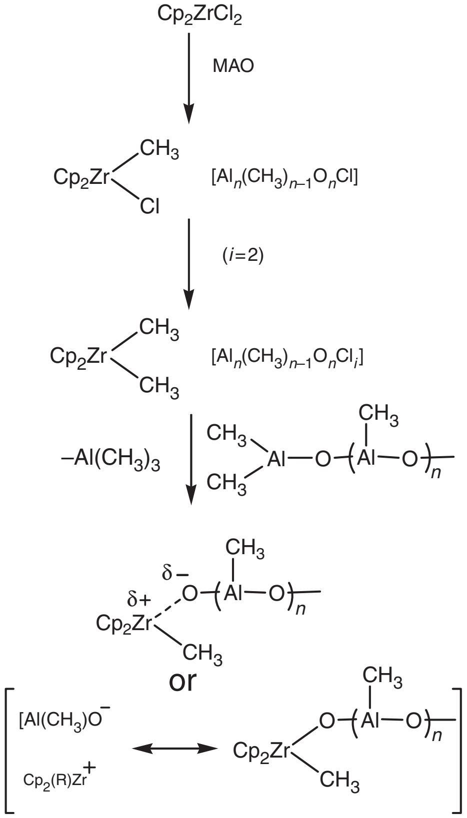
About 85–105 million tons of polyolefin (essentially homo and co-polymers of ethylene and propylene) are produced globally each year. A large number of metallocene catalysts for olefin polymerization have been prepared during the past decade. Homogeneous olefin polymerization catalysts require the action of a co-catalyst [42–45]. In the category of co-catalyst aluminum alkyls are most active co-catalyst, even in heterogeneous systems [46–49]. The majority of these catalysts consist of a zirconium complex with the general formula $LL'ZrCl_2$ activated by MAO. The structure of catalyst directly influences the catalytic activity and selectivity in olefin polymerization [50]. Metallocenes are dominant in the polymerization of olefins, showing higher activities than those without Cp ring [51].

In this review, we surveyed Zr complexes showing catalytic activity for homogeneous olefin polymerization and variation of catalytic activity in these complexes, surveying complexes synthesized from January 2006 to early period 2009 and summarizing their catalytic activities. The main factor observed in this respect is the steric bulk which on increasing reduces the catalytic activity in general [5–10, 52]. Electron count, electron distribution, and inductive effect also control the catalytic activity [53, 54].

We have focused on comparative catalytic activity tested under similar reaction conditions like ethylene pressure, kind of solvent, temperature, amount of catalysts, type of co-catalyst, etc. We have divided the Zr complexes into different categories: (1) Zr complexes containing cyclopentadienyl (Cp) and (2) Zr complexes without Cp.

2. Zirconium complexes containing Cp

Cp_2ZrCl_2 and its derivatives are excellent Ziegler–Natta catalysts having high potential in practical applications [17, 35] to produce polyolefin with defined microstructures and narrow molecular weight distributions [51]. Three challenges are foci for development of new metallocene catalysts [22, 42]: (i) increasing productivity to lower the catalyst cost, (ii) fitting catalyst systems and compositions to existing polymerization processes (gas phase, slurry or solution) by way of heterogenization (for the first two cases),



Scheme 1. Mechanism showing formation of the active center for Cp_2ZrCl_2–MAO catalyst system.

and (iii) developing a wider range of polymers and copolymers with improved physical properties (e.g., processability, mechanical, and optical properties) to control molecular weight, molecular weight distribution, and the incorporation of co-monomer and molecular polymer chain architecture. Therefore, it is necessary to modify metallocene catalysts in order to produce polyolefins with wider molecular weight distributions and avoid blending polyolefins for better performance [55].

During the review period, many catalysts containing Cp ring were reported. We summarize here their catalytic activity variation with structure; complexes having Cp ring show better catalytic activity for olefin polymerization (with few exceptions) [56–58] than those having no Cp ring. These high activities are attributed to the structures. In most cases these were two Cp rings bonded with Zr(IV), generally of formula Cp_2ZrCl_2, which on activation with co-catalyst produces 16-electron-active species (Cp_2ZrRCl). This active species promotes the coordination of olefin double bond with Zr, producing the 18-electron intermediate for polymerization that in case of non-Cp systems could not be formed. This decreases the ease of polymerization in non-Cp systems.

Besides electron count, steric bulk and electron cloud play important roles in controlling the catalytic activity. For simplicity, the complexes containing Cp ring are divided into three categories: (i) constrained geometry catalyst (CGC) system, (ii) mononuclear Cp complexes, and (iii) polynuclear Cp complexes. Mononuclear Cp

Table 1. Polymerization activity of CGC.

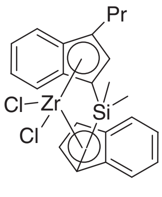
Structure no.	Activity[a] (kg PE (mol Zr)$^{-1}$ h^{-1})	Pressure (Bar)	Temp. (°C)	Co-catalyst and ratio	Reference no.
1	24,253	2.0	70	MAO 1000	64
2	23,245	2.0	70	MAO 1000	64
3	22,315	2.0	70	MAO 1000	64
4	20,457	2.0	70	MAO 1000	64
5	18,243	2.0	70	MAO 1000	64
6	15,245	2.0	70	MAO 1000	64
7	4720	2.0	20	MAO 1000	67
8	4173	1.5	70	MAO 2000	69
9	3200	0.6	40	TIBA/AB 400/3	62
10	2806	11.0	80	MAO 1000	54
11	2716	11.0	60	MAO 1000	54
12	2333	1.5	70	MAO 2000	69
13	2185	2.0	20	MAO 1000	86
14	1763	11.0	80	MAO 1000	54
15	1500	2.0	20	MAO 1000	67
16	1490	2.0	20	MAO 1000	86
17	1367	2.0	20	MAO 1000	67
18	1335	11.0	60	MAO 1000	54
19	1233	2.0	20	MAO 1000	67
20	Negligible	–	–	–	86
21	Negligible	–	–	–	86

MAO = methylaluminoxane; TIBA/AB = tri-isobutylaluminum/[PhNHMe$_2$][B(C$_6$F$_5$)$_4$].
[a] All these activities are reported in toluene.

complexes show the highest activities due to less steric bulk. The catalysts based on metallocenes are single active center catalysts giving high degree of molecular regularity of the polyolefins obtained. This is reflected by a relatively low dispersity index and lack of long-chain branching [59]. Polynuclear catalysts produce polymers with broader molecular weight distribution [60]. An important reason for the development of multinuclear metallocene catalysts is that these catalysts display unique catalytic behavior which depends on the nature of the bridging unit and cooperative effects of the metals in the same metallocene molecule [61]. CGC complexes give thermally stable activated complexes and provide high molecular weight polymers, also with a high content of α-olefin in ethylene/α-olefin co-polymerization, enabling their use in commercial processes [62, 63].

2.1. *CGC system*

Complexes **1**–**21** show catalytic activities in decreasing order, that is, complex **1** shows highest activity and **21** shows least activity; their catalytic activities are summarized in table 1.



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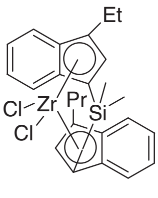

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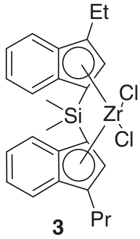

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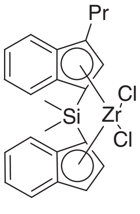

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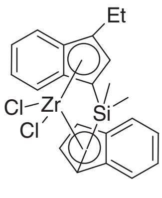

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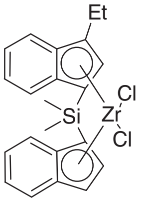

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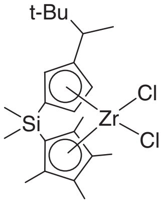
The decreasing order of activities mainly arises from steric bulk. In **1**–**6** the meso complexes show less activity than rac, due to the availability of active metal center from two sites, whereas in meso complexes one metal site is completely blocked for the coordination of olefin. Otherwise steric bulk controls the activity.



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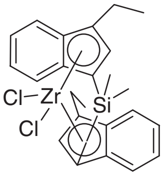

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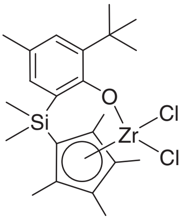

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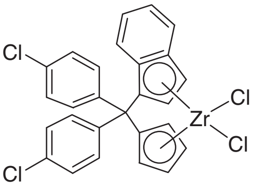

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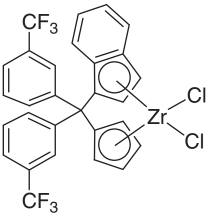
When similar groups are substituted the activity decreases as shown by **8** and **12** [64]. For different groups electron-donating inductive effect controls the activity in **1**–**6**. Complex **7** shows less activity than **1**–**6** due to more crowding on metal.



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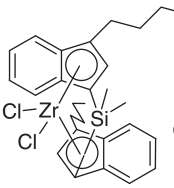

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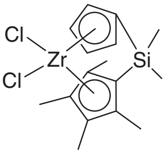

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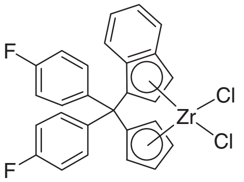

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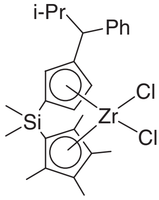

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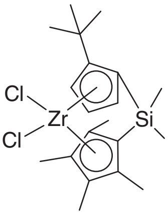
Complex **9** has less crowding at the metal but without a 16-electron-active species, during the activation by co-catalyst, decreases its activity compared to **1**–**8**. Complex **13** is less crowded than **7** but electron–donating inductive effect of alkyl enhances the activity of **7**.



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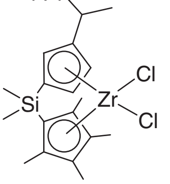

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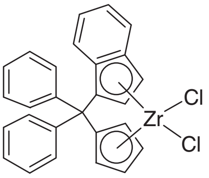

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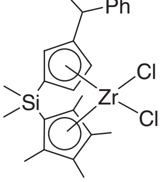

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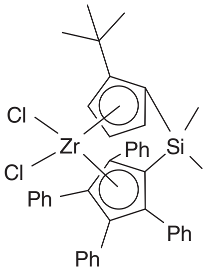
The activities of **7**, **9**, **13**, **15**–**17**, and **19** are comparable. The large decrease in the activities of **20** and **21** is due to large crowding of phenyl groups. The higher activity of **10** than **11** and **14** is due to less electron-withdrawing effect of Cl compared with CF_3 and F.

Table 2. Polymerization activity of mononuclear Cp complexes.

Structure no.	Activity[a] (kg PE (mol Zr)$^{-1}$ h^{-1})	Pressure (Bar)	Temp. (°C)	Co-catalyst and ratio	Reference no.
22	174,000	30.4	25	MAO 15000	55
23	158,000	30.4	25	MAO 15000	55
24	156,000	30.4	25	MAO 15000	55
25	146,000	30.4	25	MAO 15000	55
26	40,747	2.0	20	MAO 1000	87
27	34,960	2.0	20	MAO 1000	87
28	16,747	2.0	20	MAO 1000	87
29	13,347	2.0	20	MAO 1000	87
30	13,233	2.0	20	MAO 1000	87
31	12,033	2.0	20	MAO 1000	87
32	8850	6.0	25	MAO 3000	88
33	8707	2.0	20	MAO 1000	87
34	8607	2.0	20	MAO 1000	87
35	8160	30.4	25	MAO 200	55
36	8080	30.4	25	MAO 500	55
37	7333	2.0	20	MAO 1000	87
38	4820	2.0	20	MAO 1000	87
39	4033	2.0	20	MAO 1000	87
40	3347	2.0	20	MAO 1000	87
41	3340	6.0	25	MAO 2000	88
42	2300	1.0	25	MAO 4000	27
43	1630	10.13	25	MAO 200	55
44	1460	10.13	25	MAO 200	55
45	1166	5.0	40	MAO 4000	89
46	1030	10.13	25	MAO 200	55
47	470	1.0	25	MAO 1000	27
48	410	1.0	25	MAO 1000	27
49	270	1.0	25	MAO 1000	27

MAO = methylaluminoxane.

[a] All these activities are reported in toluene.



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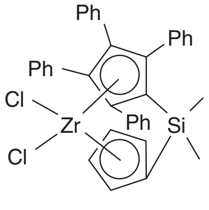

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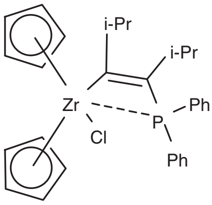
The activity in **10**, **11**, **14**, and **18** is attributed to the strain produced by bulky groups, opening the metal center for coordination with olefins.

2.2. *Mononuclear Cp complexes*

Mononuclear Cp complexes **22–49** are summarized in table 2 in decreasing order of activities. The activities of **22–25** decrease with increase in steric bulk, but remarkable decrease in activity for **35**, **36**, **43**, **44**, and **46** is contributed by less possibility for the formation of the active species, which is produced in **21**–**25** by the removal of chloride during activation by co-catalyst.



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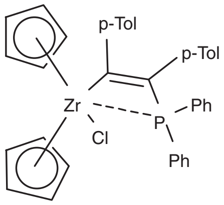

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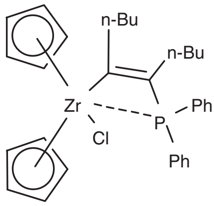

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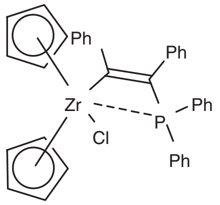

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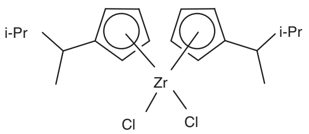
The activities of **35** and **36** are higher than **43**, **44**, and **46** due to the presence of phenyl groups which enhance removal of *n*-Bu and Me during the activation by co-catalyst to give the active species; the activities of **43**, **44**, and **46** are comparable on the basis of steric bulk. Much decrease in activities of **33**, **34**, and **37**–**40** is due to the increase in steric bulk.



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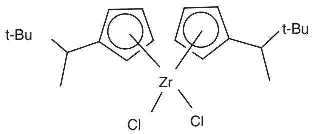

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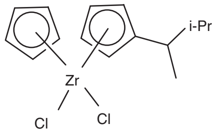

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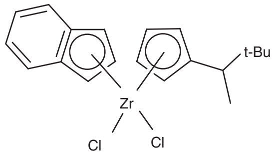

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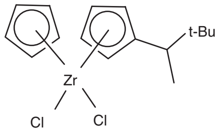

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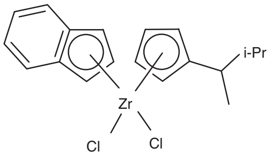

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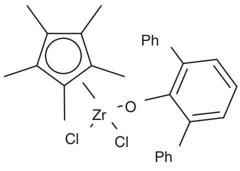

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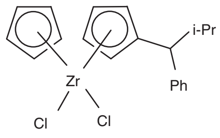

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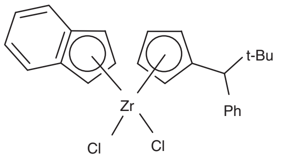

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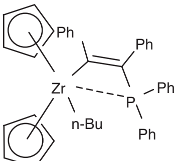

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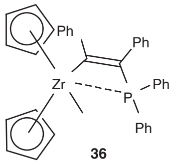

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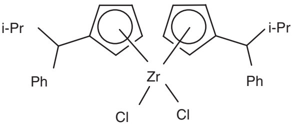

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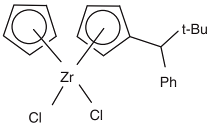

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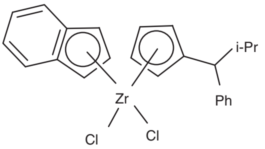

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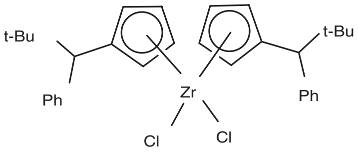
The activity of **32** is more than **41** because in **32** the oxygen is less disturbed compared to **41**; in this case the phenyl rings push the oxygen connected ring out of the plane and make the Zr center available for coordination, but t-Bu groups in **41** cannot do the same.



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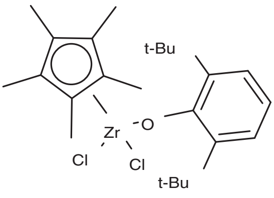

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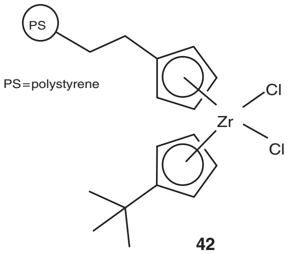

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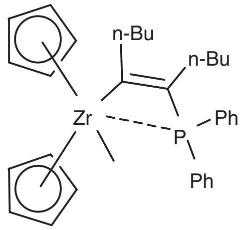
Complex **45** shows less activity even with small ligands due to the lack of 18-electron-activated intermediate for polymerization.



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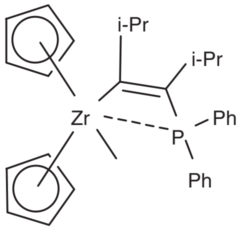

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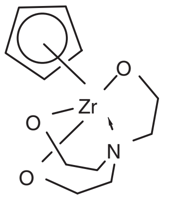

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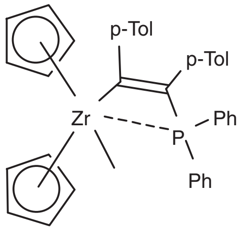

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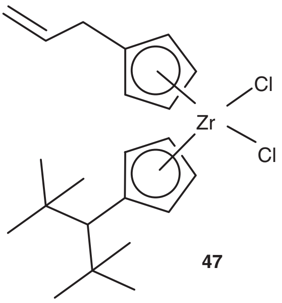

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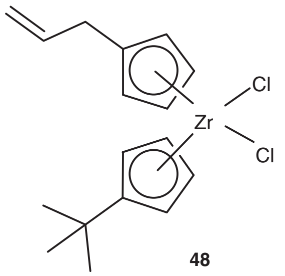

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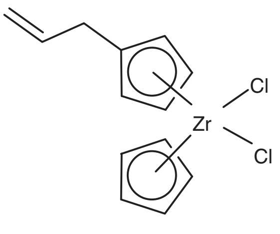

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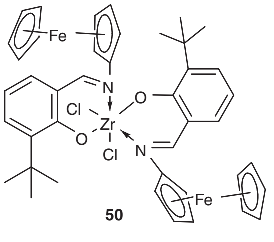
Complexes **47**–**49** show less activity due to the electron-withdrawing effect of allyl compared with **42**. The order of activity in **47**–**49** arises from the electron-donating inductive effect of attached alkyl groups.



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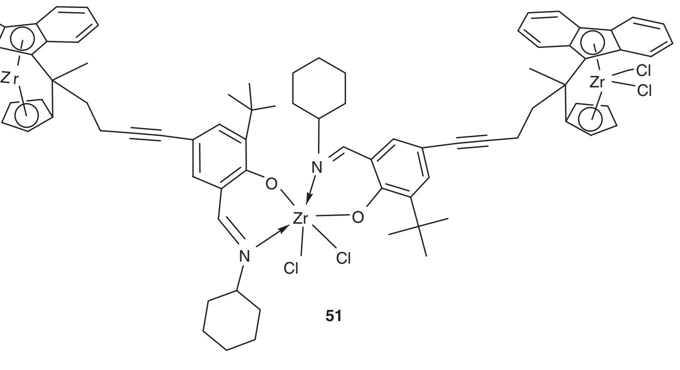

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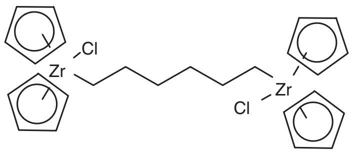

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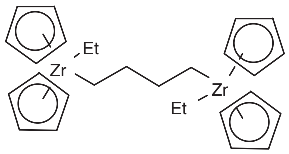

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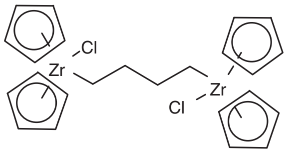

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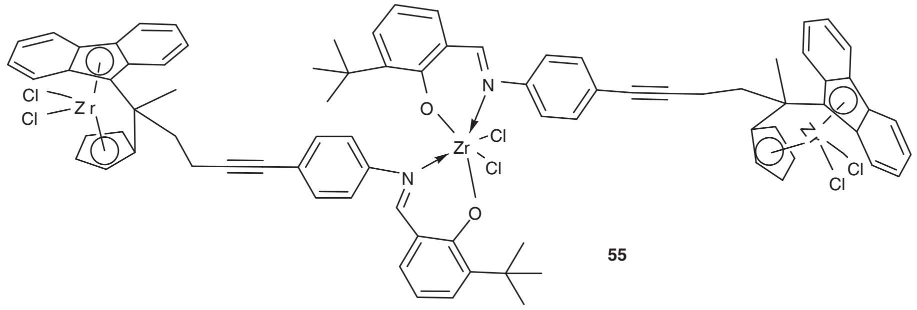

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2.3. *Polynuclear Cp complexes*

Polynuclear Cp ring complexes **50**–**74** are in decreasing activity order as summarized in table 3. The high activity of **50** is attributed to the variable metal centers present.

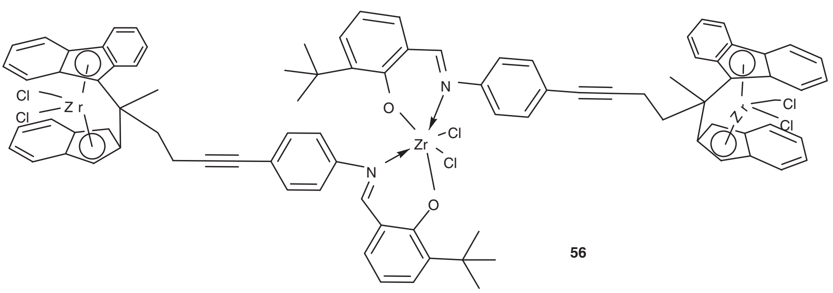
Table 3. Polymerization activity of polynuclear Cp complexes.

Structure no.	Activity[a] (kg PE (mol Zr)$^{-1}$ h^{-1})	Pressure (Bar)	Temp. (°C)	Co-catalyst and ratio	Reference no.
50	26,000	1.0	23	MAO 10000	90
51	24,500[b]	10.0	35	MAO 500	68
52	20,070[b]	10.0	60	MAO 2500	60
53	14,410[b]	10.0	60	MAO 2500	60
54	13,320[b]	10.0	60	MAO 2500	60
55	7770[b]	10.0	35	MAO 500	68
56	5630[b]	10.0	35	MAO 500	68
57	2840[b]	10.0	35	MAO 500	68
58	2830[b]	10.0	60	MAO 2500	60
59	2580[b]	10.0	35	MAO 500	68
60	1060[b]	10.0	35	MAO 500	68
61	887	1.0	40	MAO 1000	91
62	716	1.0	40	MAO 1000	92
63	710[b]	10.0	35	MAO 500	68
64	668	1.0	50	MAO 1000	38
65	640	1.0	40	MAO 1000	92
66	209	1.0	50	MAO 1000	38
67	209	1.0	40	MAO 1000	91
68	Negligible[b]	–	–	–	68

MAO = methylaluminoxane.

[a] All these activities are reported in toluene.

[b] These activities are reported in *n*-pentane.



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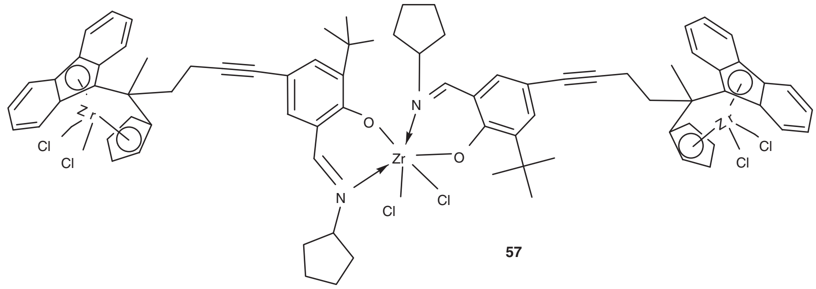

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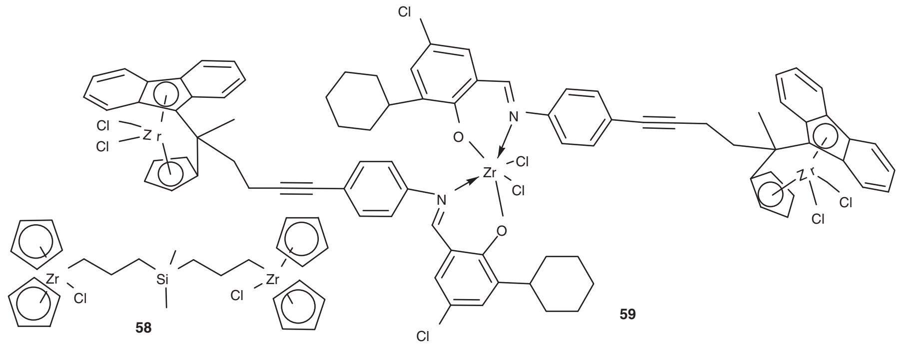

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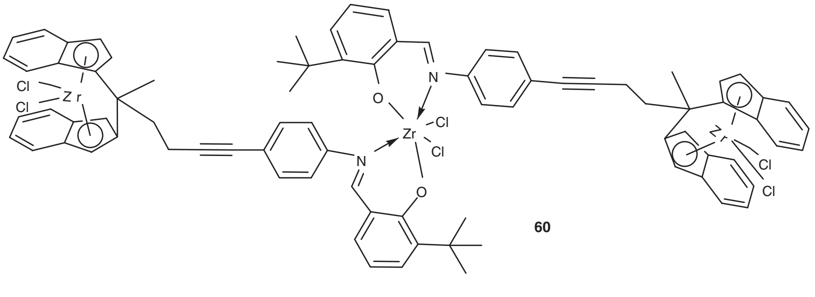

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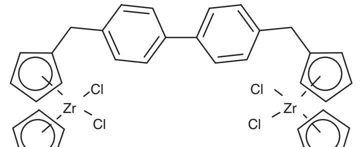

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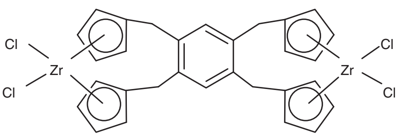

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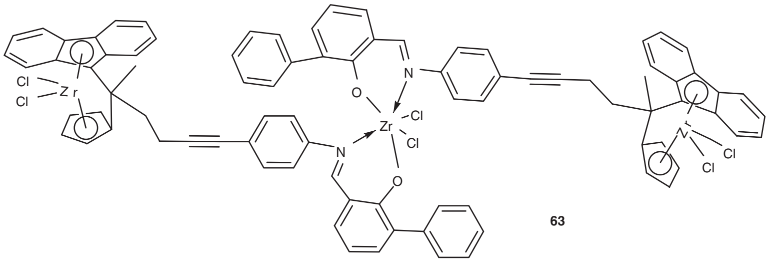
The activity of **51** is contributed by the central Zr as in **109** and also due to multiple sites present. The activities of **55**, **57**, **60**, and **63** are comparable from inductive effect and steric bulk.



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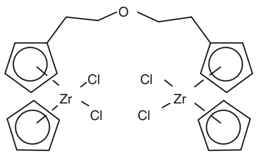

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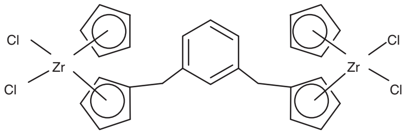

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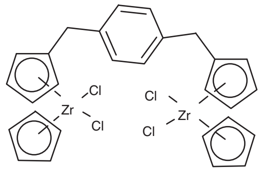

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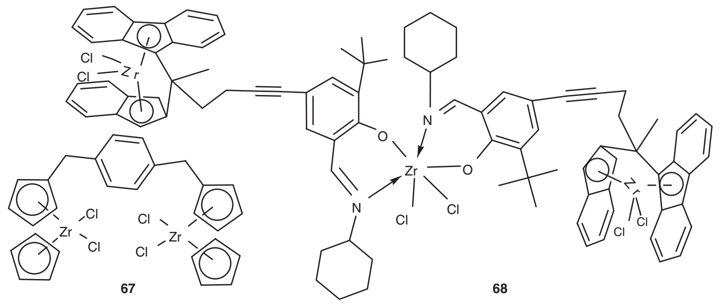
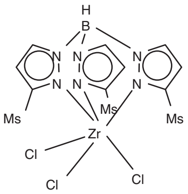


67 **68**



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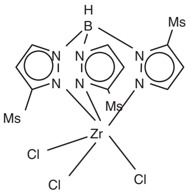

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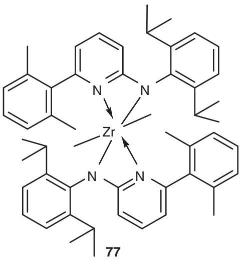

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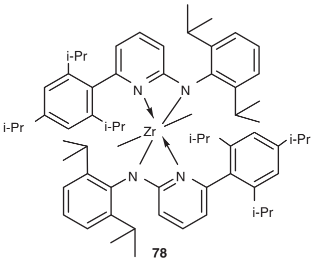

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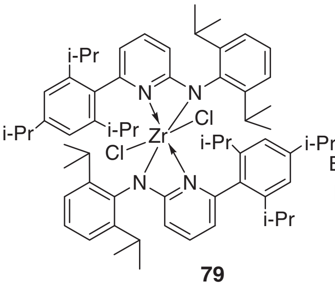
The activities of **52–54** and **58** are comparable on the basis of inductive effect, bond strength, and size of ligand, but more than the activities of **61**, **62**, and **64–67** due to strain and steric factors.



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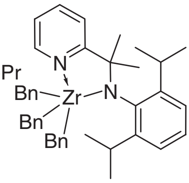

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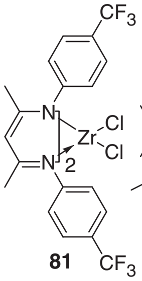

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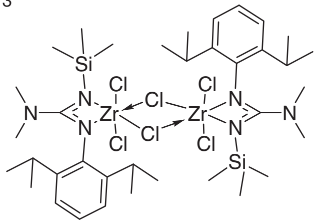

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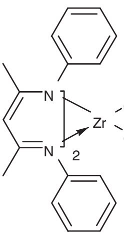

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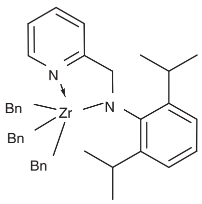

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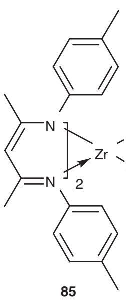

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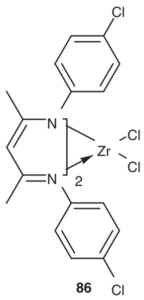

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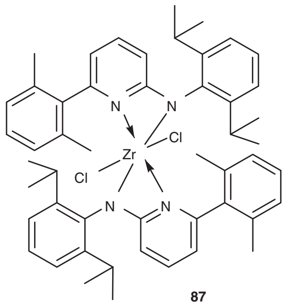

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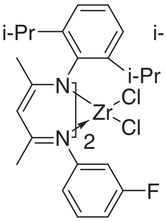

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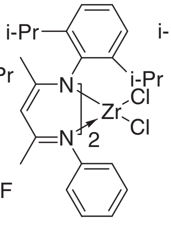

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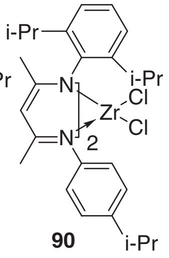

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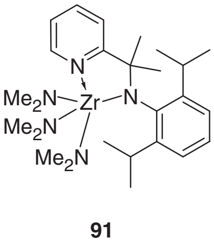

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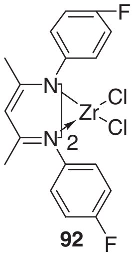

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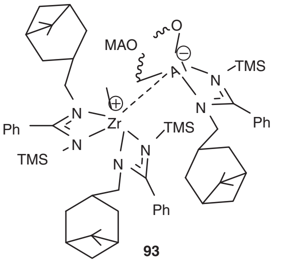

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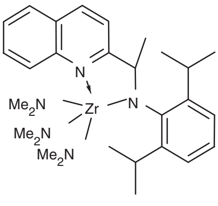

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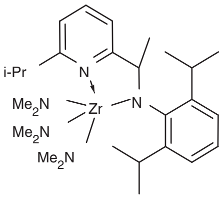

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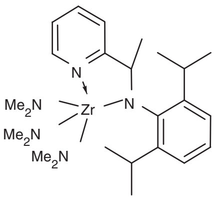

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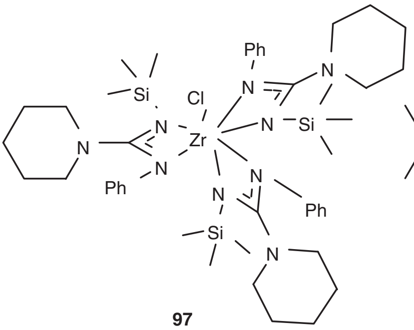

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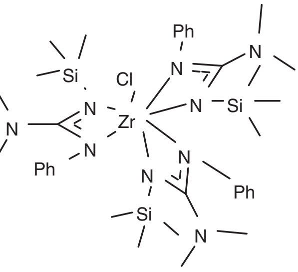

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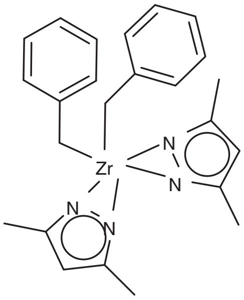

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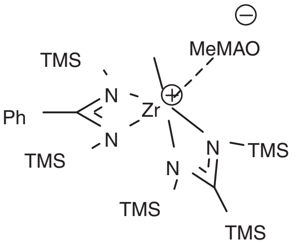

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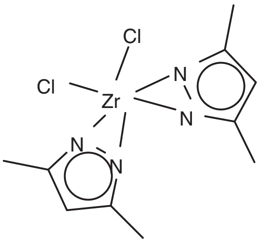

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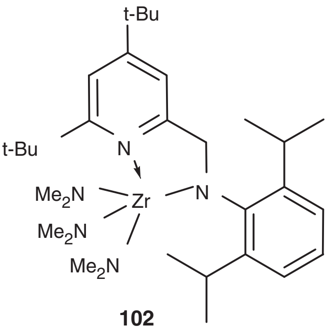

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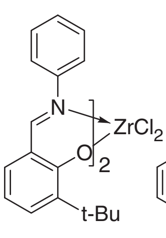

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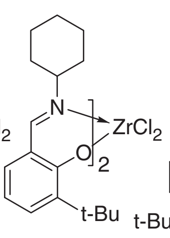

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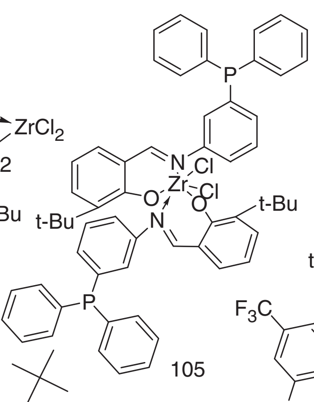

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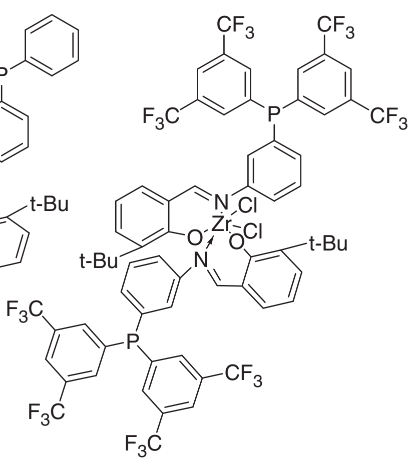

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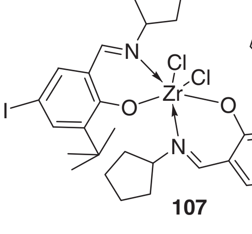

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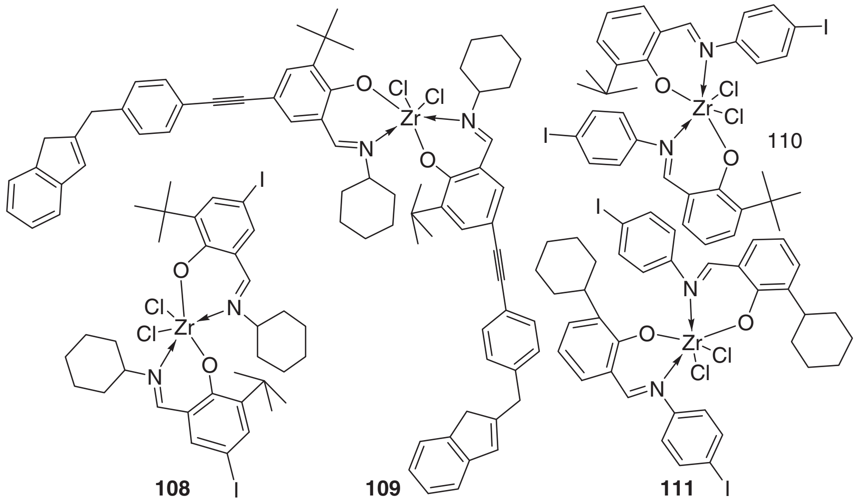
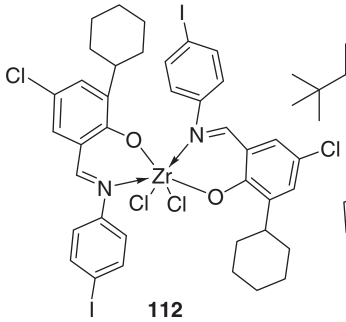


108 **109** **110** **111**

3. Zirconium complexes without Cp

The disadvantage of using metallocene complexes to produce polyolefin is the limited temperature stability of the catalyst and the tendency to produce lower molecular weight materials under convenient commercial operating conditions [65, 66]. Many efforts have been made in commercial and academic labs to develop other coordination compounds in which the selectivity and/or productivity is improved. The number of non-metallocene-based catalysts for the polymerization of ordinary olefins has increased markedly in the past decade. Some of these catalysts offer activity that is comparable to metallocene catalysts [56, 58, 68]. The majority of non-metallocene type catalysts contain ‘‘hard’’ donating ligands, such as a bis (alkoxide) [70, 71] bis (amido) [72–76], and N, O chelating ligands [77–80]. Especially, group 4 transition metal complexes bearing phenoxyimine chelating ligands are reported to show exceptionally high activities for ethylene polymerizations in the presence of MAO [37, 57, 59, 68]. Some of the most successful catalysts contain nitrogen-based ligands; amido ligands are useful for preparing early transition metal polymerization catalysts [72, 73]. The development of ‘‘post-metallocene’’ high-performance single-site catalysts allows accurate design of polymer microstructures through precise control, not only of the stereochemistry of the polymerization, but also of the termination reactions (e.g., living polymerization) [81, 82]. Extremely efficient and versatile catalysts are octahedral bis (phenoxy-imine) Group IV-B complexes [26, 37, 56, 77–80], which have displayed high activities for ethylene polymerization [26, 37, 56, 57] and versatile behavior in polymerization of α-olefins that allow the synthesis of polymers with distinctive architectural features [83, 84]. Numerous studies show that the stereo and regio-specificity of these catalysts in the polymerization of propylene are significantly affected by the ligand structure, the nature of the metal centre and co-catalyst. For ease of comparison non-metallocene-based Zr complexes are divided into three categories.



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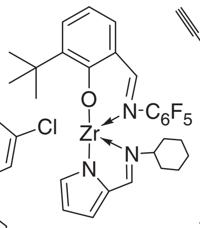

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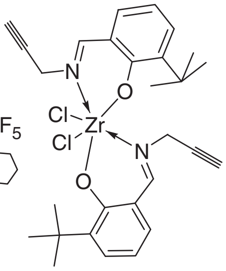

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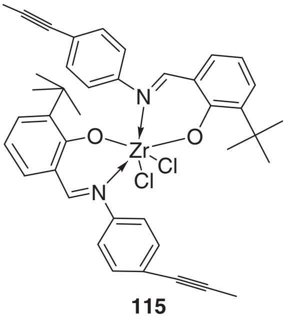


115

3.1. *Nitrogen-donor-chelating complexes*

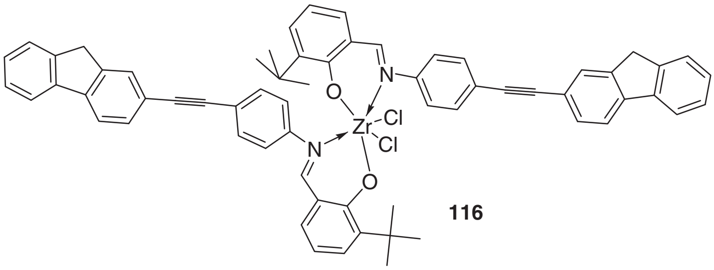
Nitrogen-donor-chelating complexes **75**–**102** are numbered according to decreasing activity and their activities are summarized in table 4. Complexes **75** and **76** differ in the location of Ms (mesityl) substituent on Tp, with **75** being more crowded at Zr than **76**.

Table 4. Polymerization activity for only nitrogen chelating complexes.

Structure no.	Activity[a] (kg PE (mol Zr)$^{-1}$ h^{-1})	Pressure (Bar)	Temp. (°C)	Co-catalyst and ratio	Reference no.
75	346,000	9.8	60	MAO 37500	56
76	264,100	9.8	60	MAO 37500	56
77	4440	5.0	80	TIBAO 50	72
78	3760	5.0	100	TIBAO 50	72
79	2760	5.0	80	MAO 500	72
80	1905	2.0	25	MAO 1000	73
81	762	1.0	70	MAO 2000	53
82	648	10.13	80	MAO 2000	74
83	490	1.0	50	MAO 2000	53
84	438	2.0	25	MAO 1000	73
85	406	1.0	50	MAO 2000	53
86	341	1.0	50	MAO 2000	53
87	320	5.0	80	MAO 500	72
88	315	1.0	50	MAO 2000	53
89	269	1.0	50	MAO 2000	53
90	240	1.0	50	MAO 2000	53
91	170	2.0	25	MAO 1000	73
92	140	1.0	50	MAO 2000	53
94	77	2.0	25	MAO 1000	73
95	70	2.0	25	MAO 1000	73
96	42	2.0	25	MAO 1000	73
97	15.2	10.13	20	MAO 1000	75
98	10.5	10.13	20	MAO 1000	75
99	9.51	4.05	25	MAO 1000	76
101	Negligible	–	–	–	76
102	Negligible	–	–	–	73

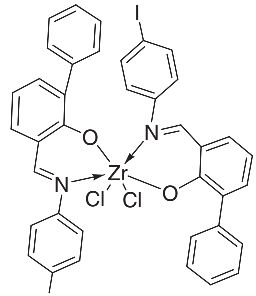
MAO = methylaluminoxane; TIBAO = (tetra-iso-butyl-aluminoxane).

[a] All these activities are reported in toluene.



116

Under the standard conditions, polymerization with **75** is restricted to 12 min runs, due to a high stirring load, resulting from a high yield of high molecular weight polymer. The data show that **75** is more productive than **76** at 60°C. To obtain a comparison of these catalysts which is not complicated by possible mass transport effects, polymerization was run at 60°C with a very low catalyst loading. Under these conditions **75** exhibited somewhat higher productivity than **76** due to a lower k_d value (k_d = deactivation rate constant determined from kinetic profiles). Complex **75** gave a higher M_v than **76** under the same conditions, possibly due to steric inhibition of chain transfer to Al of co-catalyst [56].



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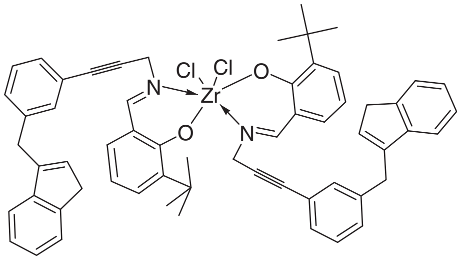
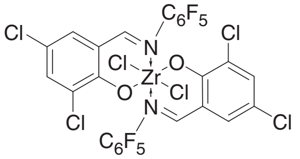


118

In comparing **77**, **78**, **79**, and **87** slight changes in the steric demand of the bulky ligand periphery can be used to tune the nature of the formed polymers by maintaining selectivity [72]. Comparing **80**, **84**, **91**, **94**, **95**, **96**, and **102** the (chelate ligand)Zr(benzyl)$_3$ systems (**84** and **80**) tested give very active ethene polymerization catalysts. The latter is even in the high activity region.



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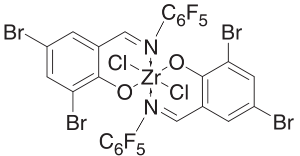

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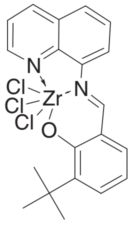

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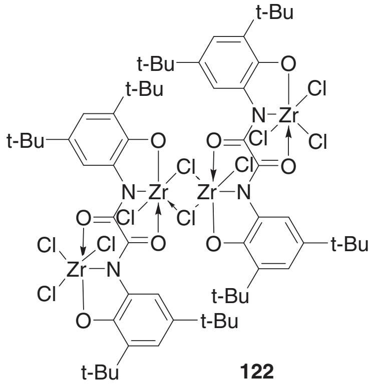
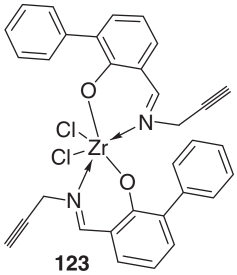


122

Apparently, introduction of some steric bulk in the bridging carbon inside the chelate is advantageous with respect to activity. The (chelate ligand)Zr(NMe2)$_3$ systems (**91**, **94**–**96**, and **102**) are markedly less active ethene polymerization catalysts. Again a series of examples investigated revealed that the introduction of some steric bulk at the α-carbon inside the chelate ring gradually increases the catalyst activity. However, the presence of a bulky alkyl substituent (e.g., i-Pr, t-Bu) in the pyridine 6-position diminished the catalyst activity or shut it off completely [73].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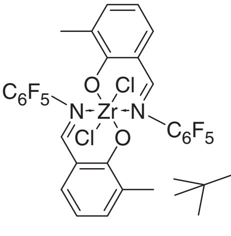
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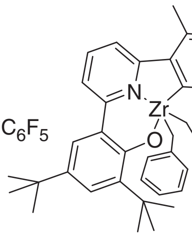
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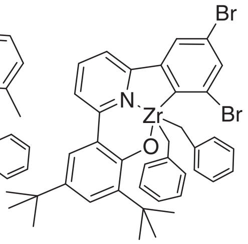
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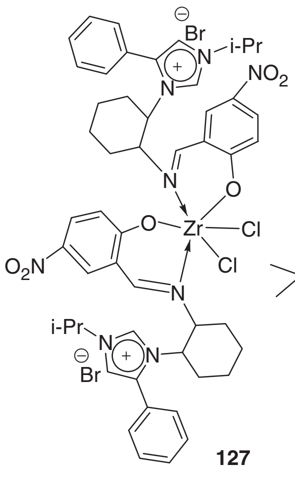
Comparing **81**, **83**, **85**, **86**, **88**, **89**, **90**, and **92** the electronic nature of the para-substituents on aromatic rings exerted great influence on the polymerization of ethylene.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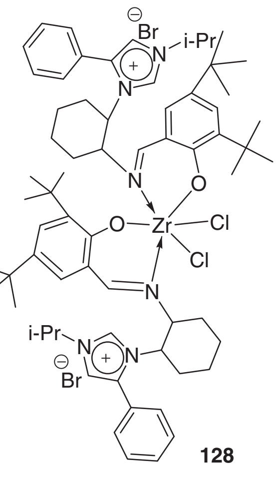
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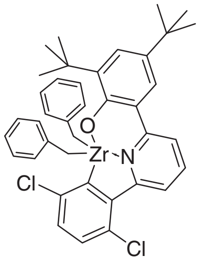
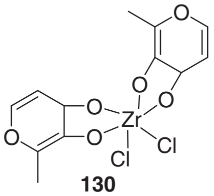

129

The catalytic activity for ethylene polymerization increased in the order **92** < **86** < **85** < **83** < **81**. Complex **81** exhibits the highest catalytic activity among them. These results indicate that the CF$_3$ substituents in **81** improved the catalytic activity significantly, probably due to the increase in electrophilicity of metal center and so accelerating the coordination/insertion rate of ethylene monomer. The lower activity of **85** than **83** indicates that the increase of electron-donating ability of the para-substituent is disadvantageous to catalytic activity. The electron-donating groups on phenyl decrease the electrophilicity of the zirconium center through the chelating pi-system of the ancillary ligand, obviously unfavorable for coordination and insertion of ethylene. Based on this, **86** and **92** bearing electron-withdrawing para-chloro or floro should display increased catalytic activity.



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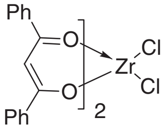

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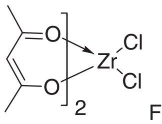

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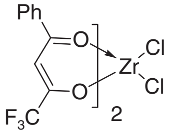

133

Unexpectedly, **86** and **92** show lower catalytic activities than the unsubstituted **83**, and **86** is slightly more active than **92**. The influence of halogen substitution at the ancillary ligands on the polymerization performance of the corresponding metal catalysts has been investigated in some cases, but conflicting results are obtained [53].

Complex **82** shows higher activity than similar guandinato complexes **97** and **98** due to binuclear active sites. Steric bulk and electronic cloud control the variation of catalytic activities in **97** and **98**. Complex **101** has no activity as compared to **99** due to non-generation of catalytically active species in solution, probably resulting from decomposition of the dimethyl zirconium intermediate, when the dialkylation of the corresponding dichloro derivative occur with MAO, before abstraction of the methyl ligand [76].

3.2. *Mixed-donor-chelating complexes*

Mixed-donor-chelating complexes **103–129** are numbered in decreasing activity (table 5).

Planar geometry and resonance delocalization of C=N with phenyl ring reduce the electron density on nitrogen, making the metal center electrophilic, hence enhancing the coordination of Zr with alkene in **103** which increase its activity, whereas in **104**, out-of-plane cyclohexyl crowding on Zr along with electron-donating inductive effect is responsible for decrease in activity. Complex **106** shows less activity than **105**, explained on the basis of electron-withdrawing inductive effect of CF_3. In comparison of **107–112**, **114–118**, and **123** the data show that exchange of the butyl for a cyclohexyl (**111**) in **110** slightly decreases the polymerization activity, since the steric bulk at the α-carbon bonded to the aldehyde ring is lowered. In addition, chloro at para position in **112** leads to further decrease in activity due to its electron-withdrawing effect. The exchange of alkyl or cycloalkyl groups at position 3 of the aldehyde ring against a more electron-withdrawing phenyl substituent (**117**) destabilizes the cationic active center resulting in reduced activity.

Polymerization activity decreases with increasing electronegativity of the substituents on the aldehyde ring. Complexes **114**, **115**, and **123** are the first ones containing terminal alkynyl groups that are active in polymerization of ethylene. Therefore, the affinity of the cationic zirconium centers toward ethylene is high enough to produce polyethylene instead of polyacetylene derivatives.

Complexes **114** and **115** containing three ter-butyl-substituted aldehyde rings show higher activities than **123** bearing electron-withdrawing substituents on the aldehyde rings. The high molecular weights M_w of the resulting polyethylene have noticeable comparison to the very low M_w obtained with **107** and **108** having cycloalkyl groups at the imino moieties.

Table 5. Polymerization activity of mixed-donor complexes.

Structure no.	Activity[a] (kg PE (mol Zr)$^{-1}$ h^{-1})	Pressure (Bar)	Temp. (°C)	Co-catalyst and ratio	Reference no.
103	61,600[c]	1.0	30	$AlEt_3$ 15000	57
104	57,800[c]	1.0	30	$AlEt_3$ 10000	57
105	31,000	1.0	50	MAO 2000	58
106	26,000	1.0	50	MAO 2000	58
107	15,600[b]	10.0	35	MAO 500	68
108	14,650[b]	10.0	35	MAO 500	68
109	10,300[b]	10.0	35	MAO 500	68
110	8320[b]	10.0	35	MAO 500	68
111	7780[b]	10.0	35	MAO 500	68
112	5100[b]	10.0	35	MAO 500	68
113	4200	1.0	50	MAO 600	37
114	4105[b]	10.0	35	MAO 500	68
115	2080[b]	10.0	35	MAO 500	68
116	1900[b]	10.0	35	MAO 500	68
117	1760[b]	10.0	35	MAO 500	68
118	1030[b]	10.0	35	MAO 500	68
119	466	1.0	18	MAO 150	77
120	408	1.0	18	MAO 150	77
121	210	1.0	50	MAO 100	78
122	201[c]	4.0	60	MAO 4000	79
123	168[b]	10.0	35	MAO 500	68
124	128	1.0	18	MAO 150	77
125	70	1.0	25	MAO 500	36
126	58	1.0	25	MAO 500	36
127	4.87	2.8	50	MAO 1200	80
128	3.85	2.0	22	MAO 500	80
129	Negligible	–	25	MAO 500	36

MAO = methylaluminoxane; $AlEt_3$ = triethylaluminum.
[a] All these activities are reported in toluene.
[b] These activities are reported in *n*-pentane.
[c] These activities are reported in *n*-hexane.

Complex **123** containing phenyl-substituted phenoxyimine ligands yielded the highest molecular weight polyethylene in this series. Due to the stronger electron-withdrawing effect of the alkynyl groups, mononuclear bis(phenoxyimine)zirconium dichloride, **116**, containing indenyl-alkynyl or fluorenyl-alkynyl substituents on their ligand frameworks consistently show lower polymerization activities compared to their iodo-substituted "precursor" complexes.

However, **115** contain a terminal ethynyl function and **116** display similar activities. Since the steric bulk caused by the indenyl substituents in **118** is significantly higher than that of propynyl groups of **114**, it is more difficult for ethylene to reach the active metal center leading to reduced activity. In contrast to this result, the activity is less influenced if the alkynyl substituent is introduced at position 5 of the aldehyde ring [68].

Complexes **125**, **126**, and **129** can be compared on the basis of inductive effect, and also possibly because of more access to the metal center with steric hindrance exerted by substituents diminished [36].

On comparing **119**, **120**, and **124**, the polymerization results obtained with **119** and **120** and those obtained with an analogos phenoxy-imine catalyst bearing methyl substituents on the phenol rings (**124**) provided evidence that introduction of halogen substituents on the ligand skeleton has beneficial effects on the catalytic activity [77].

Table 6. Polymerization activity of oxygen chelating complexes.

Structure no.	Activity[a] (kg PE (mol Zr)$^{-1}$ h^{-1})	Pressure (Bar)	Temp. (°C)	Co-catalyst and ratio	Reference no.
130	180	1.6	60	MAO 2500	70
131	26.4	1.0	60	MAO 210	71
132	24.3	1.0	60	MAO 210	71
133	8.66	1.0	60	$AlEt_3$ 50	71

MAO = methylaluminoxane; $AlEt_3$ = triethylaluminum.
[a] All these activities are reported in toluene.

3.3. *Oxygen-donor-chelating complexes*

Complex **130** shows more activity than **131–133** due to smaller size of ligand. The variation of catalytic activity in **131** and **132** is due to better electron-donating ability of phenyl (by resonance) as compared to CH_3 on the β-diketone.

Consequently, it causes enhancement of the interaction between the zirconium and ethylene, accelerating the insertion into the growing chain. The lower activity of **133** is attributed to change of co-catalyst, because $AlEt_3$ is not as good as MAO for catalyst activation [71]. The activity data for these complexes are shown in table 6.

4. Conclusion

Zr complexes show catalytic activity for homogeneous olefin polymerization and many variables influence the catalytic activities in homogeneous polymerization, such as ethylene pressure, solvent, temperature, amount of catalyst, and type of co-catalyst. The structure of the complex directly influences the catalytic activity and selectivity in olefin polymerization. By keeping other factors the same the main factor is the steric bulk which on increasing reduces the catalytic activity.

Electron-withdrawing effect mainly decreases the catalytic activity by destabilizing the complex with lack of π-bonding and hence decreasing the activity. In non-metallocene complexes with only nitrogen donors, electron-withdrawing increases the catalytic activity, due to the increase in electrophilicity of the metal center enhancing the coordination of metal with olefin [53, 85]. The role of halogens remains variable.

Work in the field of Zr complexes for olefin polymerization should emphasize complexes with smaller size ligand and electron rich to get better catalytic activity. For the production of polymers with broader molecular weight distribution, catalysts with constrained geometry and electron donor sites on the ligands should be preferred. Further work should include *computational* modeling and lab work to explore the role of halogens in ancillary ligand sites for non-metallocene complexes.

Acknowledgments

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