

Non-Cp type homogeneous catalytic systems for olefin polymerization

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Abstract

Development of homogeneous metallocene catalysts for olefin polymerization has been briefly overviewed prior to detailed examination of the chemistry of non-Cp type homogeneous catalytic systems. In order to emphasize the structural characteristics of non-Cp catalysts, they were initially classified according to the coordination numbers of 4–7 and then further subclassified according to the ligand types. Over 100 line drawings and 200 references are utilized.

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1. Introduction

Terms of “evolutionary and revolutionary developments” have been introduced by Cotton when he reviewed the advances of coordination chemistry in 1980 [1]. Cyclical view of revolution → evolution → revolution in technology development of polymer chemistry was raised by Sinclair and the commercialization of homogeneous metallocenes and other single site catalysts was considered as revolutionary one along with the postulation of polymers by Staudinger, development of low density polyethylene and commercialization of linear polyethylene and polypropylene [2]. Currently, about eleven new metallocene-based polyolefin resins such as plastomers, elastomers, interpolymers and various copolymers are under production worldwide but the increasing rate of their market share has been extremely

sluggish due to high production cost. Nonetheless, from the polymer property point of view, homogeneous catalytic systems are still attractive since they can produce polymers with properties that are hard to be embodied by Ziegler–Natta catalytic systems.

The historical progress of homogeneous catalysts for olefin polymerization, outlined in Fig. 1, was initiated in 1957 by Natta and Breslow [3] who observed that the homogeneous Cp_2TiCl_2 (Cp = cyclopentadienyl)/ AlR_3 system could produce polyethylene. But it was nearly twenty years later when a breakthrough in metallocene catalysts was made by Kaminsky and colleagues via the recognition of the importance of water in $\text{Cp}_2\text{TiCl}_2/\text{AlR}_3$ system [4] followed by the discovery in 1980 of cocatalyst methylaluminoxane (MAO), partially hydrolyzed AlMe_3 , which could activate group 4 metallocenes for the polymerization of both ethylene and α -olefins [5]. Since then, over two decades, an extraordinary amount of research efforts has been directed toward the development of new homogeneous catalysts for olefin polymerization and the understanding of the

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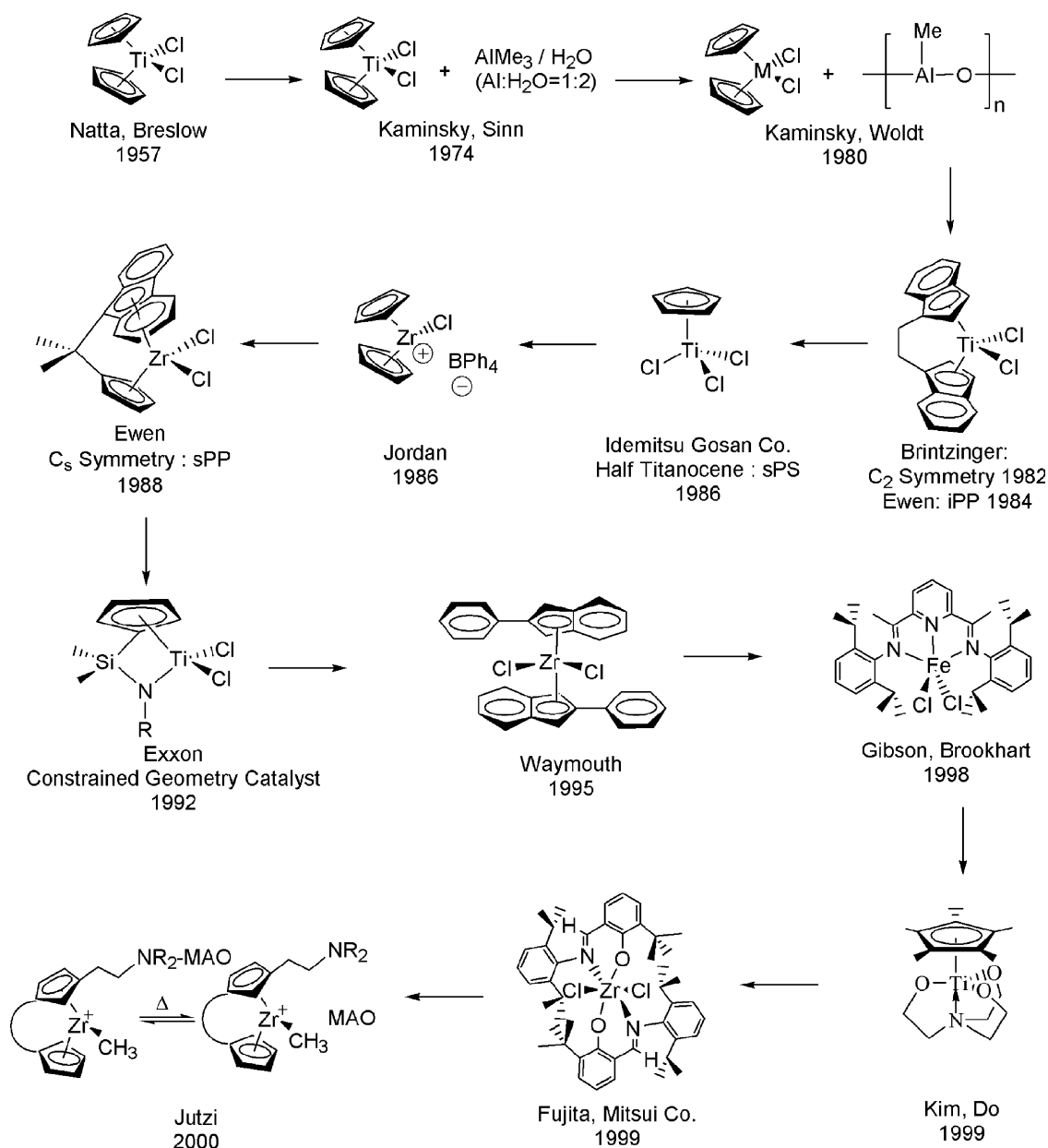


Fig. 1. Revolutionary progress of homogeneous metallocene catalysts for olefin polymerization.

fundamentals of their chemistry, resulting in the publication of huge number of papers and review articles [6–9]. A series of important findings in homogeneous catalysts for olefin polymerization, worthy of highlighting, is illustrated in Fig. 1 in chronological order and includes C₂ symmetric *rac*-ansa-ethylene bridged bis(indenyl) titanium dichloride for isotactic polypropylene [10], Idemitsu Gosan Co.'s half titanocene for syndiotactic polystyrene [11], Jordan's MAO free cationic metallocene system [Cp₂ZrCl](BPh₄) [12], Ewen's C_s symmetric isopropyl bridged *ansa*-zirconium dichloride for syndiotactic polypropylene [13], Exxon's constrained geometry catalyst (CGC) as versatile olefin polymerization catalyst [14], Waymouth's bis(3-phenyl)indenyl zirconium dichloride for isotactic-atactic block poly-

dpropylene [15], Brookhart and Gibson's late-metal single site catalysts for ethylene polymerization [16,17], Kim's syndiotactic polystyrene catalyst containing transannular interaction between titanium and nitrogen [18], Fujita's super active phenoxy-imine group 4 polyethylene catalysts (FI catalysts) [19] and Jutzi's dialkyl-aminoethyl-functionalized *ansa*-metallocene for the modulation of molecular weight distribution of polyethylene [20]. Among the foregoing highlighted subjects of homogeneous catalysts, state-of-the-art non-Cp olefin polymerization catalysts will be covered in this review.

In particular, non-metallocene olefin polymerization catalysts have been intensively studied in recent years owing to the merits of the increased opportunities for observing new polymerization behavior and the

increased patentability of the observations. Non-metallocene systems as well as CGC systems have been previously reviewed by Gibson from the central metal point of view [21]. Thus, in this review non-Cp olefin polymerization catalysts will be examined from the coordination number as well as the ligand type points of view to emphasize their structural characteristics. Group 10 non-Cp olefin polymerization catalysts will be excluded from this review since they are exclusively 4-coordinated complexes and were well reviewed earlier [21,22].

2. 4-Coordinated complexes

2.1. Cp-analog ligands

Ligands such as boratabenzenes [23–32], phosphinimides [33–39], tropidynyl ligand [40] and hydrido(trispyrazolyl)borate ligand [41] that are considered as electronically and sterically analogous to Cp have been employed in synthesizing numerous olefin polymerization catalytic systems. Some examples 1–7 are illustrated in Fig. 2.

Boratabenzene derivatives were utilized by Bazan and Ashe [23–32] in preparing new non-Cp catalytic systems that show good catalytic activities for ethylene polymerization in the presence of MAO. For example, bent-type complexes **1** are active for ethylene homopolymerization

with the activity of 325 kg PE/(mol h atm) for **1b** or 950 kg PE/(mol h atm) for **1e** [23–27,31]. *ansa*-type precatalysts **2** afforded ethylene/1-octene copolymers [26]. Chromium complexes of boratabenzene **5** are also reported [32]. The compound **5a** could not be activated by cocatalyst $B(C_6F_5)_3$ but was activated by MAO for ethylene polymerization to give the high activity of 3640 kg PE/(mol h atm).

Stephan and his colleagues beautifully demonstrated the utility of phosphinimides, new ligand systems with suitable steric effect, in developing new group 4 non-Cp ethylene polymerization catalysts [33–38]. The compound **6** with R = *t*-butyl could produce polyethylene in the presence of cocatalyst trityl tetrakis(pentafluorophenyl)borate with the activity of 62,000 kg PE/(mol h atm) and polymer M_w of about 100,000 [34]. Dinuclear iron complexes based on bridging phosphinimide ligands are also reported and the compound **7** represents one of them [39].

2.2. Amide ligands

Dianionic diamide chelate ligands in which two amide functionalities are linked by a spacer represent the class of amide ligands and have been frequently used as ancillary ligands in deriving new non-metallocene catalysts [42–66]. The report of propylene bridge as a spacer by McConville's group in 1996 constitutes the

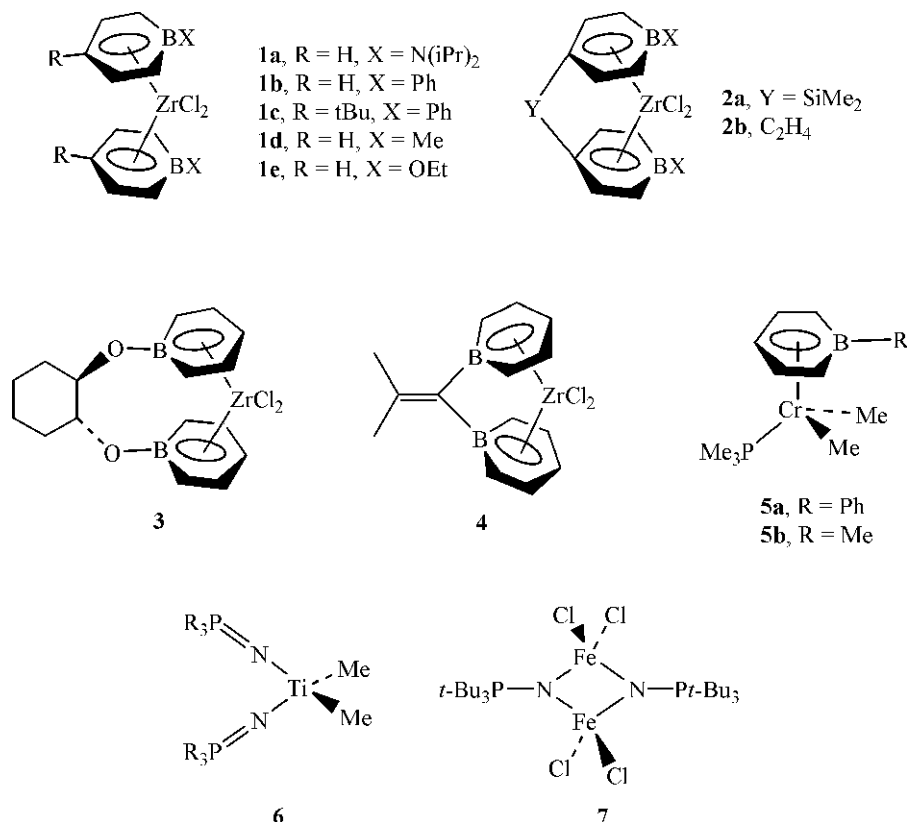


Fig. 2. Examples of 4-coordinated complexes with ligands that are analogous to Cp.

first example of this class [42–44]. Displayed in Fig. 3 are selected summary of 4-coordinated complexes based on chelate type of ligands (**8–18**). The systems with propylene bridge as a spacer, **8**, are known to show various catalytic behavior such as living polymerization of higher α -olefin with **8b**/ $\text{B}(\text{C}_6\text{F}_5)_3$ [43], highly active polymerization of 1-hexene with **8b**/MAO (350,000 g poly(1-hexene)/mmol of catalyst h) [42] and production of isotactic polypropylene and ethylene/2-butene copolymer [45–47].

As an alternative spacer, various kinds of bridging units were employed as can be seen in **9–18** [48–66]. A set of McConville's analogues such as the compounds **9** and **10** where the spacer length is similar to McConville's propylene bridge but the flexibility of a spacer is reduced due to the introduction of an aromatic ring has been reported [51–57]. The effect of such a tuning on the polymerization behavior is not straightforward. For example, the Ti and Zr analogue of **9** with the cocatalyst MAO show low activities for ethylene polymerization as several hundreds kg PE/mol atm h while the Ti analogue of **9** could be highly activated by Ph_3CB

$(\text{C}_6\text{F}_5)_4\text{Al}^i\text{Bu}_3$ for ethylene/1-butene copolymerization in 12,400 kg of polymer/(mol h) activity at 6 (kg/cm^2) of ethylene pressure [51–54]. The use of longer spacer as in **11** also gives rise to high activity of 5200 kg PE/mol_{cat} h for ethylene polymerization [58]. Boron and indium atoms play interesting role as spacers since the compounds **12** and **13** are very active for ethylene/1-octene copolymerization [59,60]. It is worthy of mention that amide complexes of vanadium **17d** [50] and chromium **18** [66] are also reported.

2.3. Neutral N–N chelate ligands

Neutral N–N chelate ligands tend to form complexes with late transition metals and diimine complexes of nickel and palladium constitute large portion of a class of non-metallocene catalysts with neutral N–N chelate ligands. Nonetheless, as stated in Section 1, only non-group 10 systems will be focused. Fig. 4 illustrates some examples. Diimine Cu complex **19** could polymerize ethylene at 30 bar with the activity of 300 kg PE/(mol h) [67] and bis(benzimidazole) complex of Cu **20** was found

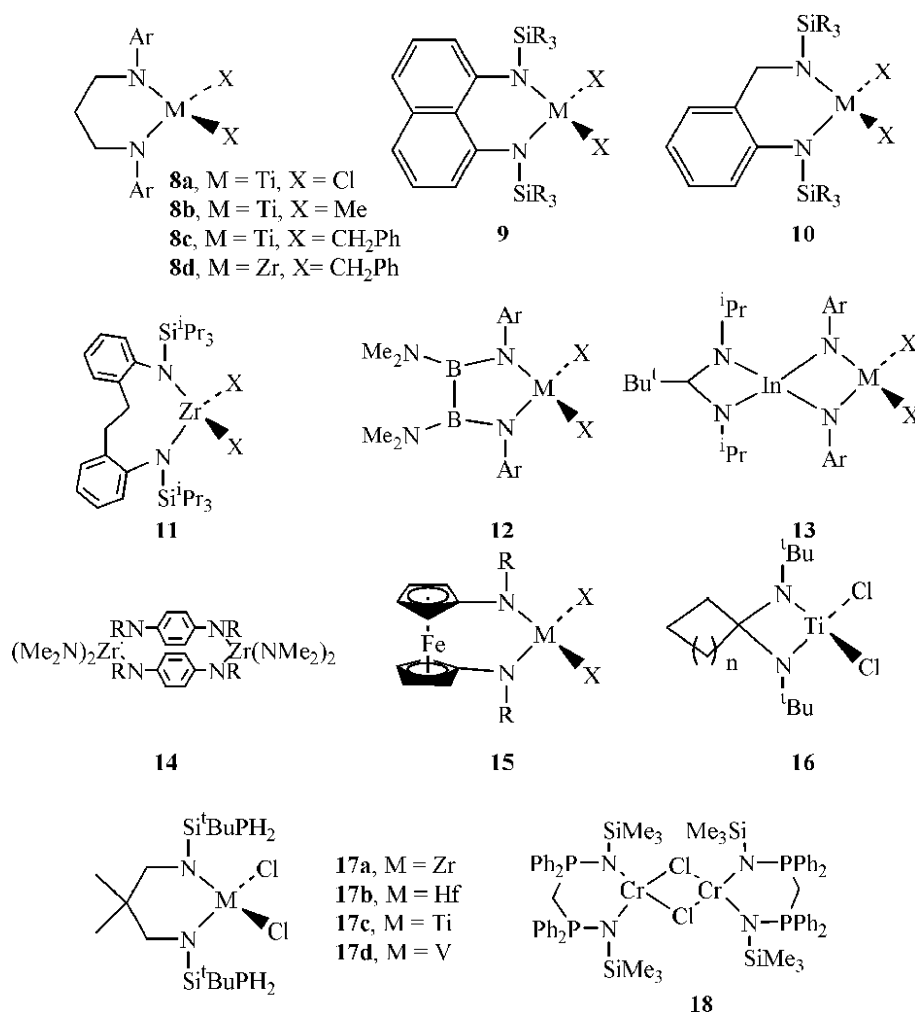


Fig. 3. Examples of 4-coordinated complexes based on chelating diamide ligands.

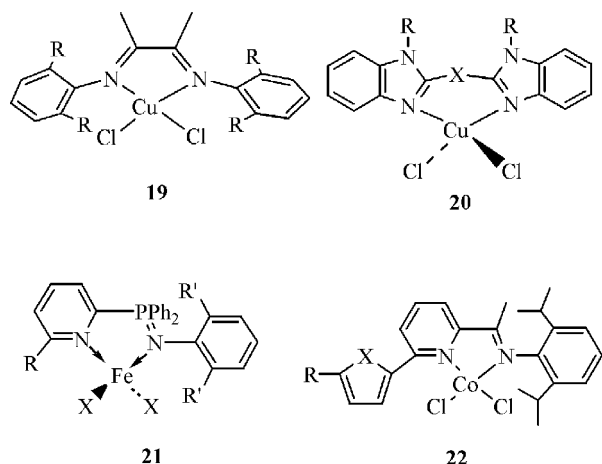


Fig. 4. Examples of 4-coordinated complexes based on neutral N–N chelate ligands.

to be active for homopolymerizations of ethylene and acrylate as well as ethylene/acrylate copolymerization [68]. Fe complex **21** with pyridine-phosphinimine ligand showed unusual ethylene polymerization behavior in the presence of MAO since C4-oligomer was obtained as the only product in low activity [69]. Four-coordinated cobalt complex **22** also produced oligomer when it was activated for ethylene with MAO [70].

2.4. Other ligands

Selected examples, **23–29**, of 4-coordinated complexes based on miscellaneous ligands are shown in

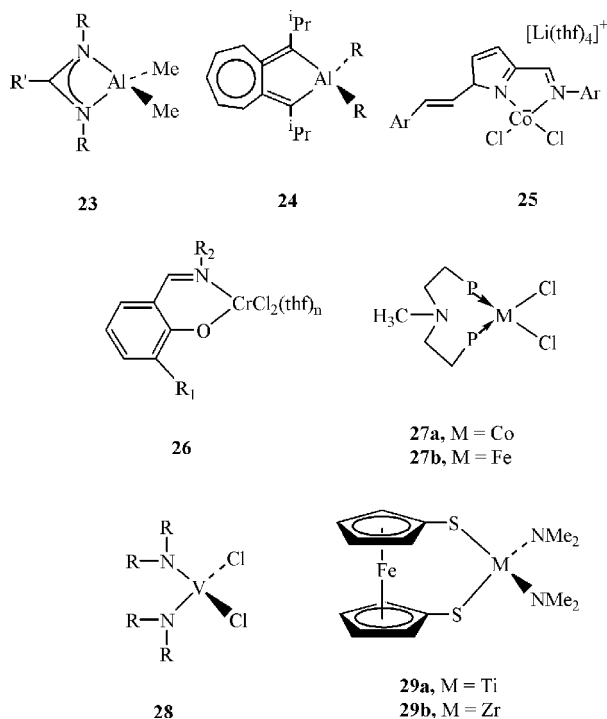


Fig. 5. Examples of 4-coordinated complexes based on miscellaneous ligands.

Fig. 5 [71–80]. Jordan and colleagues reported the synthesis of Al complexes such as **23** and **24** and their polymerization characteristics [71–75]. The compound **23** could be activated for ethylene polymerization by 1 eq of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and the activity of 3.05 kg PE/(mol h atm) was observed [71]. The compound **25** showed similar activity toward ethylene polymerization [72,73]. The system of anionic cobalt complex of a chelate containing imine and amide nitrogen centers **25** and MAO is active for ethylene and propylene [76]. Polyethylene could be prepared in high activity of several thousands kg PE/(mol h atm) with the use of salicylaldimine complex of Cr **26** and cocatalyst MAO [77]. Diphosphine ligand has been well utilized in synthesizing Co and Fe complexes **27** that were active for oligomerization of ethylene with MAO [78].

3. 5-Coordinated complexes

3.1. Bidentate ligands

3.1.1. Amidinate ligands

Amidinate ligands are monoanionic bidentate N–C–N chelates that tend to form 6-coordinate complexes with group 4 metals and a limited number of examples of 5-coordinated amidinate metal complexes is known as illustrated in Fig. 6.

Ethylene oligomerization could be effected by bis(amidinate) complex of vanadium **30** [81] and the catalytic system of yttrium compound **31**/[PhNMe₂H] $[\text{B}(\text{C}_6\text{F}_5)_4]$ produced polyethylene with narrow M_w/M_n of 1.1–1.2 in the activity of 1.04 kg PE/(mol h atm) [82]. The catalytic behavior of Ti species **32** with respect to the polymerization of propylene, 1,3-butadiene and styrene could be controlled by adjusting R group and polymerization condition [83]. The compounds **33** are structurally unique in that amidinate ligand bridges two metal centers and could be activated for ethylene polymerization by pre-alkylation with AlR_3 followed by the treatment with MAO or borate [84].

3.1.2. β -diketiminate ligands

The use of monoanionic β -diketiminate ligands in the development of non-metallocene olefin catalysts is limited and thus only few examples of 5-coordinated complexes are available as illustrated in Fig. 7. Chromium β -diketiminate complexes **34** and **35** are cases in point [85–87]. For ethylene polymerization, the combinations of **34**/Et₂AlCl [85] and **35**/various aluminum cocatalysts [86] gave the activity of about 50 kg PE/(mol h atm).

3.1.3. Other bidentate ligands

Examples of additional 5-coordinated complexes **36–39** derived from other bidentate ligands are given in Fig. 8 [88–91]. Tantalum complex **36** showed low

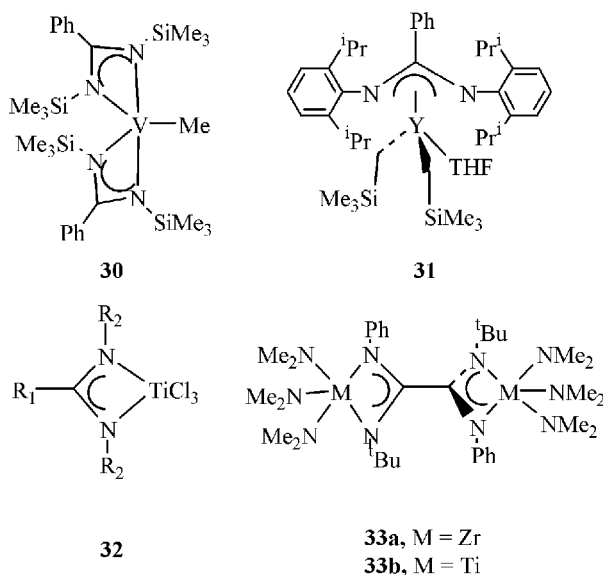


Fig. 6. Examples of 5-coordinated complexes based on amidinate ligands.

activity for ethylene/1-octene copolymerization when it was activated by Al imidazolidine cocatalyst [88]. Cr complex of salicylaldehyde **37** was activated for ethylene by MAO or alkyl aluminum chloride [89] and the successive treatment of dinuclear Ti precatalyst **38** with trimethyl aluminum and MAO resulted in very efficient ethylene polymerization catalytic systems that could produce high molecular weight polymer (M_w of 700,000) with the activity of about 1000 kg PE/(mol h) [90].

3.2. Tridentate ligands

3.2.1. Neutral bis(imino)pyridine ligands

A large number of non-metallocene catalysts based on neutral tridentate bis(imino)pyridine ligands has been reported since Gibson and Brookhart independently observed in 1998 that the polymerization behavior of **40** is outstanding [16,17,92–124]. Some examples are given in Fig. 9.

For the compounds **40**, Fe catalyst is superior to Co one in terms of the activity and could be activated with MAO to produce linear polyethylene up to the high activity of 11,020 kg PE/(mol h atm) [92–94]. Since the aryl

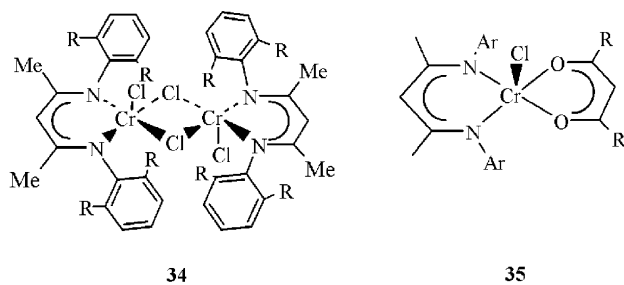


Fig. 7. Examples of 5-coordinated complexes derived from β -diketiminate ligands.

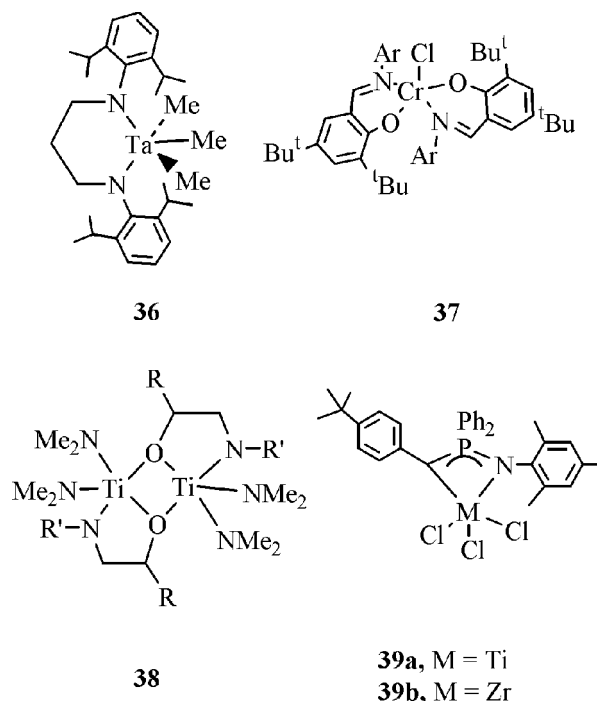


Fig. 8. Examples of 5-coordinated complexes based on other bidentate ligands.

substituents in **40** that are perpendicular to the MN_3 plane are considered to affect the active center, efforts to modify these aryl groups have been reported along with the variation of M and X of MX_2 unit, giving rise to catalytically efficient systems of **41–45** [95–102]. Mechanistic studies [115–120] and immobilization [121–124] of the foregoing 5-coordinated precatalysts containing neutral bis(imino)pyridine ligands have been also carried out.

3.2.2. Tridentate diamide ligands

Schrock and his colleagues developed various tridentate diamide ligand systems by introducing additional donor atoms into diamide systems. The ligand types of $[NON]^{2-}$ [125–130,133,143] and $[NNN]^{2-}$ [132,135–142] are among the most common tridentate diamide ligands. Examples of complexes derived from these ligands, illustrated in Fig. 10, include **46** [125–131], **47** [132–140], **48** [141,142] and **49** [143].

When these complexes with various R were tested for the polymerization of 1-hexene in the presence of cocatalyst $[Ph_3C]B(C_6F_5)_4$, the zirconium species caused living polymerization while the titanium complexes were not active at all. The compound **47** with M = Zr and D = N could be activated by $B(C_6F_5)_3$ for ethylene and propylene polymerization [132] but the compound **47** with M = V and D = N required Me_2AlCl for ethylene polymerization [140].

3.2.3. Other tridentate ligands

In Fig. 11, examples of 5-coordinated complexes **50–58** based on other tridentate ligands that were

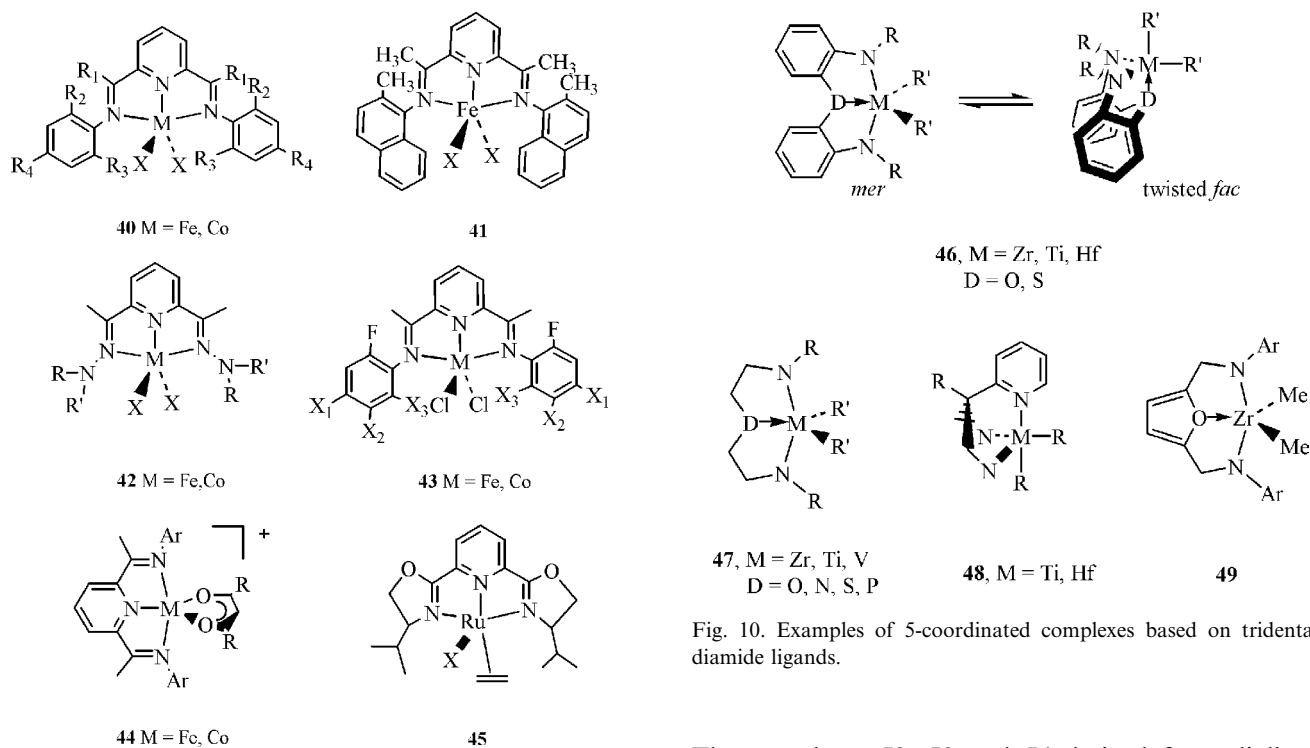


Fig. 9. Examples of 5-coordinated complexes containing neutral bis(imino)pyridine ligands.

not mentioned earlier are illustrated [144–152]. The aluminum complexes of monoanionic tridentate ligands **50** and **58** with $B(C_6F_5)_3$ are active for ethylene polymerization with a very low activity [144,152].

The complexes **52**, **53** and **54** derived from dialkoxy type ligands are also active for olefin polymerization: **52**/MAO shows low activity for ethylene and propylene polymerization [146], **53**/MAO produces bimodal poly-1-hexene [147] and **54**/modified MAO is very active for the production of polyethylene with the activity of several thousands kg PE/(mol h) at 4 atm ethylene pressure [148].

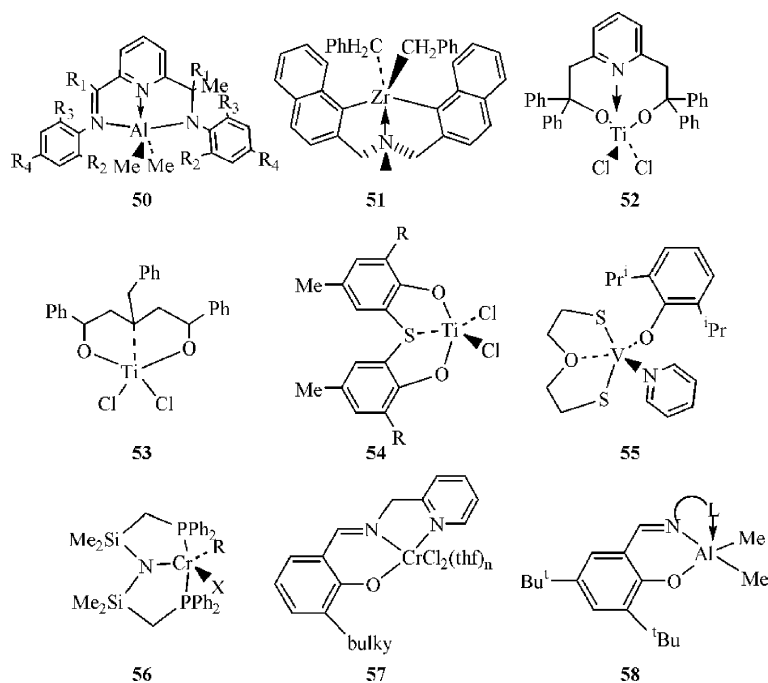


Fig. 11. Examples of 5-coordinated complexes based on miscellaneous tridentate ligands.

4. 6-Coordinated complexes

4.1. Bidentate N–N chelate ligands

Some selected 6-coordinated complexes based on bidentate N–N chelate ligands are shown in Fig. 12. Among amidinate complexes **59**, **60** and **61** [153–158], Eisen's systems **59** with MAO were found to produce isotactic polypropylene in the activity of several tens to hundreds kg PP/(mol h atm) [153–155] while **61** [157] produces polyethylenes in low activity. β -Diketiminato ligand has been utilized and the activation of its zirconium complexes **62** and **63** with MAO produced polyethylenes in the activities of several tens kg PE/(mol h) at 75 psi ethylene pressure [159] and several hundreds kg PE/(mol h) 100 psi ethylene pressure [160], respectively. Pyrrolide-imine ligand has been actively employed in developing various metal complexes [161–166] such as **64**. When the complexes **64** were activated by MAO for ethylene polymerization, the activity range of several tens to thousands kg PE/(mol h atm) was observed for Zr [165], Hf [164] and Cr [163] complexes while the high activity of 14,100 kg PE/(mol h atm) was seen only for Ti complex [161,162]. The Ti complex of **64** also produces ethylene/norbornene copolymers. The last example of Fig. 12 is imidazole-based dinuclear Cr complex **65** that was activated by MAO to produce

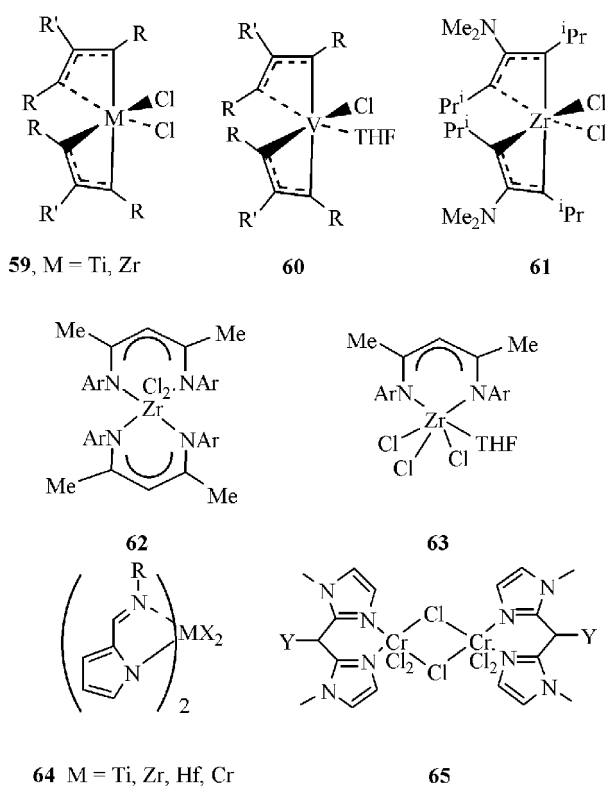


Fig. 12. Examples of 6-coordinated complexes based on bidentate N–N chelate ligands.

oligomeric polyethylene in several hundreds kg PE/(mol h) activity at 40 bar ethylene pressure [167].

4.2. Bidentate N–O chelate ligands

FI catalytic systems **66** reported by Fujita et al. [18,168–191] are phenoxy-imine based complexes and constitute the most extensively studied 6-coordinated complexes based on bidentate N–O chelate ligands whose examples are illustrated in Fig. 13. FI catalysts show outstanding polymerization behavior toward various monomers. The coupled use of **66** with MAO showed metal dependant activities ranging from several thousands kg PE/(mol h atm) for Zr [168–174] to several tens of thousands kg PE/(mol h atm) for Ti [175–182]. In particular, titanium complex of **66** with fluorinated phenyl group at R₃ position was found not only to catalyze living polymerization of ethylene but also to produce polyethylene with multimodal molecular weight distribution [175–182]. In addition, FI catalysts are also active for syndiotactic living polymerization of propylene, ethylene/propylene copolymerization and polymerization of 1-hexene as well as conjugated diene [183–191]. The details of FI catalysts have been described in the review written by Fujita and his colleagues [192].

Other complexes of bidentate N–O chelate ligands are also worthy of comment. Chromium complex of reduced Schiff-base N,O-chelate ligand **67** was activated by Et₂AlCl to produce for ethylene polymerization in 130 kg PE/(mol h atm) activity [193], zirconium ketoiminato complex **68** is inactive for ethylene polymerization [194], and the system of dinuclear complex of trivalent vanadium **69** and cocatalyst Et₂AlCl shows good activity for ethylene polymerization [195].

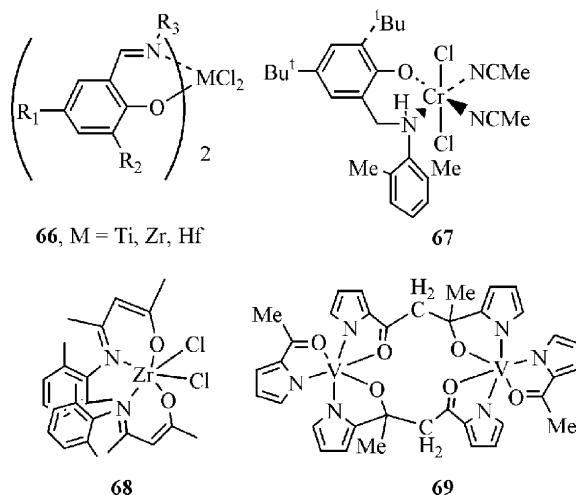


Fig. 13. Examples of 6-coordinated complexes based on bidentate N–O chelate ligands.

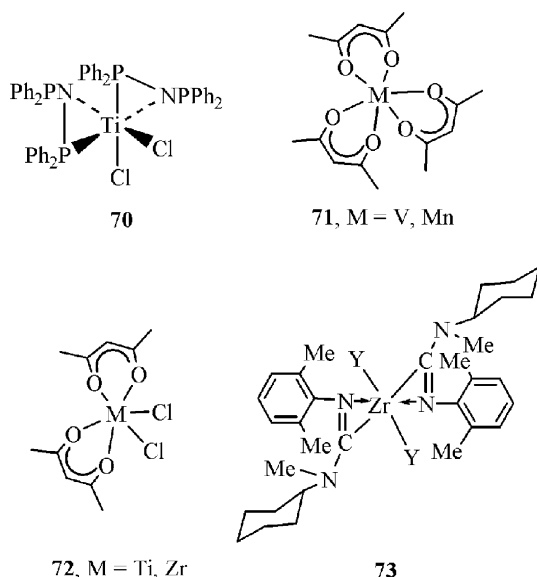


Fig. 14. Examples of 6-coordinated complexes based on other bidentate chelate ligands.

4.3. Other bidentate ligands

Examples of 6-coordinated complexes derived from other bidentate chelate ligands are given in Fig. 14. Ti complex **70** and MAO form an active catalytic system for the production of elastomeric polypropylenes [196]. Homoleptic vanadium complex of acetylacetonate ligand **71** can be activated by aluminum alkyl chloride for ethylene/propylene copolymerization [197] but manganese analogue of **71** shows negligible activity for ethylene polymerization [198]. Group 4 heteroleptic complexes of acetylacetonate ligand **72** are all active for propylene polymerization in the presence of MAO, producing elastomeric polypropylene [199]. η^2 -Formamidinyl Zr complex **73** was activated by $[\text{NHMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ for homopolymerizations of ethylene and 1-hexene [200].

4.4. Tridentate ligands

Various types of 6-coordinated complexes based on tridentate chelate ligands have been reported [201–219] and in Fig. 15 some representative examples are illustrated. Tris(pyrazolyl)borate ligand, a sterical analogue of Cp ligand, has been employed in synthesizing various metal complexes **74** [201–203] and among them Ti and Zr species could be efficiently activated by MAO to produce polyethylene in very high activity of several thousands kg PE/(mol h atm). Triazacyclohexane ligand was found useful in preparing non-metallocene complex systems **75** and **76** [204–207] and in particular **76**/MAO system produced polyethylenes in very high activity of several tens of thousands kg PE/(mol h atm) [205]. On the other hand, the use of phos-

phorous analogue of triazacyclohexane ligand as in **77** led to the observation of low activity (several tens kg PE/(mol h atm)) for ethylene polymerization [208]. The ancillary utility of bis(imino)pyridyl ligand has been tested and its compounds **78** show various ethylene polymerization activity from several hundreds to several thousands kg PE/(mol h atm) depending on the type of metal [209–211].

Chelate ligands with mixed donor atoms or with different bridging length between donor atoms have been also utilized. Cr(III) complex **79**/MAO is very active for ethylene trimerization [212,213], bis(carbene)pyridine complex of Cr **80** shows the activity of 40,440 kg PE/(mol h atm) for ethylene oligomerization [214] and zirconium complex with O–N–O chelate sites **81** produces polyethylene with the activity of 703 kg PE/(mol h atm) [215]. The use of chelate ligand with different bridging length between donor atoms led to the synthesis of vanadium complex **82** that could be activated by Et_2AlCl for ethylene polymerization, showing the activity of 447 kg PE/(mol h atm) [216].

4.5. Other ligands

Selected examples, **83–85**, of 6-coordinated complexes based on miscellaneous ligands are shown in Fig. 16. Okuda et al. has reported group 4 complexes **83** that contain O–S–S–O tetradentate ligand. The sys-

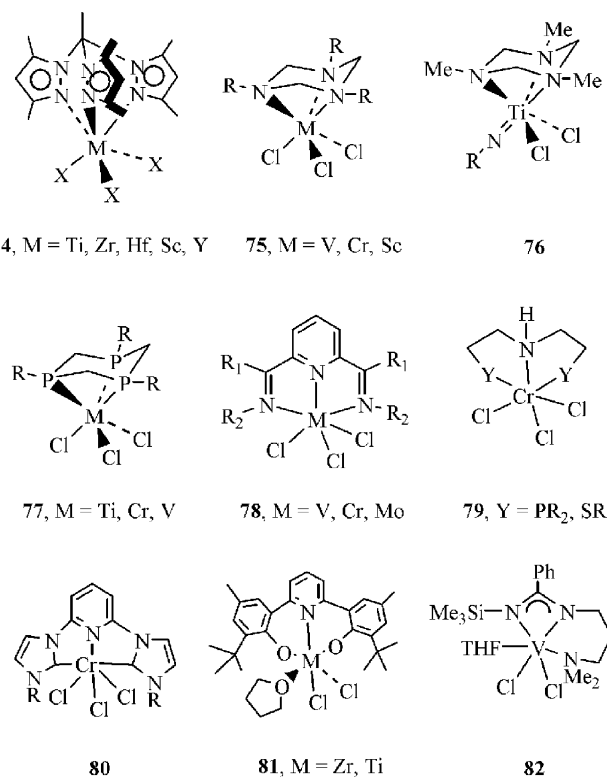


Fig. 15. Examples of 6-coordinated complexes based on tridentate chelate ligands.

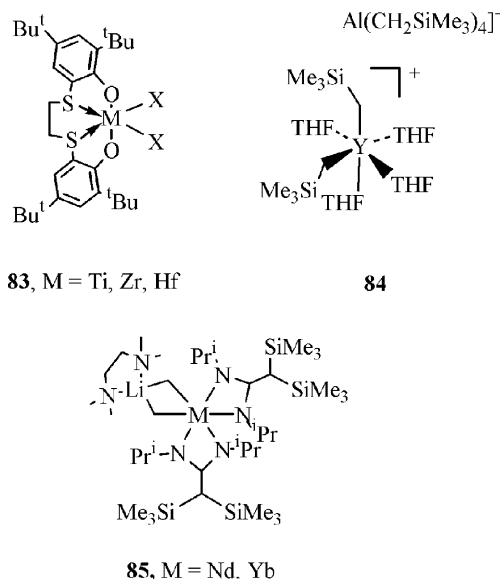


Fig. 16. Examples of 6-coordinated complexes based on miscellaneous ligands.

tem of Ti analogue of **83** and MAO was found active for isotactic polymerization of 4-methyl-1,3-pentadiene [220]. In addition, all three **83** complexes produce isotactic polystyrenes [221]. The compound **84** that contains cationic yttrium center with two non-chelating ligands and four THF molecules is interesting and requires cocatalyst AlR_3 to produce polyethylene with the activity of 1351 kg PE/(mol h atm) [222]. The compounds **85** are unique in that they are heterodinuclear species of lanthanide and lithium and were found active for styrene polymerization with the activity of several hundreds kg PS/(mol h) [223].

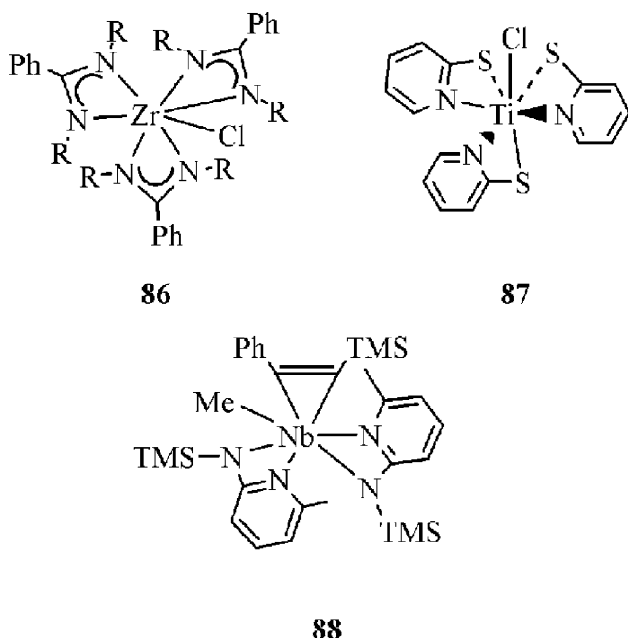


Fig. 17. Examples of 7-coordinated complexes.

5. 7-Coordinated complexes

The examples of non-metallocene catalytic systems with 7-coordination are limited and three cases are illustrated in Fig. 17. Benzamidinate based zirconium complex **86** was activated by MAO to give the activity of 9230 kg PP/(mol h) at 12 atm for the production of isotactic polypropylene [154]. Tris(pyridine-2-thiolate) complex of Ti **87** also requires MAO to catalyze ethylene and styrene polymerizations with the activity of 38 kg PE/(mol h atm) and 470 kg PS/(mol of Ti mol of styrene h atm), respectively [224]. Amidoniobium complex **88** requires initial reaction with $B(C_6F_5)_3$ followed by the use of *i*-Bu₃Al as a scavenger for the production of polyethylene with low activity [225].

6. Concluding remarks

The discovery of homogeneous catalysts for olefin polymerization has brought a revolution in polymer synthesis since the homogeneous catalysts-based polymers can possess excellent physical properties or stereo-regularities that are difficult or impossible to be achieved by other known polymerization methods. Currently, we are in the evolutionary development stage according to the cyclical view of revolution? evolution? revolution in technology development of polymer chemistry [2] and the followings among others can be singled as future research directions of the chemistry of homogeneous catalytic systems: the design of new ligand systems, the use of homogeneous catalytic systems for the polymerization of other monomers and the enhancement of the processibility of homogeneous catalysts-based polyethylene.

The report of cyclophane-based highly active late-transition-metal catalysts for ethylene polymerization by Guan et al. [226] is in strong support of the first view of the future research directions. The well-defined special cavity and sterically hindered microenvironment provided by cyclophane ligand frameworks are expected to bring fine-tuning of the catalytic properties. As to the second research direction, the efforts to use homogeneous polymerization catalysts for the polymerization of other monomers such as lactides, lactones and epoxides can be recognized [227–230]. The last direction of improving the processibility of homogeneous catalysts-based polyethylene might be justified by noting that its bulk production has been hampered by significant processing problems caused by lack of branching and narrow molecular weight distribution in spite of its excellent properties such as high clarity and high impact strength [7b,231]. Thus, the enhancement of the processibility of homogeneous catalysts-based polyethylene without losing the excellent properties has become an important research subject in recent years, with particular focus on introducing branches and modulating the molecular weight distribu-

tion [17,232–238], but homogeneous catalytic systems that can produce branched polyethylene with bimodal molecular weight distribution are yet to be observed [239]. To close on a positive note, I would like to add that the cyclical view of revolution → evolution → revolution in technology development would allow us to expect many more years of productive research in homogeneous catalysts leading to a revolutionary development in organometallic chemistry.

Acknowledgements

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