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Review

Organometallic catalysts for copolymerization of cyclic olefins

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Contents

Abstract

This article provides an overview on recent progress in the addition copolymerization of ethylene or α-olefins with cyclic olefins by various organometallic catalysts. Special emphasis is placed on the catalyst structures that govern the copolymerization activity, comonomer incorporation, and the tacticity, molecular weight and thermal property of the resulting copolymers.

Keywords: Copolymerization; Cyclic olefins; Ethylene; Metallocene catalysts; α-Olefins

1. Introduction

Polyolefins are a multibillion dollar a year industry and a variety of high performance polymer products have been widely applied in our everyday lives. In general, the potential applications of a polymer are determined by its physical and mechanical properties, which mainly depend on the polymer composition and architectures. Vinyl-polycycloolefins consisting of strained rings, which are formed via addition polymerization of cyclic olefins, can generally exhibit unique physical properties that differ from those of polyolefins with acyclic structures [1]. However, such vinyl-polycycloolefins produced are usually insoluble or have high melting points ($T_m > 400\,^\circ C$) or high glass transition temperatures (T_g) which are close to their decomposition temperatures. Therefore, such polycycloolefins are generally difficult to process and are of little commercial interest. To improve the processability of polycycloolefins, the introduction of a comonomer such as ethylene or α-olefins into the polycycloolefin chains via a coordinative–insertive (addition) mechanism can be a useful method, because the

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resultant cyclic olefin copolymers (COCs) have lower rigidity.

The first cyclic olefin copolymers were reported in the early 1960s, which were prepared by the copolymerization of ethylene with a monocyclic olefin monomer such as cyclopentene (CPE), cycloheptene (CHP), cyclooctene (COE), or cyclohexene (CHE) by use of Ziegler–Natta catalysts $TiCl_4/AlEt_2Cl$ or vanadium-based catalysts such as $VCl_4/Al(C_6H_{13})_3$ and $V(acac)_3/AlEt_2Cl$ [2]. A significant breakthrough in this area was achieved about 30 years later when Kaminsky et al. discovered that the C_2-symmetric metallocene-based catalysts such as $[Et(Ind)_2]ZrCl_2$/MAO could catalyze the addition copolymerization of ethylene with various cyclic olefins such as CPE, CHP, COE and norbornene (N) [3]. Compared with the conventional Ziegler–Natta catalysts and vanadium catalysts, the group 4 matallocene catalysts showed much higher activity, and more importantly they could be fine-tuned by ligand modification to control the structures and properties of the resultant copolymers [4]. Subsequently, various homogeneous organometallic catalysts, including half-sandwich [5] and cyclopentadienyl-free group 4 metal catalysts [6] and late transition metal catalysts [7] have been reported, and more recently cationic rare earth metal half-sandwich alkyls have also been found to show excellent activity for the copolymerization of various cyclic olefins [8]. By choosing an appropriate catalyst system, a variety of cyclic olefins, including monocyclic, dicyclic and multicyclic olefins with or without functional groups, can now be copolymerized with ethylene or α-olefins to give the corresponding COCs with controlled microstructures. Some of these copolymers not only have good processability, but could also show excellent thermal, optical and mechanical properties such as excellent resistance to heat and chemicals, excellent transparency, high refractive index, high stiffness or softness. These remarkable properties make COCs a new class of engineering plastics with potential for commercial applications in various areas such as video and compact discs, optical lenses, light-conducting fibers, blister foils, medical equipments, and capacitors.

The copolymerization of cycloolefins and the resultant COCs have so far been included in part in some overviews on metallocene or non-metallocene catalysts [4–8]. Very recently, Tritto et al. gave a detailed review on the mechanism of copolymerization of ethylene and norbornene [4a]. The purpose of this article is to give a thorough account of literatures on the addition copolymerization of various cyclic olefins with ethylene or α-olefins by homogenous organometallic catalysts. The discussions are divided into sections based on the types of the active metal centers and the ancillary ligands of the catalysts. Emphases are placed on the catalysts' structure–performance relations.

2. Group 3 metal catalysts

Cationic rare earth (group 3 and lanthanide) metal alkyls have recently emerged as a new class of catalysts for the polymerization and copolymerization of various olefins including cyclic olefins [8,9]. The combination of half-sandwich scandium bis(alkyl) complexes such as $Cp'Sc(CH_2SiMe_3)_2(THF)$ (**1**) (**a**: $Cp' = C_5Me_4SiMe_3$; **b**: $Cp' = C_5H_3(SiMe_3)_2$-1,3; **c**: $Cp' = C_5Me_5$) (Fig. 1) with 1 equiv. of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$ showed excellent activity for the copolymerization of ethylene (E) and norbornene (N) [10]. Under appropriate conditions (25 °C and 1 atm ethylene), the **1a**/$[Ph_3C][B(C_6F_5)_4]$ system afforded an amorphous E–N alternating copolymer with $M_n = 85$ kg/mol, PDI = 2.19, $T_g = 118$ °C and N content = 44 mol%, with an activity of as high as 25200 kg/(mol$_{Sc}$ h). It is particularly noteworthy that although this catalyst system showed very low activity for the homopolymerization of norbornene, the insertion of a norbornene monomer into a Sc–CH_2CH_2R bond and that of an ethylene monomer into a Sc–norbornyl bond were very fast, and the former was even more preferred to successive ethylene insertion when an adequate amount of norbornene was present. This unique nature thus led to rapid and exclusive formation of the alternating E–N copolymers without successive NN sequences under appropriate E/N molar ratios. If a relatively small amount of norbornene was used under 1 atm of ethylene, an E–N copolymer with an ethylene block P(E-*co*-N)-*b*-PE could be obtained when the reaction was terminated in an appropriate period of time (Scheme 1). The Cp′ ligands in these complexes showed a significant influence on the catalytic activity, with an order of **1a** ($C_5Me_4SiMe_3$) > **1c** (C_5Me_5) > **1b** ($C_5H_3(SiMe_3)_2$-1,3). The analogous Sc complex with an unsubstituted Cp′ ligand ($Cp' = C_5H_5$) showed no activity for the copolymerization under the same conditions. As an activator, $[PhMe_2NH][B(C_6F_5)_4]$ was also effective, but $B(C_6F_5)_3$ was inert under the same conditions. The Y and lanthanide analogues did not show an activity under the same conditions, indicating that the activity was metal dependent.

The complex **1a**/$[Ph_3C][B(C_6F_5)_4]$ system also showed excellent activity for the copolymerization of dicyclopentadiene (DCPD) with ethylene under mild conditions, constituting the first example of alternating, regioselective copolymerization of DCPD with ethylene (Scheme 1) [11]. The amorphous

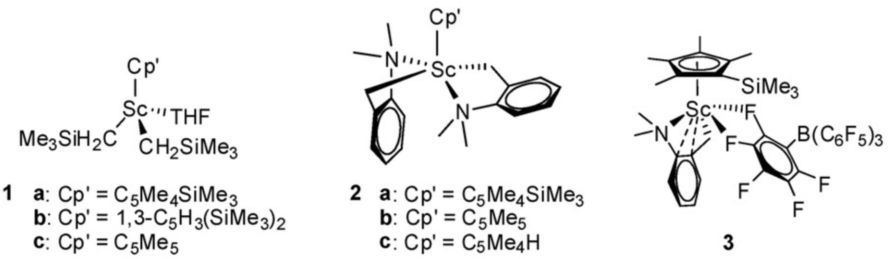
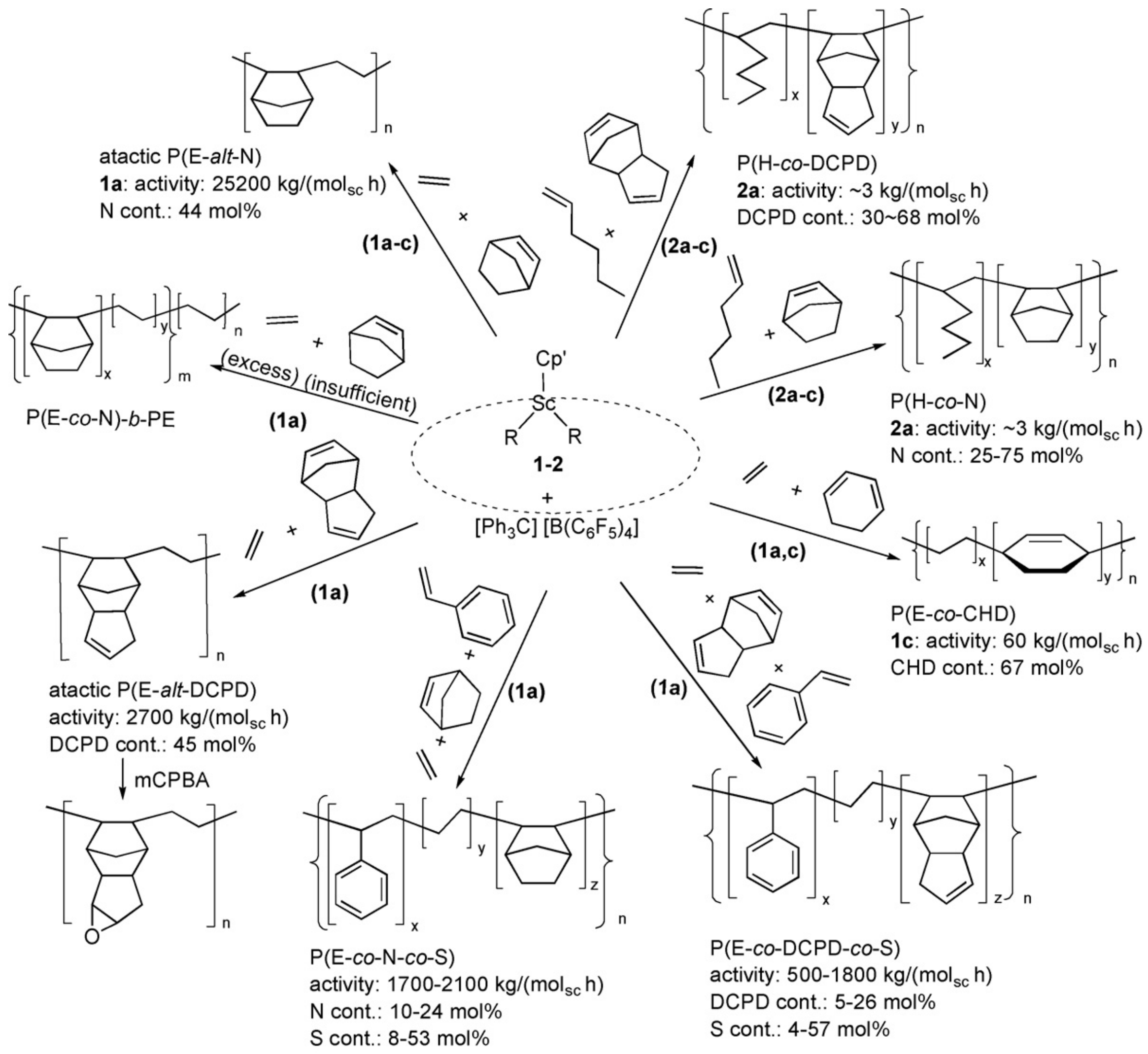


Fig. 1. Neutral and cationic half-sandwich scandium alkyl complexes.



Scheme 1. Copolymerization of cyclic olefins by scandium catalysts.

E–DCPD copolymers with DCPD content up to 45 mol% and $M_n \approx 200$ kg/mol could be obtained with an activity of 2700 kg/(mol$_{Sc}$ h) under 1 atm of ethylene at 25 °C. The resulting E–DCPD copolymers contained cyclopentene units, suggesting that the copolymerization proceeded exclusively through enchainment of the norbornene double bond. Insoluble cross-linking polymer products were not observed. The resulting copolymers could be assigned to atactic alternating E–DCPD copolymers with both *meso* and *racemic* sequences, in which continuous DCPD–DCPD units were negligible. Epoxidation of the alternating E–DCPD copolymers could be easily achieved by use of *m*-chloroperbenzoic acid (*m*CPBA) as an oxidant, which quantitatively converted the olefinic group into epoxy group (Scheme 1).

By use of the **1a**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst, the terpolymerization of ethylene, norbornene and styrene (S) and the terpolymerization of ethylene, DCPD and styrene were also achieved for the first time (Scheme 1) [11]. The corresponding poly(E-*co*-N-*co*-S) or poly(E-*co*-DCPD-*co*-S) terpolymers with S content of 4–57 mol% and N or DCPD content of 5–26 mol% could be easily prepared by changing the norbornene/styrene or DCPD/styrene feed ratio under 1 atm of ethylene. The polymers obtained are random terpolymers containing isolated or alternating N (or DCPD) units, isolated S units and syndiotactic S–S sequences, while no S–N or S–DCPD sequences were found in the terpolymer backbones.

The complexes **1a**–**c**/activator systems were also examined for the polymerization and copolymerization of 1,3-cyclohexadiene (CHD) with ethylene (E) (Scheme 1) [12]. On treatment with an activator such as [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [PhNMe$_2$H][B(C$_6$F$_5$)$_4$], **1a** and **1c** showed extremely high 1,4-*cis*, regio- and stereoselectivity (>99%) for the polymerization of CHD, while **1b** afforded polymers containing mixed 1,2- and *cis*/*trans*-1,4-CHD units under the same conditions. The copolymerization of CHD with ethylene by **1a**,**c**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] gave the corresponding random copolymers with a wide range of CHD contents (10–67 mol%) in a *cis*-1,4-regular fashion.

By use of *o*-*N*,*N*-dimethylaminobenzyl CH$_2$C$_6$H$_4$NMe$_2$-*o* as an alkyl ligand in place of CH$_2$SiMe$_3$, the THF-free scandium half-sandwich bis(aminobenzyl) complexes [Cp′Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$] (**2**) (**a**: Cp′ = C$_5$Me$_4$SiMe$_3$; **b**:

$Cp' = C_5Me_5$; **c**: $Cp' = C_5Me_4H$) could be obtained (Fig. 1) [13]. On treatment with 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$, these complexes could serve as efficient catalysts for the copolymerization of 1-hexene (H) with cyclic olefins such as N and DCPD (Scheme 1). With respect to DCPD, the reaction took place only at the norbornene double bond, while the cyclopentene C=C double bond remained unchanged. The 1-hexene incorporation in the copolymers could be easily controlled in a wide range (25–75 mol%) by changing the N/H or DCPD/H feed ratio. An almost linear relationship between T_g and the 1-hexene content of the copolymers was observed.

The contact ion-pair complex $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)(\kappa^2F\text{-}C_6F_5)B(C_6F_5)_3$ (**3**) was isolated from the 1:1 reaction of **2a** and $[PhMe_2NH][B(C_6F_5)_4]$, and was structurally characterized by X-ray analysis (Fig. 1) [13]. Complex **3** alone could serve as a "single-component" catalyst for the copolymerization of 1-hexene with N or DCPD, in a similar manner as that of the **2a**/$[PhMe_2NH][B(C_6F_5)_4]$ combination.

3. Group 4 metal catalysts

3.1. Metallocene complexes

3.1.1. Bis(cyclopentadienyl) complexes

A number of group 4 metal complexes bearing various linked and unlinked cyclopentadienyl ligands have been reported for the copolymerization of cyclic olefins with ethylene or α-olefins. The representative structures of these complexes are shown in Fig. 2, and their typical copolymerization reactions are illustrated in Scheme 2.

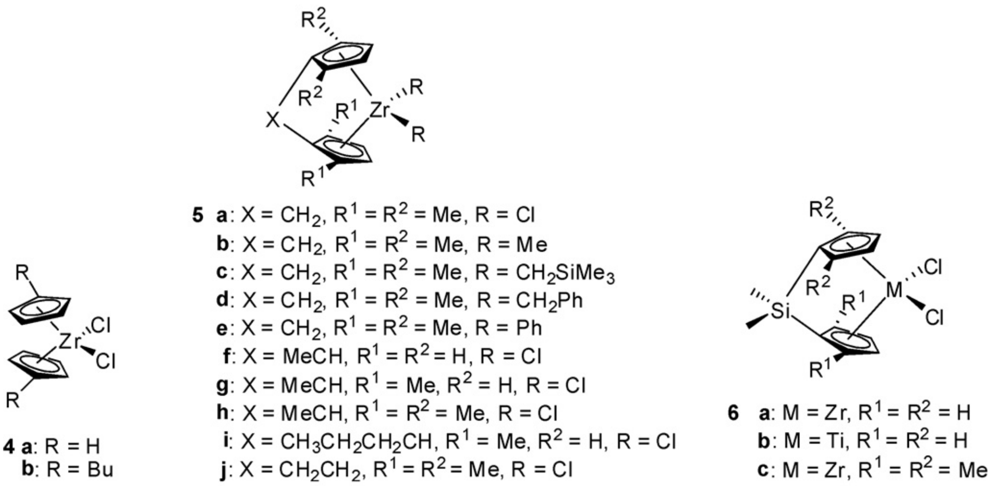
In the presence of methylaluminoxane (MAO) as a cocatalyst, the bis(cyclopentadienyl)zirconium complex $(Cp)_2ZrCl_2$ (**4a**) could serve as an effective catalyst for the copolymerization of ethylene with norbornene (activity = 500–60 kg/(mol$_{Zr}$ h)) to give the corresponding random E–N copolymers (N content = 7–68 mol%, $T_g < 180\,°C$, $T_m < 207\,°C$) containing isolated N units, alternating sequences and long N block sequences (Scheme 2) [14].

The **4a**/MAO catalyst system was also effective for the regioselective copolymerization of 5-vinyl-2-norbornene (VN) with ethylene with the maximum incorporation of VN of 14 mol% in the resultant copolymers (activity ca. 3.5 kg/g$_{Zr}$) (Scheme 2) [15]. The enchainment of the diolefin VN occurred selectively at the cyclic double bond, leaving the exo vinyl double bond unchanged. The pendant vinyl group in the copolymers could be quantitatively functionalized to the hydroxy or epoxy group using standard organic chemical transformations under mild reaction conditions.

The copolymerization of ethylene with 2,5-norbornadiene (NBD) by **4a**/MAO yielded the corresponding copolymers containing 2–19 mol% of NBD units (activity: 8–0.7 kg/(g$_{Zr}$ h) (Scheme 2) [16,17]. The reaction occurred exclusively through one of the two equally reactive endo cyclic double bonds, and no cross-linking was observed. An analogous complex bearing the butyl-substituted cyclopentadienyl ligands, $(BuCp)_2ZrCl_2$ (**4b**), showed higher activity and gave higher molecular weight copolymers than those of **4a** under the same condition, probably due to enhanced electron density at the metal centre. However, a slight drop in NBD incorporation in the copolymers was observed because of the increase in steric hindrance in **4b**.

The regioselective copolymerization of NBD (at only one of the two C=C double bonds) with 1-hexene could also be achieved by use of the **4a** and **b**/MAO systems under various conditions, though the resulting copolymers had rather low molecular weights (1000–2000 g/mol) (Scheme 2) [18]. The incorporation on NBD could reach as high as 37 mol% with an activity of 89 kg/(mol$_{Zr}$ h). End group analysis of the co-oligomers revealed that both 1,2-insertion and 2,1-insertion of 1-hexene units (regio errors) occurred in the H–NBD copolymerization.

The copolymerization of ethylene with dicyclopentadiene (DCPD) by the **4a**/MAO system at 40 °C and 1 bar ethylene afforded the copolymers with the DCPD content less than 2 mol% [19]. The **4a**/MAO system served as an efficient catalyst for the copolymerization of ethylene with dimethanooctahydronaphthalene (DMON) to give the corresponding copolymers with DMON contents of 25–35 mol% (Scheme 2) [20].

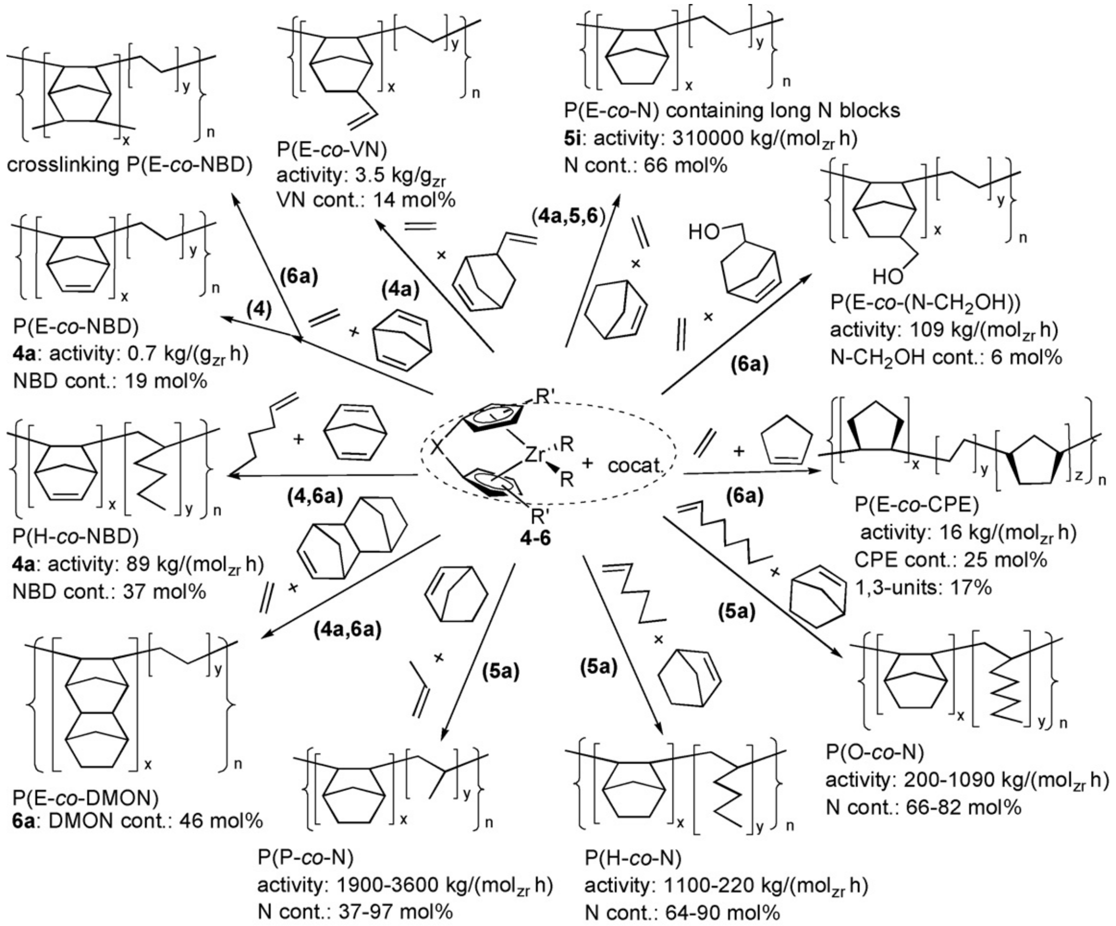


4 a: R = H
b: R = Bu

5 a: X = CH_2, $R^1 = R^2$ = Me, R = Cl
b: X = CH_2, $R^1 = R^2$ = Me, R = Me
c: X = CH_2, $R^1 = R^2$ = Me, R = CH_2SiMe_3
d: X = CH_2, $R^1 = R^2$ = Me, R = CH_2Ph
e: X = CH_2, $R^1 = R^2$ = Me, R = Ph
f: X = MeCH, $R^1 = R^2$ = H, R = Cl
g: X = MeCH, R^1 = Me, R^2 = H, R = Cl
h: X = MeCH, $R^1 = R^2$ = Me, R = Cl
i: X = $CH_3CH_2CH_2CH$, R^1 = Me, R^2 = H, R = Cl
j: X = CH_2CH_2, $R^1 = R^2$ = Me, R = Cl

6 a: M = Zr, $R^1 = R^2$ = H
b: M = Ti, $R^1 = R^2$ = H
c: M = Zr, $R^1 = R^2$ = Me

Fig. 2. Group 4 metal complexes bearing two cyclopentadienyl ligands.



Scheme 2. Copolymerization of cyclic olefins by bis(cyclopentadienyl) group 4 metal catalysts.

The *ansa*-zirconocene complex $[CH_2(2,5\text{-}Me_2Cp)_2]ZrCl_2$ (**5a**) bearing the methylene-bridged bis(2,5-dimethylcyclopentadienyl) ligands showed much higher activity and higher norbornene incorporation ability in the E–N copolymerization than those of the unlinked analogue **4a** under the similar conditions, because of the wider open metal center and more electron-donating ligand environment of **5a** [21]. Under appropriate conditions, the **5a**/MAO catalyst could show activity as high as 206000 kg/(mol$_{Zr}$ h). The analogous cationic hydrocarbyl complexes, generated by reaction of $[CH_2(2,5\text{-}Me_2Cp)_2]ZrR_2$ (**5b–e**) (**b**: R = Me; **c**: CH_2SiMe_3; **d**: CH_2Ph; **e**: Ph) with an activator such as $B(C_6F_5)_3$, $[Me_2PhHN][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$, were also active for the E–N copolymerization [22]. The nature of the hydrocarbyl groups could affect the stability of the cationic species and ultimately the olefin polymerization activity, i.e., the more electronic donating, the less catalytic active for the copolymerization. The activity of the activators decreased in the order of $[Me_2PhHN][B(C_6F_5)_4] > [Ph_3C][B(C_6F_5)_4] > B(C_6F_5)_3$ for a given alkyl group.

A detailed study on the influence of the linkers and the Cp-substituents of the *ansa*-metallocene Zr complexes on the copolymerization of ethylene with norbornene was reported [23–25]. Among complexes $[X(2,5\text{-}R^2Cp)(2,5\text{-}R^1Cp)]ZrCl_2$ (**5f–j**) (**f**: X = MeCH, $R^1 = R^2 = H$; **g**: X = MeCH, R^1 = Me, R^2 = H; **h**: X = MeCH, $R^1 = R^2$ = Me; **i**: X = $CH_3CH_2CH_2CH$, R^1 = Me, R^2 = H; **j**: X = CH_2CH_2, $R^1 = R^2$ = Me) (Fig. 2), the activity decreased in the order of **5i > 5g > 5a > 5h > 5j > 5f**, among which the methylmethylene-bridged bis(unsubstituted-Cp) complex **5f** showed the lowest activity, while the propylmethylene-bridged (2,5-dimethylcyclopentadienyl)-(unsubstituted-cyclopentadienyl) complex **5i** showed the highest activity, as a result of the interplay of steric and electronic effects of the ancillary ligands. Under appropriate conditions (80 °C, 100 psig ethylene), the **5i**/MAO system showed activity as high as 310 000 kg/(mol$_{Zr}$ h) with norbornene incorporation up to 66 mol% (M_w = 49 kg/mol, PDI = 2.3, T_g = 186 °C) (Scheme 2). The resulting random copolymers contained isolated N units, alternating sequences and long N microblocks.

The **5a**/MAO system was also investigated for the copolymerization of norbornene with various α-olefins such as propylene (P), 1-hexene (H), and 1-octene (O) (Scheme 2) [26]. The copolymerization activity decreased as the co-monomer changed from propylene to bulkier α-olefins. The molecular weight dramatically decreased with the increase of the α-olefin feed ratio, suggesting that the coordination of α-olefins to the active site of the catalyst renders the growing polymer chain susceptible to chain transfer reaction. The increase of the α-olefin content in the copolymers resulted in a dramatic decrease in their glass transition temperature (T_g) and molecular weigh (M_w). The P–N copolymer containing the highest P content of 63 mol% (M_w = 5.9 kg/mol, PDI = 1.19, T_g = 96 °C) was obtained with an activity of 1900 kg/(mol$_{Zr}$ h), while the H–N copolymer with the maximum H content = 36 mol% (M_w = 5.5 kg/mol, PDI = 1.35, T_g = 98 °C) and the O–N copolymer with the maximum O content = 34.4 mol% (M_w = 8.5 kg/mol, PDI = 1.51, T_g = 85 °C) were obtained with the activity of 1100 kg/(mol$_{Zr}$ h) and 200 kg/(mol$_{Zr}$ h), respectively.

The Me_2Si-bridged complex $[Me_2Si(Cp)_2]ZrCl_2$ (**6a**), in combination with MMAO (methylisobutylaluminoxane), was reported to copolymerize ethylene and cyclopentene (CPE) to give preferentially the copolymers with *cis*-1,2-CPE units under appropriate conditions [27]. At high CPE concentrations, however, the E–CPE copolymers containing a mixture of 1,2-and 1,3-CPE units (at CPE content = 25 mol%, 1,3-CPE units = 17%) were obtained, suggesting that the isomerization of the 1,2-substituted cyclopentane terminal to the 1,3-substituted one could take place at high CPE concentrations.

The titanocene complex $[Me_2Si(Cp)_2]TiCl_2$ (**6b**) exhibited higher activity but lower norbornene incorporation ability than the zirconocene analogue **6a** for the E–N copolymerization, because **6b** was more active than **6a** in the homopolymerization of ethylene under the given conditions [28]. The effect of the aluminoxane cocatalyst was also investigated. The combination of EBAOI3 (containing a 3:7 (mol/mol) mixture of $AlEt_3$ and Al(*iso*-Bu)$_3$) with **6a** showed lower activity (21 kg/(mol$_{Zr}$ h)) than the **6a**/MAO system (62 kg/(mol$_{Zr}$ h)), because the reactivity of the metal–alkyl bonds usually decreased in the order of methyl > ethyl > isobutyl. However, the resulting E–N copolymers in the case of EBAOI3 contained higher N contents (∼60 mol%) than those obtained in the case of MAO (N content ≤ 44 mol%). The monomer distributions in the copolymers prepared with different aluminoxanes (MAO and EBAO) were also different. However, a linear relationship between the norbornene content and the T_g of the resulting copolymers was observed in both cases.

As observed in the methylene-linked *ansa*-metallocene complexes **5a–j**, the silylene-linked zirconocene complex with 2,5-dimethyl-substituted Cp ligands, $[Me_2Si(2,5\text{-}Me_2Cp)_2]ZrCl_2$ (**6c**), showed much higher activity (27000 kg/(mol$_{Zr}$ h) than that of the methyl-free analogue **6a** (21 kg/(mol$_{Zr}$ h)) for the copolymerization of ethylene and norbornene under similar conditions, yielding a high molecular weight E–N copolymer with similar high N incorporation (N content = 53 mol%, M_w = 144 kg/mol, PDI = 2.0, T_g = 154 °C) (Scheme 2) [24].

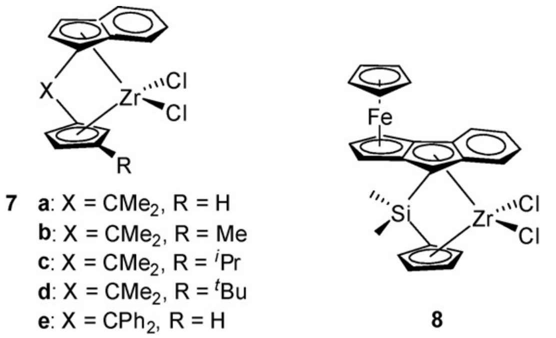
The copolymerization of ethylene with 5-norbornene-2-methanol (N–CH_2OH), which was pretreated with trimethylaluminum (TMA), was achieved by use of the **6a**/MAO system, which afforded the corresponding hydroxy-functionalized COCs with a maximum N–CH_2OH incorporation of 6 mol% and an activity of 109 kg/(mol$_{Zr}$ h) (Scheme 2) [29]. This was in contrast to the **4a**/MAO system which showed negligible N–CH_2OH incorporation under the similar conditions. The higher N–CH_2OH-incorporation ability of **6a** is apparently due to its more open coordination environment at the metal center.

The copolymerization of ethylene or 1-hexene with 2,5-norbornadiene (NBD) by **6a**/MAO was also investigated (Scheme 2) [16,18]. In contrast to the high regioselectivity observed in the case of **4a**/MAO, the E–NBD copolymerization catalyzed by **6a**/MAO occurred through both of the two C=C double bonds of the NBD unit and yielded the insoluble cross-linking copolymer products [16], due to the more open metal center of **6a** which could allow the second C=C double bond to participate in the copolymerization reactions. However, **6a** could promote the regioselective copolymerization of 1-hexene and NBD to give the corresponding cooligomers (NBD content = 18 mol%, M_n = 1.5 kg/mol), similar to what was observed in the case of **4a** [18]. Higher regio errors (85 mol% 2,1-insertion) in the H units of the resulting copolymers were observed in comparison with those in the case of **4a** (52 mol% 2,1-insertion) under the same conditions. The copolymerization of ethylene with dimethanooctahydronaphthalene (DMON) by the **6a**/MAO system gave the corresponding copolymers with higher DMON contents (40–46 mol%) than those obtained by the **4a**/MAO system (25–35 mol%) (Scheme 2) [20].

3.1.2. Mixed (indenyl)(cyclopentadienyl) complexes

In comparison with the bis(cyclopentadienyl) complexes, the mixed (indenyl)(cyclopentadienyl) analogues usually showed higher activity for the copolymerization of cyclic olefins, affording higher molecular weight copolymers with relatively shorter cyclic olefin microblocks. Moreover, a dramatic steric effect was observed when bulky alkyl substituents were introduced at the 3-position of the cyclopentadienyl ligand in such C_s-symmetric complexes, which led to the enhancement of the total polymerization activity and the molecular weight of the copolymers but to the decrease in incorporation of cyclic olefin monomers. This is probably because the indenyl ligand is more sterically demanding and electronically donating than the Cp group and can lead to formation of a looser ion-pair in the active catalyst species and cause stronger nonbonding interactions between a polymer chain and the ligand, which thus hampers the formation of the long cyclic olefin microblocks. Examples of the linked (indenyl)(cyclopentadienyl) Zr complexes are given in Fig. 3. Their typical copolymerization reactions are shown in Scheme 3.

In the copolymerization of ethylene with norbornene by the catalyst systems $[Me_2C(Ind)(3\text{-}R\text{-}Cp)]ZrCl_2$ (**7**)/MAO (**a**: R = H; **b**: Me; **c**: ^{i}Pr; **d**: ^{t}Bu), the introduction of a bulky alkyl group such as ^{i}Pr or ^{t}Bu at the 3-position of the Cp ligand showed dramatic influences on the catalyst activity and the microstructures of the resultant copolymers [23,30,31]. The catalytic activity increased in the order **7d** > **7c** > **7b** > **7a**. The **7a** and **b**/MAO systems gave the random copolymers with N content up to 69 mol%, which consisted of isotactic alternating sequences, *meso*-NN diads, and a small amount of *meso*,*rac*-NNN triads. In contrast, **7c** and **7d** afforded the copolymers with the N content ≤ 55 mol%, which contained isolated N units, isotactic alternating sequences, and *meso*-NN diads, without NNN triads being observed. Addition of aluminum or zinc alkyls (AlR_3 or ZnR_2, R = Me or Et) lowered the molecular weight of the E–N copolymers obtained by **7a**/MAO, indicating that the copolymer chain growing at the Zr catalyst center could be



7 **a**: X = CMe_2, R = H
b: X = CMe_2, R = Me
c: X = CMe_2, R = ^{i}Pr
d: X = CMe_2, R = ^{t}Bu
e: X = CPh_2, R = H

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Fig. 3. Group 4 metal complexes bearing mixed (indenyl)(cyclopentadienyl) ligands.

transferred to Al or Zn by alkyl-polymeryl exchange [32]. However, when triisobutylaluminium ($Al(^iBu)_3$, TIBA) was added, an increase in the molecular weight of the resulting copolymers was observed, showing that TIBA could suppress the polymer chain exchange between the Zr catalyst center and the trimethylaluminum (TMA) species contained in MAO. This is probably because TIBA tends to react with TMA to form stable dimers with the bridging Me groups, which is too bulky to react with the catalytically active alkyl zirconocene cation.

When pretreated with $Al(^iBu)_3$ (TIBA), 5-norbornene-2-methanol (N–CH_2OH) could be copolymerized with ethylene by the **7a**, **c** and **d**/MAO systems [33]. However, the incorporation of N–CH_2OH was generally lower than that of norbornene. Among **7a**, **c** and **d**, the catalytic activity decreased in the order **7d** > **7c** > **7a**, while the N–CH_2OH incorporation ability decreased in the order **7a** > **7c** > **7d**. An E–(N–CH_2OH) copolymer (M_w = 11.6 kg/mol, PDI = 3.1, T_g = 41 °C) with the N–CH_2OH content of 15.3 mol% was obtained by use of the **7a**/MAO system (5200 kg/(mol$_{Zr}$ h)) (Scheme 3). Similarly, 5-norbornene-2-carboxylic acid (N–CO_2H), when protected with TIBA, could also be copolymerized with ethylene by the **7a**, **c** and **d**/MAO systems. However, the resulting copolymers contained a mixture of the N–CO_2H unit (up to 9 mol%) and the N–CH_2OH (up to 2 mol%), suggesting that a partial reduction of the N–CO_2H unit into the corresponding hydroxy species occurred during the prereaction with TIBA.

The terpolymerizations of ethylene, norbornene and polar norbornene derivatives prereacted with TIBA were also carried out by using the **7a**, **c** and **d**/MAO systems [33b,34]. A number of terpolymers with various components such as E–N–(N–CH_2OH) (N content = 10 mol%, N–CH_2OH content = 12 mol%), E–N–(N–CO_2H) (N content = 9 mol%, N–CO_2H content = 6 mol%), and E–(N–CH_2OH)–(N–CO_2H) (N–CO_2H content = 7 mol%, N–CH_2OH content = 8 mol%) could be prepared by the **7a**/MAO system under appropriate conditions (Scheme 3). As a protecting group for N–CH_2OH, the bulky trialkylsilyl groups such as isopropyldimethylsilyl (IPDMS), tert-butyldimethylsilyl (TBDMS), triethylsilyl (TES), and triisopropylsilyl (TIPS) could also be used, albeit not as effective as TIBA [35].

The copolymerization of ethylene with norbornadiene (NBD) was also investigated by use of the Ph_2C-bridged complex $[Ph_2C(Ind)(Cp)]ZrCl_2$(**7e**)/MAO system [17]. Because of the wider coordination space at the metal center of **7e** (resulting from the short diphenylmethylene-bridge) than that of **4a**, the **7e**/MAO system gave the copolymers with higher NBD incorporation, but with lower regioselectivity. An E–NBD copolymer (NBD content = 25 mol%) containing both unsaturated bicyclic units and tetra-substituted bicyclic units was obtained with an activity of 4000 kg/(mol$_{Zr}$ h) at 60 °C and 2.5 bar ethylene.

The **7e**/MAO system served as a well-suited catalyst for the copolymerization of ethylene with bulky multicycloolefins such as dimethanooctahydronaphthalene (DMON) and trimethanododecahydroanthracene (TMDA) [36]. The amorphous E–DMON copolymer with the DMON content up to 85 mol% (M_n = 13 kg/mol, T_g = 216 °C) could be produced (activity ∼31 kg/(mol$_{Zr}$ h)) at high temperature (90 °C) (Scheme 3). The E–TMDA copolymer with TMDA content up to 20 mol% (M_n = 17 kg/mol) could be prepared by **7e**/MAO with an activity of 33 kg/(mol$_{Zr}$ h) at 50 °C.

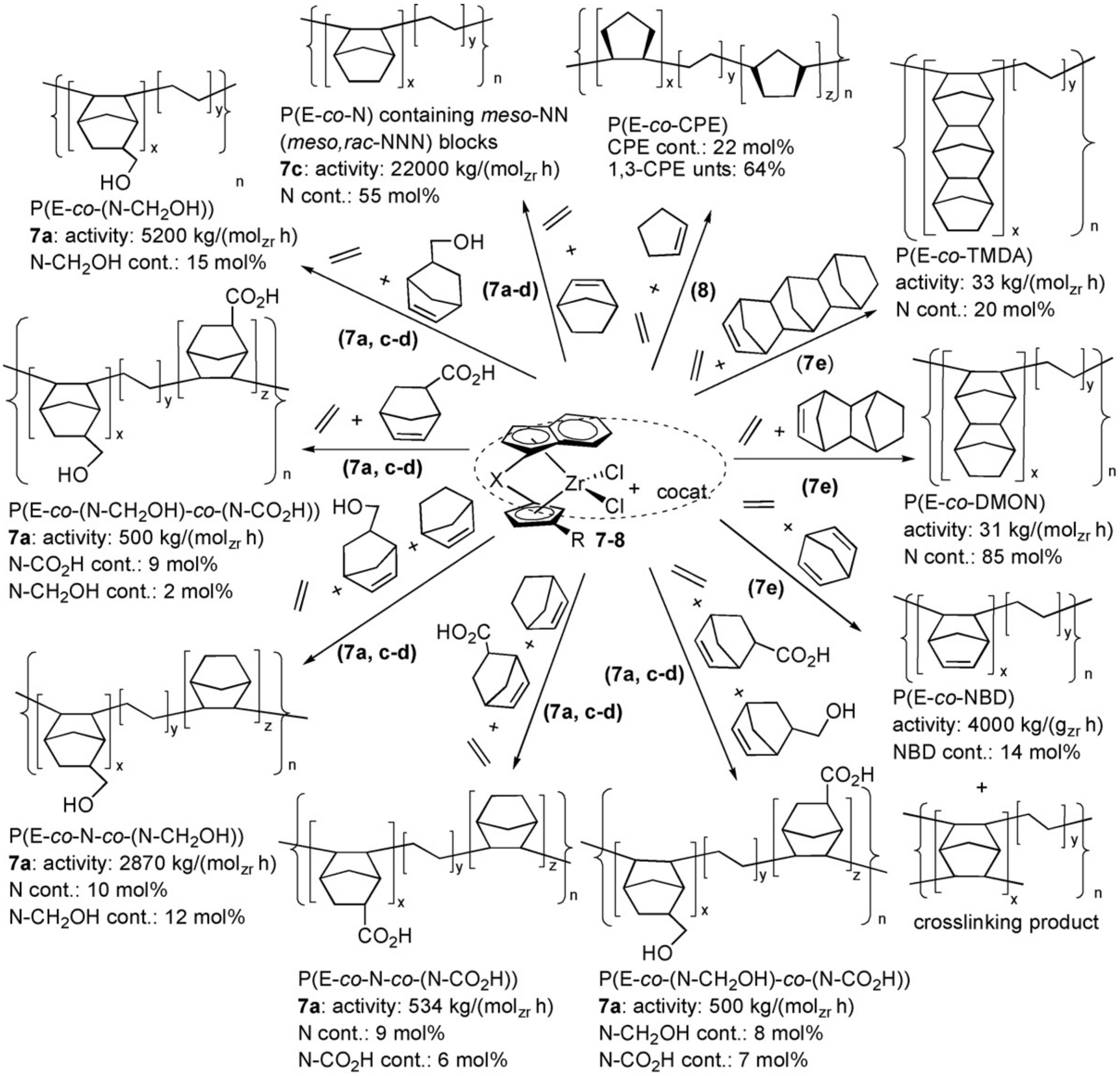
The copolymerization of ethylene with cyclopentene (CPE) by $[Me_2Si(ferroceneindenyl)(Cp)]ZrCl_2$ (**8**)/MAO was reported to afford the E–CPE copolymers with CPE content up to 22 mol% (M_w = 3 kg/mol, T_m = 105 °C) (Scheme 3) [37]. The resulting copolymers contained a significant amount of atactic CPE blocks. Up to 64% of the CPE units were incorporated via 1,3-enchainment.

3.1.3. Bis(indenyl) complexes

The bis(indenyl) zirconium complexes are the first metallocene complexes reported for the copolymerization of cyclic olefins, and various monomers have been examined by use of this class of complexes. In comparison with the analogous bis(cyclopentadienyl) complexes, the bis(indenyl)-ligated complexes generally show stronger nonbonding interactions between the polymer chain and the ancillary ligands, and increase largely the activation energy for propagation of a cyclic monomer and the chain transfer. As a consequence, the activity, the degree of cyclic monomer incorporation, and the microstructure and glass transition temperature of the resulting copolymers are very sensitive to the steric constraints of the bis(indenyl) Zr catalysts. The structures of typical complexes bearing the unlinked bis(indenyl) ligands (**9**), the methylene- or ethylene-linked bis(indenyl) ligands (**10**) and the silylene-linked bis(indenyl) ligands (**11**) are shown in Fig. 4. The copolymerization reactions catalyzed by these complexes are summarized in Scheme 4.

The unlinked bis(indenyl) complex $[(Ind)_2]ZrCl_2$ (**9**)/MAO system was not very effective for the copolymerization of ethylene with dimethanooctahydronaphthalene (DMON), affording the corresponding copolymers with lower DMON contents of 10–15 mol% than those obtained by **4a**/MAO system (25-35 mol%) [20].

The methylene-bridged bis(indenyl) complex [*rac*-$H_2C(3\text{-}^tBuInd)_2]ZrCl_2$ (**10a**)/MAO system, in which there is a sterically demanding ^{t}Bu substituent on each of the indenyl ligands, could hardly incorporate norbornene (<1 mol%) in the copolymerization with ethylene (Fig. 4, Scheme 4) [38]. In contrast, the sterically less demanding $[Me_2C(Ind)_2]ZrCl_2$ (**10b**), $[CH_2CH_2(Ind)_2]ZrCl_2$ (**10c**) and

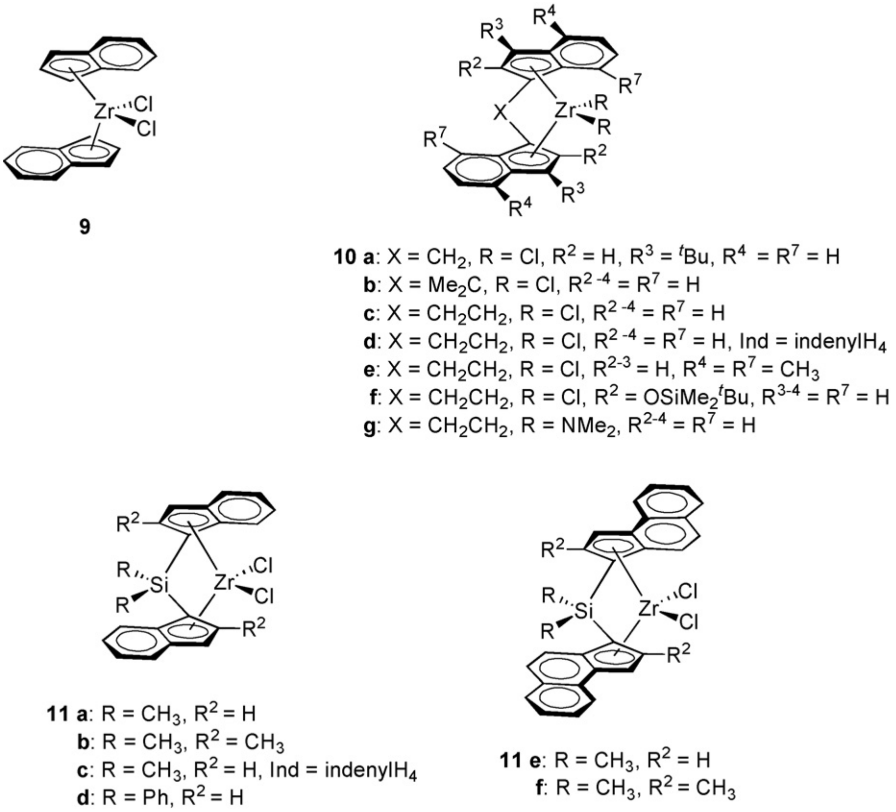


Scheme 3. Copolymerization of cyclic olefins by linked (indenyl)(cyclopentadienyl) group 4 metal catalysts.

[CH$_2$CH$_2$(C$_9$H$_{10}$)$_2$]ZrCl$_2$ (**10d**) (bearing two partially hydrogenated indenyl ligands)/MAO systems showed higher activity (920–8000 kg/(mol$_{\mathrm{Zr}}$ h)) and higher norbornene incorporation (up to 63 mol%), giving the E–N copolymers containing isolated N units (EENEE), isotactic alternating sequences (*meso*-NENE), isotactic *meso*-NN diads, and *meso*,*meso*- and *meso*,*rac*-NNN triads [3b,33c,38–48]. At a high N concentration and low polymerization temperature (30 °C), the *rac*-**10c**/MAO and [*rac*(90%)-/*meso*(10%)-CH$_2$CH$_2$(4,7-Me$_2$-Ind)$_2$]ZrCl$_2$ (**10e**)/MAO systems showed quasi-living characters for the E–N copolymerization (activities = 920, 560 kg/(mol$_{\mathrm{Zr}}$ h), respectively), producing the E–N copolymers with narrow molecular weight distributions (N content = 59, 36 mol%, M_{n} = 202, 72 kg/mol, PDI = 1.35, 1.18, respectively) (Scheme 4) [38]. Kinetic studies indicated that the presence of N monomer in solution seemed to be one of the main factors responsible for the unusual quasi-living character of the polymerization. Addition of aluminum or zinc alkyls (AlR$_3$ or ZnR$_2$, R = Me or Et) had rather similar effects on [*rac*-CH$_2$CH$_2$(2-^{t}BuMe$_2$SiO-Ind)$_2$]ZrCl$_2$ (**10f**) as noted above for **7a**, especially with regard to chain shortening and suppression of unsaturated chain ends, indicating the transfer of polymer chains from the Zr center of a catalyst to Al or Zn [32].

The copolymerization of propylene with norbornene was investigated by use of the **10c**/MAO system [49,50]. The activity of the P–N copolymerization appeared to be rather lower than that of E–N copolymerization, however, a higher N incorporation could be achieved in the P–N copolymerization than that in the E–N copolymerization (41 mol% vs. 23 mol%) under the similar conditions. The resulting P–N copolymers had statistical structures containing isolated N units, isotactic PP diads and isotactic alternating NPN sequences. With respective to propylene, both 1,2- and 1,3-insertion units were observed.

The **10c**/MAO and **10c**/MMAO (methylisobutylaluminoxane) systems were also examined for the copolymerization of other cyclic olefins such as cyclopentene (CPE), cycloheptene (CHP), and cyclooctene (COE) with ethylene or propylene (Scheme 4) [3a, 27]. In the E–CPE copolymerization by



9

10 a: X = CH_2, R = Cl, R^2 = H, R^3 = ^{t}Bu, R^4 = R^7 = H
b: X = Me_2C, R = Cl, R^{2-4} = R^7 = H
c: X = CH_2CH_2, R = Cl, R^{2-4} = R^7 = H
d: X = CH_2CH_2, R = Cl, R^{2-4} = R^7 = H, Ind = indenylH_4
e: X = CH_2CH_2, R = Cl, R^{2-3} = H, R^4 = R^7 = CH_3
f: X = CH_2CH_2, R = Cl, R^2 = $OSiMe_2{}^t$Bu, R^{3-4} = R^7 = H
g: X = CH_2CH_2, R = NMe_2, R^{2-4} = R^7 = H

11 a: R = CH_3, R^2 = H
b: R = CH_3, R^2 = CH_3
c: R = CH_3, R^2 = H, Ind = indenylH_4
d: R = Ph, R^2 = H

11 e: R = CH_3, R^2 = H
f: R = CH_3, R^2 = CH_3

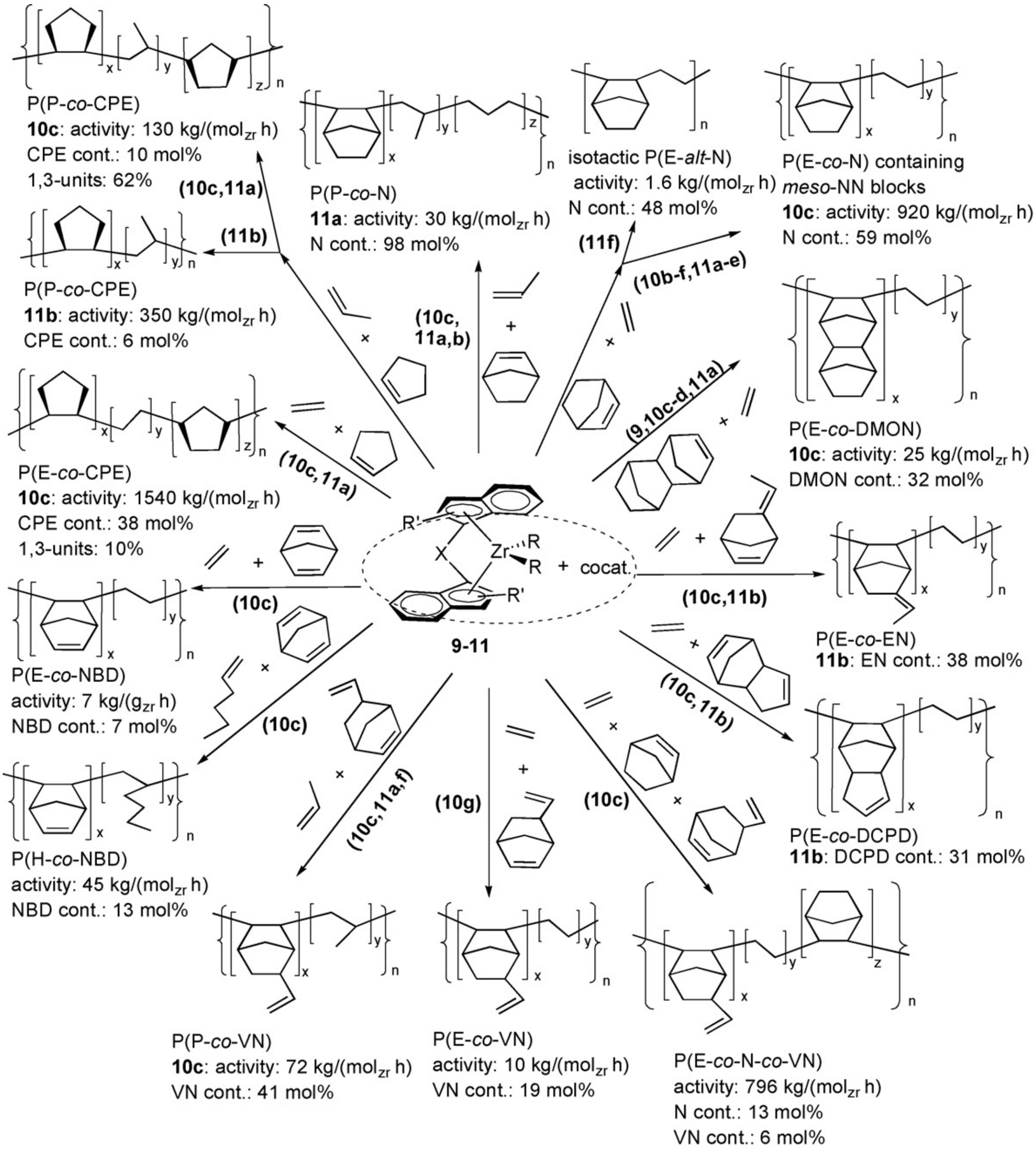
Fig. 4. Group 4 metal complexes bearing two indenyl ligands.

10c/MMAO, the incorporation of CPE in the regio-error 1,3-fashion was observed even under low CPE feed, in contrast with what was observed in the case of **6a**/MMAO. The highest CPE incorporation observed in the **10c**/MMAO system was 38 mol% (with 1,3-CPE units = 10%), with a catalytic activity of 1540 kg/(mol_{Zr} h). The copolymerizations of CHP, COE, and cyclohexene (CHE) with ethylene were more difficult. The maximum incorporations of CHP and COE were 3 mol% and 1 mol%, respectively, while CHE incorporation was not observed in the copolymerization with ethylene by **10c**/MMAO. The copolymerization of propylene (P) with CPE by **10c**/MAO produced the P–CPE copolymers containing CPE contents up to 10 mol% with both *cis*-1,2- and *cis*-1,3-insertion units (1,2/1,3 = 37.6/62.4) [51].

When pretreated with trimethylaluminum (TMA), 5-norbornene-2-methanol (N–CH_2OH) could also be copolymerized with ethylene by the **10c**/MAO system, with the maximum N–CH_2OH incorporation of 3 mol%, which was lower than those in the **6a**/MAO + TMA system and the **7a**/MAO + TIBA system as mentioned above [29,33].

The copolymerization of 2,5-norbornadiene (NBD) with ethylene or 1-hexene by the **10c**/MAO system took place regioselectively at only one of the two C=C double bonds, as in the case of **4a**/MAO [16,18]. For the E–NBD copolymerization, the sterically less demanding **10c**/MAO system showed higher activity (6.7 kg/(g_{Zr} h) and higher NBD incorporation (7 mol%) than the **4a**/MAO system (activity = 3.0 kg/(g_{Zr} h), NBD incorporation = 4 mol%) under the similar conditions. In the H–NBD copolymerization (NBD incorporation up to 13 mol%) by **10c**/MAO, higher regio errors (90 mol% of 2,1-insertion) in the H units were observed, in comparison with those in the case of **4a** (52 mol% of 2,1-insertion) and **6a** (85 mol% of 2,1-insertion).

The regioselective copolymerization of 5-vinyl-2-norbornene (VN) with propylene via the endocyclic double bond could be achieved by the combination of **10c** with $[Ph_3C][B(C_6F_5)_4]/Al(^iBu)_3$ (activity > 72 kg/(mol_{Zr} h)), to give the corresponding random copolymers containing high VN contents (up to 41 mol%) (M_w = 14 kg/mol, PDI = 3.9) (Scheme 4) [52,53]. This is probably due to the higher flexibility of the CH_2CH_2 bridge in **10c**, which could facilitate the incorporation of VN. At high VN loadings, the cross-linking reaction occurred. The functionalization of the copolymers could be readily achieved via transformation of the pendant vinyl side chains into ester or epoxy groups. The regioselective copolymerization of VN with ethylene by the combination of [*rac*-$CH_2CH_2(Ind)_2$]$Zr(NMe_2)_2$ (**10 g**) with $[Ph_3C][B(C_6F_5)_4]/Al(^iBu)_3$ was also investigated, which yielded the corresponding E–VN copolymers with VN content up to 19 mol% (Scheme 4) [54]. The cross-linking reaction, however, took place during prolonged polymerization. The terpolymerization of ethylene, norbornene and VN could be carried out by use of the **10c**/MAO system, which afforded the amorphous E–N–VN terpolymers with N content up to 13 mol% and VN content up to 6 mol% (activity: ~796 kg/(mol_{Zr} h)) [55]. Compared to the E–N copolymerization under the similar



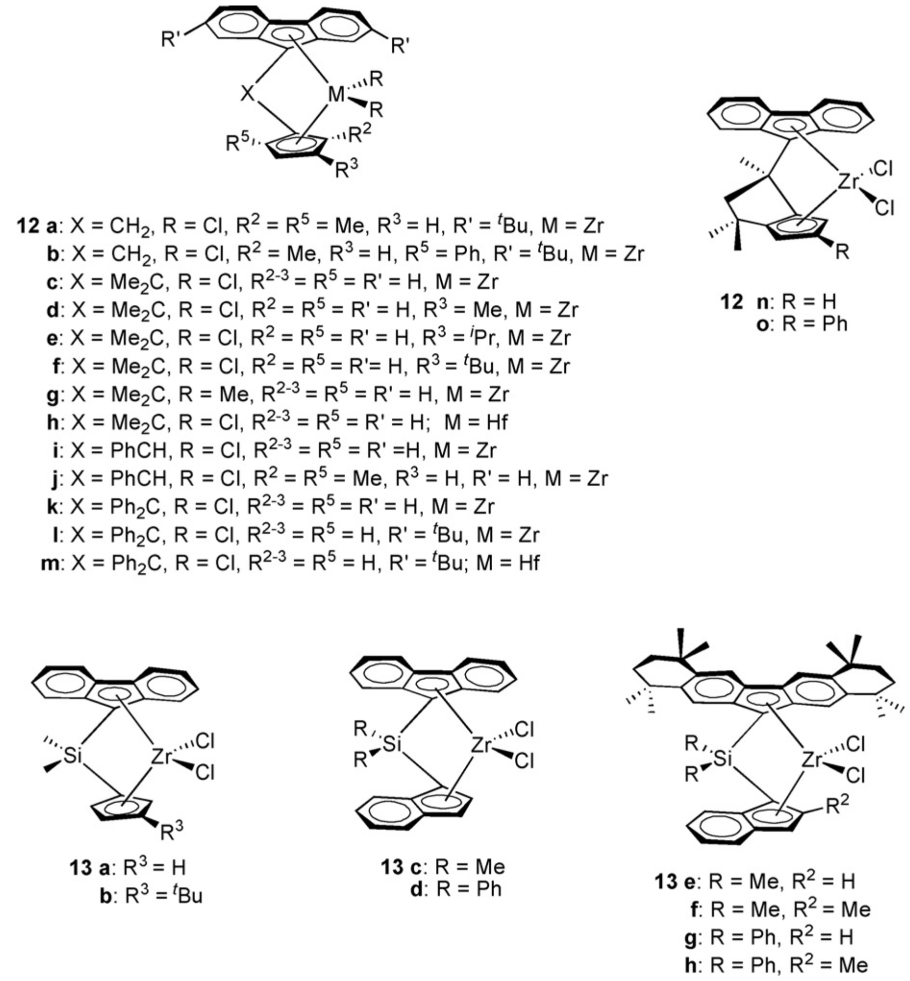
Scheme 4. Copolymerization of cyclic olefins by bis(indenyl) group 4 metal catalysts.

conditions, the introduction of the third comonomer VN in the terpolymerization diminished the incorporation of norbornene into the polymer product. The VN units were distributed in the terpolymers almost entirely in an isolated form via insertion of the cyclic double bond.

The **10c**/MAO system was also examined for the copolymerization of ethylene with cyclic dienes such as 1,3-cyclopentadiene (CPD) and dicyclopentadiene (DCPD) (Scheme 4) [19,53,56]. In the E–DCPD copolymerization, the reaction took place selectively at the norbornene unit of the DCPD molecule, leaving the cyclopentene unit unchanged. The maximum DCPD incorporation in the resultant copolymers was 13 mol% [19]. In the copolymerization of CPD with ethylene, the resulting copolymer contained both CPD and DCPD units (total content = 3 mol%), suggesting that the dimerization of CPD into DCPD occurred in the polymerization system [56].

The copolymerization of ethylene with dimethanooctahydronaphthalene (DMON) was also carried out by use of the **10c** and **d**/MAO systems [20,57]. The DMON incorporation rate of **10c** (up to 32 mol%) was higher than that of **10d** (<15 mol%), but lower than that of **6e** (up to 85 mol%) under the same conditions [36,57]. Attempts to terpolymerize ethylene, propylene, and cyclooctadiene (COD) [58] or ethylidene norbornene (EN) [59] by use of **10c**/MAO or **10c**/[Ph_3C][$B(C_6F_5)_4$]/Al(*i*-Bu)$_3$ led to incorporation of only a small amount of the cyclic copolymers (<2 mol%) in the resulting copolymers.

Significant ligand substituent effects were observed in the E–N copolymerization by the silylene-bridged bis(indenyl)



12 a: X = CH_2, R = Cl, $R^2 = R^5$ = Me, R^3 = H, R' = ^{t}Bu, M = Zr
b: X = CH_2, R = Cl, R^2 = Me, R^3 = H, R^5 = Ph, R' = ^{t}Bu, M = Zr
c: X = Me_2C, R = Cl, $R^{2\text{-}3} = R^5$ = R' = H, M = Zr
d: X = Me_2C, R = Cl, $R^2 = R^5$ = R' = H, R^3 = Me, M = Zr
e: X = Me_2C, R = Cl, $R^2 = R^5$ = R' = H, R^3 = ^{i}Pr, M = Zr
f: X = Me_2C, R = Cl, $R^2 = R^5$ = R'= H, R^3 = ^{t}Bu, M = Zr
g: X = Me_2C, R = Me, $R^{2\text{-}3} = R^5$ = R' = H, M = Zr
h: X = Me_2C, R = Cl, $R^{2\text{-}3} = R^5$ = R' = H; M = Hf
i: X = PhCH, R = Cl, $R^{2\text{-}3} = R^5$ = R' =H, M = Zr
j: X = PhCH, R = Cl, $R^2 = R^5$ = Me, R^3 = H, R' = H, M = Zr
k: X = Ph_2C, R = Cl, $R^{2\text{-}3} = R^5$ = R' = H, M = Zr
l: X = Ph_2C, R = Cl, $R^{2\text{-}3} = R^5$ = H, R' = ^{t}Bu, M = Zr
m: X = Ph_2C, R = Cl, $R^{2\text{-}3} = R^5$ = H, R' = ^{t}Bu; M = Hf

12 n: R = H
o: R = Ph

13 a: R^3 = H
b: R^3 = ^{t}Bu

13 c: R = Me
d: R = Ph

13 e: R = Me, R^2 = H
f: R = Me, R^2 = Me
g: R = Ph, R^2 = H
h: R = Ph, R^2 = Me

Fig. 5. Group 4 metal complexes bearing linked (fluorenyl)(cyclopentadienyl) ligands.

complexes $[R_2Si(R^2\text{-Ind})_2]ZrCl_2$ (**11**) (**a**: R = Me, R^2-Ind = indenyl; **b**: R = Me, R^2-Ind = 2-Me-indenyl; **c**: R = Me, R^2-Ind = indenylH_4; **d**: R = Ph, R^2-Ind = indenyl; **e**: R = Me, R^2-Ind = [*e*]-benzindenyl; **f**: R = Me, R^2-Ind = 2-Me-[*e*]-benzindenyl)/MAO systems [31,39,43,47,50,60–63]. The diphenylsilylene-bridged complex **11d** was less active than its dimethylsilylene-linked analogue **11a**, but both could afford the random E–N copolymers with N contents up to 58 mol%, which consisted of a mixture of isolated N sequences, alternating sequences, *meso*-NN diads and *meso*,*meso*-NNN triad blocks. The Me-substituted indenyl analogue **11b**/MAO showed a higher activity (1.6 kg/(mol$_{Zr}$ h)) and similar N incorporation (∼60 mol%), which yielded the corresponding copolymers with a larger amount of three or more N blocky microstructures. The bis(benzindenyl) complex **11e** produced the random E–N copolymers containing predominantly the *meso*-NN diads with N content = 54 mol%. In contrast, the analogous 2-Me-substituted benzindenyl complex **11f** yielded predominantly the isotactic alternating E–N copolymers (N content: 44–48 mol%) with a small amount of *meso*-NN diads and NNN triads under the same conditions. The less formation of the NN diads in the case of **11f** could be due to stronger nonbonding interactions (steric repulsion) among the ancillary ligands, the growing polymer chain, and the incoming norbornene monomer, which could limit successive N insertion. The tendency of the formation of the alternating E–N copolymers was found to be **11f** > **10c** > **11a** [47]. In the copolymerization of propylene with norbornene by the **11a**/MAO system, the corresponding P–N copolymers with a wide range of N contents (11–98 mol%) were obtained [64]. The random copolymers obtained are amorphous, with glass transition temperatures increasing linearly from 22 to 255 °C with increase of the N content. The **11b**/MAO system was also reported to be active for the P–N copolymerization [50].

In the copolymerization of cyclopentene (CPE) with ethylene by the **11a**/MMAO system, CPE was preferentially incorporated via *cis*-1,2-insertion at low CPE concentrations, while formation of the 1,3-CPE units was observed at high CPE concentrations (total CPE content: ∼28 mol%, 1,2-/1,3- = 94.6/5.6), as observed in the case of **6a** and **10c**/MMAO [27,65]. However, the 1,2-insertion selectivity of the **11a**/MMAO system was generally higher than that of the **10c**/MMAO system. In the copolymerization of propylene with CPE, the **11b**/MAO system incorporated CPE exclusively via the *cis*-1,2-insertion fashion (CPE content = 6 mol%), in contrast to the **11a**/MAO system, which produced a P–CPE copolymer with mixed 1,2- and 1,3-CPE units (CPE content = 8 mol%, 1,2-/1,3- = 68.5/31.5) [51].

The regioselective copolymerization of propylene and VN was achieved by using **11a** and **11f** in the presence of either $[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ or MAO [52]. The activity and the degree of VN incorporation were strongly sensitive to the steric constraints. The sterically less demanding **11a**/$[Ph_3C][B(C_6F_5)_4]/Al(^iBu)_3$ system showed higher activity (20 kg/(mol$_{Zr}$ h)) and higher VN incorporation (34 mol%) than the sterically hindered **11f**/MAO system (activity: 2.0 kg/(mol$_{Zr}$ h), VN content = 20 mol%). The syntheses of the E–EN copolymers (EN content up to 38 mol%) and P–EN copolymers (EN content up to 21 mol%) by copolymerization of ethylene or propylene with EN (5-ethylidene-2-norbornene) in the presence of **10c**/$[Ph_3C][B(C_6F_5)_4]/Al(^iBu)_3$ or **11b**/$[Ph_3C][B(C_6F_5)_4]/Al(^iBu)_3$ were also reported (Scheme 4) [53]. The copolymerization of ethylene with dimethanooctahydronaphthalene (DMON) by the **11a**/MAO system gave the E–DMON copolymers with DMON contents of 10–20 mol%, as in the case of **10c**/MAO [20].

3.1.4. Mixed (fluorenyl)(cyclopentadienyl) complexes

Representative mixed (fluorenyl)(cyclopentadienyl) Zr complexes with different linkers and different substituents on the Cp ring are shown in Fig. 5. Their copolymerization reactions are summarized in Scheme 5. In comparison with the above described bis(cyclopentadienyl), bis(indenyl), and mixed (indenyl)(cyclopentadienyl) analogues, the mixed (fluorenyl)(cyclopentadienyl) complexes are more sterically demanding and more susceptible to the substituents on the ligands with respect to catalytic activity and cyclic olefin monomer incorporation. Therefore, the comonomer sequences (microstructures) of the resulting copolymers could be better controlled by introduction of appropriate substituents on the ancillary ligands.

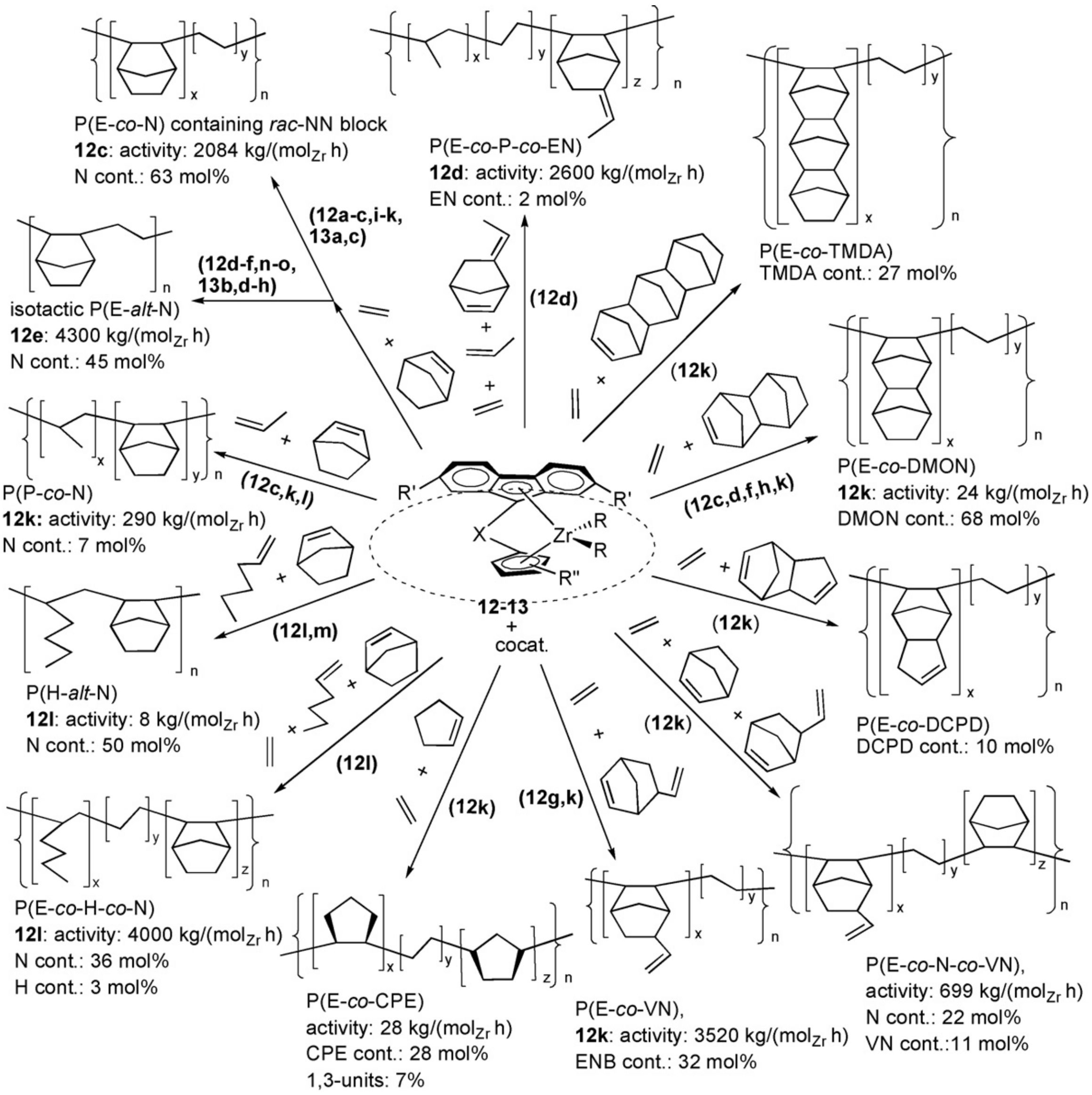
In the presence of MAO, the CH_2-bridged complexes $[CH_2(2,7\text{-}^tBu_2Flu)(2\text{-}R^2\text{-}5\text{-}R^5Cp)]ZrCl_2$ (**12**) (**a**: $R^2 = R^5 = Me$; **b**: $R^2 = Me$, $R^5 = Ph$) [66] and the Me_2C-bridged complexes $[Me_2C(Flu)(Cp)]ZrCl_2$ (**12c**) [23,39,60] were effective for the E–N copolymerization. Among these complexes, the substituent-free, less sterically demanding complex **12c** exhibited the highest activity (2084 kg/(mol$_{Zr}$ h)) and the highest norbornene incorporation ability (N content up to 63 mol%) to give an E–N copolymer with $M_w = 143$ kg/mol and $T_g = 200\,°C$. The 2,5-$Me_2C_5H_3$-ligated complex **12a** showed higher activity and higher norbornene insertion performance than the 2-Me-5-Ph-C_5H_3-ligated analogue **12b** under the same conditions. The resulting E–N copolymers contained mainly atactic alternating sequences and some amount of racemic NN sequences [31,41,43,67].

The effects of the substituent at the 3-position of the Cp ligands on the E–N copolymerization was examined by use of the Me_2C-bridged complexes $[Me_2C(Flu)(3\text{-}R^3Cp)]ZrCl_2$ (**12d–f**) (**d**: $R^3 = Me$; **e**: $R^3 = {}^iPr$; **f**: $R^3 = {}^tBu$) [23,39,63,68–73]. The introduction of an alkyl group such as methyl (**12d**) or isopropyl (**12e**) at the 3-position of the Cp ring prevented the formation of norbornene microblocks, yielding almost perfectly isotactic alternating E–N copolymers (N content ca. 46 mol%), which contained only a small amount of isolated norbornene units. Productivities with these two catalysts increased along with the increase of hindrance of the R substituent ($Me < {}^iPr$) under the similar conditions (20, 4300 kg/(mol$_{Zr}$ h), respectively), while the isopropyl-substituted complex (**12e**) incorporated a slightly less amount of norbornene (45 mol%) than the methyl-substituted complex (**12d**) (46 mol%). When the more sterically demanding ^tBu group was introduced at the 3-position of the Cp ring (**12f**), the catalytic activity (142 kg/(mol$_{Zr}$ h)), the norbornene incorporation (39 mol%), and the molecular weight of the copolymer ($M_w = 8.9$ kg/mol) dropped greatly. The tendency for producing alternating sequences decreased in the order: **12e** > **12d** > **12f**, different from the order of the steric hindrance of the ancillary ligands.

The phenylmethylene-bridged complexes $[X(Flu)(2\text{-}R^2\text{-}5\text{-}R^5Cp)]ZrCl_2$ (**12i–k**) (**i**: $X = Ph(H)C$, $R^2 = R^5 = H$; **j**: $X = Ph(H)C$, $R^2 = R^5 = Me$; **k**: $X = Ph_2C$, $R^2 = R^5 = H$)/MAO systems showed similar activities and similar norbornene incorporation (up to 79 mol%) as compared with the analogous dimethylmethylene-bridged complex **12c**, giving the random E–N copolymers consisting of atactic alternating sequences and a certain amount of racemic NN diads [14,21,50,60,74]. The pentalene-bridged complexes $[(Flu)(3\text{-}R\text{-}Me_3Rpen)]ZrCl_2$ (**12n** and **o**) (**n**: R = H; **o**: R = Ph) afforded predominantly the corresponding alternating E–N copolymers without NN sequences under the same conditions [4b,39,75]. The introduction of a phenyl substituent at the 3-position of the Cp ring (**12o**) resulted in the decrease of activity (100 kg/(mol$_{Zr}$ h)) and N incorporation (36 mol%) in comparison with the substituent-free analogue **12n** (activity: 600 kg/(mol$_{Zr}$ h), N incorporation; 42 mol%). However, the molecular weight of the copolymer prepared by **12o** ($M_w = 830$ kg/mol) was higher than that obtained by **12n** ($M_w = 370$ kg/mol).

The **12c**/MAO, **12k**/MMAO and $[Ph_2C(2,7\text{-}^tBu_2Flu)(Cp)]ZrCl_2$ (**12l**)/MAO systems were also active for the copolymerization of propylene with norbornene [50,76]. The copolymerization of 1-hexene with norbornene by **12l**/MAO afforded the alternating H–N oligomers ($M_w < 1$ kg/mol) with the norbornene incorporations of about 50 mol%, in spite of different N/H feed ratios (from 20 to 90 mol%) [76]. The activity of the **12l**/MAO system for the terpolymerization of ethylene, 1-hexene and norbornene was higher than that for the H–N copolymerization. A relatively high molecular weight terpolymer ($M_w > 30$ kg/mol) which contained 36 mol% of norbornene and 3 mol% of hexene was obtained when 10 mol% of ethylene was present in the feed. The hafnium complex $[Ph_2C(2,7\text{-}^tBu_2Flu)(Cp)]HfCl_2$ (**12 m**) showed much lower activity than that of **12l** for the H–N copolymerization.

The copolymerization of ethylene with cyclopentene (CPE) was examined by the **12k**/MMAO system [27]. Similar to the **6a**/MMAO and **11a**/MMAO systems, the **12k**/MMAO system also incorporated CPE preferentially via the *cis*-1,2-insertion. However, the isomerization of the 1,2-substituted cyclopentane terminal to the 1,3-substituted one proceeded at a high CPE feed, which produced the E–CPE copolymer containing ca. 7% of the 1,3-CPE units (total CPE content = 28 mol%).



Scheme 5. Copolymerization of cyclic olefins by linked (fluorenyl)(cyclopentadienyl) group 4 metal catalysts.

The $[Me_2C(Flu)(Cp)]ZrMe_2$ (**12g**)/$[Ph_3C][B(C_6F_5)_4]$/$Al(^iBu)_3$ system could promote the regioselective copolymerization of VN with ethylene through the endocyclic double bond (Fig. 5, Scheme 5) [54]. In comparison with the bis(indenyl) complex **10g**, complex **12g** showed lower activity and lower VN incorporation (VN content < 10 mol%). The **12k**/MAO system showed better performance for the regioselective E–VN copolymerization to give the copolymer with VN incorporation up to 32 mol% in an activity of 3520 kg/(mol$_{Zr}$ h) at 60 °C (Scheme 5) [77]. The resulting copolymer contained mostly isolated VN sequences. The **12k**/MAO system was also active for the terpolymerization of ethylene, norbornene and VN, producing the amorphous E–N–VN terpolymers with higher cycloolefin contents (N content = 22 mol%, VN content = 11 mol%) (activity = 699 kg/(mol$_{Zr}$ h)) than those obtained by **10c** under the same conditions [55].

The **12k**/MAO system was also effective for the regioselective copolymerization of ethylene with dicyclopentadiene (DCPD) through enchainment of norbornene rings at 40 °C and 1 bar ethylene, affording the copolymers with the maximum DCPD content up to 10 mol% (Scheme 5) [19]. The copolymerization of ethylene with DMON by the **12c**/MAO $[Me_2C(Flu)(Cp)]HfCl_2$ (**12h**)/MAO, and **12k**/MAO systems yielded the random E–DMON copolymers (DMON content = 28, 73 and 68 mol%, respectively) with moderate activities (940, 16 and 24 kg/(mol$_{Zr}$ h), respectively) at 30 °C [36], while the **12d**/MAO and **12f**/MAO systems gave the alternating E–DMON copolymers (DMON content = 40, 44 mol%, respectively) with low activities (1.3 and 0.4 kg/(mol$_{Zr}$ h), respectively) [39]. The copolymerization of ethylene with TMDA by **12k**/MAO gave the E–TMDA copolymers with TMDA content up to 27 mol% at 50 °C (Scheme 5) [36]. The

E–P–EN terpolymerization and the E–P–H–EN and E–P–O–EN quarterpolymerizations by the **12d**/MAO system were also investigated, which incorporated EN of less than 8 mol% in the resulting polymer products [78,79].

The Me_2Si-bridged complexes $[Me_2Si(Flu)(3\text{-}R^3Cp)]ZrCl_2$ (**13a** and **b**) (**a**: $R^3 = H$, **b**: $R^3 = {}^tBu$)/MAO systems were also investigated in the E–N copolymerization, in which the substituent-free-Cp-ligated **13a** showed higher activity and higher N incorporation than the ^{t}BuCp-ligated **13b** [23,39a]. High molecular weight E–N random copolymers ($M_w = 190$ kg/mol) with N content up to 64 mol% could be obtained by use of the **13a**/MAO system with an activity of 432 kg/(mol$_{Zr}$ h). The resulting copolymers showed the similar microstructures with those obtained by **12c**. Similar to **12f**, the introduction of a ^{t}Bu group (**13b**) at the 3-position of the Cp ring also confined the formation of norbornene microblocks, yielding almost perfect alternating E–N copolymers with a small amount of isolated norbornene units. The tendency of **13b** to produce a copolymer with an alternating structure is lower than that of **12f**. The silylene-linked (indenyl)(fluorenyl) complexes (**13c–h**) showed lower activities and lower N incorporations than **13a** in the E–N copolymerization, apparently due to its larger steric hindrance [39].

3.2. Half-sandwich complexes

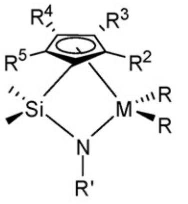
3.2.1. Constrained geometry complexes (CGCs)

In comparison with the metallocene complexes bearing two cyclopentadienyl (or indenyl or fluorenyl) ligands, the constrained geometry complexes (CGCs) which bear the silylene-linked cyclopentadienyl (or indenyl or fluorenyl)-amido ligands usually provide a more open and more electrophilic metal center. As a result of the interplay of the steric and electronic effects, CGCs usually show lower activity than the metallocenes toward cyclic olefins, and can result in the formation of the alternating copolymers in the copolymerization of ethylene with cyclic olefins such as norbornene, cyclopentene, cycloheptene, and cyclooctene. Examples of typical CGCs are shown in Fig. 6. The copolymerization reactions by CGCs are summarized in Scheme 6.

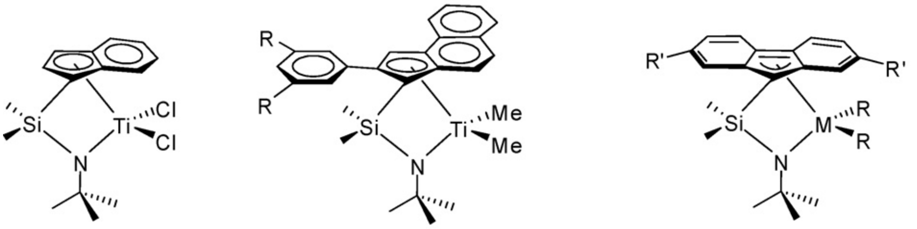
The cyclopentadienyl type CGCs $[Me_2Si(C_5Me_4)NR']TiCl_2$ (**14**) (**a**: $R' = Me$; **b**: $R' = Et$; **c**: $R' = {}^iPr$; **d**: $R' = {}^tBu$)/MAO systems were reported to effect the copolymerization of ethylene with cyclohexadiene (CHD) [80]. The E–CHD copolymers with CHD contents of 25–31 mol% could be obtained by use of the sterically less demanding complexes **14a–c**, while the bulkier **14d** showed lower CHD incorporation rate (ca. 12 mol%) under the same conditions. The copolymers prepared by **14a**, **b**, and **d** contained predominantly 1,4-CHD units that are randomly distributed in the polyethylene backbones, whereas **14c** yielded a copolymer with both 1,2- and 1,4-CHD units.

The copolymerizations of ethylene with norbornene by **14d** and $[Me_2Si(Cp')N^tBu]MR_2$ (**14e–h**) (**e**: $M = Ti$, $R = Me$, $Cp' = C_5Me_4$, **f**: $M = Zr$, $R = Cl$, $Cp' = C_5Me_4$; **g**: $M = Ti$, $R = Cl$, $Cp' = C_5H_2Me_2\text{-}2,4$; **h**: $M = Ti$, $R = Cl$, $Cp' = C_5H_3{}^tBu\text{-}3$) with MAO as a cocatalyst afforded the E–N copolymers containing mainly atactic alternating sequences and isolated norbornene units with a small amount of *meso*- and *racemic*-NN diads [23,43,47,62,73,75,81,82]. Among these catalysts, the fully-substituted-cyclopentadienyl-ligated Ti complexes **14d** and **e** showed the highest activity (480 and 280 kg/(mol$_{Ti}$ h), respectively) and the highest norbornene incorporation (46 and 44 mol%, respectively) under the similar conditions. However, the steric nature of the Cp ligands did not show a clear effect on the molecular weight of the resulting copolymers ($M_w = 100$–400 kg/mol). The tendency of **14d** for producing alternating sequences is lower than those of the (cyclopentadienyl)(fluorenyl) complexes **12d–f** and **13b** but higher than those of the bis(indenyl) complexes **10c**, **11a** and **11f**. Moreover, quasi-living characters, which was more pronounced at low temperatures and short reaction time, were observed in the case of **14d**, when the copolymerization was carried out at high norbornene concentrations [83]. The Zr analogue **14f** was notably less active than **14d**, but yielded the copolymer products with microstructures similar to those produced by **14d**. Replacement of the ^{t}Bu substituent of the amido group in **14d** with $CH(CH_3)$(1-naphthyl), i.e., $[Me_2Si(C_5Me_4)N\{CH(CH_3)(1\text{-naphthyl})\}]TiCl_2$ (**14i**), did not affect the microstructure of the resulting copolymers, though lowering of the catalyst activity was observed [23]. The analogous bulky adamantylamido complexes $[Me_2Si(C_5H_3{}^tBu\text{-}3)NC_{10}H_{13}]MMe_2$(**14j–k**) (**j**: $M = Zr$, **k**: $M = Hf$) with $[Me_2PhHN][B(C_6F_5)_4]$ as a cocatalyst, however, yielded the isotactic alternating E–N copolymers (activity: ~1100 kg/(mol$_M$ h), N content: ~49 mol%), which are similar to those prepared by the mixed Flu/Cp-ligated catalysts **12d–f**, but are in contrast with the atactic E–N copolymers produced by **14d–i** [84].

The **14d**/MMAO (methyl isobutyl aluminoxane) system, which showed no activity for the cyclopentene homopolymerization, could promote the copolymerization of ethylene with cyclopentene to give the corresponding atactic alternating copolymers with regiospecific microstructures comprised of only 1,2-enchained cyclopentene units [85–87]. The E–CPE copolymers with CPE incorporation up to 40 mol% ($M_n = 8.3$ kg/mol, $T_g = -22\,°C$, $T_m = 127\,°C$) could be obtained with an activity of 10 kg/(mol$_{Ti}$ h) at 25 °C. The **14d**/MMAO system was also effective for the copolymerization of ethylene with a wide range of cyclic olefins such as CHP, COE, N, CPD, COD, NBD, and DCPD [86,87]. In the copolymerization of ethylene with cyclic mono-olefins, the reactivity observed was in the order $N \approx CHP > COE > CPE$. The cyclic olefins were incorporated only in the 1,2-insertion mode to give the copolymers with the cyclic olefin contents ranging from 19 to 47 mol%. This exclusive regioselectivity may be attributed to a lower tendency of the half-sandwich titanium catalysts to undergo β-hydrogen elimination than those of the zirconocene catalysts. In the copolymerization of ethylene with cyclodiolefins, an activity order of $DCPD >> COD > NBD > CPD$ was observed, with cyclic monomer incorporation of 8–15 mol%. NBD was incorporated regioselectively via the 1,2-insertion fashion. However, crosslinking fractions were detected in the case of larger cyclodiolefins such as COD and DCPD. CPD was incorporated via a



14 a: M = Ti, R = Cl, R' = Me, R^{2-5} = Me
b: M = Ti, R = Cl, R' = Et, R^{2-5} = Me
c: M = Ti, R = Cl, R' = ^{i}Pr, R^{2-5} = Me
d: M = Ti, R = Cl, R' = ^{t}Bu, R^{2-5} = Me
e: M = Ti, R = Me, R' = ^{t}Bu, R^{2-5} = Me
f: M = Zr, R = Cl, R' = ^{t}Bu, R^{2-5} = Me
g: M = Ti, R = Cl, R' = ^{t}Bu, R^2 = R^4 = Me, R^3 = R^5 = H
h: M = Ti, R = Cl, R' = ^{t}Bu, R^3 = ^{t}Bu, R^2 = R^4 = R^5 = H
i: M = Ti, R = Cl, R' = $CH(CH_3)$-1-naphthyl, R^{2-5} = Me
j: M = Zr, R = Me, R' = adamantyl, R^3 = ^{t}Bu, R^2 = R^{4-5} = H
k: M = Hf, R = Me, R' = adamantyl, R^3 = ^{t}Bu, R^2 = R^{4-5} = H



15 a

15 b: R = H
c: R = ^{t}Bu
d: R = CF_3

16 a: M = Zr, R = Cl, R' = H
b: M = Ti, R = Me, R' = H
c: M = Ti, R = Me, R' = ^{t}Bu

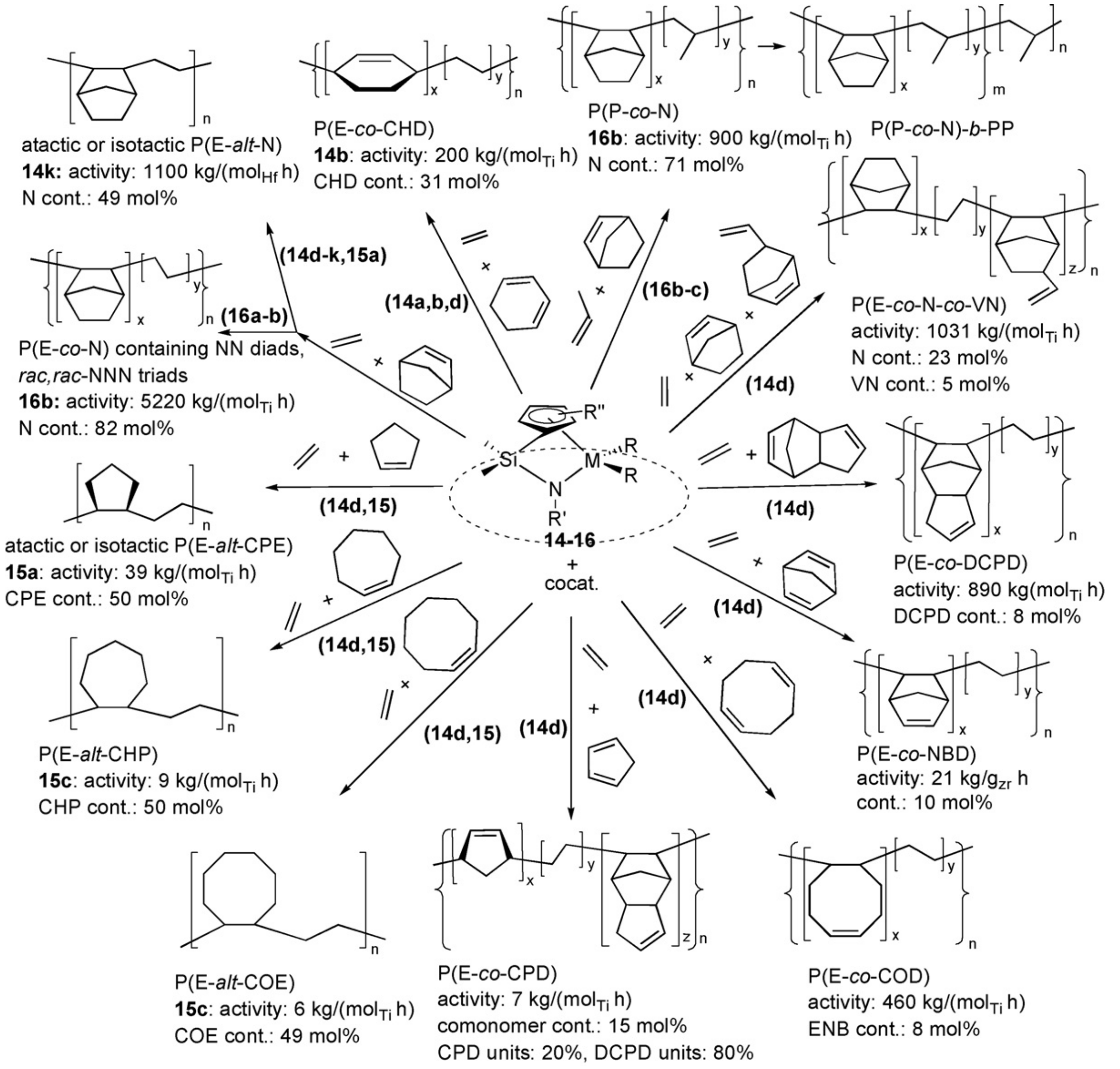
Fig. 6. Constrained geometry group 4 metal complexes.

variety of insertion modes (1,2-, 1,4-insertions, and in the dimer DCPD form).

The terpolymerization of ethylene, norbornene and VN could also be carried out by use of the **14d**/MAO system, which afforded the amorphous E–N–VN terpolymers with N content up to 23 mol% and VN content up to 5 mol% (activity: ~1031 kg/(mol$_{Ti}$ h)) (Scheme 6) [55]. Compared to the E–N copolymerization under the similar conditions, the introduction of the third comonomer VN in the terpolymerization did not diminish the incorporation of norbornene into the polymer product, in contrast with what was observed in the case of the metallocene catalysts **10c** and **12k**.

The $[Me_2Si(Ind)N^tBu]TiCl_2$ (**15a**)/MMAO system was also effective for the E–N copolymerization [81]. In comparison with the Cp analogue **14d**, the indenyl complex **15a** showed lower activity (921 kg/(mol$_{Ti}$ h)) and lower norbornene incorporation (35 mol%) under the similar conditions, yielding the E–N copolymers containing mainly atactic alternating sequences and isolated norbornene units. However, in the copolymerization of ethylene with CPE, **15a** showed higher activity (39 kg/(mol$_{Ti}$ h)) and higher CPE incorporation (50 mol%) than **14d** under the same conditions, yielding a semi-crystalline isotactic alternating E–CPE copolymer (M_n = 33.9 kg/mol, T_g = 16 °C, T_m = 183 °C) [85,87]. The larger indenyl-derivative-ligated analogues $[Me_2Si(Ind')N^tBu]TiMe_2$ (**15b–d**) (**b**: Ind′ = 2-C_6H_5-benz[6,7]indenyl; **c**: 2-(3,5-$^tBu_2C_6H_3$)-benz[6,7]indenyl; **d**: 2-(3,5-$(CF_3)_2$-C_6H_3)-benz[6,7]indenyl) were also effective for the E–CPE copolymerization, although they showed slightly lower activity (5–17 kg/(mol$_{Ti}$ h)) and CPE incorporation (47–48 mol%) than **15a** under the same conditions [87]. The isotactic alternating copolymers containing exclusive 1,2-enchainment of CPE units were observed in all the cases of **15a–d**. The copolymerization of ethylene with CHP or COE by **15a–c**/MMAO was also reported to give the corresponding isotactic alternating copolymers (CHP and COE contents up to 50 mol%) (Scheme 6).

The η^3-fluorenyl-ligated complexes $[Me_2Si(Flu)N^tBu]MR_2$ (**16a** and **b**) (**a**: M = Zr, R = Cl; **b**: M = Ti, R = Me) with Me_3Al-free MAO (dried MAO), MMAO, or $[Ph_3C][B(C_6F_5)_4]/Oct_3Al$ as a cocatalyst were active for the homopolymerization of norbornene, and therefore showed higher activity and higher N incorporation than other types of CGCs such as **14e** and **f** for the E–N copolymerization, probably because of the more open metal centers in **16a** and **b** [23,82]. The random E–N copolymers with N content up to 82 mol% and T_g up to 237 °C could be prepared by **16b**/$[Ph_3C][B(C_6F_5)_4]/Oct_3Al$ with activity up to 5220 kg/(mol$_{Ti}$ h) at 80 °C. Living characters were observed when the E–N copolymerization by the **16b**/dried MAO system was carried out at 0 °C and high N concentrations [88]. The random E–N copolymers prepared by **16a** and **b** contained a significant amount of *meso*- and *rac*-NN diad and *rac*,*rac*-NNN triad sequences, in contrast with the preferred formation of the alternating ENEN sequences in the case of **14e** and **f**.



Scheme 6. Copolymerization of cyclic olefins by constrained geometry group 4 metal catalysts.

The copolymerization of propylene with norbornene by the **16b**/dried MAO system afforded high molecular weight P–N copolymers (M_n up to 156 kg/mol, PDI = 1.11–1.16, T_g up to 249 °C) with norbornene content up to 71 mol% (activity ~900 kg/(mol$_{Ti}$ h)) (Scheme 6) [89]. The resulting copolymers contained a random distribution of the comonomers and long norbornene sequences. The glass transition temperatures of the copolymers increased linearly against the N content in the copolymers. Introduction of the ^{t}Bu substituents at the 3,6-positons of the fluorenyl ligand in **16b** could improve the living character of the P–N copolymerization, and the novel block copolymers consisting of syndiotactic PP (*s*PP) and poly(P-*co*-N) sequences could thus be obtained by use of the [$Me_2Si(3,6-{}^tBu_2Flu)N^tBu]TiMe_2$ (**16c**)/MMAO system (Scheme 6) [90]. Both melting point (133–135 °C) and glass transition temperature (93–311 °C) that correspond to the crystalline *s*PP sequences and amorphous poly(P-*co*-N) sequences, respectively, could be observed in the resulting copolymers.

3.2.2. $Cp'MX_3$ and $Cp'M(R)X_2$ complexes

The half-sandwich complexes ($(C_5R_5)MX_3$) (**17a–e**) (**a**: M = Ti, R = H, X = Cl; **b**: M = Ti, R = Me, X = Cl; **c**: M = Ti, R = Me, X = Me; **d**: M = Zr, R = H, X = Cl; **e**: M = Zr, R = Me, X = Cl) (Fig. 7), in combination with a cocatalyst such as MAO or $B(C_6F_5)_3$, could promote the copolymerization ethylene with norbornene (Scheme 7) [91]. The unsubstituted Cp-ligated titanium trichloride complex **17a**/MAO system showed higher activity and higher norbornene incorporation (23 mol%) than the fully substituted analogue **17b/**MAO (N content = 11 mol%), both of which were, respectively, lower than those observed in the analogous zirconium systems **17d** and **e/**MAO (N content ≈28 mol%). Among **17a–e**, the Ti methyl complex **17c**/$B(C_6F_5)_3$ system showed the highest norbornene incorporation (up to 44 mol%). The E–N copolymers produced by the **17c**/$B(C_6F_5)_3$ system contained more alternating NENE sequences than those by the **17a**, **b**, **d** and **e/**MAO systems.

The half-titanocene dichloride complexes with an aryloxo ligand $(Cp')Ti(OC_6H_3{}^iPr_2\text{-}2,6)Cl_2$ (**18**) (**a**: $Cp' = {}^tBuC_5H_4$; **b**:

Cp′ = 1,2,4-$Me_3C_5H_2$; **c**: Cp′ = C_5Me_5; **d**: Cp′ = Indenyl) were also investigated for the E–N copolymerization by use of MAO or MMAO as a cocatalyst [92–94]. Among these catalysts, the **18d**/MAO system showed the highest norbornene incorporation ability (up to 49 mol%, activity ≈1520 kg/(mol_{Ti} h)). The N repeat units (including diads), in addition to atactic alternating and isolated N sequences, were observed in the E–N copolymers prepared by **18a**, **b** and **d**. The copolymers produced by **18c** possessed few N repeat units. The DFT calculation indicates that the stability of the π-complex formed after N insertion affects the catalytic activity, while the N incorporation is affected by the energetic preference of coordination between N and ethylene to the alkyl-cationic species.

In comparison with **18c** and **d**, the half-titanocene dichloride complexes with a ketimide ligand (Cp′)Ti(N = C^tBu_2)Cl_2 (**18e–f**) (**e**: Cp′ = C_5H_5; **f**: Cp′ = C_5Me_5) showed remarkable activity for the E–N copolymerization in the presence of MAO as a cocatalyst [94]. It is noteworthy that the C_5H_5-ligated complex **18e** showed higher activity and higher norbornene incorporation than the C_5Me_5-ligated analogue **18f** under the same conditions. High molecular weight copolymers ($M_n > 444$ kg/mol) with N incorporation up to 74 mol% could be obtained by use of **18e**/MAO at 25 °C, with an activity as high as 31 500 kg/(mol_{Ti} h). The resulting copolymers possessed a mixture of N repeat units (diads, triads) and the alternating and isolated N sequences. The glass transition temperature of the copolymers increased linearly with increase of the N content.

The copolymerization of ethylene with CPE was also investigated by use of the **18a–d**/MAO systems (Scheme 7) [93]. Among these catalysts, **18a** exhibited the highest catalytic activity (5980 kg/(mol_{Ti} h)) and the highest CPE incorporation (17 mol%) at 25 °C. The CPE unit was incorporated via the 1,2-insertion mode and was distributed in the copolymers in the isolated and alternating forms. No or a negligible amount of 1,3-inserted units were observed since these catalysts have a lower tendency to undergo β-hydrogen elimination. In the copolymerization of ethylene with cyclohexene (CHE) by **18a–d**/MAO, a significant influence of the Cp′ ligands on the CHE incorporation was observed [95]. The *tert*-BuCp-ligated complex **18a** and the Me_3Cp-ligated **18b** gave higher CHE incorporation (∼15 mol%) than the indenyl complex **18d** (3 mol%), whereas the C_5Me_5-ligated analogue **18c** incorporated only a trace amount of CHE in the copolymer products under the same conditions. The highest CHE incorporation (up to 16 mol%) was achieved by **18a** with an activity of 423 kg/(mol_{Ti} h) at 25 °C. The resultant copolymers possessed isolated CHE units and a small amount of alternating sequences, in which the CHE units were incorporated selectively in a 1,2-insertion manner, without 1,3-insertion units being observed.

The C_5H_5/(N = P^tBu_3)-ligated Ti complex (C_5H_5)Ti(N = P^tBu_3)Cl_2 (**18g**) in combination with MAO served as good catalyst for the copolymerization of ethylene with cyclohexadiene (CHD) [80a]. An E–CHD copolymer with CHD content = 17 mol% and M_n = 347 kg/mol was obtained with high activity (1600 kg/(mol_{Ti} h)) at 60 °C. CHD was incorporated regioselectively in a 1,4-fashion. The 1,3-$(SiMe_3)_2C_5H_3$/NMe_2-ligated analogue {1,3-$(SiMe_3)_2C_5H_3$}Ti(NMe_2)Cl_2 (**18 h**) was also effective for the E–CHD copolymerization, which gave a higher CHD incorporation (up to 56 mol%) but showed lower regioselectivity (both 1,2- and 1,4-CHD insertions) and lower activity (ca. 60 kg/(mol_{Ti} h)) under the same conditions.

The activity of the dicarbollide-ligated half-sandwich complexes ($C_2B_9H_{11}$)M(NEt_2)$_2$($NHEt_2$) (**19**) (**a**: M = Ti; **b**: Zr) for the copolymerization of ethylene with norbornene was investigated by using various cocatalysts, including MAO and alkylaluminium compounds such as $AlMe_3$ (TMA), Al^iBu_3 (TIBA), $AlH(^iBu)_2$ (DIBALH), and $AlEt_2Cl$ (DEAC)) [91]. In general, the Zr complex **19b** was more active than the Ti analogue **19a**. The **19a** and **b**/TIBA systems (Al/M = 10) exhibited higher activity (2.2 and 77 kg/(mol_M h), respectively) and incorporated more N units in the copolymers (38 and 45 mol%, respectively) than the corresponding MAO-activated systems (N content < 29 mol%). Among all these catalyst systems, the **19b**/DIBALH system exhibited the highest activity (with N incorporation = 43 mol%) under the same conditions. The resulting E–N copolymers contained isolated norbornene units and alternating NENE sequences.

3.3. Cyclopentadienyl-free complexes

In comparison with metallocene complexes, the analogous cyclopentadienyl-free complexes could provide a more electrophilic active site and more sterically open coordination space, and usually result in low degree of polymerization stereocontrol without successive cyclic olefin insertion. In some cases, they

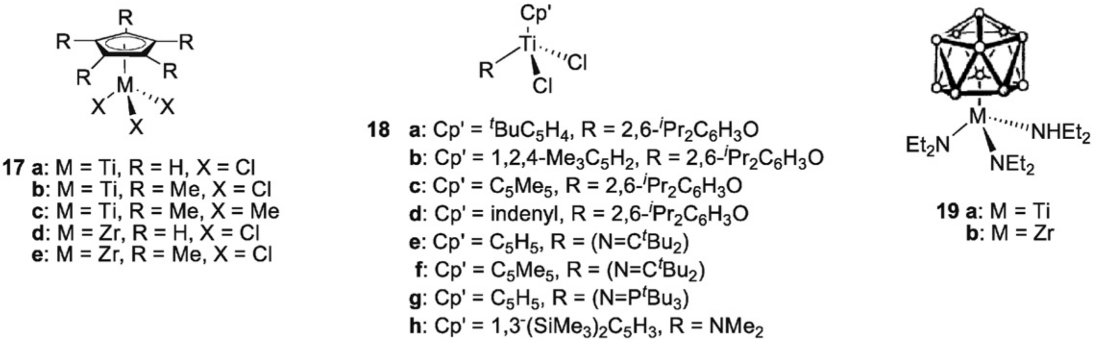
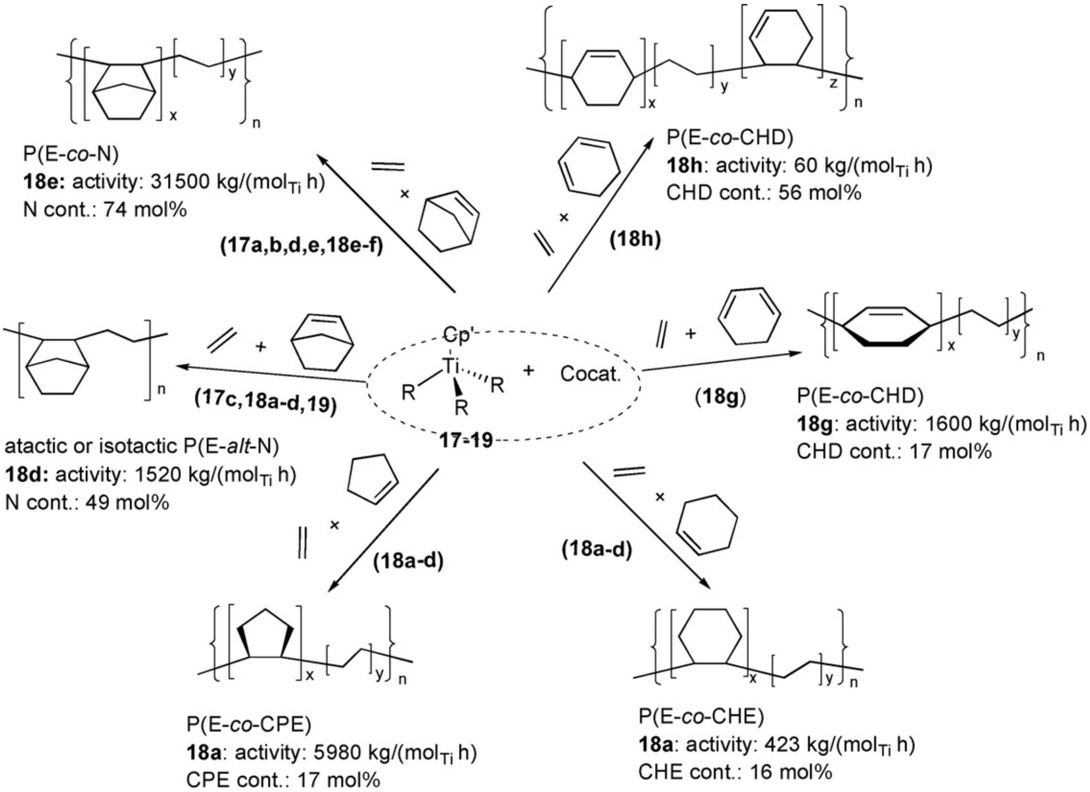


Fig. 7. Half-sandwich group 4 metal complexes of Cp′MX_3 and Cp′MRX_2 types.



Scheme 7. Copolymerization of cyclic olefins by half-sandwich group 4 metal catalysts of $Cp'MR_3$ type.

can show living character for the copolymerization of ethylene with cyclic olefins.

The living E–N copolymerization could be achieved by the bis(imino-pyrrolyl)titanium complexes $[2\text{-}(RN=CH)C_4H_3N]_2TiCl_2$ (**20a–d**) (**a**: R = cyclohexyl; **b**: R = 4-^{t}Bu-cyclohexyl; **c**: R = cyclooctyl; **d**: R = Ph)/MAO systems (Fig. 8) at room temperature and 1 atm ethylene [6,96]. The **20a–d**/MAO systems all afforded high molecular weight alternating E–N copolymers with narrow molecular weight distributions (M_n = 127–600 kg/mol, PDI = 1.10–1.24, T_g = 120–130 °C, N contents = ca. 50 mol%, activity = 576–3186 kg/(mol$_{Ti}$ h)), although they were not active for the homopolymerization of norbornene. The resulting copolymers were atactic alternating copolymers containing some isolated N units and a small amount of N diads. The chain-end analysis of the copolymers showed that the polymerization is initiated by norbornene insertion and terminated by norbornene insertion into the E-last-inserted species. Relative formation energies estimated by DFT calculations indicated that the facile coordination of norbornene to the E-last-inserted metal species and its fast insertion into this species as well as the living character of ethylene polymerization under limited conditions played key roles in the achievement of the highly controlled living copolymerization. Unique block copolymers such as poly(E-*co*-N)$_A$-*b*-poly(E-*co*-N)$_B$, PE-*b*-poly(E-*co*-N) could be synthesized from ethylene and norbornene by using these living catalysts. Transmission electron microscopy (TEM) indicated that the PE-*b*-poly(E-*co*-N) consisted of crystalline and amorphous segments which were chemically linked.

The bis(imino-indolyl-)titanium complex $[3\text{-}Cl\text{-}2\text{-}(2,6\text{-}F_2C_6H_4\text{-}N=CH)indolyl]_2TiCl_2$ (**21**)/MAO system (Fig. 8) was also active for the E–N copolymerization (activity ~1700 kg/(mol$_{Ti}$ h)) at 80 °C and 5 atm ethylene, affording the copolymers with the N content up to 41 mol% (M_w = 55 kg/mol) (Fig. 8) [97]. The resulting copolymers contained isolated norbornene units, alternating sequences, and a small amount of norbornene micro-blocks, since the **21**/MAO system was also active toward the homopolymerization of norbornene.

The bis(phenoxy-imino)titanium complex $[(C_6F_5NCH)(2,4\text{-}{}^tBu_2C_6H_2O]_2TiCl_2$ (**22**)/MAO system (Fig. 8) served as an efficient catalyst for the living E–CPE copolymerization [98]. An almost perfect atactic alternating E–CPE copolymer with the CPE content of 47 mol% (M_n = 21000, PDI = 1.34, T_g = 10.1 °C) was obtained with an activity of 0.03 kg/(mol$_{Ti}$ h). The CPE units were incorporated solely via *cis*-1,2-enchainment at 0–25 °C. When the polymerization was carried out at 40 °C and low ethylene pressure (<1 psig ethylene), 1,3-enchainment of CPE (1–6%) was also observed. The glass-transition temperatures of the E–CPE copolymers prepared by **22**/MAO, which ranged from −27.3 °C (27 mol% CPE) to 10.1 °C (47 mol% CPE), were found to be linearly dependent on the CPE content. By use of the living nature of the **22**/MAO system, a new class of E–CPE block copolymers with varying E/CPE ratios, such as (PE-*b*-poly(E-*co*-CPE) and PE-*b*-poly(E-*co*-CPE)$_A$-*b*-poly(E-*co*-CPE)$_B$), were synthesized through a sequential polymerization procedure and repetitively raising and lowering the ethylene pressure in the E–CPE copolymerization.

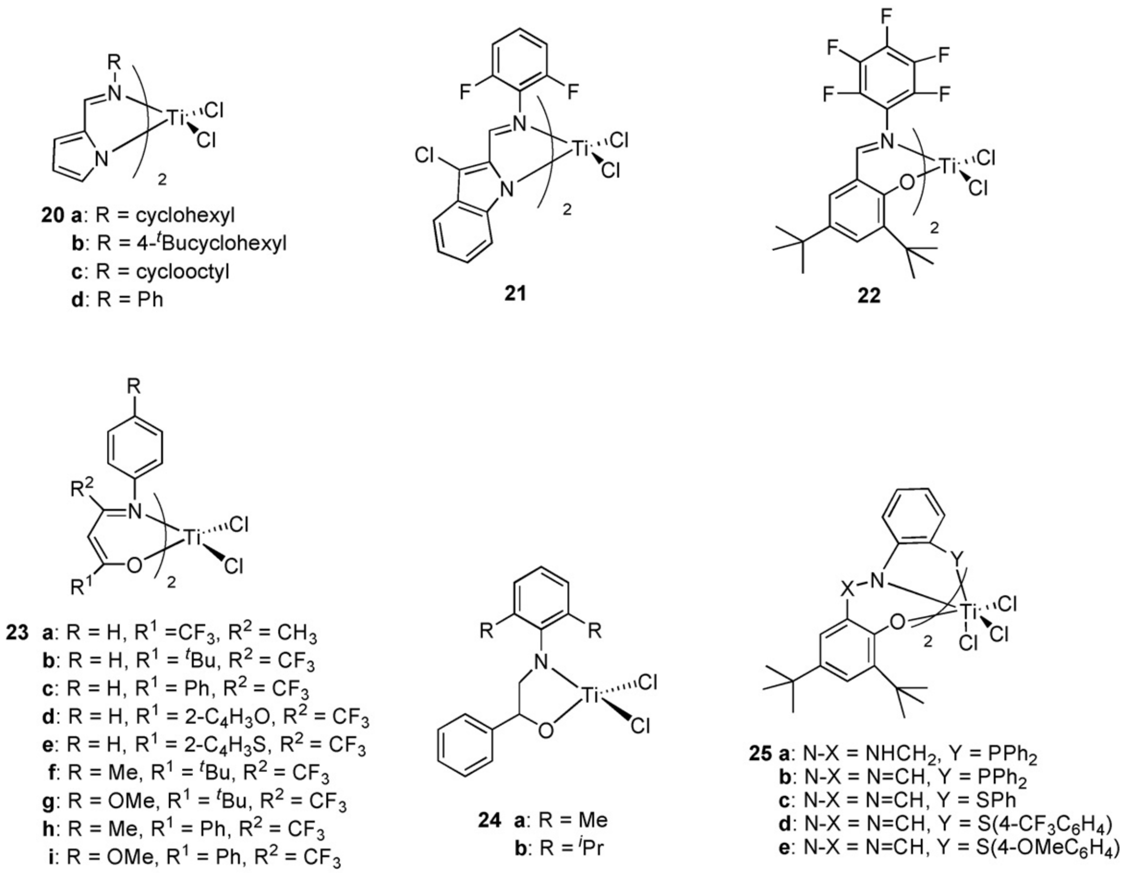


Fig. 8. Group 4 metal complexes bearing [*N*,*N*]- and [*N*,*O*]-chelating ligands.

The bis(β-enaminoketonato)titanium complexes $[(4\text{-RC}_6\text{H}_4)\text{N}=\text{C}(\text{R}^2)\text{CH}=\text{C}(\text{R}^1)\text{O}]_2\text{TiCl}_2$ (**23a**–**i**) (**a**: R = H, $\text{R}^1=\text{CF}_3$, $\text{R}^2=\text{CH}_3$; **b**: R = H, $\text{R}^1={}^t\text{Bu}$, $\text{R}^2=\text{CF}_3$; **c**: R = H, $\text{R}^1=\text{Ph}$, $\text{R}^2=\text{CF}_3$; **d**: R = H, $\text{R}^1=2\text{-C}_4\text{H}_3\text{O}$, $\text{R}^2=\text{CF}_3$; **e**: R = H, $\text{R}^1=2\text{-C}_4\text{H}_3\text{S}$, $\text{R}^2=\text{CF}_3$; **f**: R = Me, $\text{R}^1={}^t\text{Bu}$, $\text{R}^2=\text{CF}_3$; **g**: R = OMe, $\text{R}^1={}^t\text{Bu}$, $\text{R}^2=\text{CF}_3$; **h**: R = Me, $\text{R}^1=\text{Ph}$, $\text{R}^2=\text{CF}_3$; **i**: R = OMe, $\text{R}^1=\text{Ph}$, $\text{R}^2=\text{CF}_3$)/MMAO systems (Fig. 8) exhibited quasi-living nature for the E–N copolymerization at 25 °C and 1 atm of ethylene [99]. The substituents R, R^1, and R^2 showed significant influences on the catalyst activity. Among these catalysts, the **23a/**MMAO system displayed the highest catalytic activity (2360 kg/(mol$_{\text{Ti}}$ h)) and the highest norbornene incorporation (55 mol%), affording a high molecular weight E–N copolymer with narrow molecular weight distribution ($M_\text{n}=480$ kg/mol, PDI = 1.38, $T_\text{g}=144$ °C). Linear relationships between the molecular weight and the yield of the polymers (or polymerization time), as well as narrow molecular weight distribution, were observed in all the cases of **23a**, **c**, **d** and **h/**MMAO, which indicated the quasi-living nature of these systems. The resulting copolymers are atactic alternating copolymers containing some isolated norbornene sequences and a small amount of NN diad sequences. By using the quasi-living characteristics of the **23a**/MMAO system, a new diblock polymer PE-*b*-P(E-*co*-N) consisting of the crystalline PE and the amorphous P(E-*co*-N) segments was synthesized.

The **23a**–**d**/MMAO systems served as effective catalysts for the E–CPE copolymerization, although they did not show any activity for the CPE homopolymerization [100]. Complexes **23a** and **c** showed higher CPE incorporation than **23b** under the same conditions. A high molecular weight copolymer containing the CPE content of ca. 39 mol% ($M_\text{w}=106.9$ kg/mol, PDI = 1.81, $T_\text{g}=4.9$ °C, $T_\text{m}=128.4$ °C) was obtained by using the **23a**/MMAO system with an activity of 141 kg/(mol$_{\text{Ti}}$ h) at 30 °C and 1 atm ethylene. The copolymer contained atactic alternating sequences and isolated CPE units via exclusive *cis*-1,2-enchainment. The **23c**/MMAO system showed quasi-living nature at lower temperatures (<15 °C), which allowed the synthesis of an A–B diblock polymer PE-*b*-P(E-*co*-CPE).

The phenylamino-alkoxy titanium complexes $[(2,6\text{-C}_6\text{H}_3\text{R}_2)\text{NHCH}_2\text{CH}(\text{Ph})\text{O}]\text{TiCl}_2$ (**24a** and **b**) (**a**: R = Me; **b**: R = ^{i}Pr)/MAO systems (Fig. 8) were investigated for the E–N copolymerization, in which the sterically less demanding **24a** always showed higher N incorporation (up to 43 mol%) than **24b** (<36 mol%) under the same conditions [101]. The resulting copolymers contained isolated N units and alternating *meso*- and *racemic*-ENEN sequences. A linear relationship between the N content and T_g of the copolymers was observed. Among the tridentate phenoxy-imine complexes $[(\text{N–X})(\text{C}_6\text{H}_4\text{Y})(2,4\text{-}{}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}]_2\text{TiCl}_3$ (**25a**–**e**) (**a**: N–X = NH–CH$_2$, Y = PPh$_2$; **b**: N–X = N = CH, Y = PPh$_2$; **c**: N–X = N = CH, Y = SPh; **d**: N–X = N = CH, Y = S(4-CF$_3$C$_6$H$_4$); **e**: N–X = N = CH, Y = S(4-OMeC$_6$H$_4$)), the **25b**/MAO system (Fig. 8) gave the maximum norbornene incorporation of 35.3 mol% with an activity of 140 kg/(mol$_{Ti}$ h) at 50 °C and 1 atm ethylene [102]. The combination of Ti(NEt$_2$)$_4$ or Zr(NEt$_2$)$_4$ with MAO was also reported to catalyze the copolymerization of ethylene with norbornene, which gave the random E–N copolymers with norbornene contents of 45 and 34 mol%, respectively [91a].

4. Vanadium catalysts

The combinations of vanadium salts such as VCl$_4$ and V(acac)$_3$ with alkyl aluminum compounds such as Al(C$_6$H$_{13}$)$_3$ and AlEt$_2$Cl are among the first catalyst systems reported for the copolymerization of cyclic olefins [2]. The VCl$_4$/Al(C$_6$H$_{13}$)$_3$ or V(acac)$_3$/AlEt$_2$Cl system could copolymerize ethylene with a variety of cyclic olefins such as cyclopentene (CPE), cyclohexene (CHE), cycloheptene (CHP), and *cis*-cyclooctene (COE), with the activity decreasing in the order CPE > CHP > COE > CHE [2b]. The alternating E–CPE and E–CHP copolymers with the CPE or CHP content up to ca. 50 mol% could be obtained, while the incorporation of COE (<22 mol%) or CHE (<19 mol%) in the corresponding copolymers was lower under the similar conditions.

The (arylimido)(aryloxo)vanadium complexes (2,6-R$_2$C$_6$H$_3$O)(2,6-Me$_2$C$_6$H$_3$N)VCl$_2$ (**26a–c**) (**a**: R = Me; **b**: R = ^{i}Pr; **c**: R = Ph) (Fig. 9), with MAO or Et$_2$AlCl as a cocatalyst, was investigated for the copolymerization of ethylene with norbornene, which afforded the atactic alternating E–N copolymers with N content up to 46 mol% [103]. The substituents on the aryloxide ligand showed a significant influence on the catalytic activity of the catalysts and the molecular weight of the resulting copolymers (**26a** > **26b** > **26c**), but did not strongly affect the N incorporation and microstructure of the copolymers. The copolymers contained isolated N units, atactic alternating ENEN sequences, and a small amount of N repeating units (NN diad). In the **26a**/Et$_2$AlCl catalyst system, the Al/V molar ratio showed a significant influence on the molecular weight of the resulting E–N copolymers, indicating that the chain transfer from V to Al should be a dominant chain transfer process in this system. However, in the **26a**/MAO system, the molecular weight of the resulting copolymers was independent of the Al/V molar ratio.

The bis(benzimidazole)amino vanadium complexes [(C$_6$H$_4$NH)N = CCH$_2$N(CH$_3$)CH$_2$C = N(C$_6$H$_4$NH)]VCl$_3$ (**27a**) and [(C$_6$H$_4$N)NCCH$_2$N(CH$_3$)CH$_2$C = N(C$_6$H$_4$NH)]V = O(OPr)$_2$ (**27b**) (Fig. 9) were also effective for the E–N copolymerization in the presence of simple alkylaluminum compound such as Me$_2$AlCl at 50 °C and 0.5 bar ethylene [104]. On activation with Me$_2$AlCl, **27b** showed higher activity (11,250 kg/(mol$_V$ h)) and higher N incorporation (33 mol%) than **27a** (N content <16 mol%). The copolymerization of ethylene with norbornene by the bis(phenolate)amino vanadium complex V(acac){[2-(4,6-Me$_2$C$_6$H$_2$)O]CH$_2$N(CH$_2$CH$_2$NMe$_2$) CH$_2$[2-(4,6-Me$_2$C$_6$H$_2$)O]} (**28**)/EtAlCl$_2$ system (Fig. 9)

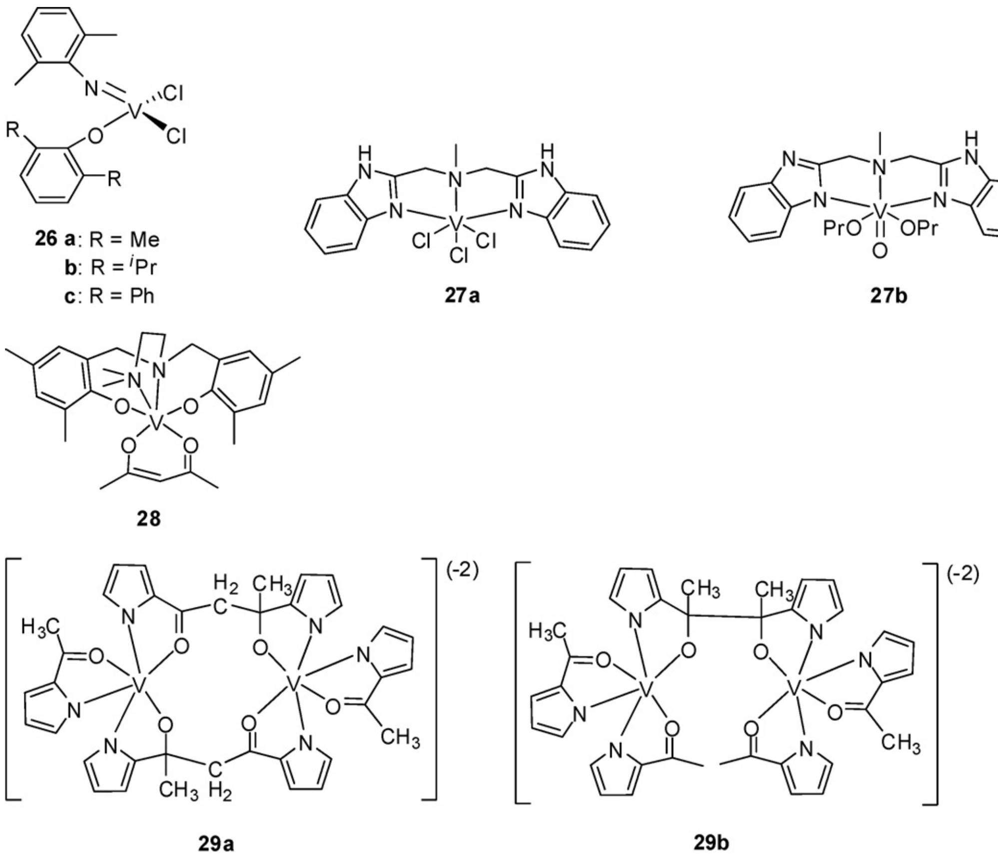


Fig. 9. Vanadium complexes for copolymerization of cyclic olefins.

afforded the E–N copolymers with moderate N incorporation (<29 mol%) in an activity of 66 kg/(mol$_V$ h) at room temperature and 2 bar ethylene [105]. When activated by Me_2AlCl, the dinuclear vanadium complexes $\{V_2[K(THF)]_2[CH_3CO(C_4H_3N)]_2\}[(C_4H_3N)C(O)CH_2C(C_4H_3N)(CH_3)O]_2$ (**29a**) and $\{VK(THF)[(C_4H_3N)C(O)CH_3]\}_2[(C_4H_3N)(CH_3)(O)CC(O)(CH_3)(C_4H_3N)]$ (**29b**) (Fig. 9) were reported to show high activity (∼3720 kg/(mol$_V$ h)) and moderate norbornene incorporation (N content <25 mol%) for the E–N copolymerization at 25 °C [106]. These catalysts were also effective for the E–P–N terpolymerization.

5. Chromium catalysts

The half-sandwich chromium complex $[C_5Me_4(NMe_2)]Cr(\eta^1,\eta^1\text{-}C_4H_8)(C_2H_4)$ (**30**)/MAO system (Fig. 10) could promote the E–N copolymerization with high activity (27000 kg/(mol$_{Cr}$ h)) at 40 °C and 6.0 bar of ethylene to give the alternating E–N copolymers (N content up to 50 mol%) containing the isolated N units and alternating sequences [23]. The dinuclear chromium complexes $[Cp'CrMeCl]_2$ (**31a** and **b**) (**a**: $Cp' = C_5Me_5$; **b**: Cp′ = Fluorenyl)/MAO systems were also active for the E–N copolymerization (Fig. 10) [107]. Random E–N copolymers (N content up to 55 mol%) containing isolated N units, alternating sequences and N blocks could be obtained.

When activated by MAO or $B(C_6F_5)_3$, the bis(allyl) complex $Cr[1,3\text{-}C_3H_3(SiMe_3)_2]_2$ (**32a**) and the tetra(alkyl) complex $Cr(CH_2SiMe_3)_4$ (**32b**) were also effective for the E–N copolymerization [108]. The allyl complex **32a**/$B(C_6F_5)_3$ system, which showed no activity for the homopolymerization of norbornene, yielded the random E–N copolymers with only limited amounts of N incorporation (N content <11 mol%). In contrast, the alkyl complex **32b**/MAO system, which was active toward to the homopolymerization of norbornene, gave the E–N copolymers with N content up to ca. 60 mol%. The NN diads were observed even in the copolymers with N incorporation as low as 10 mol%. The NNN triad sequences were observed at higher norbornene incorporation levels.

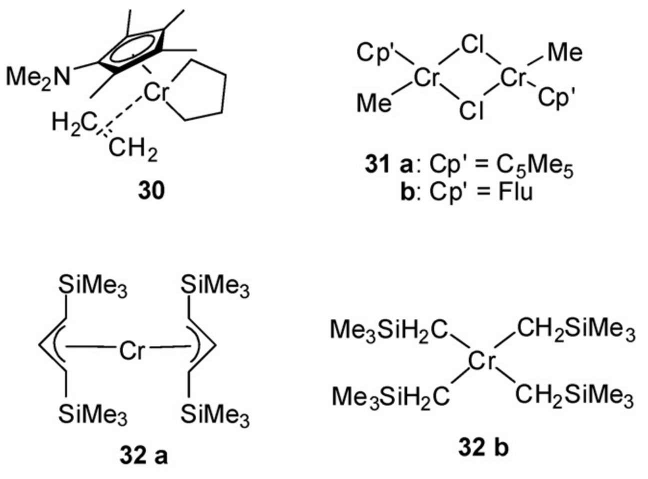


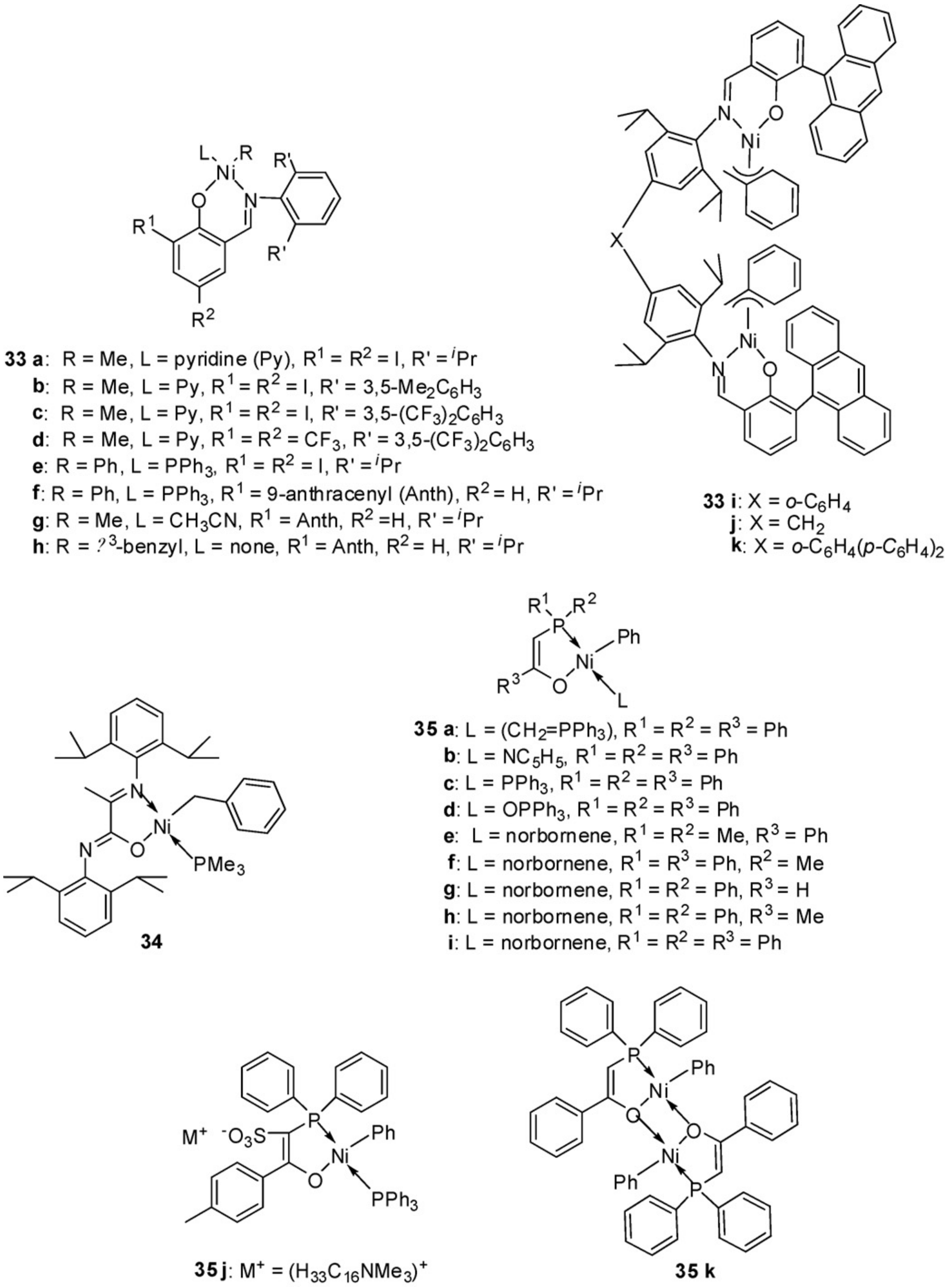
Fig. 10. Chromium complexes for copolymerization of cyclic olefins.

6. Nickel and palladium catalysts

In comparison with early transition metal complexes, late transition metal analogues are less oxophilic (or Lewis acidic) and are thus more tolerant of polar functionalities, affording the possibility of the direct copolymerization of ethylene with norbornene derivatives containing polar groups or performing the reactions in aqueous solutions.

Representative nickel and palladium complexes for the copolymerization of cyclic olefin are shown in Figs. 11 and 12, respectively. The copolymerization reactions catalyzed by the nickel and palladium catalysts are summarized in Scheme 8. The (salicylaldimino)nickel methyl complexes $[(2,6\text{-}R'_2C_6H_3)N{=}CH(2\text{-}R^1\text{-}4\text{-}R^2\text{-}C_6H_2O)]Ni(Me)(Py)$ (**33a–d**) (**a**: $R^1 = R^2 = I$, $R' = {}^iPr$; **b**: $R^1 = R^2 = I$, $R' = 3,5\text{-}Me_2C_6H_3$; **c**: $R^1 = R^2 = I$, $R' = 3,5\text{-}(CF_3)_2C_6H_3$; **d**: $R^1 = R^2 = CF_3$, $R' = 3,5\text{-}(CF_3)_2C_6H_3$) (Fig. 11) served as single-component catalysts for the copolymerization of ethylene with norbornene in both non-aqueous and aqueous solutions, without requirement of a cocatalyst [109]. The substitution pattern of these catalysts influenced, to some extent, the norbornene content of the resulting copolymers in toluene (in the order **33d** > **33b** > **33a** > **33c**), with the maximum N incorporation being less than 10 mol%. Complex **33c** could effectively promote the E–N copolymerization in water to yield the E–N copolymers with the maximum N incorporation of 6 mol% (M_n = 14 kg/mol). The (salicylaldiminato)nickel phenyl complex $[(2,6\text{-}{}^iPr_2C_6H_3)N{=}CH(2,4\text{-}I_2\text{-}C_6H_2O)]Ni(Ph)(PPh_3)$ (**33e**), in combination with $[Rh(CH_2{=}CH_2)_2(acac)]$ as a phosphine scavenger (Ni/Rh = 2/1), was also effective for the copolymerization of ethylene with norbornene in toluene or in aqueous emulsion, which afforded the relatively high molecular weight random copolymers with norbornene contents up to 19 or 14 mol% (M_n = 77 or 88 kg/mol, respectively) [110].

The analogous (salicylaldimino)nickel complexes $[(2,6\text{-}{}^iPr_2C_6H_3)N{=}CH(2\text{-}(9\text{-anthracenyl})C_6H_3O)]NiR(L)$ (**33f–h**) (**f**: R = Ph, $L = Ph_3P$; **g**: $R = CH_3$, $L = CH_3CN$; **h**: $R = \eta^3\text{-}CH_2Ph$, L = none) and the bimetallic (salicylaldiminato)nickel benzyl complexes $X\{[(2,6\text{-}{}^iPr_2C_6H_2)N{=}CH(2\text{-}(9\text{-anthracene})\text{-}C_6H_3O)]Ni(\eta^3\text{-}CH_2Ph)\}_2$ (**33i–k**) (**i**: $X = CH_2$; **j**: $X = o\text{-}C_6H_4$; **k**: $X = o\text{-}C_6H_4(p\text{-}C_6H_4)_2$) (Fig. 11) were reported to act as single-component catalysts for the copolymerization of ethylene with norbornene derivatives containing polar groups [111,112]. The E–(N–CH_2OH) copolymers (5-norbornene-methanol (N–CH_2OH) content <5 mol%) and E–(N–OC(O)Me) copolymers (5-norbornene-acetate (N–OC(O)Me) content <4 mol%) were obtained by **33f** at 40 °C and 100 psig ethylene. The copolymerization of ethylene with 5-norbornene-carboxylic acid methyl ester (N–CO_2Me) or the functional-group-containing tricyclononene (TCN) monomers such as tricyclononene *tert*-butyl ester (TCN–$CO_2{}^tBu$), tricyclononene di-*tert*-butyl ester (TCN–$(CO_2{}^tBu)_2$), TCN–anhydride, and TCN–^{n}Bu-imide by using **33 g** at 100 psig ethylene afforded the corresponding copolymers with the cyclic comonomer incorporations less than 2 mol%. However, the decrease of ethylene concentration (from 100 psig to <5 psig) increased the TCN–$CO_2{}^tBu$



33 a: R = Me, L = pyridine (Py), $R^1 = R^2$ = I, R' = ^{i}Pr
b: R = Me, L = Py, $R^1 = R^2$ = I, R' = 3,5-$Me_2C_6H_3$
c: R = Me, L = Py, $R^1 = R^2$ = I, R' = 3,5-$(CF_3)_2C_6H_3$
d: R = Me, L = Py, $R^1 = R^2 = CF_3$, R' = 3,5-$(CF_3)_2C_6H_3$
e: R = Ph, L = PPh_3, $R^1 = R^2$ = I, R' = ^{i}Pr
f: R = Ph, L = PPh_3, R^1 = 9-anthracenyl (Anth), R^2 = H, R' = ^{i}Pr
g: R = Me, L = CH_3CN, R^1 = Anth, R^2 = H, R' = ^{i}Pr
h: R = ?^{3}-benzyl, L = none, R^1 = Anth, R^2 = H, R' = ^{i}Pr

33 i: X = o-C_6H_4
j: X = CH_2
k: X = o-C_6H_4(p-C_6H_4)$_2$

34

35 a: L = (CH_2=PPh_3), $R^1 = R^2 = R^3$ = Ph
b: L = NC_5H_5, $R^1 = R^2 = R^3$ = Ph
c: L = PPh_3, $R^1 = R^2 = R^3$ = Ph
d: L = $OPPh_3$, $R^1 = R^2 = R^3$ = Ph
e: L = norbornene, $R^1 = R^2$ = Me, R^3 = Ph
f: L = norbornene, $R^1 = R^3$ = Ph, R^2 = Me
g: L = norbornene, $R^1 = R^2$ = Ph, R^3 = H
h: L = norbornene, $R^1 = R^2$ = Ph, R^3 = Me
i: L = norbornene, $R^1 = R^2 = R^3$ = Ph

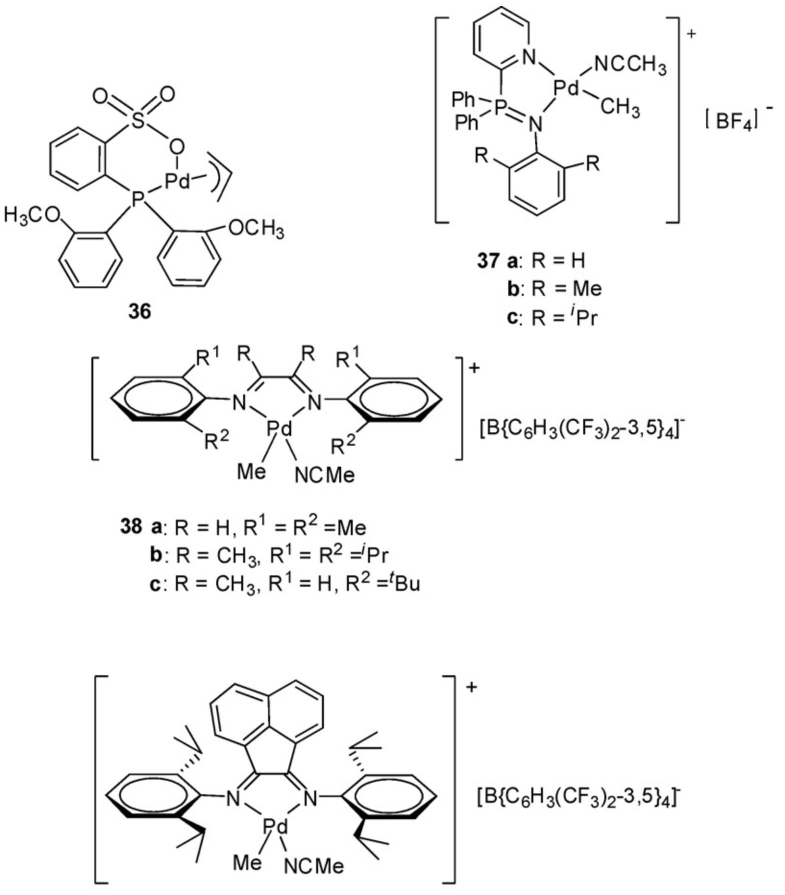
35 j: $M^+ = (H_{33}C_{16}NMe_3)^+$

35 k

Fig. 11. Nickel complexes for copolymerization of cyclic olefins.

incorporation in the copolymers from 2 to 31 mol% [110b]. The dinuclear phosphine-free benzyl complexes **33i–k** showed much higher ability for the incorporation of functionalized norbornene derivatives such as 5-norbornene-2-methyl acetate (N–CH_2OAc: 27–42 mol%) and N–CO_2Me (13–19 mol%) at 45 °C and 100 psig ethylene than the corresponding mononuclear **33h** (N–CH_2OAc content = 15 mol%, N–CO_2Me content = 7 mol%) [111]. The DFT calculation suggested that the higher cyclic comonomer incorporations were attributed to the cooperative effects of the two metal centers. Among these bimetallic complexes **33i–k**, the ability of incorporation of N–CH_2OAc and N–CO_2Me in the copolymerization with ethylene decreased in the order of **33k** > **33i** > **33j** > **33h**.

The (phenylimino)(propanamido)nickel benzyl complex [(2,6-^{i}$Pr_2C_6H_2$)N = C(CH_3)C(O) = N(2,6-^{i}$Pr_2C_6H_2$)]Ni(CH_2Ph)(PMe_3) (**34**) (Fig. 11), in combination with bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$), served as an efficient catalyst for the copolymerization of ethylene with functionalized norbornene derivatives such as 5-norbornene-2-ol (N–OH) and N–OC(O)Me [113]. The E–(N–OH) copolymer with the maximum N–OH incorporation of 18 mol% (M_n = 31 kg/mol) was obtained at 20 °C and 100 psig ethylene. The E–(N–OC(O)Me)



36

37 **a**: R = H
b: R = Me
c: R = ^{i}Pr

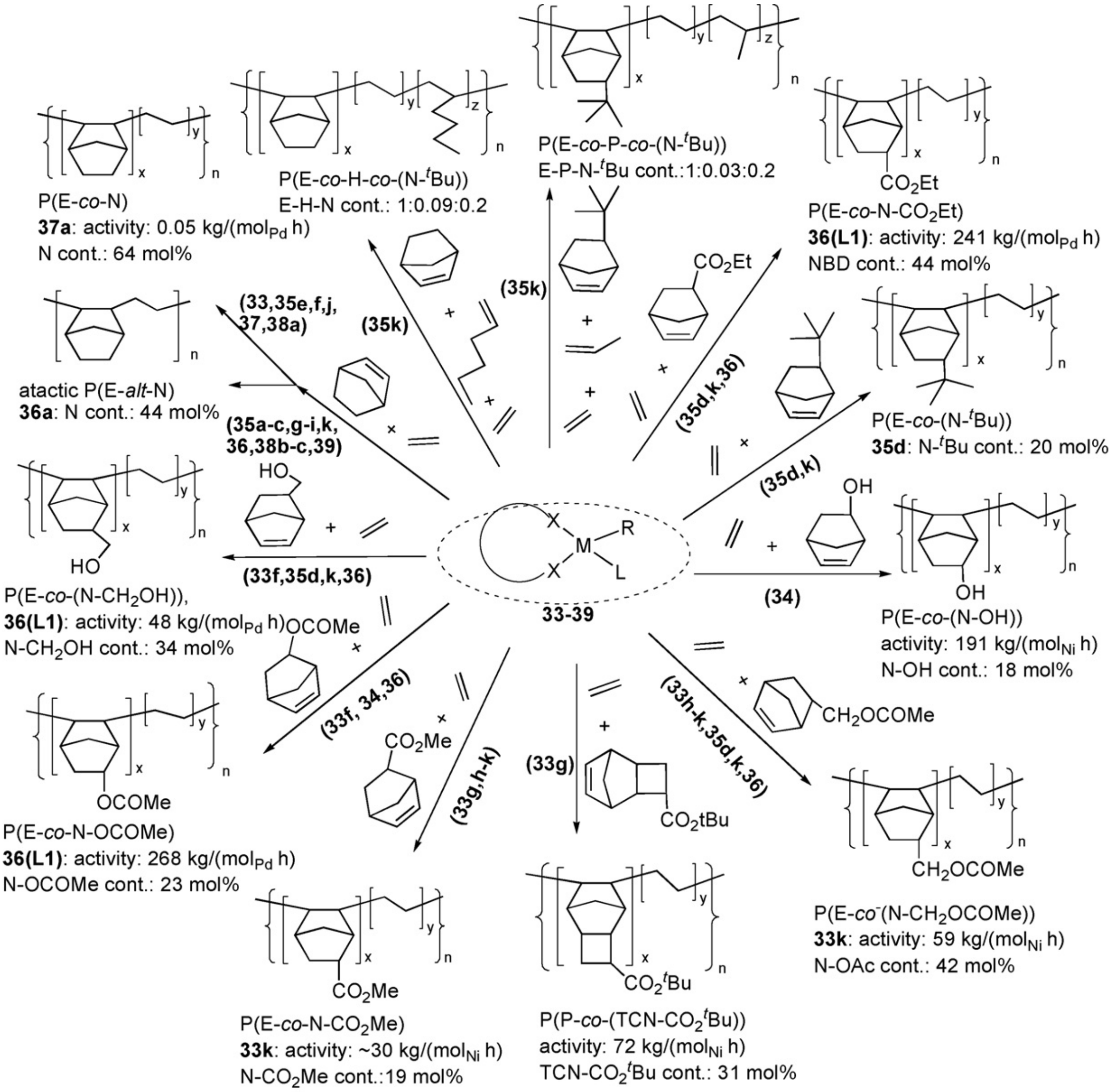
38 **a**: R = H, $R^1 = R^2$ = Me
b: R = CH_3, $R^1 = R^2$ = ^{i}Pr
c: R = CH_3, R^1 = H, R^2 = ^{t}Bu

39

Fig. 12. Palladium complexes for copolymerization of cyclic olefins.

copolymer with the N–OC(O)Me content of about 17 mol% (M_n = 30 kg/mol) was produced under the same conditions. The polymerizations are quasi-living as demonstrated by the narrow molecular weight distributions of the resulting copolymers (PDI = 1.2–1.4) and the increase of polymer molecular weight with polymerization time (8–90 min). By using the quasi-living nature of the **34**/Ni(COD)$_2$ system, block copolymers P(E-*co*-(N–OC(O)Me))$_A$-*b*-P(E-*co*-(N–OC(O)Me))$_B$ containing different ratios of ethylene and N–OC(O)Me (comonomer content in block sequences changed from 25 mol% (block A) to 1–2 mol% (block B)) were synthesized through increasing the ethylene pressure from 50 to 1100 psig during the polymerization reaction [114]. Thermal characterization and TEM examination confirmed the formation of two independent blocks which are sufficiently different in molecular composition to favor microphase separation. Moreover, the tapered block copolymer P(E-*co*-(N–OC(O)Me))-*b*-PE could also be obtained by using the **34**/Ni(COD)$_2$ system in the E–(N–OC(O)Me) copolymerization in the presence of an excess amount of ethylene [115].

The [P,O]-chelating nickel complexes ($PPh_2CH=C(O)Ph$)Ni(Ph)(L) (**35a–d**) (**a**: L = ($CH_2 = PPh_3$); **b**: L = NC_5H_5; **c**: L = PPh_3; **d**: L = $OPPh_3$) and the analogous L-free dinuclear complex ($PPh_2CH=C(O)Ph)_2$Ni (**35k**) (Fig. 11) were also active for the copolymerization of ethylene with norbornene or norbornene derivatives [116a]. In the E–N copolymerization, complexes **35a–c** and **k** produced the alternating copolymers containing some isolated norbornene units and traces of norbornene diads/triads with similar N incorporations (N content: 41–46 mol%) at 25 °C and 100 psig ethylene. Complexes **35d** and **k** could promote the copolymerization of ethylene with norbornene derivatives such as 2-(*n*-butyl)norbornene (N–^{n}Bu), 5-norbornene-carboxylic acid ethyl ester (N–CO_2Et), N–CH_2OC(O)Me, and N–CH_2OH to give the corresponding copolymers with the cyclic comonomer incorporation in the range of 6–20 mol%. The dinuclear complex **35k**, formed in the absence of any added ligand (L), was more active and yielded copolymers with a higher level of norbornene incorporation than the Ph_3PO-coordinated mononuclear complex **35d**. Moreover, both propylene and 1-hexene were successfully terpolymerized with ethylene and norbornene or with ethylene and N–^{n}Bu by using **35k**. The level of incorporation of the cyclic olefins (up to 22 mol%) in the terpolymers was higher than that of the α-olefins. The copolymerization of ethylene with norbornene by the in situ generated, norbornene-coordinated analogues [$(P(R^1)(R^2)CH=C(O)(R^3))$]Ni(Ph)(norbornene) (**35e–i**) (**e**: $R^1 = R^2$ = Me, R^3 = Ph; **f**: $R^1 = R^3$ = Ph, R^2 = Me; **g**: $R^1 = R^2$ = Ph, R^3 = H; **h**: $R^1 = R^2$ = Ph, R^3 = Me; **i**: $R^1 = R^2 = R^3$ = Ph) (Fig. 11) was also investigated [116b].



Scheme 8. Copolymerization of cyclic olefins by nickel and palladium catalysts.

The successive replacement of the methyl groups at the phosphorus atom (in **35e**) by phenyl groups (**35f–i**) caused a considerable increase in catalytic activity and at the same time, decreased the proportion of norbornene units in the resulting copolymers from 62 to 40–50 mol%. The water-soluble complex $[(H_{33}C_{16}NMe_3)(O_3S)(Ph_2P)C=C(O)(C_6H_4CH_3\text{-}4)]Ni(Ph)(PPh_3)$ (**35j**), in combination with $[Rh(CH_2=CH_2)_2(acac)]$ as a phosphine scavenger, could effectively promote the E–N copolymerization in water at room temperature and 50 bar ethylene, yielding a copolymer with the N incorporation of 15 mol% ($M_n = 1.8$ kg/mol) [109].

The phosphine–sulfonate (P–O)-chelating palladium complex $(2\text{-}MeOC_6H_4)_2P(C_6H_4(SO_3)\text{-}2)Pd(allyl)$ (**36**) (Fig. 12) together with the $B(C_6F_5)_3$ activator was effective for the copolymerization of ethylene with norbornene, giving the E–N copolymers with N content up to 31 mol% [117]. The analogous palladium species generated in situ by reaction of $(Pd(DBA)_2)$ (DBA, dibenzylideneacetone) with the ligand $(2\text{-}(MeO)\text{-}6\text{-}RC_6H_3)_2P(C_6H_4(SO_3H)\text{-}2)$ (**L1**: R = H; **L2**: R = OCH_3) showed similar or higher activities for the copolymerization of ethylene with norbornene or functionalized norbornene derivatives. The norbornene derivative contents (N–$CH_2OC(O)Me$: 38 mol%, N–CO_2Et: 44 mol%, N–OC(O)Me: 23 mol%, and N–CH_2OH: 34 mol%) in the corresponding copolymers obtained by the sterically less demanding **L1**/$Pd(DBA)_2$ system were higher than those obtained by **L2**/$Pd(DBA)_2$. The copolymerization of ethylene with norbornene in emulsion by the **L1**/$Pd_2(DBA)_3$ system was also reported, which afforded the atactic alternating E–N copolymers with the N contents up to 44 mol% ($M_n = 3.0$ kg/mol).

The E–N copolymerization by the cationic (pyridinyliminophosphorane)palladium complexes $[\{(2\text{-}C_6H_4N)PPh_2=N(2,5\text{-}R_2C_6H_3)\}Pd(CH_3)(NCCH_3)][BF_4]$ (**37a–c**) (**a**: R = H; **b**: R = Me; **c**: R = ^{i}Pr) yielded the corresponding copolymers with the norbornene incorporation up to 64 mol% [118]. Complex **37b** appeared to be much more active than **37a** and **37c**. The lower activity of **37c** was presumably due to the steric hindrance of the ancillary ligand, whereas in the case of **37a** it was probably due to the lower stability of the olefin-inserted intermediates. The cationic (α-diimino)palladium complexes $[\{(2\text{-}R^1\text{-}6\text{-}R^2C_6H_3)N=C(R)C(R)=N(2\text{-}R^1\text{-}6\text{-}R^2C_6H_3)\}Pd(Me)\text{–}(CH_3CN)][B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$ (**38a–c**) (**a**: $R = H$, $R^1 = R^2 = Me$; **b**: $R = CH_3$, $R^1 = R^2 = {}^iPr$; **c**: $R = CH_3$, $R^1 = H$, $R^2 = {}^tBu$) and $[(2,6\text{-}{}^iPr_2C_6H_3)N=C(C_{10}H_6)C=N(2,6\text{-}{}^iPr_2C_6H_3)]\text{–}Pd(Me)(CH_3CN)]B[3,5\text{-}C_6H_3(CF_3)_2]_4$ (**39**) (Fig. 12) were also investigated for the E–N copolymerization [119]. Among these complexes, the least sterically demanding complex **38a** produced copolymers with the highest N contents (up to 62 mol%, containing *rac*-NN diads) and the highest glass transition temperatures (up to 216 °C) but with the lowest molar weights ($M_w = 20\text{–}66$ kg/mol). In the case of the bulkier **38b**, **c** and **39**, higher molecular weight copolymers ($M_w = 71\text{–}490$ kg/mol, $T_g =$ ca. 104 °C) with the maximum N incorporation less than 43 mol% (N content order: **38c > 39 > 38b**) were obtained, which possessed isolated N units and atactic alternating sequences, without norbornene block sequences being observed.

7. Conclusion and outlook

As described above, great progress in the copolymerization of cyclic olefins by organometallic catalysts has been achieved in the past two decades. Changing the metal center and the ancillary ligand of an organometallic complex is obviously an important strategy for the modification of the catalyst performance and the control of the composition and microstructure of the resulting copolymer products. Cationic scandium alkyl complexes bearing mono(cyclopentadienyl) ligands have demonstrated extremely high activity and excellent alternating preference for the copolymerization of ethylene with norbornene and dicyclopentadiene, as well as excellent activity for the incorporation of styrene into the E–N and E–DCPD COCs (terpolymerization). However, organometallic catalysts based on group 3 and the lanthanide metals for the copolymerization of cyclic olefins are still very limited. Group 4 metal-based catalysts are the most extensively investigated catalyst systems for the copolymerization of cyclic olefins, and a large number of group 4 metal complexes bearing various ancillary ligands have been examined. For a given metal, more electron-donating ancillary ligands usually raise the copolymerization activity and the molecular weight of the resulting copolymers, while increase in the steric hindrance of the ancillary ligands tends to confine successive insertion of a cyclic olefin comonomer. The introduction of the alkyl substituents at the appropriate positions of the ancillary ligands in *ansa*-metallocene or half-sandwich group 4 metal catalysts has therefore led to the synthesis of a series of E–N copolymers with a wide range of N contents and controlled N distributions. Cyclopentadienyl-free, [*N*,*N*]- or [*N*,*O*]-chelating titanium complexes can provide a more electrophilic active site and more sterically open coordination space than metallocene analogues, and usually resulted in lower degree of polymerization stereocontrol without successive insertion of a cyclic olefin. The subtle interplay between the steric and electronic effects of the ancillary ligands in such Cp-free complexes could result in “quasi-living” copolymerization of ethylene with cyclic olefins in some cases. In comparison with early transition metal catalysts, late-transition-metal-based catalysts (e.g., Pd and Ni) are usually less active for the copolymerization of ethylene with cyclic olefins. However, late transition metal catalyst systems can show good tolerability to polar functional groups and can also promote the copolymerization in aqueous solutions.

It should also be pointed out that in comparison with the rather successful copolymerization of ethylene with norbornene, the copolymerizations of larger acyclic olefins such as α-olefins, conjugated dienes, or styrenes with norbornene or other cyclic olefins have achieved only limited success, which usually yielded the copolymers with low incorporation of a larger comonomer (either cyclic or acyclic) and low molecular weight in low activity. Therefore, future challenges in this area will include the development of more active catalyst systems which can efficiently copolymerize not only ethylene but also α-olefins, conjugated dienes, and styrenes with various monocyclic and multicyclic olefins in a controllable fashion, to produce diverse COCs with desired physical, mechanical and optical properties. Undoubtedly, the synthesis of new organometallic complexes with various metal centers and various sophisticatedly controlled ligand environments will continue to play an important role in these endeavors.

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Glossary

acac: Acetylacetonate.
^{n}*Bu:* *n*-Butyl.
^{t}*Bu:* *tert*-Butyl.
CHD: 1,3-Cyclohexadiene.
CHE: Cyclohexene.
CHP: Cycloheptene.
COC: Cyclic olefin copolymer.
COD: 1,5-Cyclooctadiene.
COE: Cyclooctene.
Cp: Cyclopentadienyl.
CPD: 1,3-Cyclopentadiene.
CPE: Cyclopentene.
Cy: Cyclohexyl.
DCPD: Dicyclopentadiene.
DFT: Density functional theory.
DMON: Dimethanooctahydronaphthalene.
E: Ethylene.
EN: Ethylidenenorbornene.
Et: Ethyl.
Flu: 9-Fluorenyl.
H: 1-Hexene.
Ind: Indenyl.
IndH4: 4,5,7,8-Tetrahydro-1-indenyl.
L: Generic neutral ligand.
M: Metal.
MAO: Methylaluminoxane.
MMAO: Methylisobutylaluminoxane or modified methylaluminoxane.
Me: Methyl.
MeCN: Acetonitrile.
M_n: Number-average molecular weight.
M_w: Weight-average molecular weight.
N: Norbornene.
NBD: 2,5-Norbornadiene.
N–^{n}*Bu:* 2-(*n*-Butyl)norbornene.
N–CH$_2$*OC(O)Me::* 5-Norbornene-2-methyl acetate.
N–CH$_2$*OH:* 5-Norbornene-methanol.
N–CO$_2$*Et:* 5-Norbornene-carboxylic acid ethyl ester.
N–CO$_2$*Me:* 5-Norbornene-carboxylic acid methyl ester.
N–COOH: 5-Norbornene-carboxylic acid.
N–OC(O)Me: 5-Norbornene-acetate.
N–OH: 5-Norbornene-2-ol.
O: 1-Octene.
P: Propylene.
PDI: Molecular weight distribution (or polydispersity).

PE: Polyethylene.
Ph: Phenyl.
sPP: Syndiotactic polypropylene.
^{i}*Pr:* *iso*-Propyl.
Py: Pyridyl.
R: Alkyl group.
S: Styrene.
TCN–CO$_2{}^t$*Bu,:* Tricyclononene *tert*-butyl ester.
TCN–(CO$_2{}^t$*Bu)*$_2$*:* Tricyclononene di-*tert*-butyl ester.
TEA: Triethylaluminium.
TEM: Transmission electron microscopy.
TIBA: Triisobutylaluminium.
TMA: Trimethylaluminium.
TMDA: Trimethanododecahydroanthracene.
TMS: Trimethylsilyl.
T_g*:* Glass transition temperature.
T_m*:* Melting point.
VN: 5-Vinyl-2-norbornene.