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Review

Well-defined vanadium complexes as the catalysts for olefin polymerization

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ABSTRACT

The design and synthesis of well-defined vanadium complexes as efficient catalysts for olefin polymerization remains an attractive project for organometallic and polymeric research. Recently, vanadium complexes with well-defined structures have been explored for olefin (co)polymerization by several groups around the world. This article summarizes our recent progress in well-defined vanadium complexes bearing a variety of chelating β-enaminoketonato, salicylaldiminato, iminopyrrolide and tetradentate amine trihydroxy ligands, and their applications in ethylene polymerization, ethylene/α-olefin copolymerization and ethylene/cycloolefin copolymerization. The application of the optimized catalysts in the copolymerization of ethylene and polar monomer such as 3-buten-1-ol, 5-hexen-1-ol, 10-undecen-1-ol and 5-norbornene-2-methanol is also discussed. Particular attention has been paid to the relationships between the catalytic behavior and the electronic and geometrical structure of the precatalyst.

1. Introduction

The advance of homogeneous metallocene catalyst technology in the past two decades has allowed chemists to make significant progress in understanding the relationship between structure and activity in olefin polymerization [1–3]. This significant achievement has stimulated research into the development of non-metallocene catalysts based on both early and late transition metals; this has led to extraordinary advances in producing polyolefins in a precise controlled macromolecular architecture [4–6]. New catalysts for olefin polymerization play a critically important role in the development of new materials as well as in upgrading the performance of existing polyolefins.

The impact of the vanadium based catalyst for olefin polymerization, discovered in the 1950s [7], has been considerable and continues to be the focus of much organometallic and polymeric research [8–11]. In spite of the fact that the activity of vanadium catalyst is a few orders of magnitude smaller than that displayed by Group IV based catalysts, the unique quality of the polymers produced by vanadium catalysts makes them irreplaceable for the manufacture of synthetic rubber and elastomers (EPDM) [12–14]. Actually, vanadium-based Ziegler-Natta technology is well established and widely used in the industrialized world. Vanadium catalysts have also played a critically important role in producing

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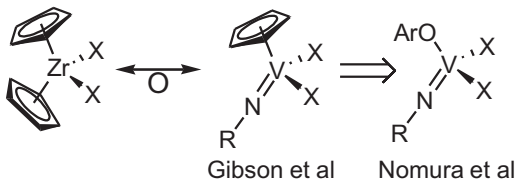


Scheme 1. Isolobal relationship between group 4 metallocene and imido complexes of group 5 complex.

high molecular weight polyethylene with narrow molecular weight distribution as well as ethylene/α-olefin or cycloolefin copolymers with high comonomer incorporations [8]. However, catalyst deactivation is an issue in polymerization with vanadium complexes in general, especially at high polymerization temperatures, due to reduction of catalytically active vanadium species to low-valent, less active, or inactive species. This problem could be overcome by reactivation of inactive vanadium(II) center to active vanadium(III) species by addition of $Cl_3CCOOEt$ or chlorinated hydrocarbons (namely 'rejuvenators' or 'promoters' in the literature), which has proven to be effective reagents for maintaining the higher (active) oxidation state of vanadium systems [15]. Designing and synthesizing ancillary ligands to stabilize active vanadium species is another powerful approach to keep vanadium in high-oxidation and subsequently prolong the catalyst life-time. Van Koten et al. [8] and Gambarotta [9] individually published two review articles on vanadium based catalysts for olefin polymerization, and gave comments on the relationship between catalyst structure and activity from different viewpoints. Recently, Redshaw [11] has described catalytic behavior of vanadium precatalysts bearing chelating aryloxides, focusing on the structure-activity relationship in ethylene polymerization in a perspective. In order to obtain the same electronic complexes of group 5 metals as the group 4 metallocenes, a monoanionic supporting ligand is used, combined with a dianionic imido ligand by the isolobal principle (Scheme 1). The first effective imido-supported group 5 metal based complexes for olefin polymerization were reported by Gibson et al. in 1994 [16–19]. Nomura and co-workers [20–29] reported vanadium(V) imido complexes with aryloxide coligands as efficient catalysts for olefin (co)polymerization.

N,O-chelating ligands such as phenoxyimine and enolatoimine, which have multiple sites for introducing or changing the substituents, have significant applications in olefin polymerization when attached to group 4 [30], group 6 [31], and group 10 metal [32–36]. N,O ligands chelated group 4 metal catalysts have been thoroughly investigated to produce PE, highly-syndiotactic PP, highly-isotactic poly(1-hexene), and ethylene/cycloolefin copolymer with high molecular weight and very narrow molecular weight distribution [37–40]. Highly active chromium catalysts with Schiff base salicylaldimine ligands were discovered by methods of high throughput catalyst screening [31,41]. The family of neutral, single-component, late transition metal olefin polymerization catalysts bearing monoaniomic N,O ligands has been reported and exhibited high activities toward ethylene polymerization and cycloolefin (co)polymerization [32,33,42]. In this review, we want to take a look at more recent developments in vanadium catalysts bearing N,O ligands, particularly those precatalysts with well-defined structures.

2. β-Enaminoketonato vanadium complexes

2.1. Mono(β-enaminoketonato) vanadium(III) complexes

The β-Enaminoketonato ligand is easily accessible and modified, which made it a versatile ligand for the design of diverse catalytic structures. As a matter of fact, before the investigation of vanadium catalysts, we found that titanium catalysts featuring unsymmetrical bidentate β-enaminoketonato ligands were highly active catalysts not only towards ethylene polymerization but also for the copolymerization of ethylene with α-olefins or cycloolefins [43–48]. Impressed by these results, we extended our interests to test the catalytic behavior of β-enaminoketonato vanadium complexes (Fig. 1) [49]. Mono(β-enaminoketonato) vanadium(III) complexes can be prepared under moderate conditions in good yields by the reaction of $VCl_3(THF)_3$ with one equivalent of the lithium salts of β-enaminoketonato ligands in tetrahydrofuran. The molecular structure (see Fig. 1) shows the metal center is a distorted octahedron and is coordinated by two THF molecules, two chlorine atoms, and one nitrogen atom and one oxygen atom of the β-enaminoketonato ligand. The two chlorine atoms are situated in the *trans*-position, while two THF molecules are in the *cis*-position to each other independent of ligand structure. With Et_2AlCl as a cocatalyst and ethyl trichloroacetate (ETA) as a promoter, vanadium complexes **1a–e** have been investigated as catalysts for ethylene polymerization. Among the five catalytic systems, precatalyst **1b** exhibited the highest activity of 27.8 kg PE/mmol$_V$ h bar, followed by precatalyst **1d** (22.8 kg PE/mmol$_V$ h bar), **1a** (21.8 kg PE/mmol$_V$ h bar), **1c** (17.5 kg PE/mmol$_V$ h bar) and **1e** (16.8 kg PE/mmol$_V$ h bar) under mild conditions. In spite of the electronic feature of ligands in **1a** and **1d** being considerably different, similar activities were observed. Similarly, steric hindrance played little role in controlling the catalytic activities, and precatalysts **1b**, **1c** and **1d** gave comparable activities in ethylene polymerization.

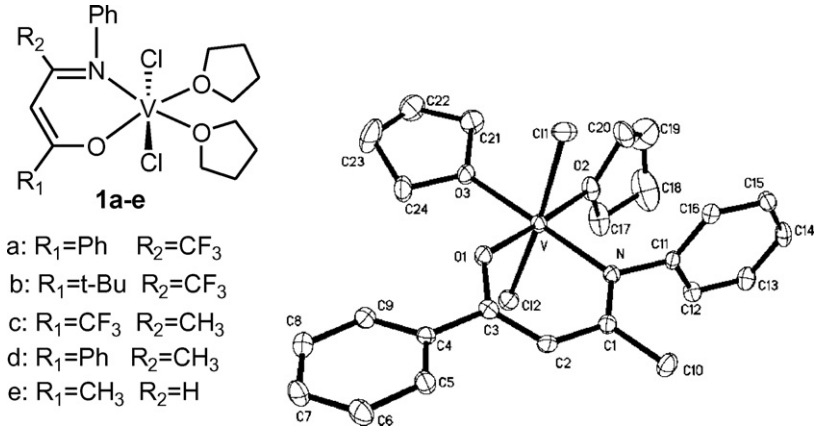


Fig. 1. Mono(β-enaminoketonato) vanadium(III) complexes [49].

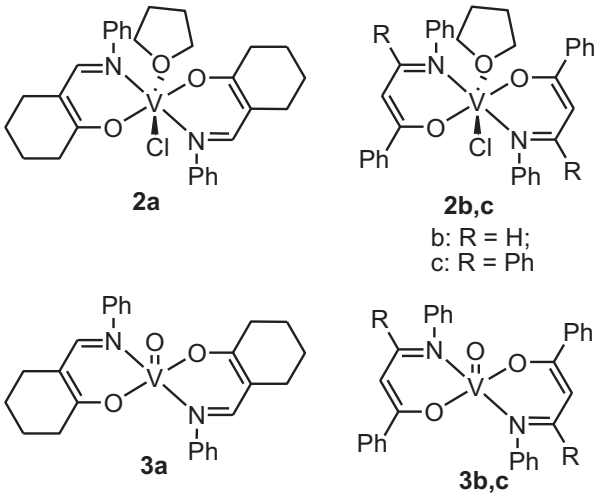


Fig. 2. Bis(β-enaminoketonato) vanadium complexes.

Since these catalysts displayed high activities for ethylene polymerization, the abilities of catalyzing ethylene/norbornene (NBE) and ethylene/1-hexene copolymerization were also investigated. Catalyst **1e** with the smallest substituent on the ligand backbone exhibited the highest activity of 6.84 kg polymer/mmol$_V$ h in ethylene/NBE copolymerization under atmospheric pressure and 0.5 mol/L NBE in the feed. Under optimized conditions, the copolymer with NBE incorporation up to 42.8 mol% can be easily obtained, indicating the promising ability to copolymerize ethylene and norbornene by these vanadium catalysts. The GPC analyses reveal that the ethylene/NBE copolymers obtained possess high molecular weights with unimodal molecular weight distributions. The copolymers obtained display glass transition temperatures (T_gs) valued between 67.3 and 105.3 °C. The analyzing microstructures of copolymers, which were investigated by NMR, revealed that norbornene was incorporated as isolated or alternating manner without any NBE-NBE sequence or long polyethylene segment. Under the same conditions (1 μmol catalyst, 1 atm ethylene pressure, Al/V = 3000 (molar ratio), ETA/V = 300 (molar ratio), V_{total} = 30 mL, 1.0 mol/L 1-hexene, polymerization at 25 °C in toluene for 10 min), catalyst **1a** exhibits the highest catalytic activity (5.82 kg polymer/mmol$_V$ h) in the ethylene/hexene copolymerization, which is a little lower than the activity of $VCl_3(THF)_3$. However, the copolymers with much higher hexene incorporation and higher molecular weight were produced by catalysts **1a–d** than that by $VCl_3(THF)_3$.

Interestingly, high catalytic activity of catalyst **1d** (9.72 kg/mmol$_V$ h) was displayed towards the copolymerization of ethylene and 10-undecen-1-ol (masked by Et_2AlCl), and the resultant copolymer with the 10-undecen-1-ol incorporation of 3.70 mol% was obtained [50]. Catalyst **1d** can also efficiently copolymerize ethylene with 5-hexen-1-ol, and a high catalytic activity (8.50 kg/mmol$_V$ h) and a mild monomer incorporation of 2.7 mol% were obtained. A significant decrease in both catalytic activity (3.90 kg/mmol$_V$ h) and monomer incorporation (0.6 mol%) were detected when 3-buten-1-ol was used as comonomer.

2.2. Bis(β-enaminoketonato) vanadium complexes

In order to obtain more information on the structure-activity relationship of the β-enaminoketonato vanadium catalyst, bis(β-enaminoketonato) vanadium(III and IV) complexes with varied ligand backbone were synthesized (Figs. 2 and 3) [51]. By comparison, a small but significant lengthening of the V–O and V–N bond distances in vanadium complex **2b** in contrast with those in the mono(β-enaminoketonato) vanadium(III) complexes (1.910–1.922 Å and 2.048–2.064 Å) was observed because the two coordinated ligands repulsed each other. A small shortening of the V–N bond distances in vanadium complex **3b** (2.084 and 2.092 Å) in contrast with those in their analogue **2b** (2.108 and 2.111 Å) was observed after the release of the coordinate space (without THF molecule in **3b**).

Comparing with mono(β-enaminoketonato) vanadium(III) complexes (**1a–e**), with introducing one more β-enaminoketonato ligand, complexes **2a–c** and **3a–c** all exhibited high activities at 70 °C (Table 1), and the highest activity of 23.76 kg PE/(mmol$_V$ h bar) was observed by **3c**, suggesting the promising thermal stability of these catalysts. The catalytic activities of vanadium(III) complexes **2b** and **2c** are much higher than that of complex **2a** under the same conditions. The catalytic activity of **2a** decreased and the molecular weight decreased, and the molecular weight distribution broadened with the increase of reaction temperature from 25 to 70 °C. The introduction of a Ph group in the imino side (catalyst **2b** *vs* **2c**) resulted in narrowing the molecular weight distribution of the resultant polymer (especially at elevated reaction temperature). It is thus assumed that the conjugate effect of the N,O ligands plays an important role for the thermal stability of the catalysts. The vanadium(III) complexes **2a** and **2b** displayed higher activities than the corresponding vanadium(IV) complexes **3a** and **3b** when polymerization operated at 25 °C, however, similar activities were observed by catalysts **2c** and **3c**. Complex **3c** exhibited the highest catalytic activity, and produced PE with the highest molecular weight under the same conditions among the three vanadium(IV) catalysts, which could also arise from the enhancement of the conjugate effect on the backbone of the ligands. These results indicate that the catalytic behavior was influenced not only by the oxidation state of the precursors but also by the ligand structures [52].

Other reaction parameters such as cocatalyst, solvent, and promoter also play an important role in controlling the catalytic behaviors. The lowest activity was observed with CH_2Cl_2 as the solvent; however, it produced PE with highest molecular weight and relatively broad molecular weight distribution. Polymerization

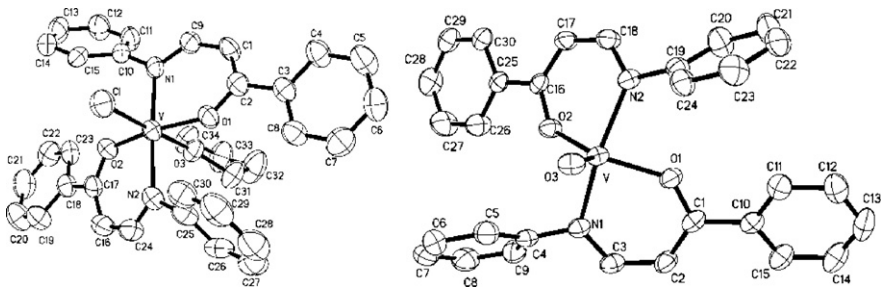


Fig. 3. Molecular structures of complexes **2b** and **3b**. [51].

Table 1
Ethylene polymerization catalyzed by **2a–c** and **3a–c** [51].[a]

Entry	Catalyst	T (°C)	Al/V (molar ratio)	Polymer (g)	Activity[b]	M_w[c] (kg/mol)	M_w/M_n[c]
1	**2a**	25	4000	0.55	13.20	58.7	2.62
2	**2a**	70	4000	0.47	11.28	21.0	4.45
3	**2b**	25	2000	0.55	13.20	52.7	2.64
4	**2b**	25	4000	0.76	18.24	35.3	2.57
5	**2b**	70	4000	0.89	21.36	14.9	2.69
6[d]	**2b**	25	2000	0.11	2.64	73.1	3.79
7[e]	**2b**	25	2000	0.19	4.56	23.4	2.60
8	**2c**	25	4000	0.75	18.00	42.6	2.55
9	**2c**	70	4000	0.75	18.00	14.3	2.25
10	**3a**	25	4000	0.34	8.16	48.4	2.16
11	**3a**	70	4000	0.63	15.20	11.2	2.60
12	**3b**	25	4000	0.35	8.40	46.5	2.63
13	**3b**	70	4000	0.57	13.68	12.4	2.90
14	**3c**	25	4000	0.77	18.48	53.2	2.77
15	**3c**	70	4000	0.99	23.76	18.4	2.24

[a] Conditions: V_{total} = 50 mL, ethylene 1 atm, catalyst 0.5 μmol, cocatalyst Et_2AlCl 2.0 mmol, ETA/V = 300 (molar ratio), 5 min.
[b] Activity in kg PE/($mmol_V$ h bar).
[c] GPC data in 1,2,4-trichlorobenzene *vs* polystyrene standard.
[d] Polymerization in CH_2Cl_2.
[e] Polymerization in hexane.

conducted in hexane was also less productive than that in toluene and polymer was obtained with lower molecular weight (See Table 1). Organoaluminum compounds, such as modified MAO, dry MAO, $AlMe_3$, and $AlEt_3$, were separately investigated as the cocatalyst in combination with complex **2b**. Only system **2b**/(modified MAO) exhibited low activity (0.09 kg PE/$mmol_V$ h bar), and trace or even no polymer was obtained by using dry MAO, $AlMe_3$, or $AlEt_3$ as the cocatalyst. The increase in Et_2AlCl concentration resulted in an increase in catalytic activity but a decrease in the molecular weight of the polyethylene, which suggests the existence of chain transfer to Al reactions. In order to obtain a better understanding of the chain transfer process, $AlMe_3$, Al^iBu_3, $ZnEt_2$ and MeMgBr were separately added as chain transfer agents. As shown in Fig. 4, polyethylenes with broad molecular weight distributions were obtained. The more dominant low M_w part PEs were formed with $AlMe_3$ and Al^iBu_3, which suggested the chain transfer to these agents was not completely reversible, however, the high M_w part predominant PEs were obtained by using MeMgBr, indicating that the chain transfer to Mg was not so easy and the halide compound was actually a catalyst support [53–55]. Saturated chain ends without vinyl termination were observed when $ZnEt_2$ was added indicating that virtually all of the polymer chains were terminated via chain transfer to aluminum or zinc. The chain transfer reaction was also influenced by the catalyst structure. The polymers with low molecular weights and unimodal distributions were obtained by vanadium(IV) catalyst **3b**.

Chain transfer reactions also play an important role in ethylene/hexene copolymerization. The introduction of 50 equiv. halide magnesium compounds resulted in a sharp decrease of catalytic activity. A typical bimodal distribution copolymer was obtained in the case of MeMgBr whereas a copolymer with high molecular weight and unimodal distribution was produced when $MgCl_2$ was used (Fig. 5). These results suggest that the halide magnesium compounds were a promising support for these catalysts. Catalytic activity was enhanced and the molecular weight of the resultant copolymer decreased with the addition of $ZnEt_2$. Most importantly, the hexene incorporation highly increased with elevated polymerization temperature. This behavior could mainly rise from the variation in the ratio of chain transfer reaction rate to chain propagation rate. The introduction of bulkier comonomer should decrease the rate of olefin insertion into the vanadium carbon bond

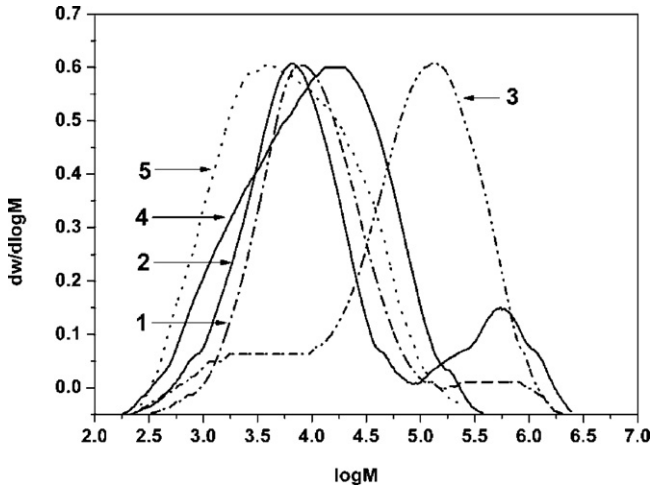


Fig. 4. The influence of chain transfer reagents on the molecular weights and molecular weight distributions of the resultant PEs produced by **2b**/Et_2AlCl [51]. (**1**: 50 equiv. of $AlMe_3$; **2**: 50 equiv. of Al^iBu_3; **3**: 50 equiv. of MeMgBr; **4**: 50 equiv. of $ZnEt_2$; **5**: 100 equiv. of $ZnEt_2$).

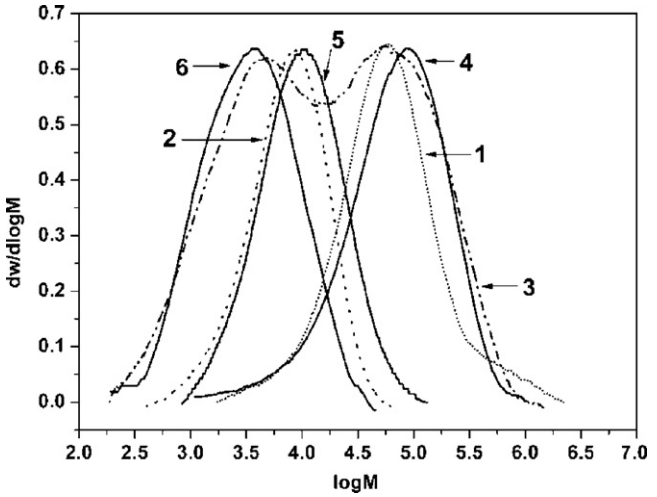
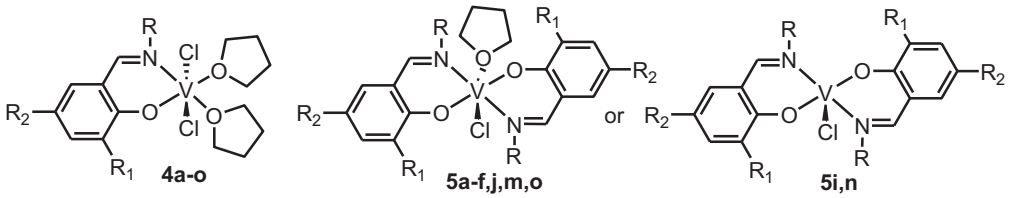


Fig. 5. The influence of chain transfer reagents on the molecular weights and molecular weight distributions of the ethylene/1-hexene copolymers produced by **2b**/Et_2AlCl [51]. (**1**: no chain transfer reagents, T = 25 °C; **2**: no chain transfer reagents, T = 70 °C; **3**: 50 equiv. of MeMgBr, T = 70 °C; **4**: 50 equiv. of $MgCl_2$, T = 70 °C; **5**: 50 equiv. of $ZnEt_2$, T = 25 °C; **6**: 50 equiv. of $ZnEt_2$, T = 70 °C).



a: $R_1 = R_2$ = H, R = Ph
b: $R_1 = R_2$ = H, R = *p*-CF_3Ph
c: $R_1 = R_2$ = H, R = *p*-CH_3Ph
d: $R_1 = R_2$ = H, R = 2,6-Me_2Ph
e: $R_1 = R_2$ = H, R = 2,6-*i*Pr_2Ph
f: $R_1 = R_2$ = H, R = Cyclohexyl
g: $R_1 = R_2$ = H, R = C_3H_2NS
h: $R_1 = R_2$ = H, R = C_7H_4NS
i: $R_1 = R_2$ = H, R = $C_7H_5N_2$
j: R_1= *t*-Bu, R_2 = H, R = Ph
k: R_1= *t*-Bu, R_2 = H, R = C_3H_2NS
l: R_1= *t*-Bu, R_2 = H, R = 2,6-*i*Pr_2Ph
m: $R_1 = R_2$ = *t*-Bu, R = Ph
n: $R_1 = R_2$ = *t*-Bu, R = 2,6-*i*Pr_2Ph
o: $R_1 = R_2$ = Br, R = Ph

Fig. 6. Mono- or bis(salicylaldiminato) vanadium(III) complexes.

(k_p) (Scheme 2), but the rate of exchange of the polymer chains between vanadium and Al (k_e) must be kept constant. The ratio of k_e/k_p in ethylene/1-hexene copolymerization could be much higher than that in ethylene homopolymerization, though it may be not high enough for the criterion of catalyzed chain growth ($k_e \gg k_p$) [56,57]. Interestingly, the comonomer composition distribution was independent of the chain transfer agents, and little dyad sequence of hexene was observed even when the hexene incorporation was increased to 13.5 mol%.

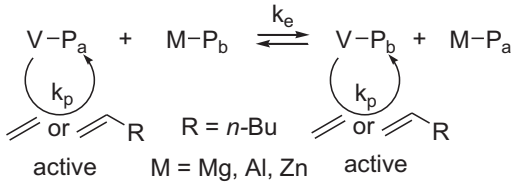
3. Salicylaldiminato vanadium complexes

Salicylaldiminato ligands have been used in transition metal organometallics and shown to afford highly active olefin polymerization catalysts [30,58]. For instance, titanium/zirconium complexes containing bis(salicylaldiminato) ligands can be used to produce polyethylene or syndiotactic polypropylene with high molecular weight and a narrow molecular weight distribution, and the catalytic behavior was highly affected by the substituents on both the phenoxy and the imino groups [4–6,37–40]. Fujita extended the application of salicylaldiminato ligands in vanadium-based olefin polymerization catalysts, and highly active olefin polymerization catalysts were obtained when salicylaldiminato ligated vanadium complexes were supported by $MgCl_2$ [53,54]. In light of the impressive results for salicylaldiminato vanadium catalysts, ligands with varied steric and electronic features at the substituents were designed and synthesized for screening the salicylaldiminato vanadium catalysts.

3.1. Mono(salicylaldiminato) vanadium(III) complexes

In the presence of excess triethylamine, the reaction of $VCl_3(THF)_3$ with 1.0 equiv. of salicylaldiminato ligand in tetrahydrofuran (THF) afforded vanadium(III) complexes **4a–o** in moderate to high yields (Fig. 6) [59]. X-ray crystallographic analysis showed that the geometry of the molecular structure was similar to those of mono(β-enaminoketonato) vanadium(III) complexes (Fig. 7). Though some bond angles and distances around the V centre were influenced by the modification of the ligands, the configuration of molecular structure almost kept constant.

Complexes **4a–o** have been investigated as effective catalysts for ethylene polymerization under atmospheric pressure. Both ligand structure and reaction temperature played an important role in determining catalytic activity (Fig. 8). Although the structures of complexes **4a–e** are rather different, they display comparable catalytic activities (17–22 kg PE/mmol$_V$ h bar) towards ethylene polymerization at 25 °C. On introducing one *para*-trifluoromethyl (electron-withdrawing group) or *para*-methyl (donating group) into N-aryl moiety of the ligand, to form complex **4b** or **4c**, catalytic activity decreased by about 10%, while complex **4e** bearing a ligand with two *ortho* isopropyl groups (bulky group) into the N-aryl moiety was more active than **4a**. Complex **4a** displays quite high activity at 50 °C, which is comparable with that at room temperature, while the catalytic activities of complexes **4b–e** rapidly decrease with the increase of temperature. Interestingly, with the introduction of the non-conjugated substituent cyclohexyl into the N-moiety of the ligand, complex **4f** exhibited much lower catalytic activity (10.8×10^3 kg PE/mol$_V$ h bar) than **4a** (22.3×10^3 kg PE/mol$_V$ h bar) at 25 °C, but different from complexes **4a–e**, complex **4f** displayed the highest catalytic activity towards ethylene polymerization at 70 °C. With the introduction of heteroatom contained group onto the N-aryl moiety of a ligand [60], complexes **4g–i** exhibited higher catalytic activities toward ethylene polymerization at 70 °C than complex **4a**, although they only showed much lower activities at ambient temperature compared with **4a**. Bulky *tert*-butyl on the aryloxy moiety of the ligand showed negative effect on catalytic activities. Introducing two bromine atoms into the aryloxy moiety of the ligand, complex **4o** displayed the lowest catalytic activity



Scheme 2. Generic mechanism for the chain transfer reactions.

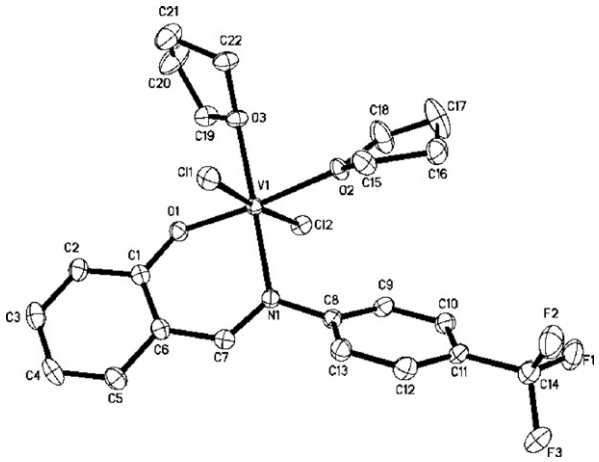


Fig. 7. Molecular structure of complex **4b** [59].

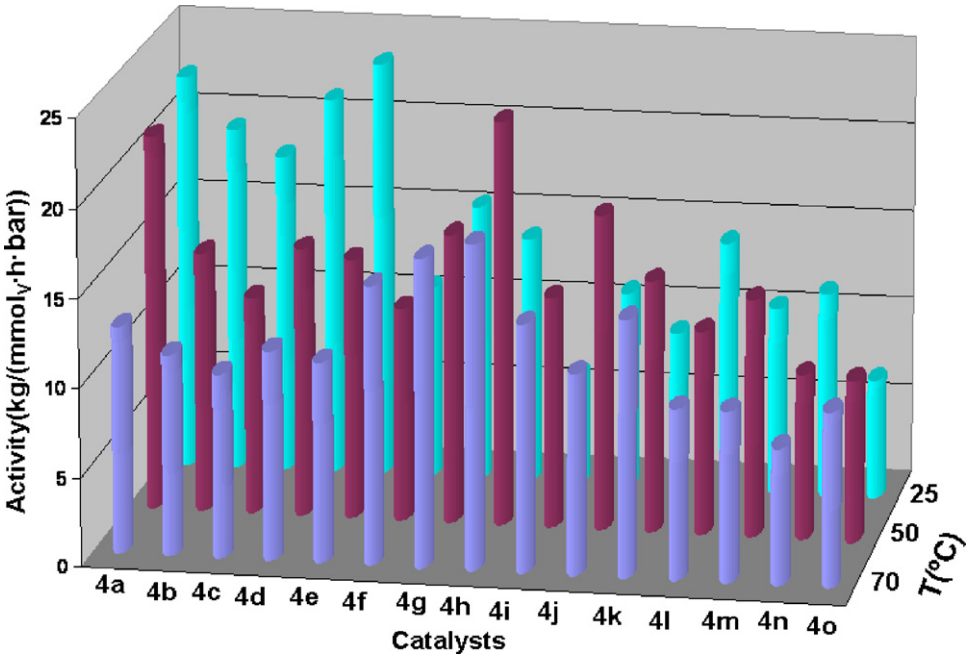


Fig. 8. Catalytic activities of mono(salicylaldiminato) vanadium(III) complexes toward ethylene polymerization at different temperatures [59,60]. (Conditions: 50 mL of toluene, ethylene 1 bar, 150 μmol of ETA, 2.0 mmol of DEAC, 0.5 μmol of catalyst, polymerization in 5 min).

(9.12×10^3 kg PE/mol$_V$ h bar) among the 15 salicylaldiminato vanadium complexes at 25 °C. It seems that both electronic and steric effects play a key role towards the decrease of catalytic activity for ethylene polymerization with the salicylaldiminato vanadium complexes.

Catalyst life-time studies were carried out with catalysts **4a**, **4g–i** and **4k** at 70 °C. Catalysts **4i** and **4d** were deactivated after the first ca. 10 min, whereas the other three catalysts **4a**, **4g** and **4h** maintained some productivity over the full 30 min run time, with the benzothiazole group containing catalyst **4h** being superior. The PEs obtained in 30 min polymerization display bimodal molecular weight distribution, probably due to the presence of two types of catalytic active species, and the relative distribution is dependent on the catalysts utilized.

Complexes **4g–i** and **4k** show high activities toward the copolymerization of ethylene and 1-hexene, and produce high molecular weight copolymers with unimodal molecular weight distributions. Copolymer with 1-hexene up to 26.7 mol % can be obtained by **4h** when 2.70 mol/L 1-hexene was in the feed. The highest catalytic activity (6.18 kg/mmol$_V$ h) was achieved at 50 °C for **4h** when polymerization ran 10 min. However, when the polymerization time was extended to 30 min, the most productive temperature was 25 °C, which showed comparable activity with that in 10 min. The molecular weights of the resultant copolymers decreased sharply with the increase of polymerization temperature. The molecular weight distribution of the resulting polymer is independent of polymerization temperature; even at 70 °C polymerization for 30 min, an unimodal molecular weight distribution copolymer was produced, indicating single-site catalytic behavior. A catalytic activity of 8.70 kg/mmol$_V$ h was obtained when **4a** was applied in the copolymerization of ethylene with the Et_2AlCl masked 10-undecen-1-ol. A copolymer with 4.00 mol% incorporation of comonomer was obtained [50].

3.2. Bis(salicylaldiminato) vanadium(III) complexes

When 2 equiv. of salicylaldimine ligands were added to $VCl_3(THF)_3$, bis(salicylaldiminato) vanadium(III) complexes were formed (Fig. 6) [59]. Molecular structures showed that the steric obstacles have a remarkable effect on the configuration of bis(salicylaldiminato) vanadium complexes. As shown in Fig. 9 (left), complex **5b** exhibits a six-coordinate distorted octahedral geometry around the V metal center, in which the equatorial positions are occupied by oxygen and nitrogen atoms of two chelating

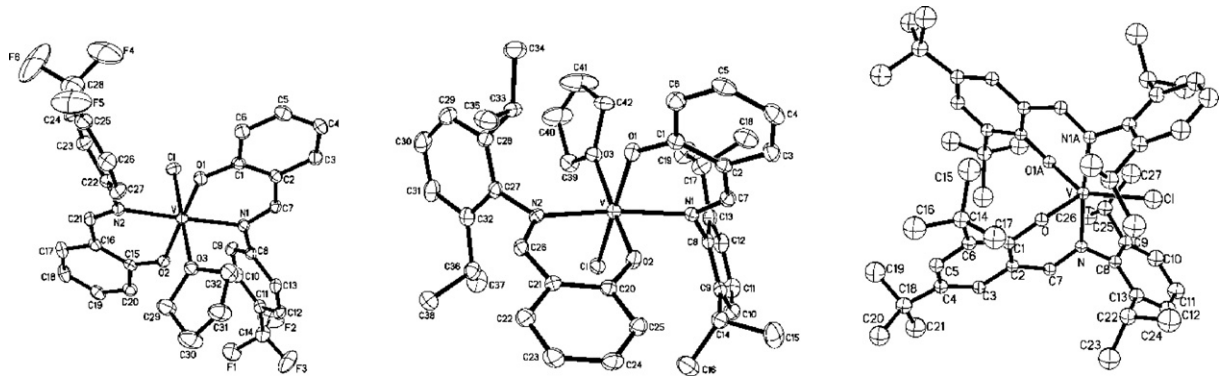


Fig. 9. Molecular structures of complexes **5b**, **5e** and **5n** [59].

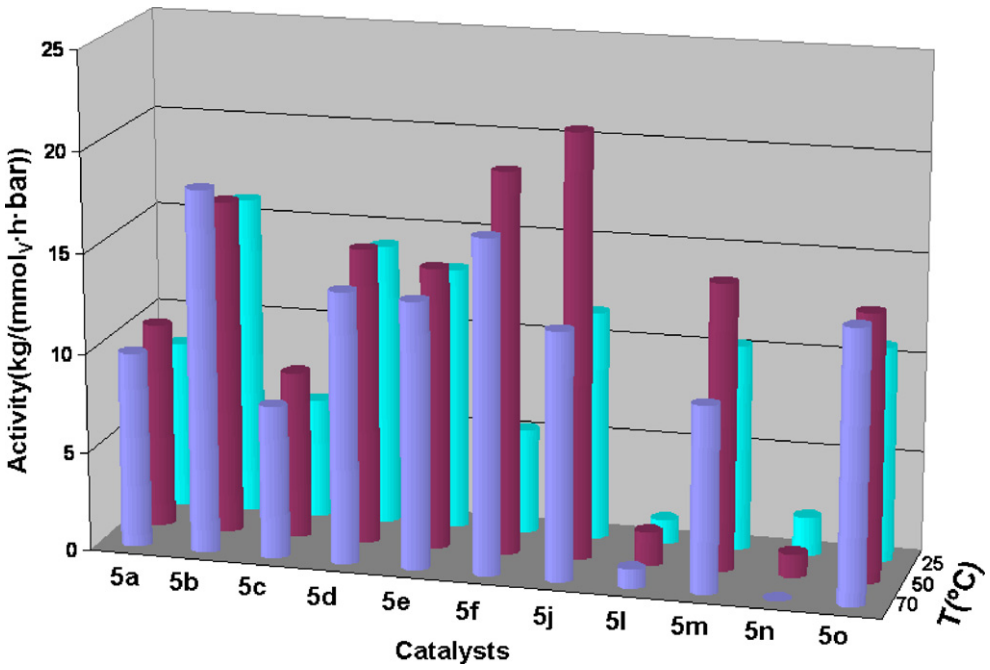


Fig. 10. Catalytic activities of bis(salicylaldiminato) vanadium(III) complexes toward ethylene polymerization at different temperatures [59]. (Conditions: 50 mL of toluene, ethylene 1 bar, 150 μmol of ETA, 2.0 mmol of DEAC, 0.5 μmol of catalyst, polymerization in 5 min).

salicylaldiminato ligands. The chlorine atom is coordinated on the axial position, and the THF occupies another axial position. A different geometry was exhibited by complex **5e** (Fig. 9 middle), in which the equatorial positions are occupied by two oxygen atoms of the salicylaldiminato ligands, and an additional oxygen atom of THF molecule as well as the chlorine atom. Two nitrogen atoms are coordinated on the axial position. The DFT calculation indicates that in complex **5e** the THF and Cl prefer to exhibit a *cis* configuration (27.11 kJ/mol lower than the corresponding *trans* configuration), while the *trans* configuration of complex **5b** shows relatively lower formation energy (11.77 kJ/mol) than the *cis* configuration. Interestingly, completely complex **5n**, different from complexes **5b** and **5e**, folds into a five-coordinate distorted trigonal bipyramidal geometry (Fig. 9 right). No THF molecule is coordinated around the vanadium metal center due to the steric effect of the ligands, as established by mass spectra as well as elemental analysis. The equatorial positions are occupied by two oxygen atoms and the chlorine atom. The nitrogen atoms are coordinated on the axial position. These results indicate that the steric effect of the ligands significantly influences the structures of the bis(salicylaldiminato) vanadium complexes. Compared with complex **5e**, although additional obstacles were introduced in aryloxy group in complex **5n**, the V–N bond distances (2.117 Å) in complex **5n** are somewhat shorter since there is no repulsion from the coordinated THF. The V–Cl bond distance in **5n** (2.261 Å) is shorter than those in **5b** (2.3405 Å) and **5e** (2.3303 Å).

Different from the case of complexes **4a–o**, the structures of ligands in **5a–o** greatly affect the catalytic behavior of these bis(salicylaldiminato) vanadium complexes towards ethylene polymerization (Fig. 10). Compared with complex **5a**, complexes **5b** and **5o** bearing CF_3-substituted and diBr-substituted salicylaldiminato ligands, respectively, exhibit higher catalytic activities, indicating that electron-withdrawing effect can improve the catalyst performance of the bis(salicylaldiminato) vanadium complexes. The catalytic activities of complexes **5d** and **5e** are much higher than that of complex **5a** under the same conditions, which shows that the steric effect of the N-moiety of the salicylaldiminato ligands is propitious to improve vanadium catalyst performance. Furthermore, the catalytic activities of complexes **5j** and **5m** are also higher than that of complex **5a**, which shows that the steric effect of the aryloxy moiety of the ligands also favors ameliorating vanadium catalyst performance. However, complexes **5l** and **5n** only display extremely low catalytic activities. The molecular structure of **5n** (Fig. 9 right) may shed some light on this result: the bulky substituents on both the N-moiety and aryloxy moiety of the salicylaldiminato ligand, which have excluded the THF molecule from the vanadium center, probably have a hindrance on the ethylene insertion reaction.

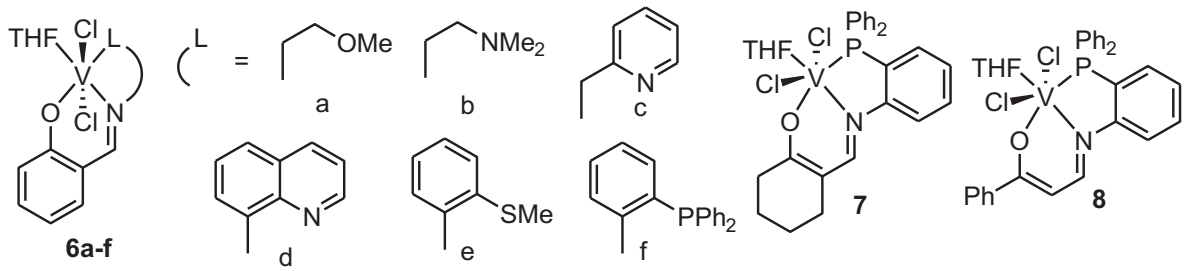


Fig. 11. Vanadium(III) complexes bearing tridentate Schiff base ligands.

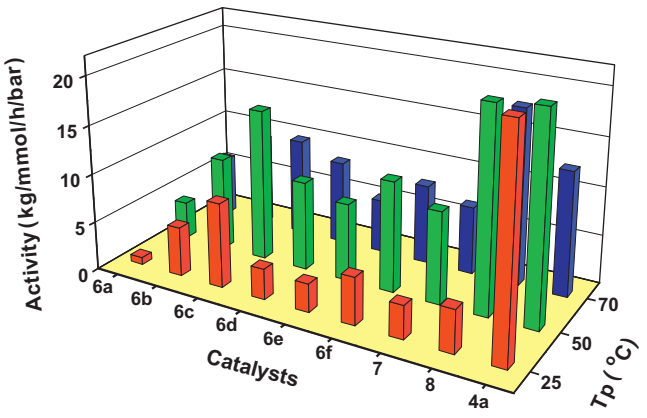


Fig. 12. Catalytic activities of complexes **6e–f**, **7** and **8** toward ethylene polymerization at different temperatures [69]. (Conditions: 50 mL of toluene, ethylene 1 bar, 150 μmol of ETA, 2.0 mmol of DEAC, 0.5 μmol of catalyst, polymerization in 5 min).

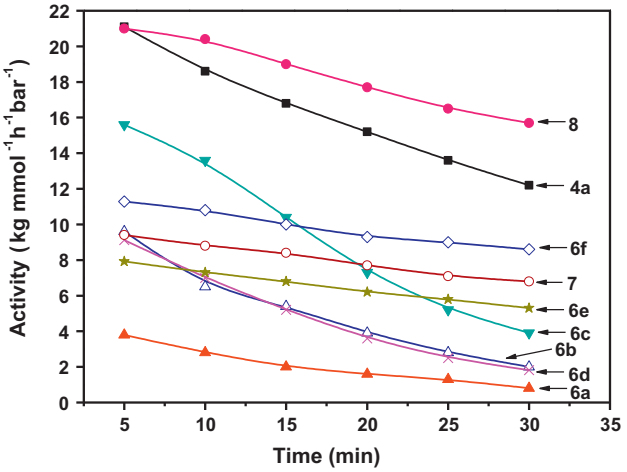


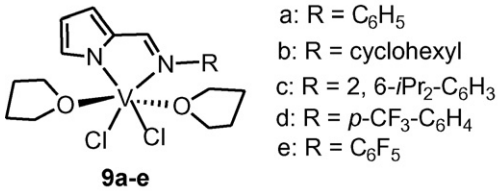
Fig. 13. Lifetime graph of ethylene polymerization for catalysts **4a**, **6a–f**, **7** and **8** [69]. (Conditions: 50 mL of toluene at 50 °C, ethylene 1 bar, 30 μmol of ETA, 0.4 mmol of DEAC, 0.2 μmol of catalyst).

3.3. Vanadium(III) complexes bearing tridentate salicylaldiminato ligands

Enhancement of catalytic activity and/or selectivity was observed following the introduction of pendant donor groups in N,O ligands with the group IV metal catalysts; this has been proposed to arise from both steric hindrance and electronic effects [61–68]. The fast deactivation of mono(salicylaldiminato) vanadium(III) complexes took place at high polymerization temperatures, while the thermal stability of the catalysts was enhanced by the introduction of a heteroatom containing group onto the N-aryl moiety of the salicylaldiminato ligands [59,60]. This encouraged us to explore the application of Schiff base ligands with π-donating pendant heteroatoms such as O, N, S, P in the vanadium catalysis (Fig. 11) [69].

As shown in Fig. 12, both pendant donor atom and the reaction temperature considerably influence catalytic activity. All catalysts are highly active toward ethylene polymerization even at high reaction temperature. The highest activity (20.64 kg PE/mmol$_V$ h bar) was obtained with catalyst **8** at 50 °C. Catalysts **6b–f** with a nitrogen, phosphine or sulfur donor displayed higher activities than catalyst **6a** bearing an oxygen donor. Among the three complexes bearing a nitrogen donor, the pyridylmethyl derivative **6c** exhibited the highest activity of 15.6 kg PE/mmol$_V$ h bar, followed by **6b** (9.6 kg PE/mmol$_V$ h bar) and **6d** (9.1 kg PE/mmol$_V$ h bar) under the optimal conditions. Although the molecular weights of polymers produced by catalysts **6a–f**, **7** and **8** decreased sharply with the increase of reaction temperature, the molecular weight distributions hardly broadened and the polydispersity indexes remained in the range of 1.9–3.0, suggesting complexes **6a–f**, **7** and **8** are single-site catalysts even at high polymerization temperature [70]. By contrast, the molecular weight distributions obviously broadened under the similar conditions when the vanadium(III) catalysts bearing bidentate Schiff base ligands were used [59]. This result indicates that the pendant donors help to stabilize the active species. The deactivation tests of catalysts **6a–f**, **7** and **8** were conducted at 50 °C in 30 min (Fig. 13). A remarkable decrease in catalytic activity of **6a–d** (at 30 min more than 70% of activity was reduced in contrast with that at 5 min) was observed, whereas catalysts **6e–f**, **7** and **8** bearing softer second-row donors (S, P) showed a smaller decrease (ca. 30%), indicating the latter four catalysts possess higher thermal stability [63–68,71,72].

The copolymerization behavior of catalysts **6a–f**, **7** and **8** was evaluated in the presence of Et_2AlCl and with ETA as the promoter. In the case of ethylene/1-hexene copolymerization, the catalytic activities depend on both the pendant donor and the electronic effect of the backbone of ligands. Catalyst **6a** bearing an oxygen donor and catalyst **7** containing weak conjugated backbone ligand exhibited low activity. Copolymers with higher molecular weights were produced by catalysts bearing a nitrogen donor. Catalyst **6f** containing the phosphorus donor exhibited the highest catalytic activity (17.28 kg/mmol$_V$ h bar) in ethylene/norbornene copolymerization (polymerization conditions: ethylene 1 bar, catalyst 0.5 μmol, cocatalyst Et_2AlCl, NBE 0.5 mol/L, Al/V = 4000 (molar ratio), ETA/V = 300 (molar ratio), copolymerization for 5 min). All of the copolymers obtained by catalysts **6a–f**, **7** and **8** displayed high molecular weights with unimodal molecular weight distributions. Moreover, the copolymers with higher molecular weights were obtained by the soft donor bearing catalysts **6e–f**, **7** and **8**



9a-e

a: R = C_6H_5
b: R = cyclohexyl
c: R = 2, 6-*i*Pr$_2$-C_6H_3
d: R = *p*-CF_3-C_6H_4
e: R = C_6F_5

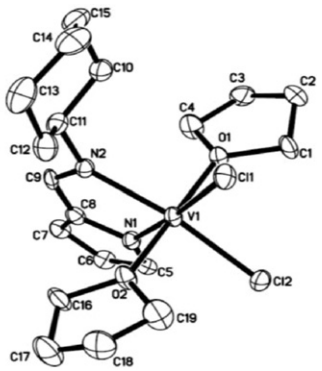


Fig. 14. Vanadium complexes bearing iminopyrrolide ligands [84].

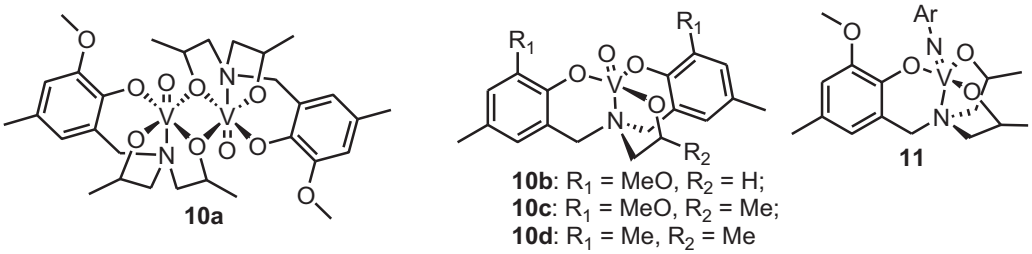


Fig. 15. Tetradentate amine trihydroxy ligands chelating vanadium(V) complexes.

rather than with **6a–d** bearing hard donors. Nonetheless, no obvious difference in NBE incorporations of the resultant copolymers was observed among catalysts **6a–f**, **7** and **8**.

4. Vanadium complexes bearing iminopyrrolide ligands

The iminopyrrolide ligands were chosen because they can form a five-membered chelating ring and the nitrogen donor atom bears stronger ability to stabilize the intermediate oxidation state of the vanadium center than does an oxygen atom [9]. Besides, iminopyrrolide ligands have been used in group 4 [73–80], group 6 [81], and group 10 metal systems [82,83] and have already been shown to afford highly active olefin (co)polymerizations. Different from mono(β-enaminoketonato) vanadium(III) complexes and salicylaldiminato vanadium(III) complexes (Fig. 14), the two chlorine atoms in the iminopyrrolide ligands chelating vanadium(III) complexes are situated in the *cis*-position, while two THF molecules are in the *trans*-position to each other [84].

Complexes **9a–e** were highly active towards ethylene polymerization at elevated temperature in the presence of Et_2AlCl. Compared with **9a**, complex **9c** bearing two *ortho*-isopropyl groups on the iminopyrrolide ligand, exhibited higher catalytic activity, indicating that steric hindrance can improve the catalyst performance of the iminopyrrolide vanadium complexes by retarding the bimolecular deactivation of vanadium catalysts. When the phenyl of the imine-moiety of complex **9a** was replaced by non-conjugated cyclohexyl to form complex **9b**, lower activity was observed, which is probably due to the lack of the stabilization of phenyl to metal center. Interestingly, the introduction of electron-withdrawing groups into the iminopyrrolide ligand will bring different results on the performance of the vanadium catalysts. For example, with trifluoromethyl at the *para*-position on the *N*-aryl moiety, complex **9d** showed lower catalytic activity than complex **9a**. However, when five fluorine atoms were introduced into the *N*-aryl moiety to form complex **9e**, comparable catalytic activity was afforded under the same conditions. Compared with mono(salicylaldiminato) vanadium(III) complexes, the vanadium(III) complexes bearing iminopyrrolide ligands exhibited higher catalytic activities toward ethylene polymerization under the similar conditions, which indicates that the nitrogen donor atom in this kind of ligands bear a stronger ability than oxygen donor in related ligands to stabilize the vanadium active species during the catalytic reaction.

Complexes **9a–e** were also evaluated as efficient catalysts for the copolymerization of ethylene with 10-undecen-1-ol. The highest activity of complex **9b** towards the copolymerization of 8.5 kg/mmol$_V$ h bar with comonomer incorporation of 3.5 mol% was detected when 10-undecen-1-ol was masked by Et_2AlCl (Reaction conditions: 1 μmol catalyst, Al/V = 4000 (molar ratio), ETA/V = 300 (molar ratio), 1 bar ethylene pressure, 0.1 mol/L 10-undecen-1-ol in feed, copolymerization at 50 °C in toluene for 10 min). Various alkylaluminum species were used to mask the functional groups, the catalytic activity towards the copolymerization and the comonomer incorporation exhibited the same sequence of $Et_2AlCl > AlMe_3 > Al^iBu_3 > AlEt_3$. A copolymer with incorporation of up to 15.8 mol% 10-undecen-1-ol could be obtained by using catalyst **9b** activated with Et_2AlCl. The systems *rac*-$Et[Ind]_2ZrCl_2$/MMAO and $VCl_3(THF)_3/Et_2AlCl$ were also studied as a comparison in this copolymerization. The catalytic activities, the M_ws of the copolymers and functional monomer incorporations were all lower than those of the **9b**/Et_2AlCl system.

5. Tetradentate amine trihydroxy ligands chelating vanadium complexes

It was proposed that ligand denticity plays an important role in improving the stability of vanadium complexes [85,86]. Many tridentate or polydentate ligands have been applied to stabilize the active vanadium complexes [11,52,85–99]. For example, vanadium complexes bearing tridentate bis(benzimidazole) amine ligands reported by Gibson's group showed high activity toward olefin polymerization [87]. Vanadium complexes with calixarene ligands were also applied to ethylene polymerization by Redshaw and co-workers [94,95]. Lorber and his colleagues found the amine

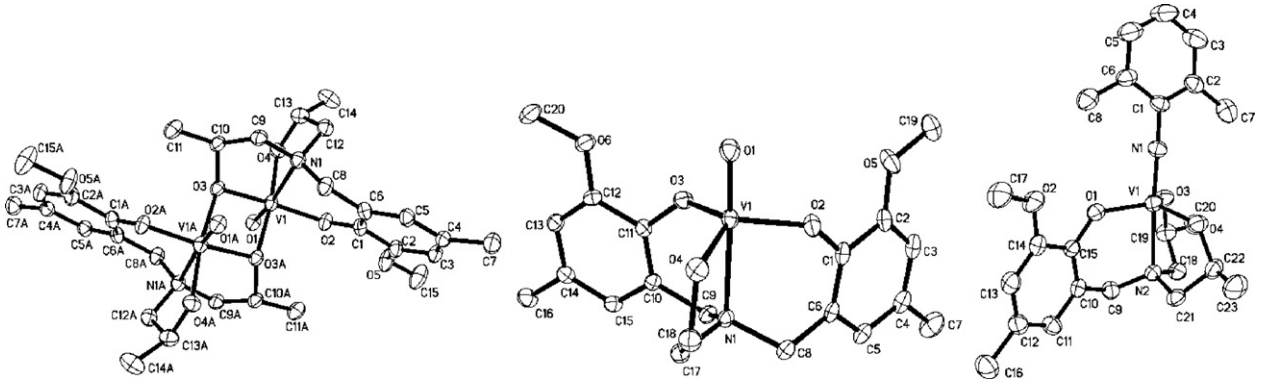


Fig. 16. Molecular structures of complexes **10a**, **10b** and **11** [100].

Table 2
Ethylene polymerization catalyzed by **10a–d** and **11**[100].[a]

Entry	Catalyst	T_p (°C)	Al/V (molar ratio)	p (C_2H_4) (bar)	Polymer (g)	Activity[b]	M_w[c] (kg/mol)	M_w/M_n[c]
1	**10a**	50	4000	4.0	0.25	6.00	167	2.4
2	**10b**	50	4000	4.0	0.56	13.44	52.1	2.6
3	**10c**	25	4000	4.0	0.51	12.24	650[d]	
4	**10c**	50	2000	4.0	0.26	6.24	110	2.7
5	**10c**	50	4000	4.0	0.78	18.72	104	3.0
6	**10c**	50	6000	4.0	0.80	19.20	99.1	3.0
7	**10c**	70	4000	4.0	0.48	11.52	92.2	2.9
8	**10d**	50	4000	4.0	0.02	0.48	–[e]	–[e]
9	**11**	50	4000	4.0	0.12	2.88	234	2.0

[a] Conditions: toluene 50 mL, catalyst 0.5 μmol, Al/V = 4000 (mol/mol), ETA/V = 300 (molar ratio), polymerization 5 min.
[b] Activity in kg of polymer/($mmol_V$ h).
[c] GPC data in 1,2,4-trichlorobenzene *vs* polystyrene standard.
[d] *Mv* was measured in decalin at 135 °C because polymer did not dissolve in 1,2,4-trichlorobenzene.
[e] Not determined.

bis(phenolate) ligand can stabilize vanadium complexes exhibiting high activity for ethylene polymerization [52].

Ligands contained aryloxide and alkoxide were designed for the vanadium(V) chemistry (Fig. 15) [100]. As shown in Fig. 16 (left), binuclear complex **10a** displayed a six-coordinate distorted octahedral geometry around each V center, which is surrounded by two ligands and is bound to each other by two bridging O atoms (the isopropoxide arm), possessing a dimeric structure. Complexes bearing ligands with two aryloxides exhibited distorted trigonal bipyramidal geometry (Fig. 16 middle), with the oxo function occupying the axial position, trans to the central nitrogen. In the imidovanadium complex **11** (Fig. 16 right), the geometry is approximately trigonal bipyramidal with N–V–N as the axes. The crystals of **11** consist of two crystallographically different independent molecules in the unit cell, in one molecule the N-aryl plane was almost in parallel with the O-aryl plane in the tetradentate ligand, whereas in the other one the N-aryl plane was almost vertical to the O-aryl plane in the tetradentate ligand.

Oxovanadium(V) complexes **10a–d** were effective catalysts for ethylene polymerization in the presence of the cocatalyst Et_2AlCl and reactivating agent ethyl trichloroacetate (Table 2). The ligand structure remarkably influenced catalytic activity and polymer property. Under similar conditions, the higher activities were observed for complexes **10b** and **10c**, which contain two aryloxides and one alkoxide, while lower activity was detected for complex **10a** presumably because of the higher electron donating property of alkoxide than aryloxide and the steric bulk of the ancillary ligands in the oxo bridged structure. Higher molecular weight polymers were produced by complex **10a**, but not by complexes **10b** and **10c**, indicating chain transfer reactions were partly hindered in the more crowded structure **10a**. Compared with **10c**, complex **10d** exhibited much lower catalytic activity (0.48 kg PE/$mmol_V$ h), indicating the ortho MeO group in the aryloxo of the ligand is indispensable for high activity in this type of catalyst. This result is quite different from the behavior of amine tris(3,5-dimethylphenolate) vanadium(V) catalyst reported by Redshaw [93], which displayed high activity toward ethylene polymerization in the presence of dimethylaluminum chloride and ETA. It was also found that the 'bite angle' of the tris(3,5-dimethylphenolate) can lead to substantially different activities, for example through introduction of a methylene linker into each arm the catalytic activity can be increased from 1000 to over 120 000 g/mmol h bar.

Imidovanadium complex **11** bearing the same trihydroxy ligand as oxovanadium complex **10a** was less productive, but produced polyethylenes with higher molecular weights probably resulting from the steric hindrance of aryl group (2,6-dimethylphenyl) on the imido group. A similar result was reported with the O,N-chelating aminophenolate vanadium catalysts [101]. Though the precursors are well defined, the active species or the alkylation pathways are obscure because paramagnetic derivatives are formed simultaneously when the vanadium(V) complexes were combined with Et_2AlCl in the *in situ* NMR experiment [93,94].

Encouraged by the high catalytic activity of these vanadium(V) complexes for ethylene polymerization, the copolymerization of ethylene with norbornene (NBE) was explored. Complex **10c** displayed the highest activity of 16.38 kg polymer/$mmol_V$ h, while complex **10d** revealed the lowest activity of 0.12 kg polymer/$mmol_V$ h (polymerization conditions: ethylene = 4 bar, Et_2AlCl/V = 4000 (molar ratio), ETA/V = 300 (molar ratio), 0.5 mol/L NBE, at 50 °C, copolymerization for 10 min). Imidovanadium complex **11** displayed slightly lower catalytic activity than oxovanadium complex **10a**, but a higher molecular weight copolymer was produced by **11**, indicating the steric hindrance of aryl group (2,6-dimethylphenyl) on the imido partly restrained the chain transfer reactions. Polymerization temperature is an important parameter in controlling the catalytic activity and molecular weight of the copolymer. A pronounced increase in catalytic activity with increasing temperature from 25 to 50 °C for catalytic system **10c**/Et_2AlCl was observed, while further elevating temperature to 70 °C led to slight loss of productivity. Similar to the behavior of the tridentate Schiff base chelated vanadium(III) catalysts, the molecular weight of the resultant copolymers obtained by **10c** decreased with elevation of reaction temperature. Nevertheless, catalyst **10c** can produce much higher M_w copolymers than vanadium(III) catalysts at 50 °C (**10c**, M_w = 341 kg/mol; **6c**, M_w = 164 kg/mol).

Interestingly, the vanadium(V) complexes were also robust catalysts for ethylene/5-norbornene-2-methanol (NB-CH_2OH) copolymerization. The highest activity of 3.30 kg polymer/$mmol_V$ h was observed by **10b**, and the copolymer with NB-CH_2OH incorporation as high as 12.1 mol% was obtained by **11** (Polymerization conditions: ethylene = 4 bar, catalyst = 1.0 μmol, Et_2AlCl = 7 mmol, ETA/V = 300 (molar ratio), 0.5 mol/L NBE-CH_2OH in feed, at 50 °C copolymerization for 10 min). The GPC analyses reveal that the ethylene/NB-CH_2OH copolymer obtained displays both high molecular weight (M_w = 157–400 kg/mol) and unimodal molecular weight distribution (M_w/M_n = 2.5–3.0). The melting temperature of the copolymers was in the range 117.6–126.6 °C with only a single peak in the DSC spectra, indicating the components of the copolymers are homogeneous.

6. Conclusions and outlook

In this article, we have reviewed a variety of well-defined vanadium complexes and, specifically, their application as catalyst precursors for ethylene polymerization, ethylene/α-olefin copolymerization and ethylene/cycloolefin copolymerization, including monomers containing polar functional groups. The success of [N,O] or [N,N] ligands chelating vanadium catalysts for the

(co)polymerization of olefins is largely attributable to their molecular and electronic structure. Indeed, the facile tuning of the [N,O] or [N,N] ligands by simple modification of the ligand architecture and insertion of various substituents, together with the ease of preparation, handling, good polar monomer tolerance and high efficiency, make these vanadium catalysts advantageous over other types of single-site catalysts for the producing different types of macromolecules from olefins, which offers remarkable opportunities for the synthesis of novel olefin-based materials.

The exact nature of the active species still remains unknown in the vanadium-based catalyst system because of the lack of a precise structural characterization of the paramagnetic intermediates, although some models were postulated by Zambelli et al. [102], Gambarotta [9], Nomura [21,29], and Redshaw [11]. The current understanding of the structural motifs of active species is largely based on the experimental evidence. With the rapid increase in computational power, quantum chemical calculations would become an increasingly powerful tool for analyzing the mechanism of vanadium catalyzing olefin polymerization.

Acknowledgements

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