Chapter 3
Olefin Polymerization with Non-metallocene Catalysts (Early Transition Metals)

Kotohiro Nomura and Wenjuan Zhang

Abstract In this chapter, recent developments of so called non-metallocene early transition metal (group 3–5) complexes as the catalyst precursors for olefin polymerization have been described. These catalysts display unique characterisitics especially for ethylene (co)polymerization, and high isospecificity ([*mmmm*] > 99.6 %) in propylene polymerization has been achieved in some catalyses. The ligand modification plays an essential key role not only for the catalytic activity, but also for control of tacticity and/or living nature in these catalyses.

3.1 Introduction

After a discovery of so called metallocene catalysts [Cp_2ZrCl_2—methylaluminoxane (MAO) catalyst] by Kaminsky et al. [1, 2], many researchers focused on design and synthesis of bridged (*ansa*) metallocene (see Reviews for metallocenes [3–6]; *Frontiers in Metal-Catalysed Polymerization* (special issue) [7–10]) and half-titanocene complex (exemplified as constrained geometry catalyst, CGC) (see Reviews for linked half-titanocenes [11–13]) for efficient ethylene/α-olefin copolymerization and isospecific polymerization of α-olefins. Nonbridged (unbridged) half-titanocene catalysts (see Reviews for nonbridged half-titanocenes [14–17]), described in Chap. 2, may also be considered as the related stream, although the basic concept in the catalyst design is somewhat different. In olefin polymerization using metallocene catalysts, it has been postulated that the cationic alkyl species, Cp_2Zr^+R, play an essential key role as the active species [3–6]. Therefore,

---

K. Nomura (✉)
Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan
e-mail: ktnomura@tmu.ac.jp

W. Zhang
Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

K. Osakada (ed.), *Organometallic Reactions and Polymerization*,
Lecture Notes in Chemistry 85, DOI: 10.1007/978-3-662-43539-7_3,

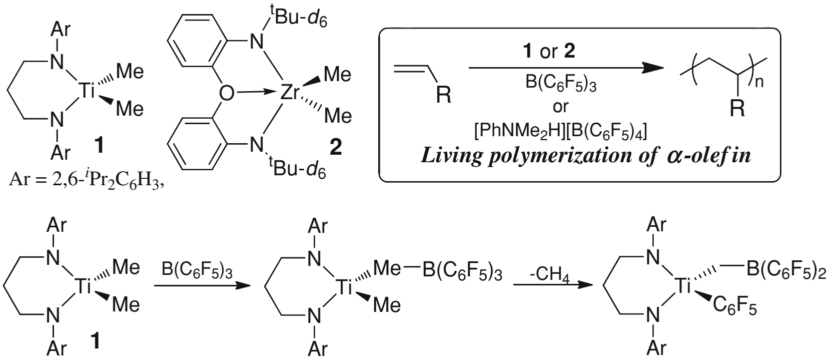
researchers only focused on generating 14e species from the catalyst precursor. Later it has been well known exemplified as $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (CGC) that 12e species also plays a role, suggesting many promising possibilities for designing efficient catalysts with various ligand. After a report concerning 1-hexene polymerization using a titanium complex containing bis(amide) ligand as the catalyst precursor by Dr. McConville [18, 19], described below, many researchers from both academic and industry invloved in the project for exploring a possibility with various early transition metals. Nowadays, tremendous number of reports have been known for this project, and some of them are very important from both academic and industrial point of view (see Reviews for post-metallocenes [20–24]; *Metal-catalysed Polymerisation* (*special issue*) [25]; Selected reviews for living polymerization [26–28]). In this chapter, efforts for designing molecular catalysts with early transition metals have been briefly reviewed.

3.2 Design, Synthesis of Molecular Catalyst with Early Transition Metals

3.2.1 Titanium, Zirconium, and Hafnium Complexes

As described above, titanium complex (**1**) containing bis(amide) ligand [18, 19] and zirconium complex with tridentate diamido ligand, $[NON]ZrMe_2$ (**2**) [29], for 1-hexene living polymerization introduced promising possibility for designing efficient catalyst, which does not contain cyclopentadienyl ligand (called non-metallocene catalyst), for olefin polymerization (Scheme 3.1). The catalytic activities by **1** in 1-hexene polymerization were suppressed upon addition of toluene, suggesting a possibility of coordination of toluene to the cationic catalytically-active species. Reaction of **1** with $B(C_6F_5)_3$ in *n*-pentane gave insoluble yellow-orange solids that was considered as a true catalyst for the living polymerization. The pentane suspensions slowly evolved CH_4 over several hours to give the pentane-soluble $[ArN(CH_2)_3NAr]Ti[CH_2B(C_6F_5)_2](C_6F_5)$, which was structurally characterized and was inactive for the polymerization of α-olefins [30]. The resultant poly(1-hexene)s prepared by **1**, **2** possessed atactic stereoregularity.

Although the resultant polymer in the above reports afforded atactic poly (1-hexene), Eisen et al. presented synthesis of isotactic polypropylene by zirconium complexes containing tris(amidinate) ligand with chiral *N*-substituents, $[N(R^*)\text{-}C\text{–}N]_3ZrCl$ (**3**) [31]. In the propylene polymerization by **3**—MAO catalyst in toluene, isotacticities for the resultant polymers were dependent upon the propylene pressure; the attempt under the atmospheric pressure of propylene was not successful. They speculated that one ancillary ligand was not acting as a spectator ligand, and MAO extracted one benzamidinate ligand from **3**. This



Scheme 3.1 Pioneering examples for living 1-hexene polymerization [18, 19, 29]

displacement reaction would afford the proposed catalytically active species **3′**. Isospecific propylene polymerization took place if zirconium complexes containing bis(amidinate) complexes (**4**), bearing achiral substituents R, at higher propylene pressures [32]. As shown in Table 3.1, the stereo-regularity in the resultant polypropylene was modulated by the pressure (from atactic to isotactic through elastomers). The different effects in the polymerization process such as the nature of solvent or cocatalyst, temperature, pressure, Al/M molar ratio (M = Ti, Zr), and the relationship between the symmetry of the complex and the polymer microstructure had been investigated [34]. The stereoregular errors were formed by the intramolecular epimerization of the growing chain at the last inserted unit. It was thus proposed that epimerization becomes faster than the stereoregular insertion of propylene at lower propylene pressure, leading to the formation of atactic polymer [34] (Scheme 3.2).

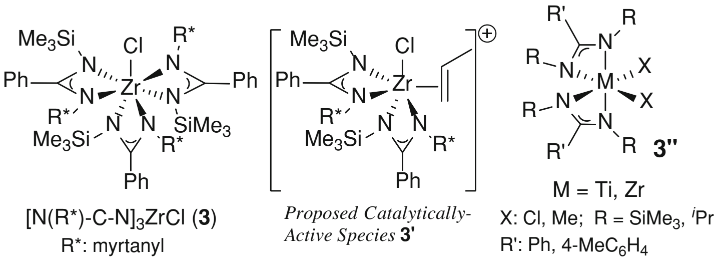
Isospecific living polymerization had been achieved by using C_2 symmetrical zirconium complex containing chelate bis(phenolate) ligand (**4b**, Scheme 3.3) [35]. Upon activation of **4b** with B(C$_6$F$_5$)$_3$, 1-hexene polymerization took place (rather efficiently), affording poly(1-hexene) with narrow molecular weight distribution (18 kg-polymer/mol-Zr·h, $M_w = 12000$, $M_w/M_n = 1.15$, >95 % isotacticity). It was thus assumed that the high isotacticity would be due to a steric bulk of the ^{t}Bu group in **4b**, because the polymerization by **4a** under the same conditions afforded atactic poly(1-hexene) with higher activity (35 kg-polymer/mol-Zr·h, $M_w = 23000$, $M_w/M_n = 1.57$) [35]. The chloride analogue (**4c**) showed remarkable activity (5400 kg-polymer/mol-Zr·h), but the polymerization did not take place in a living manner, suggesting that the electronic factor on the phenyl group plays a role for exhibiting the high activity. In contrast, the titanium analogue of **4c** showed relatively high activity (200 kg-polymer/mol-Ti·h), affording ultra high molecular weight poly(1-hexene) with low PDI value as well as with relatively high isotacticity ($M_w = 5.50$–19.0×10^5, $M_w/M_n = >1.2$, mm = 60 %) [36].

Titanium and zirconium complexes containing amine bis(phenolate) ligand (**5**) showed remarkable catalytic activity for α-olefin polymerization (Scheme 3.3)

Table 3.1 Propylene polymerization by $[Me_3SiNC(4\text{-}MeC_6H_4)NSiMe_3]_2ZrMe_2$ (**3″**)[a]

Solvent	Al/Zr[b]	Temp. /°C	Propylene /atm	Activity[c]	M_n^d $\times 10^{-3}$	M_w/M_n^d	*mmmm*[e] /%	T_m^f /°C
Toluene	250	25	9.2	110[g]	261	1.69	86	142
					36.0	2.35	11	oil
CH_2Cl_2	250	25	9.2	220	10.7	2.49	90	146
CH_2Cl_2	400	25	9.2	750	23.5	1.81	96	147
CH_2Cl_2	1000	25	9.2	790	58.1	1.42	98	149
CH_2Cl_2	250	0	5.1	50	10.2	1.85	86	138
CH_2Cl_2	250	25	9.2	220	10.7	2.49	90	146
CH_2Cl_2	250	50	17	2660	150	1.81	96	152
Toluene	$B(C_6F_5)_3$	25	9.2	280[h]	26.0	1.96	98	154
					3.00	3.1	7	oil

[a] Cited from Ref. [34]
[b] MAO (solvent removed from a 20 % solution in toluene)
[c] Activity in kg-PP/mol-Zr·h
[d] GPC data 1,2,4-trichlorobenzene versus polystyrene standards
[e] Estimated by ^{13}C NMR spectra
[f] Melting Temperature
[g] Mixture of isotactic (50 %) and atactic (50 %) fractions of polypropylene
[h] 70 % atactic and 30 % isotactic

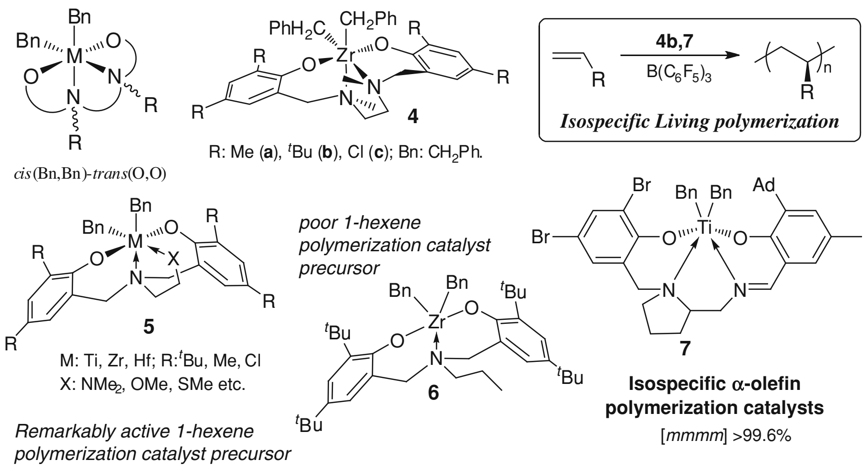

$[N(R^*)\text{-}C\text{-}N]_3ZrCl$ (**3**)
R*: myrtanyl

Proposed Catalytically-Active Species **3'**

3"
M = Ti, Zr
X: Cl, Me; R = $SiMe_3$, ^{i}Pr
R': Ph, $4\text{-}MeC_6H_4$

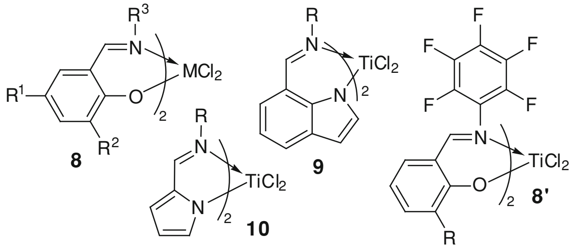
Scheme 3.2 Isospecific propylene polymerization catalysts [31–34]

[36], and the reaction by the titanium analogue (R = ^{t}Bu, X = OMe) proceeded in a living manner, affording block copolymer consisting of poly(1-hexene) and poly(1-octene). An extra arm donor ligand plays an essential role to exhibit high catalytic activity, because the activity with the zirconium analogue (**6**) was extremely low [37]. This may be due to the fact that **6** folds pseudo-trigonal bipyramidal geometry whereas the complexes **5** fold distorted octahedral geometry around the metal center, which lead to the different bond angles between two benzyl (Bn) group (117.4° in **6** and 93.7° in **5**) [37]. More recently, Kol demonstrated that octahedral C_1-symmetric titanium catalysts containing salalen ligand (**7**) are highly effective for isospecific propylene polymerization to afford polymers with extraordinary high isotacticity with high melting transition temperature ([*mmmm*] > 99.6 %, T_m = 169.9 °C) [43].



Scheme 3.3 Group 4 metal complexes containing amine bis(phenolate) ligands [35–43]

Scheme 3.4 Ti, Zr, Hf complexes containing salicylaldiminato ligands



Zirconium complexes bearing two salicylaldiminato-type ligands (**8** in Scheme 3.4) exhibited remarkable catalytic activities for ethylene polymerization [44]. As shown in Table 3.2, the activity and the molecular weight of the polymer were dependent upon the substituent on the ligand. The activity was also affected by the centered metal [45], and increasing the steric bulk especially on both the phenoxy group in *ortho* position and the imino group strongly affected the catalytic activity. Molecular weights in the resultant PE were varied by the ligand modification [44]. The zirconium complex containing *N*-(3-cumyl-5-methyl-salicylidene) cyclohexylaminato ligand showed the highest activity for ethylene polymerization (4315000 kg-PE/mol-Zr·h) at 25 °C.

Importantly, ethylene polymerization by the fluorinated phenoxy-imine analogue (**8′**) proceeded in a living manner [46], and the living polymerization of propylene afforded polypropylene with highly syndiotactic steroregularity [47, 48]. These living polymerizations took place even at room temperature, and synthesis of various block copolymers has been achieved in this catalysis [46–48]. The catalytic activity in the ethylene polymerization was high [46], whereas the activity for propylene polymerization was moderate but the polymerization

Table 3.2 Selected results for ethylene polymerization by Zr complex (**8**)—MAO catalyst systems[a]

Complex R^1, R^2, R^3	Amount /μmol	Activity[b]	$M_v \times 10^{-4}$	M_w/M_n[c]
H, ^{t}Bu, Ph	0.02	550000	0.9	2.06
Me, ^{t}Bu, Ph	0.02	331000	0.7	2
H, Me, Ph	5	400	0.3	2.31
H, ^{i}Pr, Ph	5	900	0.6	2.48
Me, adamantyl, Ph	0.02	714000	1.2	2.69
Me, cumyl, Ph	0.01	2096000	1.8	7.2
Me, cumyl, cyclohexyl	0.005	4315000	1.5	1.88
H, ^{t}Bu, 2-MeC_6H_4	0.5	40000	32	2.13
H, ^{t}Bu, 2-$^iPrC_6H_4$	0.5	58000	113	2.61
H ^{t}Bu 2-$^tBuC_6H_4$	5	100	>274[d]	[e]
H, ^{t}Bu, 3,5-$^tBu_2C_6H_3$	0.1	244000	2.6	1.79
H, ^{t}Bu, 4-$^tBuC_6H_4$	0.1	271000	0.7	2.03
H, ^{t}Bu, 2,6-$^iPr_2C_6H_3$	5	trace		
Me, adamantyl, 2-$^iPrC_6H_4$	0.1	23000	153	[e]
cumyl, cumyl, 2-$^iPrC_6H_4$	0.2	43000	220	[e]

[a] Data cited from Ref. [44], Conditions: 25 °C, ethylene 1 atm, MAO (Al) 1.25 mmol, toluene 250 mL, 5 or 30 min

[b] Activity in kg-PE/mol-Zr·h

[c] Measured by GPC

[d] Obtained from the polyethylene soluble in decalin under intrinsic viscosity measurement conditions

[e] Polymer was hardly soluble in *o*-dichlorobenzene under GPC measurement conditions

proceeds in a highly syndiospecific manner although these Ti complexes possess C_2 symmetry [47, 48]. In ethylene polymerizations using titanium complexes with various fluorine containing phenoxy-imine chelate ligands, the complexes having a fluorine atom adjacent to the imine nitrogen showed the living nature at 50 °C, whereas the complexes possessing no fluorine adjacent to the imine nitrogen afforded polyethylenes having M_w/M_n values of ca. 2 with β-hydrogen transfer as the main termination pathway. In addition to the DFT calculation results, they assumed that the presence of a fluorine atom adjacent to the imine nitrogen is the requirement for the high-temperature living polymerization, because the fluorine of the active species for ethylene polymerization interacts with a β-hydrogen in the polymer chain, resulting in the prevention of β-hydrogen transfer [46].

Based on ^{13}C NMR studies, they proposed that syndiotacticity in the propylene polymerization was governed by a chain-end control mechanism and that the polymerization is initiated exclusively via 1,2-insertion followed by 2,1-insertion as the principal mode of polymerization, and that the polypropylenes produced with the Ti complexes possess regio-block structures. Substitutions on the phenoxy-imine ligands affected both the catalytic activity and the stereo specificity, and the steric bulk of the substituent in *ortho* position of the phenoxy oxygen plays a decisive role in achieving high syndioselectivity for the chain-end controlled

Table 3.3 Selected results for propylene polymerization by **8′**—MAO catalyst systems[a]

R in **8′**	Temp./ °C	TOF[b]	$M_n^c \times 10^{-3}$	M_w/M_n^c	T_m^d/ °C	rr^e
H	25	729	189	1.51	nd[f]	
Me	25	1635	260.2	1.22	nd[f]	
^{i}Pr	25	739	153.7	1.16	nd[f]	
^{t}Bu	0	68	23.6	1.05	136	
^{t}Bu	25	87	28.5	1.11	137	87
^{t}Bu	50	70	16.4	1.37	130	
$SiMe_3$	0	72	24.7	1.08	156	94
$SiMe_3$	25	139	47	1.08	152	93
$SiMe_3$	50	113	35.1	1.23	149	90
$SiEt_3$	0	42	11.9	1.08	152	93
$SiEt_3$	25	83	24.4	1.16	151	
$SiEt_3$	50	63	20.4	1.23	148	

[a] Cited from Ref. [48], Conditions: complex 10 μmol, MAO 2.5 mmol, propylene 1 atm, 5 h

[b] Turnover frequency

[c] Determined by GPC using polypropylene calibration

[d] Melting temperature of produced PP determined by DSC

[e] Estimated by ^{13}C NMR spectra

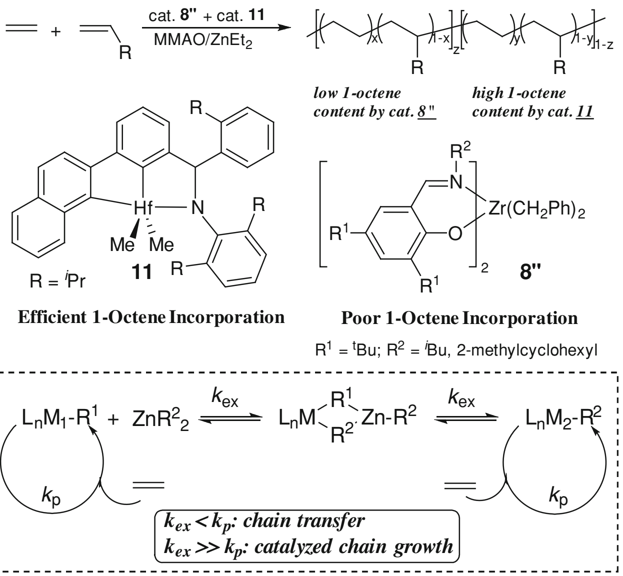
[f] Not detected

polymerization (Table 3.3) [47, 48]. The Ti complex having $SiMe_3$ group in *ortho* position of the phenoxy ligand afforded highly syndiotactic, nearly monodisperse polypropylenes (94–90 % *rr*) with extremely high melting temperatures (T_m = 156–149 °C). The polymerization behavior of the Ti complexes was explained by the proposed chain-end controlled, site-inversion mechanism for the formation of syndiotactic polypropylene by **8′**. Copolymerization of ethylene with α–olefin by **8′** also proceeded in a living manner in the presence of MAO, and various block copolymers were also thus prepared [49].

Synthesis of the related complexes such as titanium complexes containing two indole-imine ligands (**9**) [50], pyrrolide-imine ligand (**10**) were known [51], and living copolymerization of ethylene with norbornene took place if **10** was used as the catalyst precursor [52, 53].

Chain Shuttling Polymerization

Precise synthesis of microblock ethylene/1-octene copolymers which possesses two compositions (copolymers with low/high 1-octene contents) in a polymer chain was also achieved by adopting the polymerization process called “Chain Shuttling Polymerization” in the presence of two catalysts (with efficient/inefficient comonomer incorporations, different monomer reactivity, Scheme 3.5) and chain transfer reagent (Et_2Zn etc.) [54]. The resultant polymers (prepared by adding Et_2Zn during polymerization results in a block copolymer microstructure with intimately mixed interchain hard and soft segments) possess higher transparency than the polymers with two physical blend of high- and low-density polymers, and possessed higher melting temperature and low glass transition temperature (due to a



Scheme 3.5 Precise synthesis of microblock copolymers by "chain shuttling polymerization" [54]

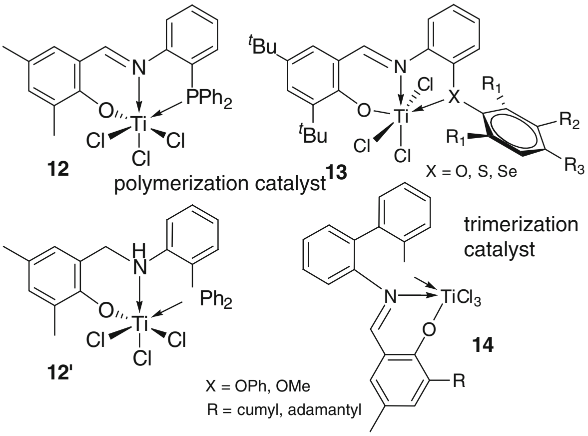
block segment with low 1-octene content). These are recognized as a new technology for evolution of new polymers on the basis of precise olefin polymerization technique [54].

The isospecific α-olefin polymerization catalyst (**11**) was developed by DOW on the basis of 1600 catalyst screenings (required only for 3 weeks) by using "high throughput screening" (Symyx Technologies) technique: this demonstrated a new methodology for the catalyst development [55, 56]. Another key issue on this process is adopting rapid chain transfer reactions enabled by presence of Et_2Zn (rapid chain transfer by Et_2Zn [57–60]): rapid polymer exchange between **8″** and **11** through Zn afforded the polymers with multiblock (microblock) microstructure.

Ligand Modification from Ethylene Polymerization Catalyst to Trimerization Catalyst

It has been known in that ethylene polymerization catalyst was tuned to the ethylene trimerization by the ligand modification. $[(\eta^5\text{-}C_5H_5)CMe_2Ph]TiCl_3$—MAO catalyst exhibited moderate catalytic activity with high selectivity for ethylene trimerization, whereas ethylene polymerization took place by $[(\eta^5\text{-}C_5H_5)CMe_3]\text{-}TiCl_3$ [61]. Titanium trichloride complexes containing monoanionic tridentate ligands (**12**,**13**) exhibited moderate to high catalytic activities for ethylene polymerization (Scheme 3.6) [62, 64]: **12** showed better catalyst performance for ethylene copolymerization with 1-hexene and norbornene [62]. In contrast, complex **14** showed remarkable selectivity in ethylene trimerization in the presence of MAO, and second order dependence of activity on ethylene pressure (suggesting the metallacycle mechanism) was observed [65]. These would suggest that the

Scheme 3.6 Titanium trichloride complexes for ethylene polymerization/trimerization [62–65]

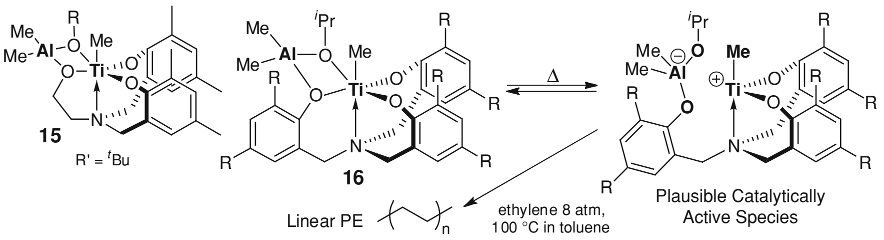


effective catalyst for the polymerization can be tuned to the effective catalyst for the trimerization by the ligand modification.

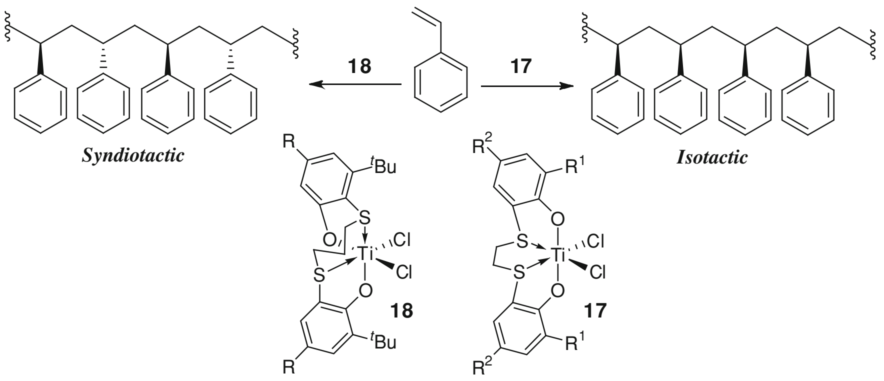
Ti–Al Hetero Bimetallic Complexes Containing Chelate Trianionic Donor Ligand
Titanium complexes with tris(aryloxo)amine or bis(aryloxo)(alkoxo)amine ligand, Ti(OR′)[(O-2,4-$R_2C_6H_2$-6-CH_2)$_3$N] or Ti(OR′)[(O-2,4-$R_2C_6H_2$-6-CH_2)$_2$ (OCH_2CH_2)N] (R = Me, ^{t}Bu; R′ = ^{i}Pr, ^{t}Bu), exhibited from moderate to high catalytic activity for ethylene polymerization especially at high temperature (100–120 °C), and the activities increased upon addition of small amount of $AlMe_3$ [66, 68]. The resultant polymers possessed unimodal molecular weight distributions, suggesting that the polymerization proceeded with a uniform catalytically-active species. The resultant heterobimetallic Ti–Al complexes (**15**, **16**) exhibited moderate catalytic activities upon heating under ethylene pressure even in the absence of any additional cocatalyst, strongly suggesting that cleavages of Ti–O bonds would generate the catalytically active cationic species in this catalysis (Scheme 3.7) [67, 68].

Isospecific/Syndiospecific Styrene Polymerization
Titanium complexes containing 1,4-dithiabutane-bridged derivatives (**17**) showed notable catalytic activities affording isotactic polystyrene with unimodal molecular weight distributions, whereas the 1,5-dithiapentane-bridged derivatives (**18**) showed low catalytic activities affording syndiotactic polystyrene (Scheme 3.8) [69]. The analogous zirconium, hafnium complexes of **17** also showed the low catalytic activity to afford isotactic polystyrene, suggesting that C_2-symmetric ligand sphere should play a crucial role for this isospecific polymerization [69, 71].

As shown in Table 3.4, the substituents on the ligand affected the activity and stereoselectivity, and these facts were evidently related to the effect of these substituents on the stereorigidity of the catalyst precursors. Complexes bearing less bulky *ortho*-substituents R^1 in the aromatic ring (H, Me, ^{i}Pr) allowed rapid interconversion on the NMR time scale, while the complexes with bulky groups (^{t}Bu, CMe_2Ph) were stereorigid at temperatures up to 100 °C. Small *ortho*-



Scheme 3.7 Ti-Al Hetero bimetallic complexes that polymerize ethylene without cocatalyst [67, 68]



Scheme 3.8 Isospecific styrene polymerization by titanium complexes containing chelate bis(phenolate) ligands [69–71]

substituents thus led to configurational lability at room temperature and resulted in the loss of both activity and stereospecificity. Syndiospecific styrene polymerization with relatively low activity was observed by titanium complexes with 1,5-dithiapentanediyl-linked bis(phenolato) ligands. Only the configurationally stable 1,4-dithiabutanediyl-linked phenolates with bulky *ortho*-substituents appeared to be capable of stabilizing a C_2-symmetric, helical ligand sphere at the titanium center and thereby provided an active site for the isospecific styrene polymerization [71].

3.2.2 Vanadium Complexes

Classical Ziegler type vanadium catalysts (ex. $VOCl_3$, VCl_4, VCl_3–$AlBr_3$, $AlCl_3$–$AlPh_3$, Al^iBu_3, $SnPh_4$) are known to display unique characteristics in olefin polymerization. In general, these catalyst systems afforded (i) high molecular

Table 3.4 Isospecific/syndiospecific styrene polymerization by titanium complexes containing chelate bis(phenolate) ligands[a]

Complex	Substituents: R^1, R^2	Activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	T_m[d]/°C
17[e]	H, H	4	1.2	82	
17[f]	H, Me	7	193.5	1.57	
		0.7	1.88		
17[e]	Me, Me	4	1.2	50	
17[e]	^{i}Pr, ^{t}Bu	5	n.d.	n.d.	
17[f]	^{t}Bu, Me	518	101.3	1.57	222
17[f]	^{t}Bu, ^{t}Bu	1543	265.4	2	223
17[f]	^{t}Bu, OMe	3	91	1.66	222
			1	1.76	
17[e]	CMe_2Ph, Me	175	70	1.9	225
17[f, g]	CMe_2Ph, CMe_2Ph	682	31.4	2.36	223
18[f]	^{t}Bu, Me	0.7	2.89	268	
18[f]	^{t}Bu, ^{t}Bu	3	n.d.	n.d.	264

[a] Cited from Ref [69], [styrene] = 3.5 mol/L (10 mL), toluene 15 ML

[b] Activity in kg-PS/[mol-Ti][styrene mol/L][h]

[c] Determined by GPC. n.d. = not determined

[d] Determined by DSC thermograms

[e] Conditions: Ti 10 µmol, [Al]/[Ti] = 500, 50 °C, 1 h

[f] Conditions: Ti 2.5 µmol, [Al]:[Ti] = 1500, 40 °C, 2 h

[g] Reaction time: 1 h

weight linear polyethylene with uniform molecular weight distribution [72–74], and (ii) high molecular weight amorphous polymers applied to syntheses of ethylene/propylene/diene copolymers (called EPDM, synthetic rubbers) [75–77], ethylene/cyclic olefin copolymers (COC). Moreover, (iii) the catalyst system [V(acac)$_3$ (acac = acetylacetonato)—Et_2AlCl] polymerizes propylene to give not only a syndiotactic "living" polymer with narrow molecular weight distribution (M_w/M_n = 1.05–1.20) [78–80], but also diblock copolymers of propylene and methyl methacrylate (MMA) [78–80]. On the basis of ESR and titration results, vanadium(III) species were postulated to play an important role as the catalytically active species [81–84], although it was estimated that fewer than 1 % of vanadium species were catalytically active in the mixture [83].

One of the main disadvantages of using this type of vanadium catalysts is the deactivation associated with the reduction to inactive vanadium(II) species. Although very high initial activities were observed by adopting these catalysts, the reduction causes very poor overall productivities. This problem could be overcome by reactivation of inactive vanadium(II) center to active vanadium(III) species by addition of re-oxidants such as hexachlorocyclopentadiene [85], ethyl trichloroacetate [86], and the polymerization proceeded without significant decrease in the activity by continuous addition of an aluminum alkyl and the re-oxidants even at high temperature (>105 °C) [86].

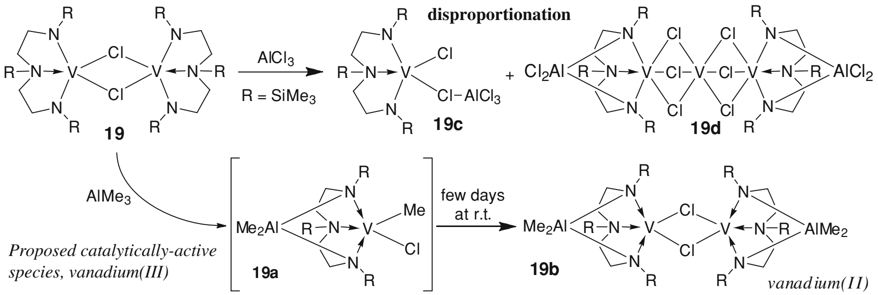
As described above, the classical Ziegler type vanadium catalysts displayed unique characteristics as the olefin polymerization catalysts. Therefore, design and synthesis of new vanadium complex catalysts directed toward the controlled polymerization has been recognized as an attractive target [11–13, 29, 87–90]. Although examples for synthesis of vanadium complexes used as the catalyst precursors for olefin polymerization were known, however, known examples which exhibit the above described unique characteristics of using these transition metal complexes had been limited until recently [20–24, 86, 87–90].

3.2.2.1 Vanadium(III), (IV) Complexes

Vanadium(III), (IV) complexes have been focused on design of the efficient polymerization catalysts, because these were assumed to play an important role as the active species in olefin polymerization. Since only a trace of *actual* active species were present due to that these species would be unstable and be readily reduced by Al cocatalyst to afford the catalytically inactive vanadium(II) species, many researchers thus concentrate on stabilization of the oxidation state of the catalytically active species by an appropriate ligand modification [23, 86].

Dinuclear vanadium(III) chloride complex (**19**) containing bis(amido)amine ligand of type, $(Me_3SiNCH_2CH_2)_2NSiMe_3$, exhibited remarkable catalytic activity for ethylene polymerization in the presence of MAO, Me_2AlCl at 50 °C [activity: 237 kg-PE/mol-V·h (MAO), 660 kg-PE/mol-V·h (Me_2AlCl); ethylene 300 psig (20.4 atm), $Al/V = 60$ (molar ratio)] [91]. Resultant polyethylene prepared by **19**—Me_2AlCl catalyst possessed high molecular weight with uniform molecular weight distribution ($M_w = 7.21 \times 10^5$, $M_w/M_n = 2.3$). The catalyst system was short-lived, does not remain to be active for no more than 20–30 min, and this may be attributed to the reduction of the vanadium(III) center to an inactive divalent species. The reaction of **19** with $AlMe_3$, Me_2AlCl and MAO in *n*-hexane initially gave a red solution, which after a few days afforded another vanadium(II) complex identified as **19b** (Scheme 3.9). This result thus suggested that no ligand dissociation occurred in the present catalyst system but aggregation with the cocatalyst. The question of how the reduction of **19** afforded the inactive divalent species (**19b**) was thus considered. The reaction of **19** with $AlCl_3$ afforded disproportionated compounds, (tetravalent) **19c** and (one divalent and two trivalent) **19d**, clearly indicating that disproportionation was the basis of a reduction of the vanadium center. These results suggested a possibility of the reduction of **19** affording **19b** and that the addition intermediate **19a**, which is likely to be the catalytically-active species, has the intrinsic instability of a vanadium-carbon bond [91].

A mixed-valent vanadium complex containing dithiolate ligand (**20c**, Scheme 3.10) showed moderate catalytic activity for ethylene polymerization in the presence of both Et_2AlCl and $MgCl_2$ [activity 254 kg-PE/mol-V·h, ethylene 6 atm, 50 °C, 15 min.] [92], but the activity was lower than those by the aryloxo analogues (**20a**, 1990 kg-PE/mol-V·h; **20b**, 1020 kg-PE/mol-V·h), under the same conditions (in *n*-hexane) [92]. The ligand in **20c** transferred to Al alkyls upon treatment with

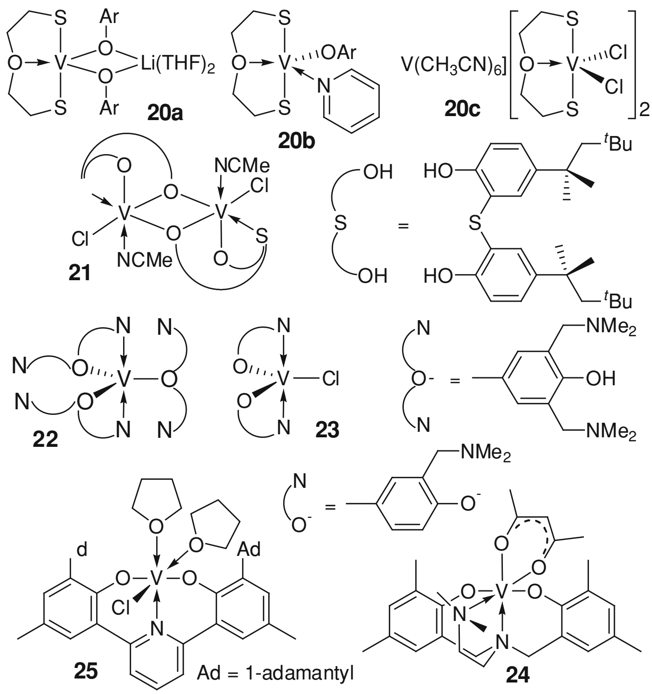


Scheme 3.9 Reaction of dinuclear vanadium(III) chloride complex containing bis(amido)amine ligand [91]

$AlMe_3$ affording vanadium(II) chloride and $[AlMe\{\mu_2\text{-}O(CH_2CH_2S)\}]_2$ [93]. Use of thiobis(phenoxy) ligand improved the activity, and the complex **21** showed remarkable activities in the presence of cocatalyst [activity = 11708 kg-PE/mol-V·h (Al^iBu_3), 8184 (Et_2AlCl), 4736 (MAO); ethylene 5 atm, Al/$MgCl_2$/V = 100/10/1 (Al^iBu_3, Et_2AlCl) or 3000/10/1 (MAO)] [94]. The resultant polymers possessed unimodal molecular weight distributions (M_w/M_n = 2.28–3.12), suggesting that these polymerizations proceeded with uniform catalytically active species.

Vanadium(III) complexes containing two or three *O*,*N*-chelating aminophenolate ligand (**22**,**23**) exhibited activities for ethylene/propylene copolymerization in the presence of $Et_2AlCl{\cdot}EtAlCl_2$ [95]. The bis(phenoxy) complex (**23**) showed higher activity [159 kg-polymer/mol-V·h·bar, 8 bar of ethylene/propylene (ratio 1/2) in pentamethylheptane at 30 °C for 10 min.] than the tris(phenoxy) complex (**22**, 27 kg-polymer/mol-V·h·bar). Olefin polymerization using a series of vanadium complexes containing an amine bis(phenolate) ligand, $[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(Me_2NCH_2CH_2)N]^{2-}$ (exemplified as complex **24**), with various oxidation states (II-V) were explored [96, 97]. Complex **24** showed notable activity in ethylene polymerization in the presence of $EtAlCl_2$, but showed negligible activity in the presence of MAO [96]. Copolymerizations of ethylene with 1-hexene, norbornene were attempted, but the activities decreased and the resultant polymers possessed a mixture of coplymers with different compositions estimated by their DSC thermograms [96]. Vanadium(III) complex containing bis(phenoxy)pyridine ligand (**25**) showed remarkable catalytic activity for propylene polymerization in the presence of MAO (activity 803 kg-PP/mol-V·h, propylene 5 atm in toluene at 0 °C for 30 min, Al/V = 3000), affording high molecular weight polymer with uniform molecular weight distribution ($M_w = 1.17 \times 10^6$, M_w/M_n = 2.03) [98]. The resultant polymer possessed large extent of regio irregular as generally seen in those prepared by vanadium catalysts.

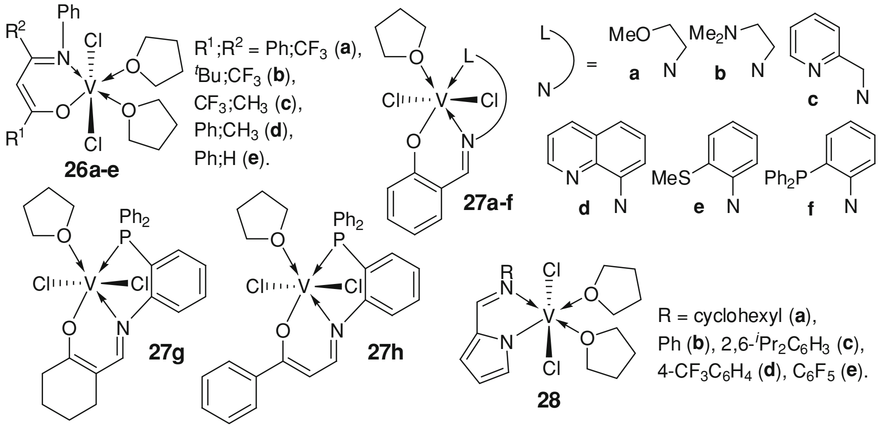
Taking into account the above reports (vanadium complexes using chelate anionic and neutral donor ligands) [91–98], as described above, control, stabilization of the oxidation state, catalytically active species) by an appropriate ligand modification seems to be a key for the efficient catalyst with vanadium(III),



Scheme 3.10 Selected vanadium complexes for olefin polymerization [91–98]

although the *actual* active species including the activation/polymerization mechanism are still not clear at the present stage.

A series of vanadium(III) complexes containing β-enaminoketonato [99, 100], phenoxy-imine [101–104], imino-pyrrolide [105] ligands (exemplified in Scheme 3.11) were tested as olefin polymerization catalyst in the presence of Et_2AlCl and Cl_3CCO_2Et. The selected results are summarized in Table 3.5 [99, 100, 103, 105]. The observed activities by certain complexes were slightly/apparently higher than those by $VCl_3(THF)_3$, and the activities decreased at 70 °C probably due to the rapid deactivation even for short period (5 min) and in the presence of excess amount of re-oxidant (300 equivalent to V). On the basis of these data, it seems that **26b** (R^1;R^2 = ^{t}Bu;CF_3) [99, 100], **26d** (R^1;R^2 = Ph;CH_3) [99, 100], **27 h** [103] showed higher activities. The related phenoxy-imine analogues showed low activities under the same conditions [101–104]. Placement of neutral donor ligands (amine, pyridine) into the phenoxy-imine ligands in **27** was not effective; the observed activity by **27 h** was relatively close to **26e**. Although both the activities and the polymerization behavior were affected by the ligand substituents, the detailed explanation by electronic/steric factors seems difficult (factors such as ligand transfer to Al, reductions etc.). In contrast, the imino-pyrrolide analogues (**28**) showed remarkable activities [105], and the activities by **28** increased in the order (ethylene 1 atm, 50 °C for 5 min): **28c** (R = 2,6-$^i Pr_2C_6H_3$) > **28b**, **e** (Ph, C_6F_5) > **28d**



Scheme 3.11 Selected vanadium(III) complexes as catalyst precursors for olefin polymerization [99, 100, 103, 105]

Table 3.5 Ethylene polymerization by **26–28**—Et_2AlCl—Cl_3CCO_2Et catalyst systems[a]

Complex	Temp. /°C	Activity /kg-PE/mol-V·h	$M_w^b \times 10^{-4}$	M_w/M_n^b
$VCl_3(THF)_3$	25	25800	22.7	2.8
$VCl_3(THF)_3$	50	23400	13.4	5.8
$VCl_3(THF)_3$	70	12600	9.9	21.9
26a	50	27400	17.7	2.6
26b	50	29000	18.6	3.0
26c	50	21800	25.9	2.9
26d	50	24000	17.3	2.9
26e	50	18700	27.1	2.9
27a	50	3840	4.0	2.4
27b	50	9600	3.5	3.0
27c	50	15600	6.2	2.2
27d	50	9120	4.8	2.5
27e	50	7920	6.3	2.0
27f	50	11300	4.6	2.5
27g	50	9360	3.0	2.2
27h	50	20600	2.4	2.0
28a	50	28200	3.5	2.1
28b	50	37800	4.3	2.2
28c	25	39600	6.3	2.4
28c	50	48600	2.5	1.7
28c	70	34200	1.0	2.2
28d	50	33000	4.4	2.4
28e	50	39000	3.0	1.9

[a] Cited from Refs. [99, 100, 103, 105], Reaction conditions: vanadium 0.2 or 0.5 µmol, Et_2AlCl and Cl_3CCO_2Et (ETA), Al/ETA/V = 4000/300/1 (molar ratio), ethylene 1 atm for 5 min

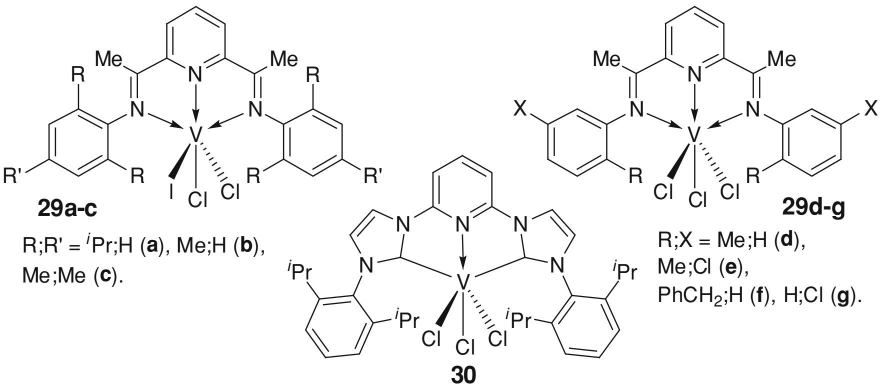
[b] GPC data in 1,2,4-trichlorobenzene versus polystyrene standards

(4-$CF_3C_6H_4$) > **28a** (cyclohexyl). The results thus suggest that both electronic and steric factors play an important role (probably for strong coordination).

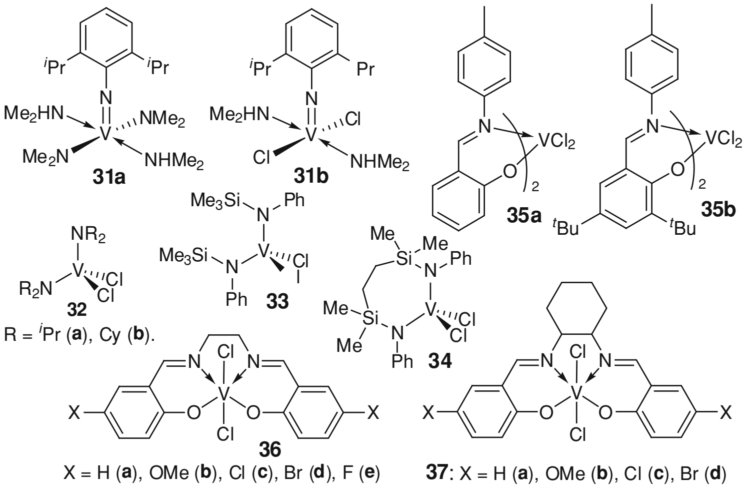
Complex **27c** showed high activity in the ethylene/norbornene copolymerization and the activity was close to that by **27h** under the same conditions, although the activity by **27c** was lower than that by **27h** in the ethylene polymerization [103]. Complexes **28** showed moderate comonomer incorporation with higher activities in ethylene/10-undecen-1-ol copolymerizations, affording the copolymers with relatively low molecular weights ($M_n = 3.1$–52.5×10^3) [105]: the M_n values decreased upon increasing the comonomer content [105].

Vanadium(III) complex containing neutral bis(imino)pyridine ligand (**29a**) exhibited remarkable catalytic activities for ethylene polymerization in the presence of MAO, affording the polymers with broad molecular weight distributions [activities 1420, 2240 kg-PE/mol-Vh, with Al/V = 600, 60 (molar ratio), respectively; ethylene 100 psig (6.8 atm), 50 °C, 15 or 30 min] (Scheme 3.12) [106]. The activities decreased at 140 °C, and the molecular weight distributions in the resultant polymers were dependent upon the Al/V molar ratios. The reaction with ethylene using the complexes (**29d**, **e**) containing mono substituted aromatic group on the imino ligand (in place of 2,6-diisopropylphenyl) afforded oligomeric mixtures and polyethylene (products by Schultz-Flory distribution) [107], (Dimerization of propylene (selectivity 80–95 %) [108]), and the reaction with propylene by **29f**, **g** afforded oligomers with relatively high C_6 selectivity (80–95 %, major products: methylpentenes) [107], (Dimerization of propylene (selectivity 80–95 %) [108]). These results suggested that the observed trend concerning the ligand effect was very similar to that observed in the ethylene polymerization/oligomerization using iron(II) complexes containing similar ligands [109–115]. The bis(carbene)pyridine complex (**30**) showed remarkable activities for ethylene polymerization, and the activity was affected by the Al cocatalyst employed [116]. The activity decreased in the order (ethylene 1 atm in toluene at r.t. for 30 min, Al/V = 500, molar ratio): 1446 kg-PE/mol-V·h (MMAO, methyl-isobutyl-aluminoxane) > 1280 (MAO) > 586 (dried MAO and Al^iBu_3) > 278 (Et_2AlCl).[59]

(Arylimido)vanadium(IV) dichloride complexes (**31**, Scheme 3.13) showed high activities for ethylene polymerization in the presence of Al cocatalyst [activity by **31b**: 59 kg-PE-mol-V·h (MAO, Al/V = 500), 120 kg-PE-mol-V·h (Et_2AlCl, Al/V = 10); ethylene 1 atm, 20 °C in toluene, 2 or 10 min], affording the polymers with uniform molecular weight distributions [117, 118]. The activities in ethylene/propylene copolymerization using vanadium(IV) complexes containing two amide ligands (**32**) were affected by the Al cocatalyst employed, and the activity by **32a** decreased in the order: $Et_2AlCl{\cdot}EtAlCl_2$ (860 kg-polymer/mol-V·h) > $EtAlCl_2$ (330) > Et_2AlCl (80) > $AlEt_3$ (24) [conditions: ethylene + propylene total 2 bar in hexane at 22 °C for 15 min, Al/V = 40 (molar ratio)] [119]. The isopropyl amide complex (**32a**) showed higher activity than the cyclohexyl analogue (**32b**) [119], and the resultant polymer possessed high molecular weight with uniform molecular weight distribution (**32a**—$Et_2AlCl{\cdot}EtAlCl_2$ catalyst, $M_w = 2.29 \times 10^6$, $M_w/M_n = 3.0$, ethylene 73 wt%). Vanadium(IV) complex with chelate bis(amide)



Scheme 3.12 Vanadium(III) complexes with neutral tridentate donor ligands [106–116]



Scheme 3.13 Selected vanadium(IV) complexes as catalyst precursors for olefin polymerization [117–123]

ligand (**34**) showed higher activity than the bis(amide) analogue (**33**) in ethylene polymerization [activities in the presence of $Et_2AlCl{\cdot}EtAlCl_2$: 213 kg-PE/mol-V·h, 54 kg-PE/mol-V·h for **34**, **33**, respectively: ethylene 1 atm in toluene at 30 °C, Al/V = 50]. Although the activity in the ethylene polymerization by **36** is close to that by **32a** (178 kg-PE/mol-V·h), **34** showed higher activity in ethylene/propylene copolymerization [120].

Vanadium(IV) complex with N,O-bidentate ligand (**35b**) showed higher activity than **35a**, probably owing to increasing the steric bulk, and the activity was highly affected by the Al cocatalyst employed [$EtAlCl_2 \gg Et_2AlCl > MAO$]. The resultant polymers possessed rather high molecular weights with moderate distributions

[121]. The salen-type tetradentate complexes (**36**, **37**) also showed from moderate to high activities for ethylene polymerization [122, 123], and the activities of **37** were higher than **36**: the activities were affected by the *ortho*- substituent in the phenoxo moiety, and by Al cocatalyst employed. However, the resultant polymer possessed broad molecular weight distributions ($M_w/M_n = 7.3–10.4$), suggesting generation of multiple catalytically active species [122, 123].

3.2.2.2 Vanadium(V) Complexes

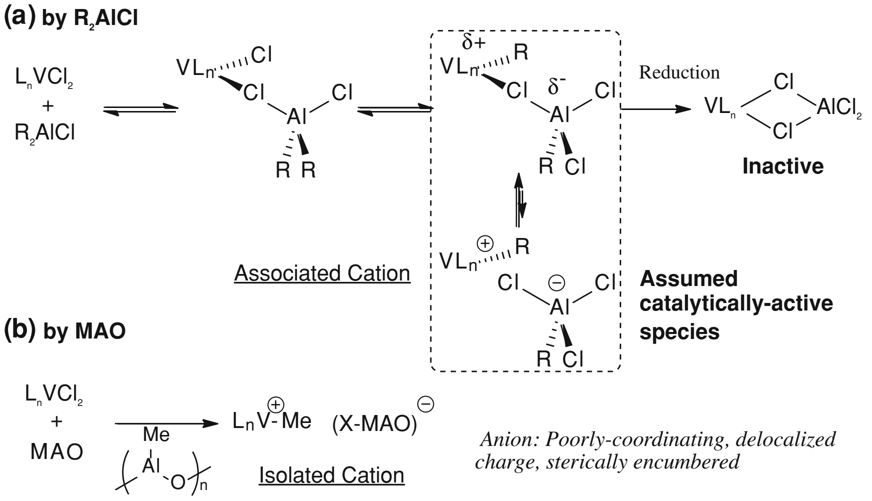
As described above, $VOCl_3$ showed moderate activities for ethylene/propylene (co)polymerization in the presence of Al alkyls, however, one of the major concerns associated with use of vanadium(V) complexes as catalysts for Ziegler-Natta polymerizations is a facile reduction to yield lower-valent complexes. Use of arylimido analogues seemed to be promising, because a series of trichloride analogues, $V(NAr)Cl_3$, can be prepared in high yields by treating $VOCl_3$ with various isocyanates (ArNCO) [124–126], and these complexes showed moderate thermal stability, as demonstrated by synthesis of $V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(CH_2Ph)_3$ from the trichloride analogues by treating with $PhCH_2MgCl$ in *n*-hexane [127]. The reported fact is noteworthy, because the most common problem encountered in attempts to synthesize vanadium(V) alkyls was the reduction of the metal center upon alkylation. Placement of appropriate alkyl substituent in the arylimido ligand is important for stabilization of the oxidation state upon the alkylation, and the approach is useful for synthesis various vanadium(V)-alkyls [128–131].

It turned out that the arylimido-aryloxo analogue (**38**) showed remarkable activities not only for ethylene polymerization [132–135], but also for ethylene/norbornene copolymerization [136] especially in the presence of halogenated Al alkyls (Et_2AlCl, Me_2AlCl, $EtAlCl_2$ etc.) [134–136], affording high molecular weight polymers with uniform distributions. Selected results in the ethylene polymerization catalyzed by $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**38**) are summarized in Table 3.6 [135]. The activity was highly dependent upon the Al cocatalyst employed, and the activities in toluene decreased in the order: ${}^iBu_2AlCl$ (52000 kg-PE/mol-V·h) > $EtAlCl_2$ (37400) > Me_2AlCl (27500) > Et_2AlCl (11700) > MAO (2930) $\gg$ $Et_2Al(OEt)$, Me_3Al, Et_3Al (trace or less). The activity did not decrease after 30 min, and was highly affected by the solvent employed; the activity of 584000 kg-PE/mol-V·h (TOF 20800000 h^{-1}, 5780 s^{-1}) was attained in CH_2Cl_2 in the presence of $EtAlCl_2$. The resultant polymers prepared in toluene possessed ultra high molecular weights with unimodal molecular weight distributions (the M_v values in the resultant polymers prepared in the presence of ${}^iBu_2AlCl$, Me_2AlCl were $9.87–12.5 \times 10^6$, 8.98×10^6, respectively). The activity decreased upon addition of CCl_3CO_2Et, which is commonly used as the effective additives in the polymerization using vanadium(III) and/or vanadium(IV) complexes. The results clearly suggest that the active species were thus different from those prepared from vanadium(III), (IV) complexes. It was assumed that the observed difference in the catalytic activities in the presence of MAO and Et_2AlCl

Table 3.6 Ethylene polymerization catalyzed by $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**38**)—Al cocatalyst systems: effect of Al cocatalyst[a]

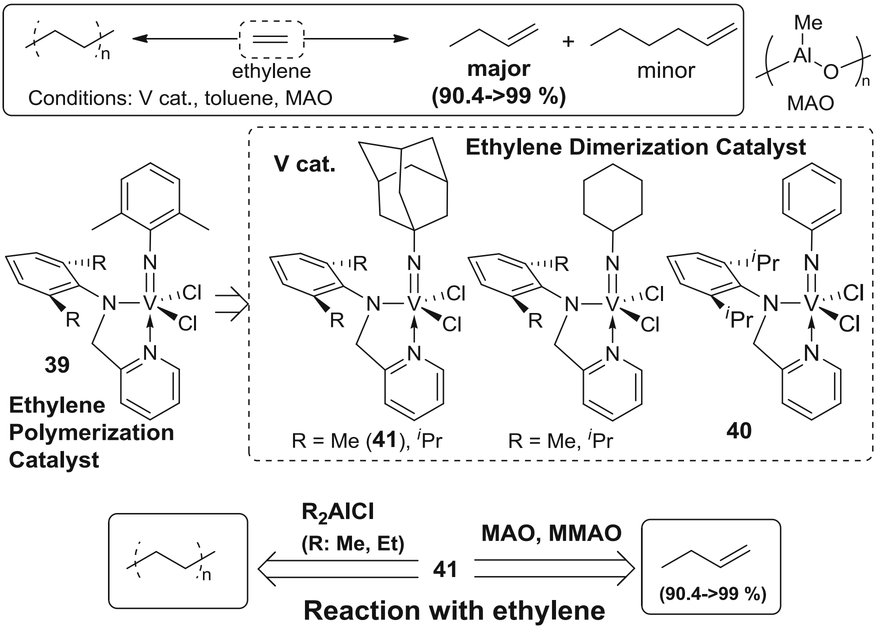
38 / μmol	Al cocat.	Time / min	Activity[b] × 10^{-3}	TOF[c] × 10^{-5}	M_w[d] × 10^{-5}	M_w/M_n[d]	M_v[e] × 10^{-6}
1.0	MAO	10	2.93	1.04	28.7	1.64	
0.05	Me_2AlCl	10	27.5	9.8	–[e]	–	8.98
0.05	Et_2AlCl	10	11.7	4.15	36.5	1.42	
0.05	Et_2AlCl	30	11.4	4.06			
0.05[f]	Et_2AlCl	10	1.08	0.4			
0.05	$^{i}Bu_2AlCl$	10	52.0	18.5	–[e]	–	9.87
0.01	$^{i}Bu_2AlCl$	10	64.8	23.1	–[e]	–	12.5
0.05	$EtAlCl_2$	10	37.4	13.3	6.02	3.04	
1.0	Et_2AlOEt	10	None	–			
1.0	Me_3Al	10	Trace	–			
1.0	Et_3Al	10	Trace	–			
1.0	$^{i}Bu_3Al$	10	trace	–			

[a] Data cited from Ref. 135, reaction conditions: toluene + cocatalyst solution = 30 mL, 0 °C (or 25 °C by MAO), ethylene 8 atm, Al cocatalyst 250 or 500 μmol (or MAO 2.5 mmol)
[b] Activity in kg-polymer/mol-V·h
[c] TOF = (molar amount of ethylene consumed)/(mol-V·h)
[d] GPC data in o-dichlorobenzene versus polystyrene standards
[e] Molecular weight by viscosity due to that the resultant polymers were insoluble in *o*-dichlorobenzene for GPC measurement
[f] Polymerization in the co-presence of $CC_{13}CO_2Et$ (10.0 equiv to V)



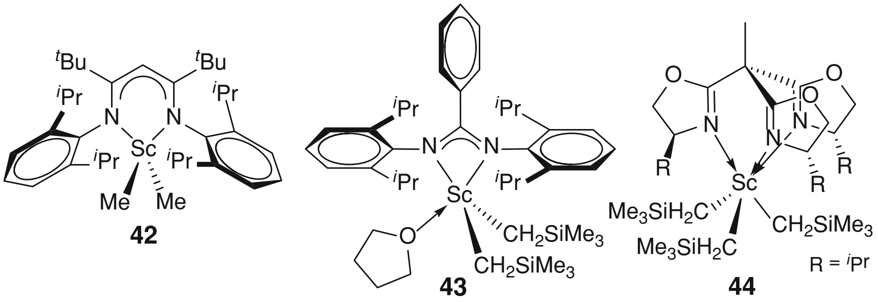
Scheme 3.14 Proposed formation of two catalytically active species [23, 134, 135, 140]

cocatalyst would be due to the different catalytically active species, catalyst/cocatalyst nuclearity effect [137, 138] generated in the two catalyst systems, as shown in Scheme 3.14 [23].



Scheme 3.15 Ethylene dimerization by (imido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligand [139, 140]

The (imido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligand, $V(NR)Cl_2[2\text{-}ArNCH_2(C_5H_4N)]$ [R = 1-adamantyl (Ad), cyclohexyl (Cy), phenyl (Ph)], exhibited remarkably high catalytic activities for ethylene dimerization in the presence of MAO, affording 1-butene exclusively (selectivity from 90.4 to > 99 %, Scheme 3.17) [139]. The phenylimido analogue (**40**) also afforded 1-butene under the same conditions, whereas the 2,6-dimethylphenylimido analogue (**39**) afforded polyethylene. The cyclohexylimido analogues also showed high activities to afford 1-butene exclusively. The adamantylimido analogues (**41**) showed the highest activities (TOF: 2730000 h^{-1}) for ethylene dimerization. These results thus clearly indicate that (i) the electronic nature of the imido ligand directly affects the activity, and (ii) the steric bulk of the imido substituents plays an essential key role toward the selectivity in this catalysis [139]. Moreover, **41**—Et_2AlCl, Me_2AlCl afforded ultra high molecular weight polyethylene, suggesting a presence of proposed reaction scheme shown in Scheme 3.15 [140]. On the basis of reactions under various conditions, and ESR and NMR experiments, it was thus proposed that cationic vanadium(V)-alkyls play an important role in these catalysis [140].

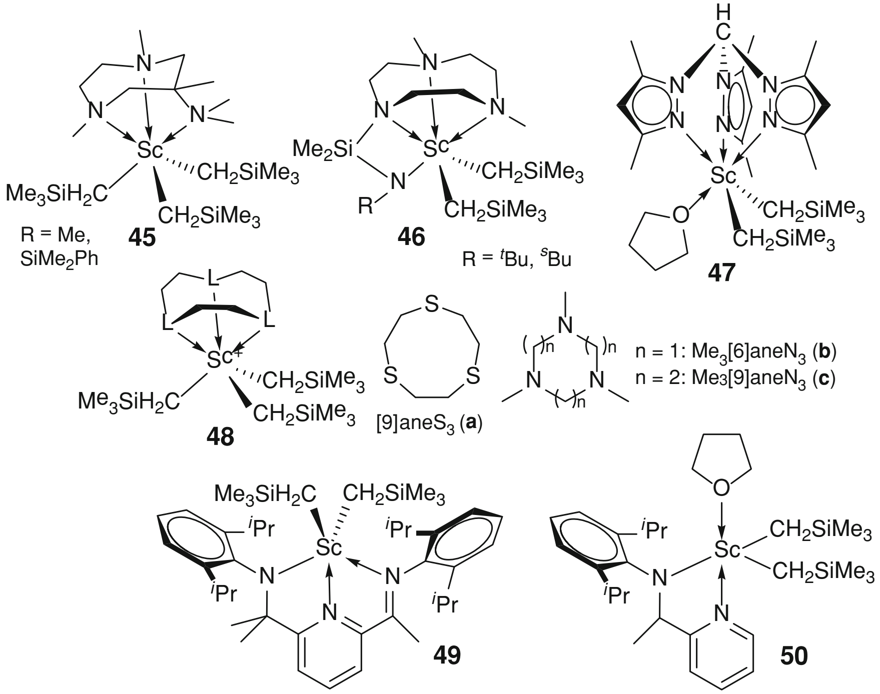


Scheme 3.16 Known scandium catalysts for olefin polymerization [141–143]

3.2.3 *Miscellaneous Early Transition Metal Complex Catalysts*

3.2.3.1 Scandium Complexes

Examples for olefin polymerization using non-metallocene type scandium complex catalysts still have been limited but demonstrate promising possibilities: examples as catalyst precursors for conjugated diene polymerization (butadiene, isoprene) have also been reported. The complex containing β-diketiminato "nacnac" (**42**, Scheme 3.16) exhibited moderate to high catalytic activities for ethylene polymerization [1200 kg-PE/mol-Sc·h (MAO, Al/Sc = 20), 300 kg-PE/mol-Sc·h $\{B(C_6F_5)_3$, ca. 1 equiv.$\}$: ethylene 300 psi, 50 °C, cyclohexane/toluene], affording high molecular weight polymers with uniform distributions ($M_w = 8.51–18.7 \times 10^5$, $M_w/M_n = 1.7–2.48$) [141]. The reaction of **42** with 1.0 equiv. of $B(C_6F_5)_3$ afforded monocationic $[(\text{nacnac})ScMe]^+[\mu\text{-}Me\text{-}B(C_6F_5)_3]^-$, and the dicationic species $[(\text{nacnac})Sc]^{2+}[\mu\text{-}Me\text{-}B^-(C_6F_5)_3]_2$ by treating **42** with 2.0 equiv. of $B(C_6F_5)_3$ exhibited moderate catalytic activity for ethylene polymerization (1 atm at r.t.) [141]. In contrast, ethylene polymerization using the admidinate analogue, $[ArNC(Ph)NAr]Sc(CH_2SiMe_3)_2(THF)$ (**43**) was low [activity 120 kg-PE/mol-Sc·h, ethylene 5 bar, $\{PhN(H)Me_2\}(C_6F_5)_4$, 30 °C 20 min], and the acitivity by the Y, Gd, Nd complexes showed higher catalytic activities ($1.0–1.5 \times 10^4$ kg-PE/mol-M·h) under the same conditions [142]. A dicationic scandium complexes containing a C_3-chiral ligand, prepared from $[^i\text{Pr-trisox}]Sc(CH_2SiMe_3)_3$ (**44**) with 2.0 equiv. of $[Ph_3C][B(C_6F_5)_4]$, exhibited remarkable catalytic activities for 1-hexene polymerization [$2.03–36.2 \times 10^3$ kg-polymer/mol-Sc·h at −30–21 °C], and the activity increased at higher temperature. The resultant polymer prepared at −30 °C possessed highly isotactic structure (*mmmm* = 90 %) with narrow molecular weight distribution ($M_w/M_n = 1.18$, $M_w = 7.50 \times 10^5$), suggesting a possibility of living polymerization [143]. In addition to promising results by half-metallocene type scandium complex in ethylene copolymerization (with styrene, cyclic olefins etc.) [144–147], these results suggest that the non-metallocene type scandium complexes



Scheme 3.17 Reported scandium dialkyl, trialkyl analogues [148–153]

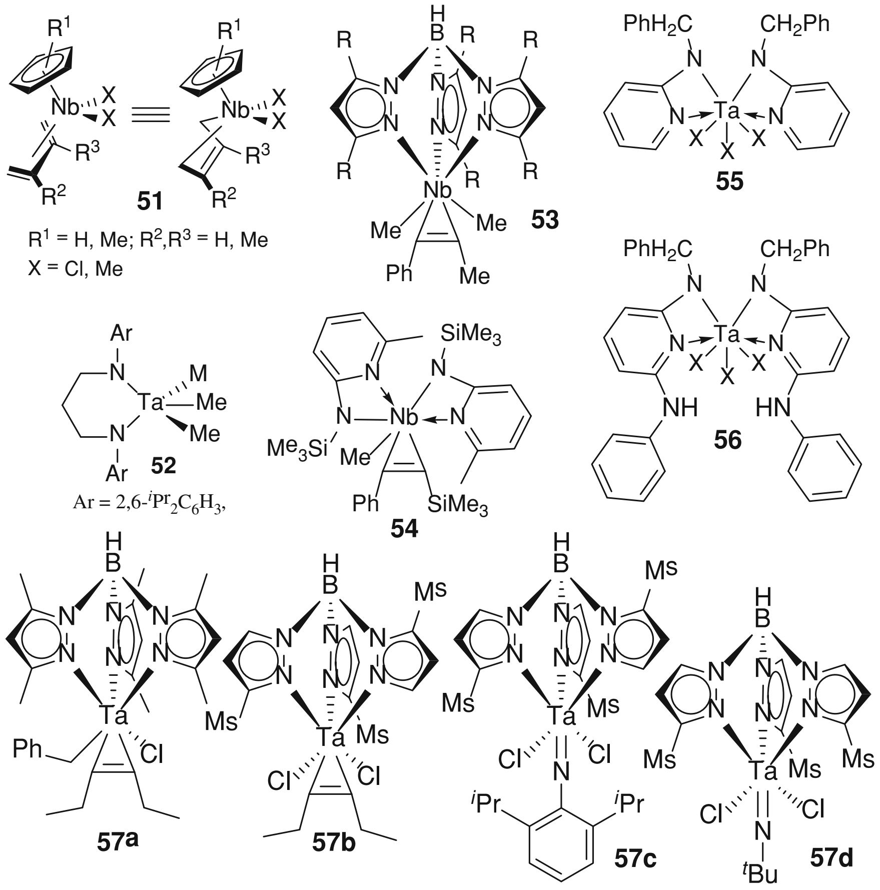
would exhibit unique characteristics as the catalyst precursors for olefin polymerization.

Scandium complexes containing [6-amino-6-methyl-1,4-diazepine] ligand (**45**, Scheme 3.17) exhibited high activities for ethylene polymerization in the presence of $[PhN(H)Me_2][B(C_6F_5)_4]$, affording polymer with unimodal molecular weight distribution [2660 kg-PE/mol-Sc·h, ethylene 5 bar, in toluene at 50 °C]: the activity increased at 70 °C (5800 kg-PE/mol-Sc·h) [148]. Although the dialkyl analogues containing monoanionic tridentate ligand, $Sc(L)(CH_2SiMe_3)_2(THF)$ [L = 6-RN-1,4,6-trimethyl-1,4-diazepine] (R = Me, $PhMe_2Si$), exhibited negligible catalytic activities for ethylene polymerization in the presence of $[PhN(H)Me_2][B(C_6F_5)_4]$, the THF-free complex exhibited high activity under the same conditions [2920 kg-PE/mol-Sc·h, ethylene 5 bar, toluene, 50 °C, 10 min], affording high molecular weight polymer with uniform distribution ($M_w = 1.2 \times 10^6$, $M_w/M_n = 1.9$) [149]. Removal of THF is thus found to be prerequisite for exhibiting remarkable activity. Ethylene polymerization using Sc complexes containing linked triazacyclononane(TACN)-amide ligands, $[Me_2Si(Me_2TACN)(NR)]Sc(CH_2SiMe_3)_2$ (**46**, R = ^{t}Bu, ^{s}Bu), were explored in the presence of borate cocatalysts [150]. These complexes exhibited high catalytic activities at 70 °C in the presence of $[Ph_3C][B(C_6F_5)_4]$ [activity = 2705 kg-PE/mol-Sc·h (R = ^{t}Bu), 1810 kg-PE/mol-Sc·h (R = ^{s}Bu): ethylene 5 bar, toluene, 10 min], affording relatively high molecular weight polymers with uniform distributions. The activity in the presence of $[Ph_3C][B(C_6F_5)_4]$ was higher than that in the presence of $[PhN(H)Me_2][B(C_6F_5)_4]$, and the activity at 70 °C was higher than that conducted at 50 °C. The yttrium analogues exhibited further higher catalytic activities under the same conditions [150].

Trialkyl complexes containing four different neutral tridentate ligands (**47**, **48a–c**) were used as the catalyst precursors for polymerization of ethylene, 1-hexene in the presence of $[Ph_3C][B(C_6F_5)_4]$ in toluene (ethylene 6 bar, 33–36 °C, 10 min). Ring size of the tridentate ligand affected the activity for ethylene polymerization [activity = 60 kg-PE/mol-Sc·h (**48b**), 4380 kg-PE/mol-Sc·h (**48c**)], and replacement of NMe group with S (**48a**) was also effective (activity = 5160 kg-PE/mol-Sc·h): the $HC(Me_2pz)_3$ analogue (**47**) also exhibited high catalytic activity (4980 kg-PE/mol-Sc·h). However, the resultant polymers possessed broad molecular weight distributions, although the 1-hexene polymerizations resulted in the polymers with uniform molecular weight distributions in most cases [151]. Taking into account these results, design of cationic Sc(III) alkyl complexes play an essential key role as the active species for olefin polymerization, and the ligand modifications which stabilize the oxidation state should be important for the efficient catalyst. Later, monoanionic bidentate or tridentate anilido-pyridine ligands (**49**, **50**) were prepared and their catalyst performances for ethylene polymerizations were explored [152, 153].

3.2.3.2 Niobium and Tantalum Complexes

The Nb complexes **51** can be considered to contain either a neutral butadiene (C_4) ligand and a Nb(III) metal center or a dianionic butadienide ($C_4{}^{2-}$) ligand and a Nb(V) center (Scheme 3.18) [154]. The activity in ethylene polymerization by Cp^*NbMe_2(butadiene) was 39 kg-PE/mol-Nb·h, affording high molecular weight polymer with narrow molecular weight distribution. PDI (M_w/M_n) values are very small (1.05) when these polymerizations were performed at low temperature (−20 °C), suggesting the polymerization proceeds in a living manner. Half-metallocene analogue, $Cp^*Ta(=N^tBu)Cl_2$, exhibited high catalytic activity for ethylene/1-octene copolymerization [40200 kg-polymer/mol-Ta·h: ethylene 500 psig (ca. 34 atm), 140 °C, 15 min] in the presence of Al imidazolide ($[HNMe(C_{18}H_{37})_2][(C_6F_5)_3AlNC_3H_3NAl(C_6F_5)_3]$), affording the copolymer with uniform molecular weight distributions [155]. The activity was higher than that by the bis(amide) analogue (**52**, 6000 kg-polymer/mol-Ta·h) [155]. Niobium complexes containing tris(pyrazolyl)borate ligand (**53**) exhibited moderate catalytic activity for ethylene polymerization in the presence of $B(C_6F_5)_3$, and the activity was affected by the R substituent: the methyl analogue (R = Me) exhibited higher activity (130 kg-polymer/mol-Nb·h) than the H analogue. Treatment of the precatalyst with MAO does not result in any polymerization [156]. Bis(pyridyl-amido) niobium(V) (**54**) showed activity for ethylene polymerization upon addition of $B(C_6F_5)_3$, but the activity was low (4.4 kg-polymer/mol-Nb·h) and rapid



Scheme 3.18 Reported niobium and tantalum complexes for olefin polymerization [154–159]

decomposition of the catalytically active species was observed [157]. Analogous bis(pyridylamide) complexes (**55**, **56**) showed very high activity, up to 23900 kg-PE/mol-Ta·h (ethylene 5 bar, 80 °C), and rapid decrease in the activity was observed at low temperature [158].

More recently, four Ta complexes bearing tris(pyrazolyl)borate ligands (**57a**–**d**) were found to exhibit catalytic activities for ethylene polymerization. Activity in the presence of $Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$ is higher than that in the presence of dried MAO; the sterically encumbered **57c**, **d** showed higher activities [activity: 77100 kg-PE/mol-Ta·h (**57c**) and 51300 kg-PE/mmol-Ta·h (**57d**)], and some of the highest values reported to date for Ta-based catalysts [159].

3.3 Summary and Outlook

As described above, tremendous number of reports have been known for this project, and some of them are very important from both academic and industrial point of view [20–28]. It is clear that fine-tuning of the ligand plays a crucial role in this catalysis. Unfortunately, recent examples for chromium complex catalysts are not listed and these are also important on relevance of their ethylene trimerization catalysts [160]. Very successful examples such as highly isospecific polymerization of α-olefins, and living polymerization, so called chain shuttling polymerization have been demonstrated among recent advances in this research subject. These several promising findings that should be very important from both academic and industrial viewpoints have been demonstrated. These efforts will pave new promising possibilities for evolution of new *fine* polyolefins with unique properties by incorporation of new comonomers and/or by adopting new synthetic strategies. We highly expect more progress in this field in the near future.

References

1. Sinn H, Kaminsky W (1980) Adv Organomet Chem 18:99
2. Sinn H, Kaminsky W, Vollmer HJ, Woldt R (1980) Angew Chem Int Ed 19:390
3. Brintzinger HH, Fischer D, Mülhaupt R, Rieger B, Waymouth RM (1995) Angew Chem Int Ed Engl 34:1143
4. Kaminsky W (1996) Macromol Chem Phys 197:3907
5. Kaminsky W, Arndt M (1997) Adv Polym Sci 127:143
6. Suhm J, Heinemann J, Wörner C, Müller P, Stricker F, Kressler J, Okuda J, Mülhaupt R (1998) Macromol Symp 129:1
7. Gladysz JA (2000) Chem Rev 100:1167
8. Ittel SD, Johnson LK, Brookhart M (2000) Chem Rev 100:1169
9. Alt HG, Köppl A (2000) Chem Rev 100:1205
10. Chen EY-X, Marks TJ (2000) Chem Rev 100:1391
11. McKnight AL, Waymouth RM (1998) Chem Rev 98:2587
12. Braunschweig H, Breitling FM (2006) Coord Chem Rev 250:2691
13. Cano J, Kunz K (2007) J Organomet Chem 692:4411
14. Stephan DW (2005) Organometallics 24:2548
15. Nomura K, Liu J, Padmanabhan S, Kitiyanan B (2007) J Mol Catal A 267:1
16. Nomura K (2009) Dalton Trans 8811
17. Nomura K, Liu J (2011) Dalton Trans 40:7666
18. Scollard JD, McConville DH (1996) J Am Chem Soc 118:10008
19. Scollard JD, McConville DH, Payne NC, Vittal JJ (1996) Macromolecules 29:5241
20. Britovsek GJP, Gibson VC, Wass DF (1999) Angew Chem Int Ed Engl 38:428
21. Gibson VC, Spitzmesser SK (2003) Chem Rev 103:283
22. Bolton PD, Mountford P (2005) Adv Synth Catal 347:355
23. Nomura K, Zhang S (2011) Chem Rev 111:2342
24. Makio H, Terao H, Iwashita A, Fujita T (2011) Chem Rev 111:2363
25. Milani B, Claver C (eds) (2009) Dalton Trans 8769
26. Coates GW, Hustad PD, Reinartz S (2002) Angew Chem Int Ed 41:2236
27. Domski GJ, Rose JM, Coates GW, Bolig AD, Brookhart M (2007) Prog Polym Sci 32:30

28. Sita LR (2009) Angew Chem Int Ed 48:2464
29. Baumann R, Davis WM, Schrock RR (1997) J Am Chem Soc 119:3830
30. Scollard JD, McConville DH, Rettig SJ (1997) Organometallics 1810:16
31. Averbuj C, Tish E, Eisen MS (1998) J Am Chem Soc 121:8755
32. Volkis V, Shmulinson M, Averbuj C, Lisovkii A, Edelmann FT, Eisen MS (1998) Organometallics 17:3155
33. Shmulinson M, Galan-Fererea M, Lisovskii A, Nelkenbaum E, Semiat R, Eisen MS (2000) Organometallics 19:1208
34. Volkis V, Nelkenbaum E, Lisovskii A, Hasson G, Semiat R, Kapon M, Botoshansky M, Eishen Y, Eisen MS (2003) J Am Chem Soc 125:2179
35. Tshuva EY, Goldberg I, Kol M (2000) J Am Chem Soc 122:10706
36. Segal S, Goldberg I, Kol M (2005) Organometallics 24:200
37. Tshuva EY, Goldberg I, Kol M, Weitman H, Goldchmidt Z (2000) Chem Commun 379
38. Tshuva EY, Goldberg I, Kol M, Weitman H, Goldchmidt Z (2001) Chem Commun 2120
39. Tshuva EY, Goldberg I, Kol M, Goldchmidt Z (2001) Organometallics 20:3017
40. Tshuva EY, Groysman S, Goldberg I, Kol M, Goldchmidt Z (2002) Organometallics 21:662
41. Groysman S, Goldberg I, Kol M, Genizi E, Gildschmidt Z (2003) Organometallics 22:3013
42. Gryosman S, Tshuva EY, Goldberg I, Kol M, Goldschmidt Z, Shuster M (2004) Organometallics 23:5291
43. Press K, Cohen A, Goldberg I, Venditto V, Mazzeo M, Kol M (2011) Angew Chem Int Ed 50:3529
44. Matsui S, Mitani M, Saito J, Tohi Y, Makio H, Matsukawa N, Takagi Y, Tsuru K, Nitabaru M, Nakano T, Tanaka H, Kashiwa N, Fujita T (2001) J Am Chem Soc 123:6847
45. Matsui S, Fujita T (2001) Catal Today 66:63
46. Mitani M, Mohri J, Yoshida Y, Saito J, Ishii S, Tsuru K, Matsui S, Furuyama R, Nakano T, Tanaka H, Kojoh S, Matsugi T, Kashiwa N, Fujita T (2002) J Am Chem Soc 124:3327
47. Mitani M, Furuyama R, Mohri J, Saito J, Ishii S, Terao H, Kashiwa N, Fujita T (2002) J Am Chem Soc 124:7888
48. Mitani M, Furuyama R, Mohri J, Saito J, Ishii S, Terao H, Nakano T, Tanaka H, Fujita T (2003) J Am Chem Soc 125:4293
49. Furuyama R, Mitani M, Mohri J, Mori R, Tanaka H, Fujita T (2005) Macromolecules 38:1546
50. Matsugi T, Matsui S, Kojoh S, Takagi Y, Inoue Y, Nakano T, Fujita T, Kashiwa N (2002) Macromolecules 35:4880
51. Yoshida Y, Matsui S, Takagi Y, Mitani M, Nakano T, Tanaka H, Kashiwa N, Fujita T (2001) Organometallics 20:4793
52. Yoshida Y, Saito J, Mitani M, Takagi Y, Matsui S, Ishii S, Nakano T, Kashiwa N, Fujita T (2002) Chem Commun 1298
53. Yoshida Y, Mohri J, Ishii S, Mitani M, Saito J, Matsui S, Makio H, Nakano T, Tanaka H, Onda M, Yamamoto Y, Mizuno A, Fujita T (2004) J Am Chem Soc 126:12023
54. Arriola DJ, Carnahan EM, Hustad PD, Kuhlman RL, Wenzel TT (2006) Science 312:714
55. Boussie TR, Diamond GM, Goh C, Hall KA, LaPointe AM, Leclerc M, Lund C, Murphy V, Shoemaker JAW, Tracht U, Turner H, Zhang J, Uno T, Rosen RK, Stevens JC (2003) J Am Chem Soc 125:4306
56. Boussie TR, Diamond GM, Goh C, Hall KA, LaPointe AM, Leclerc M, Murphy V, Shoemaker JAW, Turner H, Rosen RK, Stevens JC, Alfano F, Busico V, Cipullo R, Talarico G (2006) Angew Chem Int Ed 45:3278
57. Britovsek GJP, Cohen SA, Gibson VC, Maddox PJ, van Meurs M (2002) Angew Chem Int Ed 41:489
58. Britovsek GJP, Cohen SA, Gibson VC, Maddox PJ, van Meurs M (2004) J Am Chem Soc 126:10701
59. van Meurs M, Britovsek GJP, Gibson VC, Cohen SA (2005) J Am Chem Soc 127:9913
60. Mitani M, Nakano T, Fujita T (2003) Chem Eur J 9:2396
61. Deckers PJW, Hessen B, Teuben JH (2001) Angew Chem Int Ed 40:2516

62. Hu W, Sun X, Wang C, Gao Y, Tang Y, Shi L, Xia W, Sun J, Dai H, Li X, Yao X, Wang X (2004) Organometallics 23:1684
63. Wang C, Sun X, Guo Y, Gao Y, Liu B, Ma Z, Xia W, Shi L, Tang Y (2005) Macromol Rapid Commun 26:1609
64. Wang C, Ma Z, Sun X, Gao Y, Guo Y, Tang Y, Shi L (2006) Organometallics 25:3259
65. Suzuki Y, Kinoshita S, Shibahara A, Ishii S, Kawamura K, Inoue Y, Fujita T (2010) Organometallics 29:2394
66. Wang W, Fujiki M, Nomura K (2004) Macromol Rapid Commun 25:504
67. Gurubasavaraj PM, Nomura K (2010) Organometallics 29:3500
68. Padmanabhan S, Katao S, Nomura K (2007) Organometallics 26:1616
69. Capacchione C, Proto A, Ebeling H, Mülhaupt R, Möller K, Spaniol TP, Okuda J (2003) J Am Chem Soc 125:4964
70. Beckerle K, Capacchione C, Ebeling H, Manivannan R, Mülhaupt R, Proto A, Spaniol TP, Okuda J (2004) J Organomet Chem 689:4636
71. Capacchione C, Manivannan R, Barone M, Beckerle K, Centore R, Oliva L, Proto A, Tuzi A, Spaniol TP, Okuda J (2005) Organometallics 24:2971
72. Carrick WL (1958) J Am Chem Soc 80:6455
73. Carrick WL, Kluiber RW, Bonner EF, Wartman LH, Rugg FM, Smyth JJ (1960) J Am Chem Soc 82:3883
74. Phillips GW, Carrick WL (1962) J Polym Sci 59:401
75. Junghanns E, Gumboldt O, Bier G (1962) Makromol Chem 58:18
76. Natta G, Mazzanti G, Valvassori A, Sartori G, Fiumani D (1961) J Polym Sci 51:411
77. Christman DL, Keim GI (1968) Macromolecules 1:358
78. Doi Y, Ueki S, Keii T (1978) Macromolecules 12:814
79. Doi Y, Hizal G, Soga K (1987) Makromol Chem 188:1273
80. Doi Y, Koyama T, Soga K (1985) Makromol Chem 186:11
81. Natta G, Zambelli A, Lanzi G, Pasquon I, Mognaschi ER, Segre AL, Centola P (1965) Makromol Chem 81:161
82. Zambelli A, Pasquon I, Signorini R, Natta G (1968) Makromol Chem 112:160
83. Lehr MH (1968) Macromolecules 1:178
84. Lehr MH (1969) Macromolecules 2:217
85. Gumboldt A, Helberg J, Schleitzer G (1967) Makromol Chem 101:229
86. Christman DL (1972) J Polym Sci Part A-1 10:471
87. For recent reviews (vanadium catalysts), see: Hagen H, Boersma J, van Koten G (2002) Chem Soc Rev 31:357
88. Gambarotta S (2003) Coord Chem Rev 237:229
89. Nomura K (2005) In: Bevy LP (ed) New developments in catalysis research, NOVA Science Publishers, New York, USA, p 199
90. Redshaw C (2010) Dalton Trans 39:5595
91. Feghali K, Harding DJ, Reardon D, Gambarotta S, Yap G, Wang Q (2002) Organometallics 21:968
92. Janas Z, Jerzykiewicz LB, Sobota P, Richards RL (1999) Chem Commun 1015
93. Janas Z, Jerzykiewicz LB, Przybylak S, Richards RL, Sobota P (2000) Organometallics 19:4252
94. Janas Z, Wiśniewska D, Jerzykiewicz LB, Sobota P, Drabenta K, Szczegot K (2007) Dalton Trans 2065
95. Hagen H, Boersma J, Lutz M, Spek AL, van Koten, G (2001) Eur J Inorg Chem 117
96. Lorber C, Wolff F, Choukroun R, Vendier L (2005) Eur J Inorg Chem 2850
97. Lorber C (2009) Pure Appl Chem 81:1205
98. Golisz SR, Bercaw JE (2009) Macromolecules 42:8751
99. Tang L-M, Wu J-Q, Duan Y-Q, Pan L, Li Y-G, Li Y-SJ (2008) Polym Sci Part A Polym Chem 46:2038
100. Wu J-Q, Li B-X, Zhang S-W, Li Y-SJ (2010) Polym Sci Part A Polym Chem 48:3062
101. Wu J-Q, Pan L, Hu N-H, Li Y-S (2008) Organometallics 27:3840

102. Wu J-Q, Pan L, Liu S-R, He L-P, Li Y-S (2009) J Polym Sci Part A Polym Chem 47:3573
103. Wu J-Q, Pan L, Li Y-G, Liu S-R, Li Y-S (2009) Organometallics 1817:28
104. Houghton J, Simonovic S, Whitwood AC, Douthwaite RE, Carabineiro SA, Yuan J-C, Marques MM, Gomes PT (2008) J Organomet Chem 693:717
105. Xu B-C, Hu T, Wu J-Q, Hu N-H, Li Y-S (2009) Dalton Trans 8854
106. Reardon D, Conan F, Gambarotta S, Yap G, Wang Q (1999) J Am Chem Soc 121:9318
107. Schmidt R, Welch MB, Knudsen RD, Gottfried S, Alt HG (2004) J Mol Catal A 222:17
108. Lang JRV, Denner CE, Alt HG (2010) J Mol Catal A 322:45
109. Britovsek GJP, Gibson VC, Kimberley BS, Maddox PJ, McTavish SJ, Solan GA, White AJP, Williams DJ (1998) Chem Commun 849
110. Britovsek GJP, Bruce M, Gibson VC, Kimberely BS, Maddox PJ, Mastroianni S, McTavish SJ, Redshaw C, Solan GA, Stromberg S, White AJD, Williams DJ (1999) J Am Chem Soc 121:8728
111. Britovsek GJP, Dorer BA, Gibson VC, Kimberely BS, Solan GA (1999) WO 99/12981
112. Small BL, Brookhart M, Bennett AMA (1998) J Am Chem Soc 120:4049
113. Small BL, Brookhart M (1998) J Am Chem Soc 120:7143
114. Small BL, Brookhart M (1999) Macromolecules 32:2120
115. Bennett AMA (1998) WO 98/27174
116. McGuinness DS, Gibson VC, Steed JW (2004) Organometallics 23:6288
117. Lorber C, Donnadieu B, Choukroun R (2000) Dalton Trans 4497
118. Lorber C, Choukroun R, Donnadieu B (2002) Inorg Chem 41:4217 (synthesis)
119. Desmangles N, Gambarotta S, Bensimon C, Davis S, Zahalka H (1998) J Organomet Chem 562:53
120. Cuomo C, Milione A, Grassi A (2006) J Polym Sci Part A Polym Chem 44:3279
121. Białek M, Czaja K, Szydło E (2009) J Polym Sci Part A Polym Chem 47:565
122. Białek M, Czaja K (2008) J Polym Sci Part A Polym Chem 46:6940
123. Białek M, Czaja K (2008) Polimery 53:364
124. Devore DD, Lichtenhan JD, Takusagawa F, Maatta E (1987) J Am Chem Soc 109:7408
125. Buijink J-KF, Teubin JH, Kooijman H, Spek AL (1994) Organometallics 13:2922
126. Nomura K, Davis WM, Schrock RR (1996) Inorg Chem 35:3695
127. Murphy VJ, Turner H (1997) Organometallics 16:2495
128. Yamada J, Nomura K (2005) Organometallics 24:2248
129. Nomura K, Onishi Y, Fujiki M, Yamada J (2008) Organometallics 27:3818
130. Zhang W, Nomura K (2008) Organometallics 27:6400
131. Nomura K, Zhang W (2010) Chem Sci 1:161
132. Nomura K, Sagara A, Imanishi Y (2001) Chem Lett 36
133. Wang W, Yamada J, Fujiki M, Nomura K (2003) Catal Commun 4:159
134. Nomura K, Sagara A, Imanishi Y (2002) Macromolecules 35:1583
135. Wang W, Nomura K (2006) Adv Synth Catal 348:743
136. Wang W, Nomura K (2005) Macromolecules 38:5905
137. Macchioni A (2005) Chem Rev 105:2039
138. Li H, Marks TJ (2006) Nuclearity and cooperatively effects in binuclear catalysts and cocatalysts. Proc Natl Acad Sci USA 103:15295
139. Zhang S, Nomura K (2010) J Am Chem Soc 132:4960
140. Igarashi A, Zhang S, Nomura K (2012) Organometallics 31:3573
141. Hayes PG, Piers WE, McDonald R (2002) J Am Chem Soc 124:2133
142. Bambirra S, Bouwkamp MW, Meetsma A, Hessen B (2004) J Am Chem Soc 126:9182
143. Ward BD, Bellemin-Laponnaz S, Gade LH (2005) Angew Chem Int Ed 44:1668
144. Luo Y, Baldamus J, Hou Z (2004) J Am Chem Soc 126:13910
145. Li X, Baldamus J, Hou Z (2005) Angew Chem Int Ed 44:962
146. Cui D, Nishiura M, Hou Z (2005) Macromolecules 38:4089
147. Li X, Hou Z (2005) Macromolecules 38:6767
148. Ge S, Bambirra S, Meetsma A, Hessen B (2006) Chem Commun 3320
149. Ge S, Meetsma A, Hessen B (2007) Organometallics 26:5278

150. Bambirra S, van Leusen D, Tazelaar CGJ, Meetsma A, Hessen B (2007) Organometallics 1014:26
151. Tredget CS, Clot E, Mountford P (2008) Organometallics 27:3458
152. Zimmermann M, Törnroos KW, Waymouth RM, Anwander R (2008) Organometallics 27:4310
153. Jian Z, Cui D (2012) Dalton Trans 41:2367
154. Mashima K, Fujikawa S, Tanaka Y, Urata H, Oshiki T, Tanaka E, Nakamura A (1995) Organometallics 14:2633
155. Feng S, Roof GR, Chen EYX (2002) Organometallics 21:832
156. Jaffart J, Nayral C, Choukroun R, Mathieu R, Etienne M (1998) Eur J Inorg Chem 425
157. Spannenberg A, Fuhrmann H, Arndt P, Baumann W, Kempe R (1998) Angew Chem Int Ed 37:3363
158. Hakala K, Lofgren B (1997) Macromol Chem Rapid Commun 18:635
159. Michiue K, Oshiki T, Takai K, Mitani M, Fujita T (2009) Organometallics 28:6450
160. McGuinness DS (2011) Chem Rev 111:2321