

Design of Vanadium Complex Catalysts for Precise Olefin Polymerization

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1. INTRODUCTION

Polyolefins, such as polyethylene [high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) etc.], and polypropylene, produced by metal-catalyzed olefin coordination insertion polymerization, are important commercial synthetic polymers in our daily life, and the market capacity still increases every year. Recently, considerable attention has been paid to produce new polymers with specified functions exemplified by COCs (cyclic olefin copolymer, optical materials), syndiotactic polystyrene (thermal, chemical resistance), and others. It is widely believed that design of efficient transition metal complex catalysts that precisely control olefin coordination polymerization should play an important role in the success of this effort, and recent progress in the newly designed catalysts offers new possibilities.^{1–10} Therefore, research focused on the design of efficient molecular catalysts for precise olefin polymerization attracts considerable attention not only in the fields of catalysis

and organometallic chemistry but also in the field of polymer chemistry.^{1–10}

We can easily recognize that this was initiated by the discovery of the Ziegler–Natta catalyst (found in the autumn of 1953),^{11–16} especially initiated by the observation of the so-called “nickel effect” in the group of Ziegler.^{11,17} The effect has been known as the observed fact that traces of nickel salts present in the autoclave (made of chrome–nickel steel), which had been cleaned with nitric acid (in contrast to normal practice), affected the quantitative formation of 1-butene that had been found unexpectedly during the research in Al–alkyl-catalyzed ethylene oligomerization.^{11,17,18} Numerous studies of addition of transition metal compounds led to the discovery of the Ziegler catalyst for low-pressure polymerization of ethylene affording linear polyethylene.

It has been known that the classical Ziegler-type vanadium catalysts (e.g., VOCl_3 , VCl_4 , $\text{VCl}_3\text{–AlBr}_3$, $\text{AlCl}_3\text{–AlPh}_3$, Al^iBu_3 , SnPh_4) display unique characteristics in olefin polymerization. For example, Carrick reported in 1958 that the $\text{VCl}_4\text{–AlBr}_3\text{–AlPh}_3$ catalyst system afforded linear polyethylene with high catalytic activity (Scheme 1).¹⁹ One of the unique characteristics demonstrated in these catalyst systems was that the resultant polymer possessed high molecular weight with uniform molecular weight distribution compared with the Ti-based Ziegler catalyst (Figure 1).^{20,21} This fact strongly suggests formation of a single catalytically active species in this catalysis. They hypothesized that vanadium(II) species bridged by Al may play a role;^{19–21} however, many studies had been undertaken concerning the oxidation state of the catalytically active species, as described below.

The other unique characteristics demonstrated during the same period were that the catalyst systems afforded high molecular weight amorphous polymers in ethylene/propylene copolymerization^{22,23} and yielded syndiotactic polypropylene in propylene polymerization ($\text{VCl}_4\text{–Et}_2\text{AlCl}\text{–anisole}$ catalyst system, etc.).^{24,25} Synthesis of high molecular weight amorphous copolymers with uniform compositions attained in the ethylene/propylene copolymerization was one of the important requirements for application to the rubbery materials, and the catalyst systems were thus (eventually) applied to synthesis of so-called ethylene/propylene/diene copolymers (called EPDM)²⁶ that have been commercialized as synthetic rubbers. The catalyst system was also effective for synthesis of ethylene/cyclic olefin copolymers [COC, commercialized as “APEL” by Mitsui

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Scheme 1

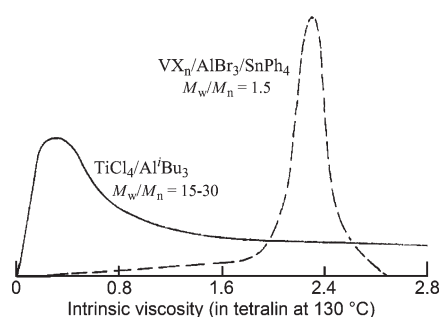
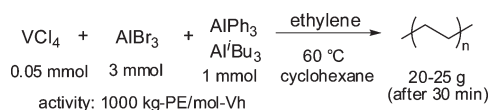


Figure 1. Differential molecular weight distributions by fractionation in the resultant polyethylenes prepared by titanium- or vanadium-based catalysts (published in 1960).²⁰

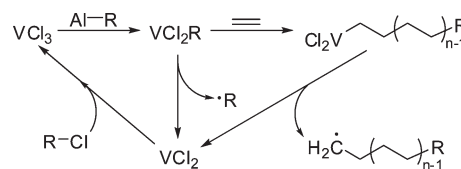
Chemicals, Inc., information and electronic materials such as pick-up lenses for DVD recorders and lenses for camera phones, copolymer of ethylene with tetracyclododecene (1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene)].

On the basis of ESR and titration results, they postulated that vanadium(III) species play an important role as the catalytically active species;^{24,25,27,28} in particular, Lehr demonstrated that a significant amount of catalyst species could not have been derived from V(IV) but must have come from inactive V(III) complexes,²⁸ although it was estimated that fewer than 1% of vanadium species were catalytically active in the mixture.²⁷

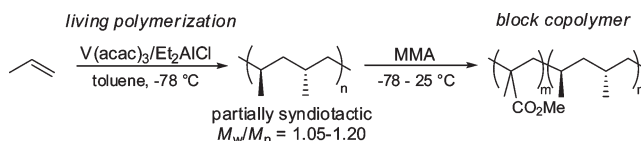
One of the main disadvantages of using this type of vanadium catalyst is the deactivation associated with the reduction to inactive vanadium(II) species. Although very high initial activities were observed by adopting these catalysts, the reduction causes very poor overall productivities. This problem could be overcome by reactivation of inactive vanadium(II) center to active vanadium(III) species by addition of reoxidants, so-called “rejuvenators” or “promoters”. Addition of hexachlorocyclopentadiene²⁹ or ethyl trichloroacetate³⁰ was known to be effective for reoxidation (even in the late 1960s), and the polymerization proceeded without significant decrease in the activity by continuous addition of an aluminum alkyl and the reoxidants even at high temperature (>105 °C).³⁰ All polyhalo-promoters cause an increase in the activity; especially esters of trichloroacetic acid appeared to be the preferred promoters. Through research exploring effect of methyl trichloroacetate (MTCA) on the oxidation state of the vanadium, it was revealed that the overall oxidation state increased by addition of MTCA into the mixture of VO(OⁱBu)₃ and Et₂AlCl [generally afforded V(IV) and V(III) or V(III) and V(II), depending on the Al/V ratio]. A mechanism shown in Scheme 2 was assumed on the basis of these facts, but it is clear that all vanadium species in the scheme are undoubtedly more complicated with the various Al species present including the fact that VCl₂ and VCl₃ are insoluble.

Another unique characteristics demonstrated was that the V(acac)₃ (acac = acetylacetonato)–Et₂AlCl catalyst system polymerizes propylene to give a syndiotactic “living” polymer with narrow molecular weight distribution ($M_w/M_n = 1.05\text{--}1.20$).³¹

Scheme 2. Assumed Scheme in Vanadium-Catalyzed Ethylene Polymerization in the Presence of Methyl Trichloroacetate (Reoxidant)³⁰



Scheme 3. Syndiospecific Living Polymerization of Propylene by the V(acac)₃–Et₂AlCl Catalyst System³¹ and Synthesis of Diblock Copolymer with Methyl Methacrylate (MMA)³³



A kinetic study proved that the propylene polymerization proceeded without any detectable chain termination as well as transfer reactions at temperatures below –65 °C. Synthesis of functional polymers with vinyl, phenyl, or hydroxyl groups at the chain end were thus prepared by adding common monomers such as butadiene, styrene, and 1,2-epoxypropane, respectively, at –78 °C during the living coordination polymerization process using this catalyst system.³² Moreover, diblock copolymer of propylene and methyl methacrylate (MMA) was prepared by adding MMA during the living coordination polymerization of propylene together with the soluble catalyst at –78 °C and subsequently by raising the polymerization temperature up to 25 °C (combination of coordination and anionic polymerization, Scheme 3).³³ Although the observed catalytic activity was unfortunately very low (ca. 4 kg of polymer/mol of V·h in the propylene polymerization) due to very low percentage of the catalytically active species, the fact has been recognized as the breakthrough for preparation of functionalized polymers by adopting the living polymerization technique using transition metal catalysts.

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 controlled polymerization has been recognized as an attractive target.^{4,10} Although examples for synthesis of vanadium complexes used as the catalyst precursors for olefin polymerization were known, known examples that exhibit the above-described unique characteristics of using these transition metal complexes had been limited until recently.^{4,10a,10b} In this review, we summarize reported examples of vanadium complexes employed as homogeneous catalyst precursors for olefin polymerization, including our recent efforts using (arylimido)vanadium(V) complex catalysts for precise olefin polymerization.^{10c} We also include our more recent examples for ethylene dimerization and ring-opening metathesis polymerization to demonstrate the unique characteristics of vanadium.

Table 1. Ethylene/Propylene Copolymerization by (1–4)–Et₂AlCl or Et₂AlCl·EtAlCl₂ Catalyst Systems^{a,34}

V cat.	V(acac) ₃ (1)		V(Cy-acac) ₃ (2)		V(^t Bu-acac) ₃ (3)		V(CF ₃ -acac) ₃ (4)	
Al cocat.	Et ₂ AlCl	Et ₃ Al ₂ Cl ₃	Et ₂ AlCl	Et ₃ Al ₂ Cl ₃	Et ₂ AlCl	Et ₃ Al ₂ Cl ₃	Et ₂ AlCl	Et ₃ Al ₂ Cl ₃
activity ^b	1988	1960	2336	1980	1492	1244	1524	1600
<i>M</i> _w ^c × 10 ^{−5}	2.19	7.02	2.18	7.16	2.90	12.65	2.77	8.01
<i>M</i> _w / <i>M</i> _n ^c	2.3	2.5	2.3	2.2	2.2	2.4	2.2	2.3
% ethylene ^d	62	52	59	53	65	57	63	54

^a Reaction conditions: vanadium 5 μmol, Al 0.2 mmol (Al/V = 40, molar ratio), Cl₃CCO₂Et 20 μmol, 200 mL of cyclohexane, ethylene/propylene 2 bar, 22 °C, 30 min. ^b Activity in kg polymer/(mol V·h). ^c GPC data in trichlorobenzene vs polystyrene standards. ^d Estimated by FT-IR spectra.

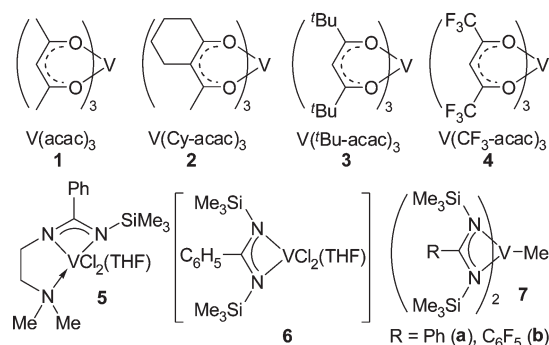
2. VANADIUM COMPLEXES DESIGNED FOR OLEFIN COORDINATION INSERTION POLYMERIZATION

As described above, it has been assumed that the vanadium(III) species plays an important role as the catalytically active species in olefin polymerization using Ziegler-type vanadium catalyst systems. Therefore, syntheses of the trivalent and the tetravalent complexes have been focused on this purpose, although these complexes would be difficult to isolate/identify due to their paramagnetic nature. As also described in the Introduction, only a trace of *actual* catalytically active species was present because the *actual* catalytically active species would be unstable and readily reduced by Al cocatalyst to afford the catalytically inactive vanadium(II) species. Therefore, many researchers concentrate on controlling the oxidation state (stabilization of the oxidation state, catalytically active species) by an appropriate ligand modification in these catalysts.

2.1. Vanadium(III) Complexes

As described above, the V(acac)₃ (1)–Et₂AlCl catalyst system polymerizes propylene in a living manner at low temperature below −65 °C, and the resultant polymer possesses highly syndiotactic stereoregularity with narrow molecular weight distributions (*M*_w/*M*_n = 1.05–1.20).³¹ Ethylene/propylene copolymerizations using various V(β-diketonate)₃ complex (1–4)–Et₂AlCl or Et₂AlCl·EtAlCl₂ catalyst systems were conducted in the presence of Cl₃CCO₂Et (Table 1).³⁴ However, it seemed that no especially useful information concerning the ligand effect for improving the catalytic activity was obtained,³⁴ although it seems that the observed activities (calculated on the basis of polymer yields) were somewhat related to the stability of the catalytically active species. Effect of substituent in β-diketonate ligand for ethylene polymerizations using V(acac)₃ (1), V(1-Ph-3-CF₃-acac)₃, V(1-MeO-3-Me-acac)₃, V(1,3-^tBu₂acac)₃ (3), V(1,2,3-Me₃acac)₃, or V[1,3-(CF₃)₂acac]₃ (4) (Scheme 4)^{34–39} was also explored in the presence of MAO (Al/V = 100), but these results did not give any useful information about the catalytically active species, because the resultant polymers possessed broad molecular weight distributions (*M*_w/*M*_n = 4.9–265).³⁵ Vanadium(III) complexes containing β-diiminato ligands, [ArNC(R)CHC(R)NAr]·VX₂ [R = Me, ^tBu; Ar = Ph, 2,6-ⁱPr₂C₆H₃, 2,4,6-Me₃C₆H₂; X = Cl, Me], showed negligible catalytic activities for ethylene polymerization in the presence of MAO, Et₂AlCl, or B(C₆F₅)₃, and transfers of the β-diiminato ligand to Al were observed in the presence of Al alkyls.³⁶

Vanadium(III) complexes containing (dimethylamino)ethyl-functionalized benzamidinate ligand (5) exhibited moderate catalytic activity for ethylene polymerization in the presence of Et₂AlCl, and the observed activity at 30 °C (447 kg PE/(mol V·h·bar); ethylene 6 bar) was higher than that by

Scheme 4

{[PhC(NSiMe₃)₂]VCl₂(THF)}₂ (6, 129 kg PE/(mol V·h·bar)) under the same conditions. However, the activity by 5 decreased at higher temperature, whereas the activity by 6 increased at 80 °C.³⁷ The molecular weight for the resultant PE prepared at 30 °C was relatively high with narrow molecular weight distribution (*M*_w = 7.6 × 10⁵, *M*_w/*M*_n = 2.1), suggesting that the polymerization took place with uniform catalytically active species.³⁷ Supported catalysts derived from 5 and 6 on MgCl₂/AlEt₃(OEt)_{3–n} showed remarkable catalytic activities [activities 1490 and 3120 kg PE/(mol V·h·bar) for 5, 6, respectively; ethylene 1.0 MPa in light petroleum (heptane etc.) at 50 °C for 1 h], affording high molecular weight polymers with uniform molecular weight distributions [*M*_w and *M*_w/*M*_n = 7.47 × 10⁵ and 2.0 and 7.62 × 10⁵ and 2.0 by 5 and 6, respectively].³⁸ These results are promising, because the supported catalysts showed higher catalytic activities than the homogeneous systems. The above polymerization results (using both homogeneous and supported catalysts) suggested that an introduction of the (dimethylamino)ethyl moiety did not play an important role for improving the catalytic activity.^{37,38} In contrast, monitoring the reaction profile suggested that the immobilized catalyst from 5 showed better stability than that from 6.³⁸

Bis(amidinate)vanadium(III) methyl complexes, [PhC(NSiMe₃)₂]VMe (7a), showed catalytic activity for ethylene oligomerization without any additional cocatalysts, affording linear olefins with Schultz–Flory distribution.^{39a} Replacement of the Ph group with C₆F₅ led to an increase in the activity (8.1 kg oligomer/(mol V·h); ethylene 8 bar at 80 °C) as well as increase in the molecular weight of the resultant oligomers (*M*_n = 1780, *M*_w/*M*_n = 2.3).

Cationic vanadium(III)–alkyl and allyl complexes containing a linked cyclopentadienyl-amine ligand (8 or 9, Scheme 5) did not afford polyethylene in the presence of isobutyl aluminoxane (ethylene 5 bar in toluene, 30 min),⁴⁰ and they showed that a

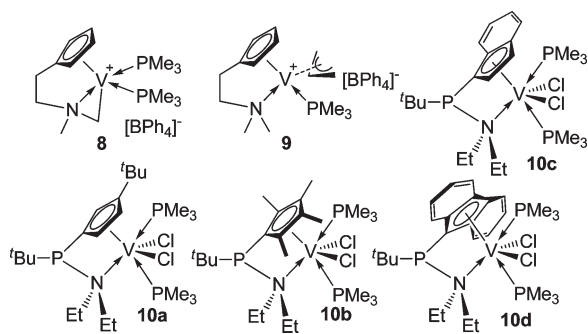
strong coordination of PMe_3 to vanadium disturbed ethylene coordination/insertion.⁴⁰ This is because the half-sandwich vanadium(III) complexes containing aminophosphanyl ligand (**10**, Scheme 5) showed low catalytic activities for ethylene polymerization in the presence of methylaluminoxane (MAO) (13–50 kg PE/(mol V·h·bar); ethylene 3 bar in toluene at 20–50 °C). A significant effect of the cyclopentadienyl fragment (in **10a–d**) on the activity was not observed.⁴¹

A dinuclear vanadium(III) chloride complex (**11**) containing a bis(amido)amine ligand of type $(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{NSiMe}_3$, exhibited remarkable catalytic activity for ethylene polymerization in the presence of MAO or Me_2AlCl at 50 °C [activity 237 kg PE/(mol V·h) for MAO and 660 kg PE/(mol V·h) for Me_2AlCl ; ethylene 300 psig (20.4 atm); Al/V = 60 (molar ratio)].⁴² The resultant polyethylene prepared by the **11**– 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 observed activities decreased at higher temperature, although the molecular weight distribution in the resultant PE remained the same. The catalyst system was short-lived, remaining 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 **11** with AlMe_3 , Me_2AlCl , and MAO in hexane initially gave a red solution, which after a few days afforded another vanadium(II) complex identified as **11b** (Scheme 6). This result thus suggested that no ligand dissociation occurred in the present catalyst system but aggregation with the cocatalyst did. The question of how the reduction of **11** afforded the inactive divalent species **11b** was thus considered. The reaction of **11** with AlCl_3 afforded disproportionated

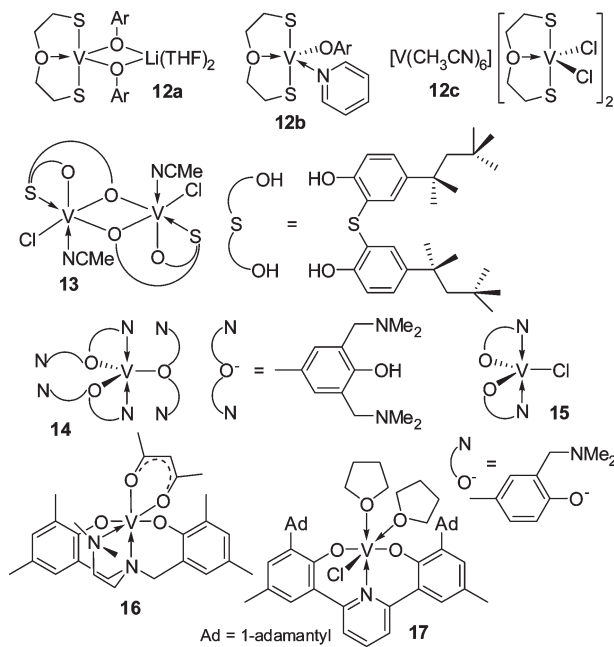
compounds, (tetravalent) **11c** and (one divalent and two trivalent) **11d**, clearly indicating that disproportionation was the basis of a reduction of the vanadium center. These results suggested the possibility of the reduction of **11** affording **11b** and that the additional intermediate **11a**, which is likely to be the catalytically active species, has the intrinsic instability of a vanadium–carbon bond.⁴²

A mixed-valent vanadium complex containing dithiolate ligand (**12c**, Scheme 7)³⁴ [prepared from $\text{VCl}(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_2 \cdot (\text{THF})_2$ by treating with $\text{O}(\text{CH}_2\text{CH}_2\text{SH})_2$ in MeCN] 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].^{43b} The observed activity was lower than that by $[\text{V}(\mu_2\text{-O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_2\{\text{O}(\text{CH}_2\text{CH}_2\text{S})_2\} \cdot \text{Li}(\text{THF})_2]$ (**12a**, 1990 kg PE/(mol V·h)) and $[\text{V}(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\{\text{O}(\text{CH}_2\text{CH}_2\text{S})_2\}(\text{pyridine})]$ (**12b**, 1020 kg PE/(mol V·h)) under the same conditions (in *n*-hexane).^{43a} The ligand transfer to Al alkyls occurred in the reaction of **12c** with AlMe_3 , affording vanadium(II) chloride and $[\text{AlMe}\{\mu_2\text{-O}(\text{CH}_2\text{CH}_2\text{S})\}]_2$

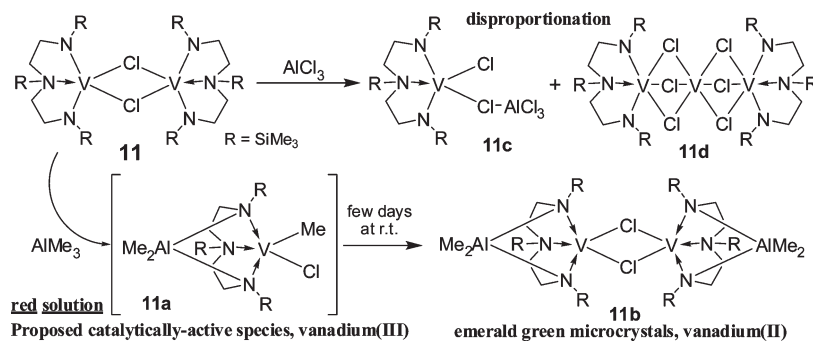
Scheme 5



Scheme 7



Scheme 6



(insoluble in *n*-hexane),^{43b} whereas the resultant products after the ligand transfer from **12a,b** would be vanadium(II) aryloxides that are soluble in hydrocarbon solvent. This observed difference was assumed due to the difference in the solubility of the *actual* catalytically active species (probably formed after dissociation of the chelate donor ligand).^{43b}

Use of thiobis(phenoxy) ligand in place of the dithiolato ligand improved the catalytic activity, and complex **13** showed remarkable catalytic activities in the presence of cocatalyst.⁴⁴ The activity was dependent upon the Al cocatalyst employed, and AlⁱBu₃ was found to be better than Et₂AlCl or MAO [activity = 11708 kg PE/(mol V·h) for AlⁱBu₃, 8184 for Et₂AlCl, and 4736 for MAO; ethylene 5 atm, Al/MgCl₂/V = 100/10/1 (AlⁱBu₃, Et₂AlCl) or 3000/10/1 (MAO)].⁴⁴ 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. The catalytic activity did not decrease after 30 min, and an effect of Cl₃CCO₂Et on the catalytic activity was not observed. Vanadium(III) complexes containing two or three *O,N*-chelating aminophenolate ligands (**14** or **15**) exhibited catalytic activities for ethylene/propylene copolymerization in the presence of Et₂AlCl·EtAlCl₂ cocatalyst.⁴⁵ Bis(phenoxy) complex **15** showed higher catalytic 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 **14** (27 kg polymer/(mol V·h·bar)). The resultant polymer prepared by **15** contained propylene (37.5 wt %) with relatively high molecular weight (M_w = 6.7×10^5).

Olefin polymerization using a series of vanadium complexes containing an amine bis(phenoxy) ligand, [(O-2,4-Me₂C₆H₂-6-CH₂)₂(Me₂NCH₂CH₂)N]²⁻ (exemplified as complex **16**), with various oxidation states (II–V) was reported (Table 2).⁴⁶ Complex **16** showed notable catalytic activity for ethylene polymerization in the presence of EtAlCl₂ but showed negligible activity in the presence of MAO.^{46a} Copolymerizations of ethylene with 1-hexene or norbornene were attempted, but the activities decreased in the presence of these comonomers and the resultant poly(ethylene-*co*-1-hexene)s possessed a mixture of copolymers with different compositions estimated by their DSC thermograms (although the molecular weight distributions in the copolymers were unimodal).^{46a} From these results, they speculated that vanadium(III) species would play an important role as the catalytically active species.

More recently, Golisz and Bercaw reported that a vanadium(III) complex containing bis(phenoxy)pyridine ligand **17** 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 polypropylene with uniform molecular weight distribution (M_w = 1.17×10^6 , M_w/M_n = 2.03).⁴⁷ Microstructure analysis in the resultant polymer by ¹³C NMR spectra indicated that the resultant polymer possessed a large extent of regioirregularity as seen in many vanadium catalysts. Taking into account the above reports (vanadium complexes using chelate anionic and neutral donor ligands),^{42–47} as described above,^{10a,10b} control of the oxidation state (stabilization of the oxidation state, catalytically active species) by an appropriate ligand modification seems to be a key for the efficient catalysis with vanadium(III), although the *actual* active species including the activation/polymerization mechanism are still not clear at present.

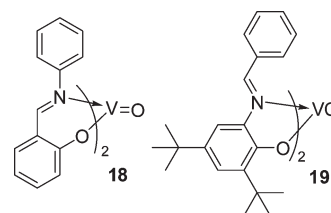
2.1.1. Vanadium Complexes Containing Chelate Anionic Donor Ligands. MgCl₂-supported vanadium catalysts

Table 2. Ethylene Polymerization Promoted by Various Vanadium Complex–EtAlCl₂ catalysts^a [L = Amine Bis-(phenolate) Ligand]^{46a}

complex	solvent	time, min	activity ^b	$M_w^c \times 10^{-4}$	M_w/M_n^c
V ^{VO} (O ⁱ Pr)[L]	toluene	5 ^d	272	11.8	2.65
V ^{VO} (N ₃)[L]	CH ₂ Cl ₂	15	22	14.6	4.6
V ^{VO} (Cl)[L]	CH ₂ Cl ₂	15	17	71.6	3.76
V ^{IV} (O ⁱ Pr) ₂ [L]	toluene	3 ^d	474	67.7	2
V ^{IV} (Cl) ₂ [L]	toluene	15	62	88.9	2.03
VCl ₄	toluene	10 ^d	22	15.2	8.13
VCl ₄ ·DME	toluene	4 ^d	200	15.2	3.19
V ^{III} (acac)[L] (16)	toluene	3 ^d	436	67.3	3.33
V ^{III} (acac)[L] (16) ^e	toluene	30	61	3.3	1.90
V ^{III} (acac)[L] (16) ^f	toluene	30	66		
V ^{III} (acac)[L] (16)	pentane	5 ^d	322	100.3	2.63
V ^{III} (Cl)(THF)[L]	toluene	15	52	45.8	2.24
V(acac) ₃	toluene	10 ^d	85	17.6	2.43
V ^{II} (tmeda)[L]	toluene	15	1	225.9	3.03

^a Reaction conditions: catalyst (ca. 0.01 mmol), solvent 10 mL, EtAlCl₂ (10 equiv), ethylene 1 bar, room temperature. ^b Activity in kg PE/(mol V·h). ^c GPC data in 1,2,4-trichlorobenzene at 140 °C vs polystyrene standards. ^d Formation of polymer gel. ^e Copolymerization with 1-hexene (8 mmol), 1-hexene content 10.6 mol %. ^f Copolymerization with norbornene (8 mmol), norbornene content 29 mol %. DME: 1,2-dimethoxyethane, tmeda: *N,N,N',N'*-tetramethylethylenediamine.

Scheme 8



consisting of bis(phenoxy-imine)vanadium complexes (**18** or **19**, Scheme 8), MgCl₂, 2-ethyl-1-hexanol, and AlEt₃ exhibited remarkable catalytic activities for ethylene polymerization in the presence of both Et₂AlCl and Cl₃CCO₂Et (Table 3).⁴⁸ The activities of **18** and **19** were higher than that of VOCl₃, and the activities also increased at higher temperature (75 °C). It was assumed that the combination of the phenoxy-imine ligand and MgCl₂/Et_mAl(OR)_n gave rise to the unprecedented V-based olefin polymerization catalyst system. The observation that a remarkable improvement was obtained by using a MgCl₂ support seems somewhat analogous to the trend previously reported by Sobota et al.⁴⁴ Copolymerization of ethylene with propylene by **18** was carried out, and the resultant polymer possessed high molecular weight (M_w = 6.97×10^5) but relatively broad molecular weight distribution (M_w/M_n = 4.72), and the composition was not uniform as confirmed by GPC/FT-IR.⁴⁴

Later, a series of vanadium(III) complexes containing β-enaminoketonato,⁴⁹ phenoxy-imine,^{50–53} and imino-pyrrolide⁵⁴ ligands shown in Scheme 9 were prepared and tested as olefin polymerization catalysts in the presence of Et₂AlCl and Cl₃CCO₂Et (for reoxidation of the deactivated species, as described above). The selected results are summarized in

Table 4.^{49–52,54} The observed catalytic activities of certain complexes were higher than those of $\text{VOCl}_3(\text{THF})_3$ under the same conditions, and the catalytic activities decreased at 70 °C probably due to the rapid deactivation even for a short

Table 3. Effect of Additives in Ethylene Polymerization by VOCl_3 -, 18-, or 19- Et_2AlCl Catalysts^{a 48}

complex	additives (molar ratio) ^b	temp, °C	activity, kg PE/(mol V·h)
VOCl_3	none	25	12600
VOCl_3	none	50	8100
18	none	25	20000
18	none	50	13300
19	none	25	16700
19	none	50	8900
VOCl_3	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n^c$ (800/2400)	25	8300
VOCl_3	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n^c$ (800/2400)	75	5400
18	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n^c$ (800/2400)	25	18700
18	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n^c$ (800/2400)	75	65100
19	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n^c$ (800/2400)	25	11300
10	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n^c$ (800/2400)	75	43800

^a Reaction conditions: complex 1.0 μmol , Et_2AlCl 0.4 mmol (Al/V = 400), $\text{Cl}_3\text{CCO}_2\text{Et}$ 0.4 mmol, toluene 400 mL, ethylene 1 atm, 15 min.

^b Molar ratio based on vanadium. ^c Prepared by adding AlEt_3 into a solution containing MgCl_2 and 2-ethyl-1-hexanol.

polymerization period (5 min) as well as in the presence of an excess amount of reoxidant (300 equiv to V). On the basis of these polymerization data, it seems that **20b** ($\text{R}^1, \text{R}^2 = \text{tBu}, \text{CF}_3$),⁴⁹ **20d** ($\text{R}^1, \text{R}^2 = \text{Ph}, \text{CH}_3$),⁴⁹ **21a** ($\text{R}^1, \text{R}^2, \text{R} = \text{H}, \text{H}, \text{Ph}$),⁵⁰ and **23h**⁵² showed higher catalytic activities, suggesting that the complexes containing β -enaminoketonato ligand (**20**, **23h**) showed higher catalytic activities than the complexes containing phenoxy-imine ligands (**21**, **22**). Placement of neutral donor ligands (amine, pyridine) into the phenoxy-imine ligands in **23** was not effective; the observed catalytic activity by **23h** was relatively close to **20e** and improvement in the activities were seen in the complexes containing phenoxy-imine ligands. 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.). As another attempt, modification of the phenoxy-imine ligand with a imidazolium salt led to significant decreases in the catalytic activity.⁵³

In contrast, vanadium(III) complexes containing iminopyrrolide ligands (**24**) showed remarkable catalytic activities under the same conditions.⁵⁴ The catalytic activities by **24** (ethylene 1 atm, 50 °C for 5 min) increased in the order: **24c** ($\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) > **24b,e** ($\text{R} = \text{Ph}, \text{C}_6\text{F}_5$) > **24d** ($\text{R} = 4\text{-CF}_3\text{C}_6\text{H}_4$) > **24a** ($\text{R} = \text{cyclohexyl}$). The results thus suggest that both electronic and steric factors play an important role (probably for strong coordination). The catalytic activity decreased at

Scheme 9

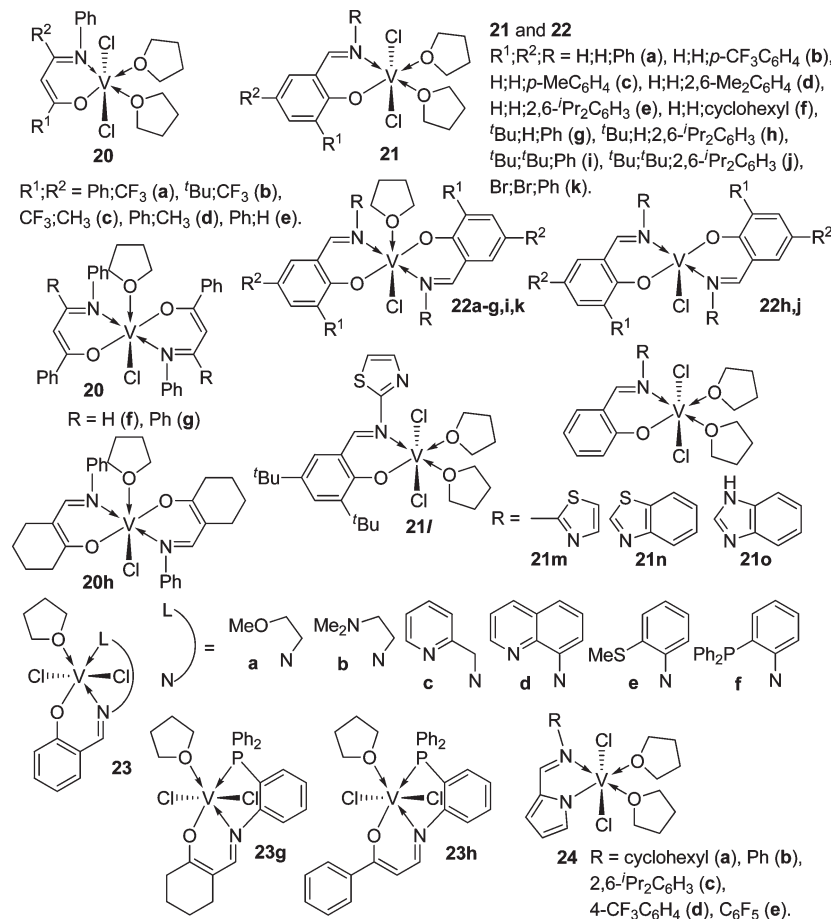


Table 4. Ethylene Polymerization by (20–24)–Et₂AlCl–Cl₃CCO₂Et Catalyst Systems^{a 49–52,54}

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	20400	24.6	2.6
VCl ₃ (THF) ₃	25	25800	22.7	2.8
VCl ₃ (THF) ₃	50	18700	15.5	5.3
VCl ₃ (THF) ₃	50	23400	13.4	5.8
VCl ₃ (THF) ₃	70	12600	9.9	21.9
20a	50	27400	17.7	2.6
20b	25	27800	25.6	3.0
20b	50	29000	18.6	3.0
20c	50	21800	25.9	2.9
20d	25	22800	25.5	2.9
20d	50	24000	17.3	2.9
20e	50	18700	27.1	2.9
20f	25	18240	3.5	2.6
20g	25	18000	4.3	2.6
20h	25	13200	5.9	2.6
21a	25	22300	13.8	2.7
21a	50	21100	5.7	3.8
21a	70	12700	3.8	12.0
22b	50	14600	4.7	3.7
21e	50	14600	7.3	3.5
21f	50	12000	5.4	3.2
21g	50	17800	5.4	3.4
21k	50	9120	5.8	4.0
22a	25	8400	17.1	1.9
22a	50	10300	6.1	2.2
22a	70	9840	1.5	2.6
22b	50	16800	5.7	2.8
22b	70	18200	3.2	3.0
22e	50	14200	7.0	2.4
22f	50	19200	3.9	2.8
23a	50	3840	4.0	2.4
23b	50	9600	3.5	3.0
23c	50	15600	6.2	2.2
23d	50	9120	4.8	2.5
23e	50	7920	6.3	2.0
23f	50	11300	4.6	2.5
23g	50	9360	3.0	2.2
23h	50	20600	2.4	2.0
24a	50	28200	3.5	2.1
24b	50	37800	4.3	2.2
24c	25	39600	6.3	2.4
24c	50	48600	2.5	1.7
24c	70	34200	1.0	2.2
24d	50	33000	4.4	2.4
24e	50	39000	3.0	1.9

^a Reaction conditions: vanadium 0.2 or 0.5 μ mol, Et₂AlCl and Cl₃CCO₂Et (ETA), Al/ETA/V = 4000/300/1 (molar ratio), ethylene 1 atm for 5 min (data summarized from refs). ^b GPC data in 1,2,4-trichlorobenzene vs polystyrene standards.

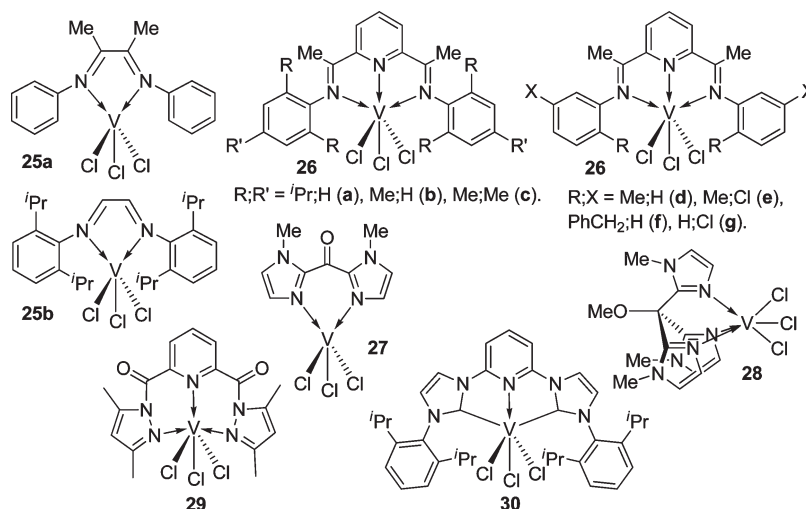
70 °C, and the resultant polymers possessed relatively low molecular weights with uniform distributions ($M_w = (1.0–6.3) \times 10^4$).

Copolymerization of ethylene with 1-hexene or norbornene using complexes **20**, **21i–o**, and **23** were examined, and these complexes can efficiently incorporate the comonomer into polymer chains, affording the copolymers with uniform molecular weight distributions.^{49,51,52} However, the observed catalytic activities decreased upon increase of the initial comonomer concentrations and the M_w values in the resultant copolymers decreased except in the ethylene/norbornene copolymers prepared by **23**.⁵² Ethylene copolymerizations with 10-undecen-1-ol using **20d–**, **21a–**, or [PhN=CHC(Ph)=CHO]VCl₂(THF)₂–Et₂AlCl–Cl₃CCO₂Et catalyst systems afforded copolymers containing a hydroxyl group in the side chain, although both the catalytic activities and the M_w values in the resultant copolymers significantly decreased upon comonomer incorporation.⁵⁵ Complex **23c** showed high catalytic activity in the ethylene/norbornene copolymerization, and the activity was close to that by **23h** under the same conditions, although the activity by **23c** was lower than that by **23h** in the ethylene polymerization.⁵² Complexes **24** showed a similar level of comonomer incorporation with higher catalytic activities in ethylene/10-undecen-1-ol copolymerizations under the same conditions and afforded the copolymers with relatively low molecular weights ($M_n = (3.1–52.5) \times 10^3$).⁵⁴ The M_n values decreased upon increase of the comonomer content.⁵⁴

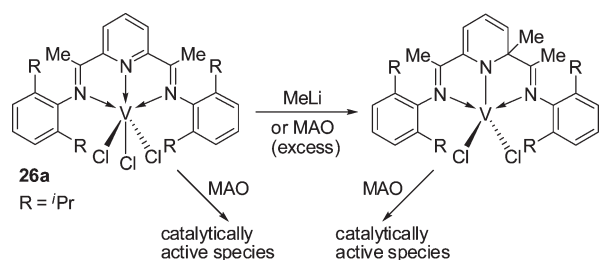
2.1.2. Vanadium Complexes Containing Chelate Neutral Donor Ligands. In 1999, Gambarotta et al. reported that a vanadium(III) complex containing a bis(imino)pyridine ligand (**26a**) exhibited remarkable catalytic activities for ethylene polymerization in the presence of MAO, affording the polymers with broad molecular weight distributions [activities 1420 and 2240 kg PE/(mol V·h), with Al/V = 600 and 60 (molar ratio), respectively; ethylene 100 psig (6.8 atm), 50 °C, 15 or 30 min] (Scheme 10).⁵⁶ The catalytic activities decreased at 140 °C, and the molecular weight distributions in the resultant polymers were dependent upon the Al/V molar ratios. The fact was explained as due to generation of another catalytically active species by attacking AlMe₃ to the pyridine ring (Scheme 11).⁵⁶ Replacement of ^tPr with Me did not improve the catalytic activities⁵⁷ but afforded oily residues if these reactions were conducted in the presence of AlⁱBu₃ in place of MAO.⁵⁷ Moreover, the reaction with ethylene using the complexes **26d** and **e** containing a mono-substituted aromatic group on the imino ligand (in place of 2,6-diisopropyl) afforded oligomeric mixtures and polyethylene (products by Schultz–Flory distribution).⁵⁸ The similar reaction with propylene using the complexes **26f** and **g** afforded oligomers with relatively high C₆ selectivity (80–95%, major products, methylpentenes).^{58c} 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 the similar ligands.^{59,60}

Vanadium(III) complexes containing chelate α -diimine ligands (**25**),⁶¹ bis(imidazole) (**27**),⁶² and tris(imidazole) (**28**)⁶² ligands were also prepared and tested for their catalytic activities for ethylene polymerization/oligomerization. However, these complexes showed low catalytic activities. Use of the bis(pyrazolyl)pyridine ligand **29** in place of **27** or **28** improved the catalytic activity in the presence of EtAlCl₂ cocatalyst.⁶³ Taking into account the above results, it seems that the tridentate ligand of bis(imino)pyridine, which was strongly bound to the metal center thus stabilizing the vanadium-alkyls, was a key factor and was probably responsible for the high catalytic activity observed in this system.

Scheme 10



Scheme 11



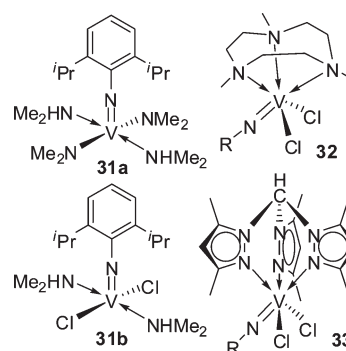
A vanadium(III) complex containing a bis(carbene)pyridine ligand (**30**) showed remarkable catalytic activities for ethylene polymerization, and the activity was dependent upon the Al cocatalyst employed.⁶⁴ The activity by **30**–Al cocatalyst (ethylene 1 atm in toluene at r.t. for 30 min, Al/V = 500, molar ratio) increased in the order: 1446 kg PE/(mol V·h) (MMAO, methyl isobutyl aluminoxane) > 1280 (MAO) > 586 (dried MAO and Al^{*i*}Bu₃) > 278 (Et₂AlCl).⁶⁴ Addition of Cl₃CCO₂Et (reoxidant used for many polymerization systems with vanadium) caused a decrease in the catalytic activity in all cases.⁶⁴

2.2. Vanadium(IV) Complexes

Lorber et al. reported that (arylimido)vanadium(IV) dichloride complexes (**31**, shown in Scheme 12) showed high catalytic activities for ethylene polymerization in the presence of Et₂AlCl cocatalyst, and the activity by **31b** in the presence of MAO (59 kg PE/(mol V·h); Al/V = 500) was lower than that in the presence of Et₂AlCl (120 kg PE/(mol V·h); Al/V = 10; ethylene 1 atm, 20 °C in toluene, 2 or 10 min). The resultant polymers possessed uniform molecular weight distributions.⁶⁵ As described below in section 2.3, introduction of a 2,6-disubstituted arylimido moiety seems to be effective in terms of stabilization of the catalytically active species.

Ethylene polymerization using various (imido)vanadium(IV) dichlorides containing 1,4,7-trimethyltriazacyclononane (TACN) or tris(3,5-dimethylpyrazolyl)methane (TPM) ligands (**32** or **33**) were explored, and the TACN analogues [**32**, R = 2,6-*i*Pr₂C₆H₃,

Scheme 12



2-^{*t*}BuC₆H₄, 2-CF₃C₆H₄, ^{*t*}Bu, or 1-adamantyl] showed negligible catalytic activities in the presence of MAO [ethylene 6 bar, Al/V = 1500 (molar ratio), 22–24 °C, 30 min].⁶⁶ The TPM-supported complexes (**33**) showed moderate catalytic activities under the same conditions, and the 2-^{*t*}BuC₆H₄ analogue produced polymer/oligomer with a bimodal molecular weight distribution [activity 30 kg PE/(mol V·h)].⁶⁶

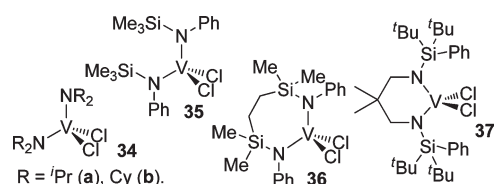
Ethylene/propylene copolymerization was performed using vanadium(IV) complexes containing bis(amide) ligands (**34**, Scheme 13)^{67–69} in the presence of Al cocatalysts, and the activity was affected by the Al cocatalyst employed.⁶⁷ The activity by the isopropyl analogue (**34a**) [ethylene + propylene total 2 bar in hexane at 22 °C for 15 min, Al/V = 40 (molar ratio)] increased in the order Et₂AlCl·EtAlCl₂ (860 kg polymer/(mol V·h)) > EtAlCl₂ (330 kg polymer/(mol V·h)) > Et₂AlCl (80 kg polymer/(mol V·h)) > AlEt₃ (24 kg polymer/(mol V·h)). The resultant polymer prepared by **34a**–Et₂AlCl·EtAlCl₂ possessed high molecular weight with uniform molecular weight distribution ($M_w = 2.29 \times 10^6$, $M_w/M_n = 3.0$, ethylene 73 wt %). The isopropyl analogue (**34a**) showed higher activity than the cyclohexyl analogue (**34b**) in the copolymerization as well as in the ethylene homopolymerization (activity 265 kg PE/(mol V·h), ethylene 1 bar).⁶⁷ A vanadium(IV) complex with a chelate

bis(amide) ligand (**35**) showed higher catalytic activity than the corresponding bis(amide) analogue (**36**) in ethylene polymerization [activities in the presence of $\text{Et}_2\text{AlCl} \cdot \text{EtAlCl}_2$: 213 and 54 kg PE/(mol V·h) for **35** and **36**, respectively; ethylene 1 atm in toluene at 30 °C, Al/V = 50 (molar ratio)]. Although the activity in the ethylene polymerization by **36** is close to that by the above isopropyl analogue (**34a**, 178 kg PE/(mol V·h)), **36** showed higher catalytic activity in ethylene/propylene copolymerization.⁶⁸ A vanadium(IV) complex containing a chelate bis(amide) complex (**37**) showed catalytic activity for ethylene polymerization in the presence of MAO, but the activity at 20 °C was low (0.7 kg PE/(mol V·h), Al/V = 500).⁶⁹

Vanadium(IV) complexes containing two *O,N*-chelating aminophenolate ligands (**38**) showed moderate catalytic activities for ethylene/propylene copolymerization in the presence of $\text{Et}_2\text{AlCl} \cdot \text{EtAlCl}_2$ cocatalyst.⁴⁵ The observed catalytic activities [222 and 189 kg polymer/(mol V·h·bar); 8 bar of ethylene/propylene (ratio 1/2) in pentamethylheptane at 30 °C for 10 min.] were slightly higher than those by the vanadium(III) monochloride analogues (**14** and **15**).⁴⁵

As described in section 2.1, MgCl_2 -supported vanadium catalysts consisting of bis(phenoxy-imine)vanadium complexes (**18** and **19**), MgCl_2 , 2-ethyl-1-hexanol, and AlEt_3 exhibited remarkable catalytic activities for ethylene polymerization in the presence of both Et_2AlCl and $\text{Cl}_3\text{CCO}_2\text{Et}$ (Table 3),⁴⁸ and the activities increased at higher temperature (75 °C). Modification of these complex catalysts were explored later by the other researchers,^{70–72} and selected results are summarized in Table 5.

Scheme 13



The *t*Bu analogue (**39b**, Scheme 14)^{45,70–72} in the vanadium complexes containing *N,O*-bidentate ligands showed higher catalytic activity than **39a**, probably because of improved stability by increasing the steric bulk, and the activity was highly affected by the Al cocatalyst employed [$\text{EtAlCl}_2 \gg \text{Et}_2\text{AlCl} > \text{MAO}$]. The resultant polymers possessed rather high molecular weights with moderate distributions.⁷¹ In the presence of Et_2AlCl and ethyltrichloroacetate (ETA, as the reoxidant, Al/ETA/V = 4000/300/1, molar ratio), (oxo)vanadium(IV) complexes containing two β -enaminoketonato ligand (**40a–c**) showed relatively high catalytic activities that were similar to those observed by the analogous vanadium(III) chloride complexes (**20f–h**, Scheme 9). Both the activities and M_w values in the resultant polymers catalyzed by **40a–c** were relatively close to those catalyzed by **20f–h**; it is thus assumed that similar catalytically active species were present under these conditions.

Vanadium(IV) complexes containing salen-type tetradentate ligands (**41,42**) also showed moderate to high catalytic activities for ethylene polymerization.⁷⁰ The catalytic activities for ethylene polymerization using the complexes containing a cyclohexyl backbone (**42**) were higher than those using a two methylene backbone (**41**), and the activities were affected by the ortho substituent in the phenoxo moiety. The activity was also highly affected by the Al cocatalyst employed. However, the resultant polymers possessed broad molecular weight distributions ($M_w/M_n = 7.3–10.4$), and this fact would suggest several catalytically active species in the reaction mixture.⁷⁰ The ethylene polymerization using **41c** supported on $\text{MgCl}_2(\text{THF})_2$ was explored, and the prepared catalyst showed better life even after 2 h, although the molecular weight distributions in the resultant polymers were somewhat large ($M_w/M_n > 16$).⁷² Ethylene polymerization using a vanadium(IV) complex containing another *N,O*-chelate donor ligand (**43**) was reported, but the activity was low, and no description was provided of the resultant polymer.⁷³

2.3. Vanadium(V) Complexes

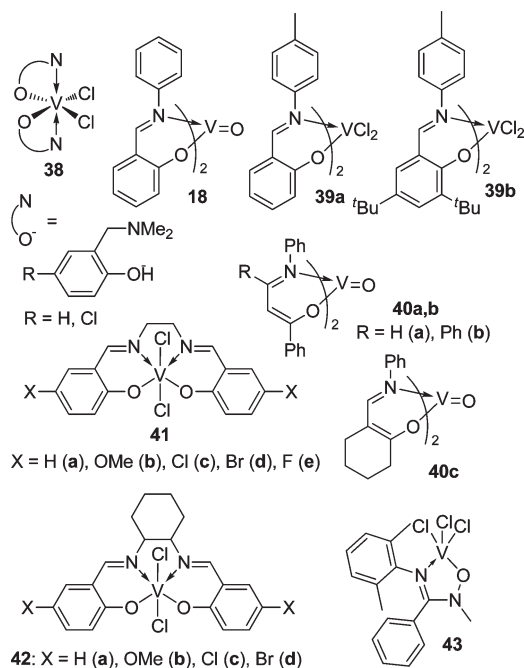
As described in the Introduction, VOCl_3 showed moderate catalytic activities for ethylene/propylene (co)polymerization in the presence of Al alkyls. One of the problems associated with the use of vanadium(V) complexes as catalysts for Ziegler–Natta

Table 5. Ethylene Polymerization by (**39–42**)–Cocatalyst Systems^a 70–72

complex (μmol)	Al cocat. (mmol)	activity, kg PE/(mol V)	$M_w \times 10^{-5}$	M_w/M_n
39a (0.08)	Et_2AlCl (7.9)	22.4	7.23	3.7
39a (0.04)	EtAlCl_2 (7.9)	208	6.49	3.7
39b (0.08)	Et_2AlCl (7.9)	111	5.66	4.4
39b (0.01)	EtAlCl_2 (7.9)	852	5.99	4.0
39b (0.08)	MAO (10.5)	30.4		
41a (0.007)	EtAlCl_2 (3.6)	354	7.20	9.3
41b (0.007)	EtAlCl_2 (3.6)	721	6.29	7.8
41c (0.007)	EtAlCl_2 (3.6)	886	6.83	7.8
41b (0.08)	Et_2AlCl (3.6)	63		
41c (0.08)	Et_2AlCl (3.6)	33		
42a (0.007)	EtAlCl_2 (3.6)	860	10.47	10.4
42b (0.007)	EtAlCl_2 (3.6)	748	6.96	7.3
42c (0.007)	EtAlCl_2 (3.6)	1070	6.85	8.4
42d (0.008)	EtAlCl_2 (3.6)	856		
42b (0.07)	Et_2AlCl (3.6)	88	14.59	27.4
42c (0.07)	Et_2AlCl (3.6)	33		

^a Reaction conditions: toluene 150 mL, ethylene 0.5 MPa for 30 min.

Scheme 14

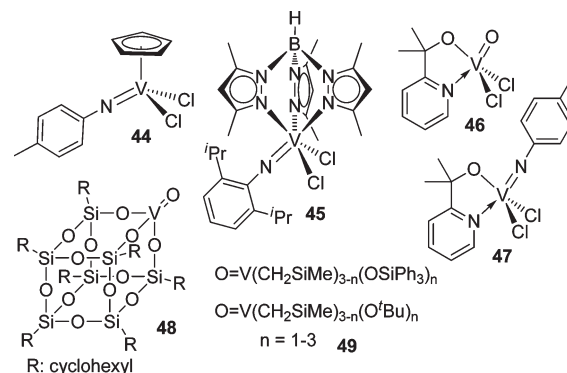


polymerizations is that hydrocarbyl compounds of vanadium(V) are easily reduced to lower-valent complexes.

(Arylimido)vanadium(V) seemed to be promising precursors in place of VOCl_3 , because a series of trichloride analogues, $\text{V}(\text{NAr})\text{Cl}_3$, can be prepared in high yields by treating VOCl_3 with various arylisocyanates (ArNCO) in octane under reflux conditions,^{74,75} and these complexes showed moderate thermal stability. In particular, Murphy and Turner demonstrated synthesis of $\text{V}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{Ph})_3$ from the trichloride, $\text{V}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}_3 \cdot (\text{THF})$, by treating with PhCH_2MgCl in hexane.⁷⁶ The reported fact is noteworthy, because the most common problem encountered in attempting 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 during the alkylation step, and the approach is useful for synthesis various vanadium(V)-alkyls.^{77,78}

Reported vanadium(V) complexes employed for ethylene polymerization until 2000 are summarized in Scheme 15.^{79–84} Gibson et al. reported the use of $[\text{CpV}(\text{N-4-MeC}_6\text{H}_3)\text{Cl}_2]$ (44) in ethylene polymerization with either Et_2AlCl or MAO as cocatalyst.⁷⁹ The activities at 25 °C were low (15 and 27 kg PE/(mol V·h), respectively; ethylene 1 bar in toluene), and no clear descriptions concerning molecular weights and their distribution in the resultant polymers were made. They reported later that the activities were improved by immobilization onto a polystyrene support through the arylimido ligand probably due to an improved stability of the catalytically active species.⁸⁰ An (arylimido)vanadium(V) complex containing a hydrotris-(pyrazolyl)borato ligand (Tp^*), $[\text{Tp}^*\text{V}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2]$ (45), polymerized ethylene (at 1 bar) and propylene (at 7 bar) in the presence of MAO.⁸¹ However, activities and molecular weights were low [14 kg PE/(mol V·h), $M_w = 47000$, $M_w/M_n = 3.0$; 7 kg PP/(mol V·h), $M_w = 3800$, $M_w/M_n = 2.0$]. The low

Scheme 15



catalytic activities shown in these reports would be considered as a consequence of the subsequent reduction of the catalytically active species in situ.

Ethylene polymerization using vanadium(V) complexes containing an O,N-chelating ligand along with either oxo (46) or imido (47) ligands were reported by van Koten and co-workers.⁸² Although the imido complex (47) showed low catalytic activities (4.8–13.2 kg PE/(mol V·h)), the oxo complex (46) showed higher activities (335–642 kg PE/(mol V·h)) under similar conditions (200 equiv of Et_2AlCl , ethylene 6 bar in toluene). The observed difference would be due to formation of different catalytically active species (with different oxidation states), but the activities of 46 and 47 were lower than those of $\text{V}(\text{N-4-MeC}_6\text{H}_4)\text{Cl}_3$ and VOCl_3 under the same conditions.

Feher et al. reported that vanadium-containing silsesquioxane (48) showed catalytic activity for ethylene polymerization in the presence of AlMe_3 as the cocatalyst affording polymer with unimodal distribution ($M_n = 21000$, $M_w = 47900$).⁸³ The presence of the silsesquioxane backbone is crucial, since the activities by the (oxo)vanadium(V)-alkyl complexes containing alkoxy or triphenylsiloxy ligands (48) were low: $\text{VO}(\text{OSiPh}_3)_3$ or $\text{VO}(\text{CH}_2\text{SiMe}_3)(\text{OSiPh}_3)_2$ showed negligible activity even in the presence of Al cocatalyst under the same conditions.⁸⁴ Although the oxidation state as well as nature of the catalytically active species were unclear, use of chelate (donor) ligands seems effective for efficient catalysts with better stability. Therefore, many examples use (oxo)vanadium(V) complexes containing chelate aryloxy/alkoxy ligands, as described below.

2.3.1. (Oxo)vanadium(V) or (Imido)complexes Containing Chelate Aryloxy/Alkoxy Ligands. (Oxo)vanadium(V) dichloride complexes containing amidinate (50) ligands, shown in Scheme 16, were used for propylene and 1,3-butadiene polymerization.⁸⁵ The activities in the propylene polymerization conducted at –60 °C were higher than that by VOCl_3 and the resultant polymer possessed syndiotactic-rich polymers if Et_2AlCl or Me_2AlCl were used as the cocatalyst: the resultant polymer was atactic in the presence of MAO. However, the activity decreased at 25 °C probably due to dissociation of the amidinate ligand. (Oxo)vanadium(V) complex containing the 2-(2-butoxyethoxy)ethanolate (51) ligand was also used for ethylene polymerization,⁸⁶ but the catalytic activity in the presence of Et_2AlCl cocatalyst was close to that by VOCl_3 even in the presence of $\text{Cl}_3\text{CO}_2\text{Et}$ (ETA) as reoxidant, and the resultant polymer possessed broad molecular weight distribution

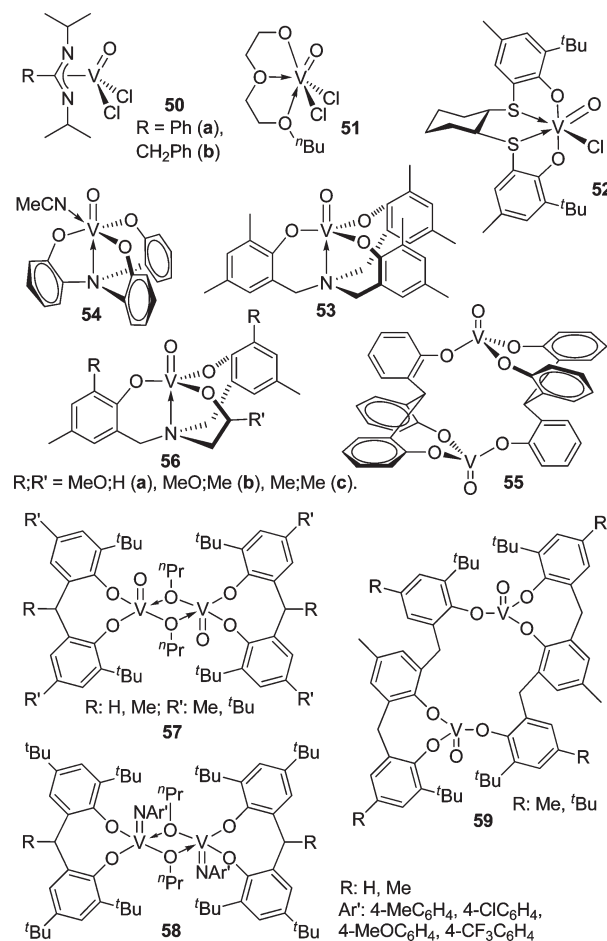
($M_w/M_n = 14.8$) with rather low molecular weights, clearly suggesting formation of several catalytically active species probably due to ligand dissociation.⁸⁶

In contrast, Okuda reported that an oxovanadium(V) complex containing an [OSSO]-type bis(phenolato) ligand (**52**) showed higher catalytic activities for ethylene polymerization in the presence of MAO cocatalyst, affording polymers with uniform molecular weight distributions.⁸⁷ Therefore, use of chelate aryloxo ligand seems to be effective for stabilization of the catalytically active species in the presence of Al cocatalysts, as also demonstrated by Redshaw below.^{10d}

The tripodal ligands shown in Scheme 16, specifically tris(3,5-di-*tert*-butyl-2-hydroxyphenyl/benzyl) methane (C-capped) and tris(2-hydroxyphenyl)amine (N-capped), utilized in a variety of polymerization studies, were used to prepare vanadyl C- and N-capped tris(phenolate) complexes by Redshaw and co-workers. The vanadyl procatalysts **53**–**55** were prepared via the reaction of the tripodal ligand with the alkoxide $[\text{VO}(\text{OPr}_n)_3]$.⁸⁸ The C-capped complex **55** was dimeric. In the presence of dimethylaluminum chloride (Me_2AlCl) and ethyltrichloroacetate ($\text{Cl}_3\text{CCO}_2\text{Et}$), **55** demonstrated significantly high activity ($123\,000\text{ kg}/(\text{mol}\cdot\text{h}\cdot\text{bar})$; 1 bar C_2H_4 , 0.2 mmol procatalyst, 80°C , 0.5 mmol Me_2AlCl , 0.5 mmol ETA for 15 min in 250 mL of toluene). However, **54** showed much lower activity ($2300\text{ kg}/(\text{mol}\cdot\text{h}\cdot\text{bar})$) relative to **55** under similar conditions, which might be due to the metal bond with MeCN. The attempt to remove the coordinated MeCN from the metal center was not successful. Introduction of an extra methylene group into each arm of the N-capped ligand allows access to the 5-coordinate vanadyl complex **53** without the coordination of any molecule like MeCN. The catalytic activity of **53** increased to $96\,500\text{ kg}/(\text{mol}\cdot\text{h}\cdot\text{bar})$. Polyethylene with very high molecular weight (M_w 5 180 000–8 670 000) was obtained by procatalysts **53**–**55** at 25°C , and a significant decrease was observed at 80°C with narrower molecular weight distribution. For ethylene/propylene copolymerization, much lower activities (highest activity $12\,400\text{ kg}/(\text{mol}\cdot\text{h}\cdot\text{bar})$ for **53**) were observed than ethylene polymerization with propylene incorporation of about 15%. More recently, (oxo)vanadium(V) complexes (**56**) containing a trianionic donor ligand, consisting of two aryloxo arms and a mono alkoxo arm, were also used as catalysts for ethylene polymerization and ethylene/norbornene copolymerization in the presence of Et_2AlCl and $\text{Cl}_3\text{CCO}_2\text{Et}$ (ETA, $\text{Al}/\text{ETA}/\text{V} = 4000/300/1$).⁸⁹ The methyl analogue (**56c**) showed the highest catalytic activity in ethylene polymerization.⁸⁹ Complex **56c** also showed moderate norbornene incorporation in the ethylene/norbornene copolymerization affording copolymers with uniform molecular weight distributions, although the observed catalytic activities in the copolymerization were lower than those in the ethylene homopolymerization.⁸⁹

Besides vanadyl C- and N-capped tris(phenolate) complexes, Redshaw et al. also reported a series of vanadyl-based catalysts (**57**–**65**), as shown in Schemes 16 and 17, for ethylene polymerization using phenolate ancillary chelate ligands.^{10d} Similarly, complexes **57** and **59**, bearing bi- and triphenolate chelate ligands, could be prepared from the reaction of the alkoxide $[\text{VO}(\text{OPr}_n)_3]$ and the parent di- or triphenol.⁹⁰ For **57** and **59**, the use of ETA resulted in a ca. 7-fold increase in activities, with a concomitant increase in thermal stability. The triphenolate

Scheme 16



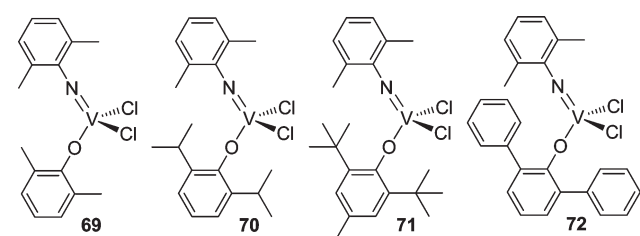
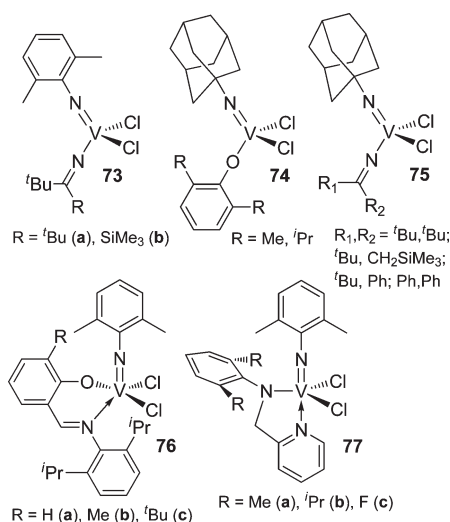
complex **59** showed much higher activity than biphenolate complex **57** as shown in Table 6. In order to know how the electronic and steric factors of procatalyst structure might affect the catalytic activity and control of the ethylene polymerization process, given that the oxo group is isoelectronic with the organoimido group, the related organoimido-containing species (for example, complex **58**) was investigated.⁹¹ Under similar conditions, the imido complexes **58** displayed higher activity than oxovanadium complex **57** (Table 6).

The air-stable oxo and imido vanadium complexes incorporating calyx[3]- or -[4]arenes **60**–**65** were prepared from the reaction of the alkoxides $[\text{V}(\text{O})(\text{OR})_3]$ and $[\text{V}(\text{N}-4\text{-MeC}_6\text{H}_4)(\text{OR})_3]_2$ and the parent LH_3 , respectively.^{10d,92} The dimeric complexes **60** and **61** incorporating calyx[3]arenes yield ultrahigh-molecular-weight ($M_w > 5\,500\,000$) linear polyethylene at 25°C . The activity increased about 4 times, and the molecular weight falls to less than 500 000 with molecular weight distribution decreasing from 3.4 to 2.0 at 80°C for **60**. A similar trend was also observed for **61**. Calix[4]-arene-based procatalysts **62**–**65** were at best an order of magnitude less active, and much lower molecular weight was observed than those observed for **60** and **61**; those containing two vanadium centers (**64** and **65**) exhibit the highest activity of this class. The vanadyl N-capped tris(phenolate) complex **66** showed much lower activity than **59** without imino groups because the presence of the “free” phenolic groups on each

Table 7. Ethylene Polymerization by V(*N*-2,6-Me₂C₆H₃)Cl₂(OAr') [Ar' = 2,6-Me₂C₆H₃ (69), 2,6-^{*i*}Pr₂C₆H₃ (70), 2,6-^{*t*}Bu₂-4-MeC₆H₂ (71), 2,6-Ph₂C₆H₃ (72)]–Cocatalyst Systems^{a,98–100}

complex (μmol)	Al cocat. (mmol)	solvent	temp, °C	activity ^b	<i>M_w</i> ^c × 10 ^{−5}	<i>M_w</i> / <i>M_n</i> ^c
69 (1.0)	MAO (2.5)	toluene	25	1770	2.73	4.65
69 (2.5)	MAO (2.5)	toluene	25	2930	17.5	1.64
70 (2.5)	MAO (2.5)	toluene	25	1050	2.38	4.92
70 (5.0)	MAO (2.0)	toluene	0	576	60.9	2.61
70 (5.0)	MAO (2.0)	toluene	25	967	20.3	2.73
70 (5.0)	MAO (2.0)	toluene	40	348		
70 (5.0)	MMAO (2.0)	<i>n</i> -hexane	25	208		
71 (5.0)	MAO (5.0)	toluene	25	242		
71 (2.0)	MAO (5.0)	toluene	60	486	7.84	2.07
72 (2.5)	MAO (2.5)	toluene	25	1090	2.65	3.89

^a Reaction conditions: solvent 30 mL, MAO (prepared by removing AlMe₃ and toluene from commercially available MAO) or MMAO (methylisobutyl aluminumoxane), ethylene 8 atm, 10 min. ^b Activity in kg polymer/(mol V·h). ^c GPC data in *o*-dichlorobenzene vs polystyrene standards.

Scheme 18**Scheme 19**

the type V(NAr)Cl₂(L), although early reports for ethylene polymerization using [CpV(*N*-4-MeC₆H₃)Cl₂] (44), [Tp*V(*N*-2,6-^{*i*}Pr₂C₆H₃)Cl₂] (45), and V(*N*-4-MeC₆H₃)Cl₂[2-OCMe₂-C₅H₄N] (47) were low.^{79–82} One reason we focused on this type is that a series of (arylimido)vanadium(V) complexes seemed to be promising available precursors (from VOCl₃ by treating with various arylisocyanates)^{74,75} with moderate thermal stability. Moreover, as demonstrated by Murphy and Turner,⁷⁶ the arylimido ligands would be effective for stabilization of the

Table 8. Ethylene Polymerization by V(*N*-2,6-Me₂C₆H₃)Cl₂[O-2-R-6-(2,6-^{*i*}Pr₂C₆H₃)N=CH]C₆H₃]–[R = H (76a), Me (76b), ^{*t*}Bu (76c)], V(*N*-2,6-Me₂C₆H₃)Cl₂[(2,6-R₂C₆H₃)NCH₂(C₅H₃N)]–[R = Me (77a), ^{*i*}Pr (77b), F (77c)], and V(NAr)Cl₂(O-2,6-Me₂C₆H₃) (69)–MAO Catalyst Systems^{a103,104}

catalyst R	MAO, mmol	temp, °C	activity ^b	<i>M_w</i> ^c × 10 ^{−5}	<i>M_w</i> / <i>M_n</i> ^c
H (76a)	3.0	25	380	16.6	2.8
Me (76b)	3.0	25	680	11.8	3.0
^{<i>t</i>} Bu (76c)	3.0	25	2150	12.2	3.1
^{<i>t</i>} Bu (76c)	3.0	50	400	4.69	4.3
69	3.0	25	880	12.7	3.4
Me (77a)	6.0	25	78	29.8	2.0
^{<i>i</i>} Pr (77b)	6.0	25	189	29.3	2.6
F (77c)	2.0	25	618	10.6	2.3

^a Reaction conditions: complex 1.0 μmol (69, 76) or 2.0 μmol (77), toluene 30 mL, ethylene 8 atm, 10 min, d-MAO (prepared by removing AlMe₃ and toluene from commercially available MAO) 3.0 mmol. ^b Activity = kg PE/(mol V·h). ^c GPC data in *o*-dichlorobenzene vs polystyrene standards.

oxidation during the alkylation step for synthesis of various vanadium(V)-alkyls by reaction with organometallic reagents, as demonstrated by us later.^{77,78} Another reason is the relevance of V(NAr)Cl₂(L) with our designed nonbridged half-titanocenes containing an anionic donor ligand of type Cp'TiCl₂(L') (Cp' = cyclopentadienyl, L' = aryloxo, ketimide, etc.),^{9b,9c,96–99} which are known to display unique characteristics especially for ethylene copolymerizations.^{9b,9c,96,97}

We first reported that (arylimido)vanadium(V) complexes containing aryloxo ligands, V(NAr)Cl₂(OAr') [Ar = 2,6-Me₂C₆H₃, OAr' = O-2,6-Me₂C₆H₃ (69), O-2,6-^{*i*}Pr₂C₆H₃ (70), O-2,6-^{*t*}Bu₂-4-MeC₆H₂ (71), O-2,6-Ph₂C₆H₃ (72), Scheme 18], exhibited notable activities for ethylene polymerization in the presence of MAO, affording ultrahigh molecular weight linear polyethylene with uniform molecular weight distributions (Table 7).^{98–100} The substituents on the aryloxo ligand affected the catalytic activity, and the activities were also affected by the Al/V molar ratio and temperature; 69 showed the highest activity and the activity decreased at 0 and 40 °C.

Table 9. Ethylene Polymerization Catalyzed by $\text{VCl}_2(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{O-2,6-Me}_2\text{C}_6\text{H}_3)$ (69**)–Al Cocatalyst Systems: Effect of Al Cocatalyst^{a100,105}**

69, μmol	Al cocat.	time, min	polymer yield, mg	activity, ^b $\times 10^{-3}$	TOF, ^c $\times 10^{-5}$	M_w , ^d $\times 10^{-5}$	M_w/M_n ^d	M_η , ^e $\times 10^{-6}$
1.0	MAO	10	488	2.93	1.04	28.7	1.64	
0.05	Me_2AlCl	10	229	27.5	9.8	<i>e</i>		8.98
0.05	Et_2AlCl	10	97	11.7	4.15	36.5	1.42	
0.05	Et_2AlCl	30	284	11.4	4.06			
0.05 ^f	Et_2AlCl	10	9	1.08	0.4			
0.05	$^i\text{Bu}_2\text{AlCl}$	10	433	52.0	18.5	<i>e</i>		9.87
0.01	$^i\text{Bu}_2\text{AlCl}$	10	108	64.8	23.1	<i>e</i>		12.5
0.05	EtAlCl_2	10	312	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	$^i\text{Bu}_3\text{Al}$	10	trace					

^a Reaction conditions: toluene + cocatalyst solution = 30 mL, 0 °C (or 25 °C for 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 vs polystyrene standards. ^e Molecular weight by viscosity because the resultant polymers were insoluble in *o*-dichlorobenzene for GPC measurement. ^f Polymerization in the copresence of $\text{CCl}_3\text{CO}_2\text{Et}$ (10.0 equiv to V).

Table 10. Solvent Effect in Ethylene Polymerization by $\text{VCl}_2(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{O-2,6-Me}_2\text{C}_6\text{H}_3)$ (69**)–Al Cocatalyst Systems^{a105}**

69, μmol	Al cocat	solvent	ethylene, atm	activity ^b	TOF, ^c $\times 10^{-4}$	M_w , ^d $\times 10^{-5}$	M_w/M_n ^d
0.05	Et_2AlCl	<i>n</i> -hexane	8	2760	9.86		
0.05	$^i\text{Bu}_2\text{AlCl}$	<i>n</i> -hexane	8	6720	24.0	26.1	3.19
0.05	EtAlCl_2	<i>n</i> -hexane	8	47300	169	13.7	3.85
0.05	Me_2AlCl	toluene	8	27500	98.0	<i>e</i>	
0.05	Et_2AlCl	toluene	8	11700	41.5	36.5	1.42
0.05	$^i\text{Bu}_2\text{AlCl}$	toluene	8	52000	185	<i>e</i>	
0.05	EtAlCl_2	toluene	8	37400	133	6.02	3.04
0.05	Me_2AlCl	$\text{C}_6\text{H}_5\text{Cl}$	8	19400	69.4	20.0	3.46
0.05	Me_2AlCl	$\text{C}_6\text{H}_5\text{Cl}$	8	19800	70.6		
0.05	Et_2AlCl	$\text{C}_6\text{H}_5\text{Cl}$	8	19000	67.7	<i>e</i>	
0.05	$^i\text{Bu}_2\text{AlCl}$	$\text{C}_6\text{H}_5\text{Cl}$	8	15800	56.5	5.63	3.80
0.05	EtAlCl_2	$\text{C}_6\text{H}_5\text{Cl}$	8	64400	230	24.4	3.14
0.05	Me_2AlCl	CH_2Cl_2	8	19700	70.2	24.2	3.38
0.05	Et_2AlCl	CH_2Cl_2	8	13200	47.1	13.4	3.93
0.05	$^i\text{Bu}_2\text{AlCl}$	CH_2Cl_2	8	45200	161	<i>e</i>	
0.01	EtAlCl_2	CH_2Cl_2	8	584000	2080	<i>e</i>	
0.01	EtAlCl_2	CH_2Cl_2	2	224000	800	12.2	2.33

^a Reaction conditions: solvent + cocatalyst solution = total 30 mL, ethylene 8 atm, 0 °C, 10 min, Al cocatalyst 250 μmol . ^b Activity in kg polymer/(mol V·h). ^c TOF = (molar amount of ethylene consumed)/(mol V·h). ^d GPC data in *o*-dichlorobenzene vs polystyrene standards. ^e Insoluble in *o*-dichlorobenzene for GPC measurement.

The catalytic activities in the propylene polymerization by **70** were significantly lower than those in the ethylene polymerization, and the resultant polymers possessed relatively high molecular weights with unimodal molecular weight distributions.⁹⁹ However, ¹³C NMR spectra for the resultant polypropylene showed that these polymers possessed no stereoregularity and contained both 1,2- and 2,1-inserted units (irregular oil). The activity in the 1-hexene polymerization by **70** at 25 °C was lower than those in both ethylene and propylene polymerizations (2.03 kg PH/(mol V·h)), although the resultant polymer possessed unimodal molecular weight distribution. The resultant polymer had no stereoregularity and contained both 1,2- and 2,1-inserted units.⁹⁹ Complex **70**–MAO catalyst showed extremely low activity for styrene polymerization.

Ethylene polymerizations using the ketimide analogues, $\text{V}(\text{NAr})\text{Cl}_2[\text{N}=\text{C}^i\text{Bu}(\text{R})]$ [**73**, R = ^{*i*}Bu (**a**), CH_2SiMe_3 (**b**)] were explored, and the activities [activity 666 kg PE/(mol V·h) (**73a**), 985 kg PE/(mol V·h) (**73b**)] were lower than that of **69** (2930 kg PE/(mol V·h)) under the similar conditions.¹⁰¹ The (adamantylimido)vanadium(V) dichloride complexes (Scheme 19) containing aryloxo (**74**) and ketimide (**75**) ligands were also explored as the catalyst precursors for ethylene polymerization in the presence of MAO, but their activities were low, and the resultant polymer possessed bimodal or multimodal molecular weight distributions, clearly suggesting that several catalytically active species play a role in the mixture.¹⁰² These ligand systems would not be suited as catalyst precursors for the ethylene polymerization in the presence of MAO.

The catalytic activities of the phenoxy-imine analogue (76a–c)–MAO catalyst systems were strongly affected by the ortho substituent in the phenoxy ligand (Table 8), and the activity increased in the order 380 (76a, R = H) < 680 (76b, R = Me) < 2150 kg PE/(mol V·h) (76c, R = ^tBu).¹⁰³ It is simply speculated that the ortho substituent stabilizes the catalytically active species, as assumed from the structural analysis, in which the Cl–V–Cl bond angle in 76c (90.49°) is smaller than those in 76a,b (91.97, 91.25°). The observed activity by 76c at 25 °C (2150 kg PE/(mol V·h)) was higher than that by the aryloxo analogue (69, 880 kg PE/(mol V·h)) under the same conditions.¹⁰³ The resultant polymers prepared at 25 °C possessed high molecular weights with unimodal molecular weight distributions ((1.18–1.66) × 10⁶, *M_w*/*M_n* = 2.8–3.1).¹⁰³ The (arylimido)vanadium complexes containing (2-anilidomethyl)-pyridine ligands (77) also exhibited moderate catalytic activities for ethylene polymerization in the presence of MAO (Table 8), and the activities increased in the order 78 (77a, R = Me) < 189 (77b, R = ⁱPr) < 618 kg PE/(mol V·h) (77c, R = F).¹⁰⁴ The resultant polymers possessed high molecular weights with unimodal molecular weight distributions.

Note that the arylimido–aryloxo analogues showed remarkable catalytic activities for ethylene polymerization in the presence of halogenated Al alkyls (Et₂AlCl, Me₂AlCl, EtAlCl₂ etc.), affording ultrahigh molecular weight polymers with uniform distributions.^{99,100,105,106} The selected results in toluene using V(NAr)Cl₂(O-2,6-Me₂C₆H₃)–Al cocatalysts systems are summarized in Table 9.^{100,105}

The activity in the ethylene polymerization was highly dependent upon the Al cocatalyst employed, and the activities in toluene increased in the order Et₂Al(OEt), Me₃Al, Et₃Al (trace

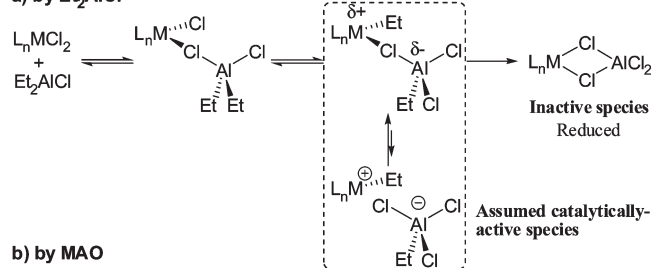
or less) < MAO (2930) < Et₂AlCl (11 700) < Me₂AlCl (27 500) < EtAlCl₂ (37 400) < ⁱBu₂AlCl (52 000 kg PE/(mol V·h)). The activity was also highly affected by the solvent employed, as shown in Table 10;¹⁰⁵ an activity of 584 000 kg PE/(mol V·h) (TOF 20 800 000 h^{−1}, 5780 s^{−1}) was attained in CH₂Cl₂ in the presence of EtAlCl₂.¹⁰⁵ The resultant polymers prepared in toluene possessed ultrahigh molecular weights with unimodal molecular weight distributions (the *M_n* values in the resultant polymers prepared in the presence of ⁱBu₂AlCl and Me₂AlCl were (9.87–12.5) × 10⁶ and 8.98 × 10⁶, respectively).

Similarly, the catalytic activities in the ethylene polymerization using (77a–c)–Et₂AlCl catalyst systems were also much higher than those in the presence of MAO,¹⁰⁴ and the activity (ethylene 8 atm, Et₂AlCl/V = 100 or 200 at 0 °C) increased in the order 77c (156, R = F) < 77a (840 kg PE/(mol V·h), R = Me) < 77b (6000, R = ⁱPr). The order is somewhat different from that observed in the presence of MAO (77a < 77b < 77c). The resultant polymers possessed ultrahigh molecular weights with uniform distributions (*M_w* = (2.18–3.12) × 10⁶, *M_w*/*M_n* = 2.7–4.1).¹⁰⁴ However, the activities in the ethylene polymerization by the ketimide analogues (75) in the presence of Et₂AlCl were similar or somewhat lower than those in the presence of MAO.¹⁰¹ This would be assumed as partial decomposition of the imino group by Al alkyls that are often observed in the complexes containing bis(phenoxy-imine) ligands.¹⁰⁷

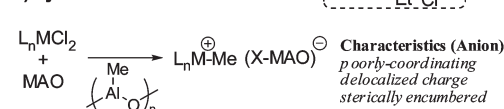
The activity of the 69–Et₂AlCl catalyst system decreased upon addition of CCl₃CO₂Et, which can be commonly used as an effective additive (for restarting the catalytic cycle from the deactivated catalyst by reoxidation to a higher oxidation state) in the ethylene polymerization using vanadium(III) or vanadium(IV) complexes like V(acac)₃ (acac = acetylacetonato) or V(β-diketonate)₃.^{10,30} The results clearly suggest that the catalytically active species were thus different from those generated from vanadium(III)/(IV) complexes. We assumed that a plausible reason for the observed difference in the catalytic activities in the

Scheme 20

a) by Et₂AlCl



b) by MAO



Scheme 21

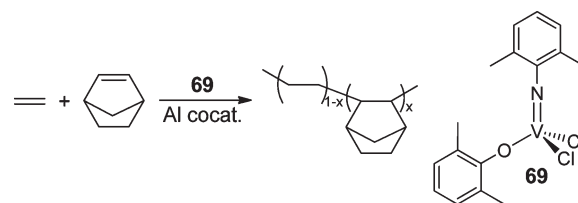


Table 11. Copolymerization of Ethylene with Norbornene (NBE) by VCl₂(N-2,6-Me₂C₆H₃)(O-2,6-Me₂C₆H₃) (69)–Al Cocatalyst Systems^{a100}

69, μmol	NBE, mmol/mL	cocatalyst	activity ^b	<i>M_n</i> ^c × 10 ^{−5}	<i>M_w</i> / <i>M_n</i> ^c	NBE, ^d mol %
1.0	0.3	MAO	1560	7.78	1.85	15.9
0.05	0.3	Et ₂ AlCl	27800	22.8	1.5	5.9
1.0	0.5	MAO	876	2.99	1.79	23.9
0.05	0.5	Et ₂ AlCl	31700	25.4	1.29	10.4
2.5	1.0	MAO	367	1.10	1.85	32.9
0.05	1.0	Et ₂ AlCl	24000	22.9	1.53	17.3

^a Polymerization conditions: toluene 30 mL, ethylene 8 atm, MAO 2.50 mmol or Et₂AlCl 0.25 mmol, 0 °C (Et₂AlCl) or 25 °C (MAO), 10 min. ^b Activity in kg polymer/(mol V·h). ^c GPC data in *o*-dichlorobenzene vs polystyrene standards. ^d NBE content in mol % estimated by ¹³C NMR spectra.

presence of MAO or Et₂AlCl cocatalyst might be due to the different catalytically active species or catalyst/cocatalyst nuclearity effect (Scheme 20)^{10c,10d,108} generated in the two catalyst systems.

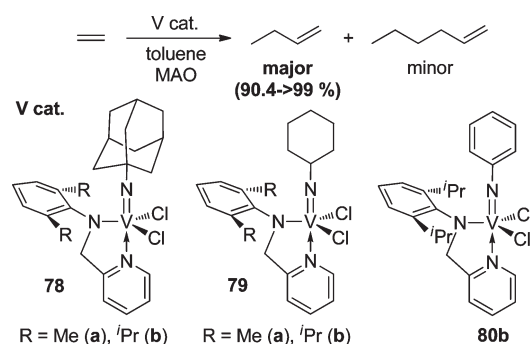
It should also be noted that the aryloxo analogue, V(NAr)Cl₂-(O-2,6-Me₂C₆H₃) (69), exhibited both remarkable catalytic activities and efficient norbornene (NBE) incorporation in the ethylene/NBE copolymerization (Scheme 21, Table 11).¹⁰⁰ Notable effects of Al cocatalyst were observed in the copolymerization: the activities, the NBE incorporation, dominant chain transfer reactions, and the M_n values for resultant copolymers were highly dependent upon the Al cocatalyst employed (MAO or Et₂AlCl). The complex 69–Et₂AlCl catalyst system exhibited remarkable catalytic activities, affording ultrahigh molecular weight poly(ethylene-co-NBE)s with narrow molecular weight distributions (M_n = (2.12–2.70) × 10⁶, M_w/M_n = 1.29–1.53), and the M_n values were independent of the NBE contents but were dependent upon the Al/V molar ratios. In contrast, the 69–MAO catalyst exhibited better NBE incorporation than the 69–Et₂AlCl catalyst, and the M_n value was independent of the Al/V molar ratio but was dependent upon the NBE contents. Modification of the aryloxo ligand affected the catalytic activity but did not strongly affect the NBE incorporation, the M_n values,

and the microstructure in the resultant copolymers.¹⁰⁰ Later, we found that both the activity and the NBE incorporation were highly affected by Al cocatalyst as well as solvent employed.^{100,105} The facts were also assumed to be explained as the catalyst/cocatalyst nuclearity effect,¹⁰⁸ although the details are not clear at this moment.

3. HIGHLY EFFICIENT ETHYLENE DIMERIZATION CATALYZED BY THE (IMIDO)VANADIUM(V) COMPLEXES CONTAINING (2-ANILIDOMETHYL)PYRIDINE LIGAND

More recently, we reported that the (imido)vanadium(V) complexes containing a (2-anilidomethyl)pyridine ligand, V(NR)Cl₂[2-ArNCH₂(C₅H₄N)] [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 90.4% to >99%, Scheme 22).¹⁰⁹ As shown in Table 12, the adamantyl imido analogues showed the highest activities (TOF 2 730 000 h^{−1} for 78a and 1 280 000 h^{−1} for 78b) for ethylene dimerization. The activity was affected by the Al/V molar ratio, the reaction temperature, and the ethylene pressure employed. Since the selectivity of 1-butene seems to be decreasing (or that of 1-hexene increases) for prolonged time as well as upon an increase of 1-butene accumulated in the reaction solution, it is

Scheme 22



Scheme 23

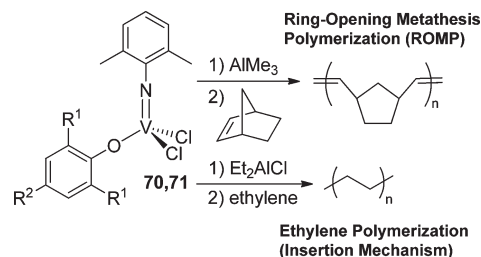


Table 12. Ethylene Dimerization by V(NR)Cl₂[2-ArNCH₂(C₅H₄N)] (78a,b, 79a,b, 80b, 77b)–MAO Catalyst Systems^{a,109}

complex (μmol)	R	time, min	Al/V ^b	activity ^c	TOF, ^d (mol V · h) ^{−1}	C ₄ ^f , % ^e	C ₆ ^f , % ^e
78a (0.5)	Ad	10	100	1350	48200	94.0	6.0
78a (0.5)	Ad	10	200	50600	1810000	94.9	5.1
78a (0.5)	Ad	10	500	51100	1830000	92.5	7.5
78a (0.5)	Ad	10	1000	40400	1440000	95.5	4.5
78a (0.5)	Ad	10	2000	6780	242000	95.0	5.0
78a (0.1)	Ad	10	1000	45800	1640000	98.0	2.0
78a (0.1)	Ad	10	1500	76500	2730000	97.0	3.0
78a (0.1)	Ad	60	1500	74800	2670000	92.1	7.9
78b (0.5)	Ad	10	1000	35700	1280000	92.1	7.9
79a (0.5)	Cy	10	200	28200	1010000	93.2	6.8
79b (0.5)	Cy	10	200	32300	1150000	95.9	4.1
80b (0.5)	Ph	10	500	18300	654000	95.1	4.9
77b (2.0)	2,6-Me ₂ C ₆ H ₃	10	500	42	1500	PE	
77b (2.0)	2,6-Me ₂ C ₆ H ₃	10	1000	66	2350	PE	
77b (2.0)	2,6-Me ₂ C ₆ H ₃	10	3000	189	6740	PE	

^a Reaction conditions: toluene 30 mL, ethylene 8 atm; 25 °C, MAO white solid [prepared by removing AlMe₃ and toluene from PMAO-S (commercial sample)]. ^b Al/V molar ratio. ^c Activity in kg ethylene/(mol V · h). ^d TOF (turnover frequency) = (molar amount of ethylene reacted)/(mol V · h). ^e By GC analysis vs internal standard.

Table 13. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene by Various Vanadium Complex V(NAr)Cl₂-(L)-MeMgBr-PMe₃ Catalyst Systems^{a110}

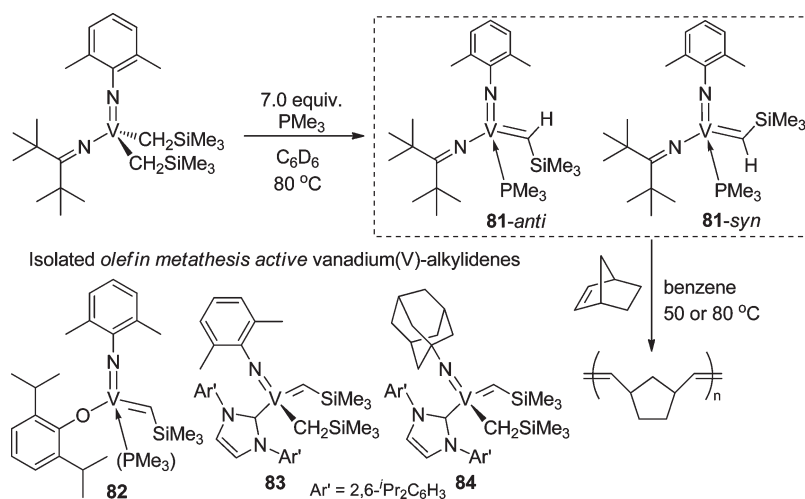
complex (μ mol)	Ar	L	temp./ $^{\circ}$ C	TON ^b	$M_n^c \times 10^{-4}$	M_w/M_n^c
73a (0.2)	2,6-Me ₂ C ₆ H ₃	N=C ^t Bu ₂	25	6850	158	1.50
73a (0.2)	2,6-Me ₂ C ₆ H ₃	N=C ^t Bu ₂	50	8820	67	2.13
73a (0.2)	2,6-Me ₂ C ₆ H ₃	N=C ^t Bu ₂	80	7010	91	1.87
73b (1.0)	2,6-Me ₂ C ₆ H ₃	N=C(CH ₂ SiMe ₃) ^t Bu	50	330	69	1.83
69 (0.2)	2,6-Me ₂ C ₆ H ₃	O-2,6-Me ₂ C ₆ H ₃	50	7440	154	1.46
70 (1.0)	2,6-Me ₂ C ₆ H ₃	O-2,6- ⁱ Pr ₂ C ₆ H ₃	50	390	35	2.25
71 (1.0)	2,6-Me ₂ C ₆ H ₃	O-2,6- ^t Bu ₂ -4-MeC ₆ H ₂	50	trace		

^a Reaction conditions: complex 0.20 or 1.0 μ mol, benzene 4.8 mL, NBE 200 mg (NBE/V molar ratio = 10600 or 2120), 50 $^{\circ}$ C, 40 min, PMe₃/MeMgBr/V = 1.0/2.1/1.0 (molar ratio). ^b TON = (molar amount of NBE consumed)/(mol V). ^c GPC data in THF vs polystyrene standards.

Table 14. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE) by V(NAd)Cl₂(L) [L= O-2,6-Me₂C₆H₃, O-2,6-ⁱPr₂C₆H₃, N=C^tBu₂, N=C(^tBu)CH₂SiMe₃]-MeMgBr-PMe₃ Catalyst Systems^{a102}

complex (μ mol)	temp, $^{\circ}$ C	time, min	yield, mg	TON ^b	$M_n^c \times 10^{-4}$	M_w/M_n^c
O-2,6-Me ₂ C ₆ H ₃ (1.0)	25	40	58.2	619	11.0	1.88
O-2,6-Me ₂ C ₆ H ₃ (1.0)	50	40	65.7	699	6.0	1.85
O-2,6- ⁱ Pr ₂ C ₆ H ₃ (1.0)	50	40	3.0	30	81.3	1.53
N=C ^t Bu ₂ (1.0)	50	25	144.9	1541	7.5	2.77
N=C(^t Bu)CH ₂ SiMe ₃ (1.0)	50	15	115.4	1223	13.0	3.03
N=C(^t Bu)CH ₂ SiMe ₃ (0.2)	50	10	82.0	4361	17.2	3.57

^a Reaction conditions: benzene 5.0 mL, NBE 200 mg, PMe₃/MgBr/V = 1.0/2.1/1.0 (molar ratio). ^b TON (turnover number) = NBE consumed (mmol)/mmol V. ^c GPC data in *o*-dichlorobenzene vs polystyrene standards.

Scheme 24

thus assumed that 1-hexene would be produced by the reaction of preformed with 1-butene and ethylene.

Also note that the cyclohexylimido analogues (**79a,b**) showed high activities, affording 1-butene with high selectivities (TOF $1\,010\,000\text{ h}^{-1}$ for **79a** and $1\,150\,000\text{ h}^{-1}$ for **79b**). The phenylimido analogue **80b** also afforded 1-butene as the major product under the same conditions although the activities were low, whereas the 2,6-dimethylphenylimido analogue (**77**) afforded polyethylene under the same conditions. These results thus clearly indicate that (1) the electronic nature of the imido ligand

directly affects the activity [**78a,b** ($\text{R} = \text{Ad}$) > **79a,b** ($\text{R} = \text{Cy}$) > **80b** ($\text{R} = \text{Ph}$)], and (2) the steric bulk of the imido substituents plays an essential role in the selectivity of this catalyst.¹⁰⁹

4. (IMIDO)VANADIUM COMPLEXES AS THE CATALYSTS FOR RING-OPENING METATHESIS POLYMERIZATION

Although the (arylimido)vanadium(V)-dichloride complexes containing an aryloxy ligand, $\text{V}(\text{NAr})\text{Cl}(\text{OAr}')$ (**69–71**),

showed negligible catalytic activity for ethylene polymerization in the presence of AlMe_3 , ring-opening metathesis polymerization (ROMP) of norbornene (NBE) took place in the presence of these catalyst systems. The facts clearly suggest that effective catalyst precursors for both olefin coordination insertion (catalyzed by cationic alkyl species) and olefin metathesis polymerization (catalyzed by alkylidene species) can be modified by selecting the Al cocatalyst (Scheme 23). The observed catalytic activities were low [TON (turnover number) = 22 (by **70**) or 29 (by **70**) after 30 min at 25 °C, $\text{AlMe}_3/\text{V} = 5$ or 10]⁹⁹ despite the resultant polymers possessing relatively high molecular weights with unimodal molecular weight distributions ($M_n = (4.0\text{--}8.5) \times 10^4$, $M_w/M_n = \text{ca. } 2.0$).⁹⁹

Later, higher catalytic activities were observed when these polymerizations were conducted in benzene in the presence of MeMgBr and PMe_3 in place of AlMe_3 .¹¹⁰ Effects of anionic donor ligands (L) and substituents on the arylimido ligands toward the activity in the ROMP using $\text{V}(\text{NAr})\text{Cl}_2(\text{L})$ [$\text{L} = \text{N}=\text{C}^t\text{Bu}_2$ (**73a**), $\text{N}=\text{C}(\text{CH}_2\text{SiMe}_3)^t\text{Bu}$ (**73b**), *O*-2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**69**), *O*-2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ (**70**), *O*-2,6- $t\text{Bu}_2$ -4- MeC_6H_2 (**71**)]- MeMgBr - PMe_3 were explored (Table 13);¹¹⁰ both **73a** and **69** showed remarkable activities, and the trends were somewhat similar to those observed in ethylene polymerization using $\text{V}(\text{NAr})\text{Cl}_2(\text{L})$ -MAO catalyst systems.^{98,101} The catalytic activity increased at 50 °C but decreased at 80 °C probably due to decomposition of catalytically active species under these conditions.¹¹⁰ The catalyst system also showed activity for ROMP of norbornadiene. The adamantylimido analogues containing aryloxo or ketimide ligands also exhibited moderate catalytic activities for ROMP of norbornene in the presence of MeMgBr and PMe_3 (Table 14).¹⁰² However, the catalytic activities (TONs) were lower than the arylimido analogues under the same conditions. On the basis of these results in the ROMP, it is clear that the catalytically active species effective for ethylene (co)polymerization can be tuned for effective catalysis in ROMP of norbornene.

It was then revealed that the reaction of $\text{V}(\text{NAr})(\text{CH}_2\text{SiMe}_3)_2$ ($\text{N}=\text{C}^t\text{Bu}_2$), prepared from the dichloro analogue (**73a**) by treating with $\text{LiCH}_2\text{SiMe}_3$, with PMe_3 (7.0 equiv) in benzene- d_6 at 80 °C afforded the alkylidene complex, $\text{V}(\text{CHSiMe}_3)(\text{NAr})(\text{N}=\text{C}^t\text{Bu}_2)(\text{PMe}_3)$ (**81**, a mixture of *syn/anti* form in solution), by α -hydrogen elimination (Scheme 24).^{77a,78} This is the common method to prepare high-oxidation-state metal alkylidenes by promoting α -hydrogen abstraction reactions from metal alkyl complexes lacking β -hydrogens, and addition of PMe_3 was required to promote the abstraction by steric crowding.¹¹¹ The complex (**81**) exhibited remarkable catalytic activity for ROMP of NBE without cocatalyst.^{77a} The activity (turnover number, TON) was low when the ROMP was conducted at 25 °C, but the activity markedly increased at higher temperature (80 °C), and the observed activity was higher than that by $\text{Ru}(\text{CHPh})(\text{Cl})_2(\text{PCy})_2$ under the same conditions due to the improved thermal stability. The aryloxo analogues (**82**)^{77c} and (imido)vanadium(V)-alkyl-alkylidene complexes (**83,84**),^{77d} as shown in Scheme 24, were also prepared in an analogous manner and these complexes also showed catalytic activities for ROMP of norbornene without any additional cocatalysts. In particular, the ROMP by **82** proceeded in a living manner at 25 °C.^{77c} These results also indicate that these vanadium(V) complexes were effective for both olefin coordination insertion polymerization and metathesis polymerization under appropriate conditions (for generating the catalytically active species).⁷⁸

5. SUMMARY AND OUTLOOK

Reported examples for olefin polymerization using various vanadium complex-cocatalyst systems have been reviewed. Most of the examples were focused on the vanadium(III) complexes based on the relevance of the proposed catalytically active species in the polymerization using classical Ziegler-type vanadium catalysts, and some systems exhibited remarkable catalytic activities even in the presence of a small amount of Al alkyls such as Et_2AlCl or Me_2AlCl affording high molecular weight polymers with unimodal molecular weight distributions. As described above, improvement of stabilization of (the oxidation state in) the catalytically active species by ligand modifications plays a key role in designing efficient vanadium(III) complex catalysts, although the mechanistic details are still not clear even at this stage. Most of the catalyst systems with vanadium(III) complexes required the presence of reoxidants such as $\text{Cl}_3\text{CCO}_2\text{Et}$ for the polymerization without significant decrease at the initial stage. Efficient complex catalyst systems without these additives should be required on the basis of better understanding of the active species in this catalysis. Although many examples were known recently concerning syntheses of vanadium complexes and their use as catalyst precursors for ethylene (co)polymerization, K.N. personally believes that examples for the mechanistic details as well as catalyst systems that exhibit unique characteristics seen in the classical systems in the 1960s have been very limited. These have to be considered for designing the new generation catalysts.

(Arylimido)(aryloxo)vanadium(V) complexes containing anionic ancillary donor ligands are highly effective not only for ethylene polymerization but also for ethylene/norbornene copolymerization affording copolymers with uniform distributions. Halogenated Al alkyls (Et_2AlCl , etc.) were more suited as cocatalysts than methylaluminoxane (MAO) for ethylene (co)polymerization, affording exceptionally high molecular weight polymers with narrow unimodal molecular weight distributions. Both Al cocatalyst and solvent directly affect the catalytic activity and comonomer incorporation, probably due to so-called catalyst/cocatalyst nuclearity effect. Highly effective ethylene dimerization complex catalysts can be tuned by modification of the imido ligand: the (adamantylimido)vanadium(V) complexes containing a (2-anilidomethyl)pyridine ligand exhibited notable catalytic activities for ethylene dimerization, and a notable effect of the imido ligand toward both the activity and selectivity was demonstrated in this catalysis. On the basis of these facts, it is clear that modification of ligands plays an essential role in this catalysis for olefin polymerization/oligomerization. These (imido)vanadium(V) complexes can be tuned from efficient catalysts for olefin insertion polymerization into efficient catalysts for ring-opening metathesis polymerization (ROMP) of cyclic olefins by modification of organometallic cocatalysts (Al, Mg). The authors believe that many unique characteristics using this catalysis can be demonstrated especially recently; the subject will expand many possibilities for establishment of more efficient and precise catalytic processes as well as for better understanding in organometallic chemistry of vanadium.

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