Synthesis of Pentavalent Imidovanadium Complexes and Their Catalyses for the Polymerization of Ethylene and Propylene

Yoshinori Sato, Yuushou Nakayama, Hajime Yasuda

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

ABSTRACT: Imidovanadium complexes with cyclopentadienyl (Cp) ligands—(Cp)V($=$NC$_6$H$_4$Me-4)Cl$_2$ (**1**), (Cp)V($=$N^{t}Bu)Cl$_2$ (**2**), and (^{t}BuCp)V($=$N^{t}Bu)Cl$_2$ (**3**; ^{t}BuCp = *tert*-butylcyclopentadienyl)—were synthesized through the reaction of imidovanadium trichloride with (trimethylsilyl)cyclopentadiene derivatives. The molecular structure of **3** was determined by X-ray crystallography. The monocyclopentadienyl complex **1** exhibited moderate activity in combination with methylaluminoxane [MAO; 10.3 kg of polyethylene (mol of V)$^{-1}$ h^{-1} atm^{-1}], whereas similar complexes with bulky ^{t}Bu groups, **2** and **3**, were less active. (2-Methyl-8-quinolinolato)imidovanadium complexes, V($=$NR)(OˆN)Cl$_2$ (R = C$_6$H$_3$^{i}Pr$_2$-2,6 (**4**) or *n*-hexyl (**5**), OˆN = 2-methyl-8-quinolinolato), were obtained from the reaction of imidovanadium trichloride with 2-methyl-8-quinolinol. Upon activation with modified MAO, complex **4** showed moderate activities for the polymerization of ethylene at room temperature. The complex **5**/MAO system also exhibited moderate activity at 0°C. The polyethylenes obtained by these complexes had considerably high melting points, which indicated the formation of linear polyethylene. Moreover, the **5**/dried MAO system showed propylene polymerization activities and produced polymers with considerably high molecular weights and narrow molecular weight distributions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1008–1015, 2005

Key words: catalysts; crystal structures; polyethylene (PE); poly(propylene) (PP)

INTRODUCTION

Imido ligands have been widely used for stabilizing high-valence transition-metal complexes and have played an important role in the development of olefin metathesis and ring-opening metathesis polymerization (ROMP) catalysts.[1] For example, a Schrock catalyst of group 6 metals with sterically hindered imido and alkoxy ligands enables the highly stereoselective polymerization of norbornene.[2] Imido ligands are also effective for the stabilization of high-valence group 5 metals such as vanadium. Imidovanadium(V) chloride complexes, V($=$NR)Cl$_3$ (R = alkyl or aryl), are synthesized from the reaction of VOCl$_3$ with RN$=$C$=$O by refluxing in octane.[3] In 1995, the first alkylvanadium(IV) complex with an imido ligand was isolated and structurally characterized.[4] Teuben et al.[3] synthesized the first imidovanadium(V) alkylidene complex, CpV($=$NAr)($=$CHPh)(PMe$_3$) (Cp = cyclopentadienyl, Ar = C$_6$H$_3$^{i}Pr$_2$-2,6), and confirmed its structure by X-ray crystallography. However, the benzylidene complex showed no activity for the ROMP of norbornene and was inert to acetone.

In recent years, several imidovanadium complexes have been reported to be catalytically active for the polymerization of ethylene. Kress et al.[5] synthesized imidovanadium(V) complexes with hydrotris(pyrazolyl)borate (Tp) ligands, which were moderately active for ethylene polymerization upon activation with methylaluminoxane (MAO). Lorber et al.[6] reported that a combination of Cp-free imidovanadium(IV), V($=$NAr)Cl$_2$(NHMe$_2$)$_2$, with AlEt$_2$Cl showed relatively high activity for ethylene polymerization at room temperature. In 2001, Nomura et al.[7] demonstrated that (arylimido)(aryloxy)vanadium(V) dichloride/dried methylaluminoxane (d-MAO) systems also exhibited similar activities for ethylene polymerization and produced high-molecular-weight polymers. A dibenzyl complex, V($=$NC$_6$H$_3$Me$_2$-2,6)(OC$_6$H$_3$^{i}Pr$_2$-2,6)(CH$_2$Ph)$_2$, was also synthesized by the treatment of its tribenzyl analogue, V($=$NC$_6$H$_3$Me$_2$-2,6)(CH$_2$Ph)$_3$, with 1 equiv of 2,6-^{i}Pr$_2$C$_6$H$_3$OH. This complex showed high activities for the ROMP of norbornene without a cocatalyst.[7] A few studies about the ethylene polymerization activities of pentavalent monocyclopentadienyl imidovanadium complexes were reported by Gibson and coworkers.[8–10] However, this type of cat-

alyst tends to be thermally unstable. In their study, a polystyrene support system was found to be effective for the stabilization of the active species for the ethylene polymerization and resulted in an improvement of the catalytic lifetime and activities.[11] In this study, we synthesized several new alkylimido and arylimido vanadium complexes with cyclopentadienyl ligands to investigate the substituent effect on their catalytic activity toward ethylene polymerization. We also prepared imidovanadium complexes with a 2-methyl-8-quinolinolate ligand and studied their catalytic activities for the polymerization of ethylene and propylene.

EXPERIMENTAL

Because of the air and moisture sensitivity of organometallic complexes, all the manipulations were carried out under an atmosphere of pure and dry argon with standard Schlenk techniques. Solvents such as heptane and n-hexane were distilled from sodium/potassium benzophenone under argon before use. Toluene was purified by distillation from sodium benzophenone. All solvents were stored over sodium. p-Tolylimidovanadium trichloride, 2,6-diisopropylphenylimidovanadium trichloride, and $tert$-butylimidovanadium trichloride were prepared according to published procedures.[4,12,13] Complexes $(Cp)V(=NC_6H_4Me-4)Cl_2$ (**1**),[4] $(Cp)V(=N^tBu)Cl_2$ (**2**),[14] and $(^tBuCp)V(=N^tBu)Cl_2$ (**3**; $^tBuCp = tert$-butylcyclopentadienyl)[15] were prepared according to the literature. Ethylene monomer was purchased from Koatsu Gas Kogyo Co. (Osaka, Japan) and used without further purification. Propylene monomer was purchased from Sumitomo Seika Co. (Osaka, Japan) and used without further purification. Modified methylaluminoxane (MMAO; 5.6 wt % solution in toluene), MAO (8.5 wt % solution in toluene), AlEt$_2$Cl, and AlMe$_3$ were provided by Tosoh Finechem Co. (Shunan, Japan) d-MAO (dried MAO) was prepared through the drying of ordinary MAO (toluene solution) in $vacuo$ at 40°C to remove AlMe$_3$ and toluene and was used as a solution in toluene. NMR spectra were measured on a JEOL JNM-LA400 400-MHz spectrometer (Tokyo, Japan). Chemical shifts of ^{1}H-NMR were calibrated with the residual signal of chloroform (δ = 7.26 ppm) in chloroform-d. Chemical shifts of ^{13}C-NMR were determined with reference to the carbon resonance of chloroform-d (δ = 77.0 ppm). Gel permeation chromatography (GPC) measurements of polyethylene (PE) were performed on a Waters C150 by Nihon-Polyolefin Co., Ltd. (Tokyo, Japan). GPC measurements of polypropylene (PP) were performed on a Tosoh SC-8010 calibrated with standard poly(methyl methacrylate)s. The melting point (T_m) and the heat of melting (ΔH_m) of the polymers were obtained with a Seiko Instruments Inc. (Chiba, Japan) SSC5100-DSC22C apparatus. Elemental analysis was performed on a PerkinElmer (Wellesley,

MA) 2400 series II CHNS/O analyzer. Electron-impact mass spectrometry spectra were recorded on a JEOL JMS-SX-102A spectrometer.

Synthesis of (2-methyl-8-quinolinolato)(2,6-diisopropylphenylimido)vanadium dichloride (4)

To a solution of 2,6-diisopropylphenylimidovanadium trichloride[3] (2.83 g, 8.42 mmol) in hexane (30 mL), 2-methyl-8-quinolinol (1.31 g, 8.42 mmol) was added at 0°C. The reaction mixture was stirred overnight. All volatiles were removed under reduced pressure. **4** was obtained as a black solid.

Yield: 2.2 g (55%). ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 8.65 (s, 1H), 8.26–7.52 (m, 4H), 7.12 (m, 3H), 3.46 (d, 2H), 3.21 (s, 3H), 1.42 (d, 12H). ANAL. Calcd. for C$_{22}$H$_{25}$N$_2$OCl$_2$V: C, 58.04%; H, 5.53%; N, 6.15%. Found: C, 57.75%; H, 5.48%; N, 6.03%.

Synthesis of n-hexylimidovanadium trichloride

To a solution of VOCl$_3$ (3 mL, 32 mmol) in hexane (60 mL), n-hexyl isocyanate (4.5 mL, 32 mmol) was added. The reaction mixture was refluxed for 5 h. All volatiles were removed under reduced pressure. n-Hexylimidovanadium trichloride was obtained as a red oil.

Yield: 5.0 g (61%). ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 4.77 (br.s, 2H), 2.02 (br.s, 2H), 1.62 (br.s, 2H), 1.35 (br.s, 4H), 0.91 (br.s, 3H).

Synthesis of (2-methyl-8-quinolinolato)(n-hexylimido)vanadium dichloride (5)

To the solution of n-hexylimidovanadium trichloride (2.4 g, 9.32 mmol) in hexane (30 mL), 2-methyl-8-quinolinol (1.45 g, 9.06 mmol) was added at 0°C. The reaction mixture was stirred overnight. All volatiles were removed under reduced pressure. **5** was obtained as a black solid.

Yield: 3.16 g (90%). ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 8.64 (s, 1H), 7.70–7.56 (br.d, 4H), 3.85 (s, 2H), 3.22 (s, 3H), 1.63 (s, 2H), 1.30 (s, 6H), 0.87 (s, 3H). ANAL. Calcd. for C$_{16}$H$_{21}$N$_2$OCl$_2$V: C, 50.68%; H, 5.58%; N, 7.39%. Found: C, 50.73%; H, 6.38%; N, 7.39%.

Polymerization of ethylene with a vanadium complex/aluminum compound

To a complex (0.06 mmol) in dry toluene (30 mL) was added a given amount of an aluminum compound, and then the mixture was stirred for 5 min at room temperature. The solution was degassed, and ethylene (1 atm) was introduced to start the polymerization. After the prescribed time, the polymerization mixture was quenched with a large amount of methanol containing a small amount of hydrochloric acid. The pre-

cipitates were collected by centrifugation and dried *in vacuo*. GPC measurements were performed.

Polymerization of propylene with a vanadium complex/aluminum compound

To complex **5** (0.06 mmol) in dry toluene (30 mL) was added a given amount of an aluminum compound, and then the mixture was stirred for 5 min at room temperature. The solution was degassed, and propylene (1 atm) was introduced to start the polymerization. After the prescribed time, the polymerization mixture was quenched with a large amount of methanol containing a small amount of hydrochloric acid. The precipitates were collected by centrifugation and dried *in vacuo*. GPC measurements were performed.

X-ray structure determination of complex 3

A single crystal of **3** suitable for X-ray diffraction was sealed in a glass capillary under an argon atmosphere and was mounted on a Rigaku (Tokyo, Japan) AFC-7R four-circle diffractometer for data collection with Mo Kα radiation. Three standard reflections were chosen and monitored every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. The structure was solved by a direct method (SHELX-97[16]) and expanded with a Fourier technique (DIRDIF99[17]). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined with the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on unique reflections. All calculations were performed with the CrystalStructure[18,19] crystallographic software package, except for refinement, for which SHELX-97 was used. The crystal data and data collection parameters of **3** are summarized in Table I. Crystallographic data for the structural analysis of **3** have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 238205). Copies of this information may be obtained free of charge (mail: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44–1223–336033; e-mail: deposit@ccdc.cam.ac.uk; or Web: www: http://www. ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Polymerization catalyses of monocyclopentadienyl imidovanadium complexes

Syntheses of monocyclopentadienyl imidovanadium complexes

We prepared nonbridged imidovanadium complexes with Cp ligands, **1**,[4] **2**,[14] and **3**,[15] according to the literature (Scheme 1). Preuss and Perner[15] reported the synthesis of complex **3**. However, the molecular structure of **3** had not been determined yet. Thus, we

TABLE I
Crystal Data and Data Collection Parameters of Complex 3

Category	Characteristic
Complex	(^{t}BuCp)V(=N^{t}Bu)Cl$_2$
Formula	C$_{13}$H$_{22}$NVCl$_2$
Formula weight	314.17
Crystal color and habit	Red, plate
Crystal size (mm)	$0.4 \times 0.2 \times 0.1$
Crystal system	Monoclinic
Space group	$P2_1/n$ (#14)
a (Å)	20.693 (2)
b (Å)	6.5699 (8)
c (Å)	12.305 (2)
β (°)	98.364 (10)
V (Å^3)	1655.1 (4)
Z	4
D_{calc} (g/cm^3)	1.261
Abs coefficient (cm^{-1})	9.03
$F(000)$	656
Diffractometer	Rigaku AFC7R
Radiation	Mo Kα (λ = 0.71069 Å)
Scan mode	$\omega-2\theta$
Temperature (°C)	25 (1)
Scan rate (°/min)	16
Scan width (°)	1.47 + 0.30 tan θ
$2\theta_{max}$ (°)	55
Collected reflections	4935
Unique reflections	3799
Variables	176
R_1 [$I > 2.00\sigma(I)$][a]	0.057
wR_2 (all data)[b]	0.152
Goodness of fit on F^2	1.01

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

performed X-ray crystallography of **3** to elucidate the effects of the substituents on the Cp ring.

The molecular structure of **3** is shown in Figure 1. The selected bond distances and angles are listed in Table II. Complex **3** has a three-legged piano-stool geometry, in which two ^{t}Bu groups are located at transoid positions to each other to avoid steric hindrance. Although the bond distance of V(1)—C(1) is slightly longer than other V(1)—C(^{t}BuCp) bond distances, the hapticity of the ^{t}BuCp ligand can be described as a distorted η^5 mode. The V(1)=N(1) distance of **3** [1.642(3) Å] is apparently longer than that of **2** [1.590(4) Å],[14] slightly longer than that of V(=N^{t}Bu)Cl$_3$ [1.621(5) Å],[12] similar to that of TpV(=N^{t}Bu)Cl$_2$ [1.638(2) Å],[5] and shorter than that of an alkylidene complex, CpV(=NAr)(=CHPh)(PMe$_3$) [1.679(5) Å].[3] The V(1)—N(1)—C(10) angle [175.6(3)°] is nearly linear, as observed for complex **2**[14] and typical imidovanadium compounds;[3,5,12] this indicates strong π donation from nitrogen to vanadium.

Polymerization catalyses of (cyclopentadienyl)imidovanadium complexes **1–3**

The catalyses of vanadium complexes **1–3** for the polymerization of ethylene were investigated in the pres-
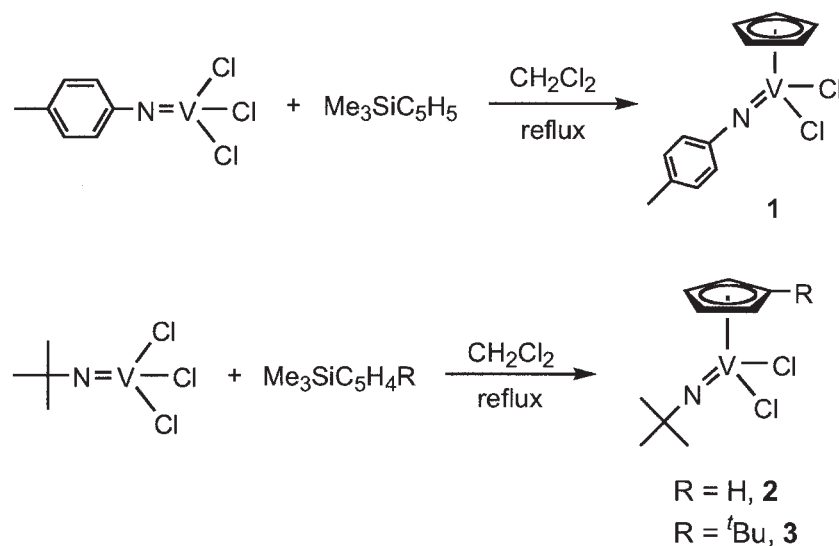
Scheme 1

ence of MAO as a cocatalyst (Table III). Without a cocatalyst, these complexes showed no catalytic activity. *p*-Tolylimido complex **1**/MAO showed moderate activity and produced PE with a bimodal molecular weight distribution. **1**/MAO exhibited higher activity at room temperature [10.3 kg of PE (mol of V)$^{-1}$ h^{-1} atm^{-1}] than at 0°C. The activity of **1**/MAO was comparable to that of Tp*V(=NAr)Cl$_2$/MAO [14 kg of PE (mol of V)$^{-1}$ h^{-1} atm^{-1}, Tp* = hydrotris(3,5-dimethylpyrazolyl)borate].[5] A tetravalent imidovanadium system, V(=NAr)Cl$_2$(NHMe$_2$)$_2$/AlEtCl$_2$ [120 kg of PE (mol of V)$^{-1}$ h^{-1} atm^{-1}],[6] was more active than these pentavalent systems. The *tert*-butylimido complex **2**/MAO system showed lower activities than the **1**/MAO system. The ^{t}BuCp complex **3** was much less active than Cp complexes **1** and **2**. It can be assumed that the bulky ^{t}Bu group of **3** hindered ethylene coordination to the active vanadium center. The activity of the **3**/MAO system decreased with the reaction time, and this indicated an instability of active species probably due to a reductive bimolecular decomposition process similar to that of other CpV(NR)Cl$_2$-type complexes.[9] Thus, the ^{t}Bu group on the Cp ring does not have sufficient bulkiness to suppress the process. The activities of these (cyclopentadienyl)imidovanadium(V) complexes (**1–3**) were still lower than those of a constrained geometry catalyst (CGC)-type vanadium(IV) complex [209 kg of PE (mol of V)$^{-1}$ h^{-1} atm^{-1}].[13] In this series of vanadium-based ethylene polymerization catalyst systems, pentavalent compounds tend to be less active than tetravalent complexes. The T_m and crystallinity (X_c) values of the PEs obtained with these monocyclopentadienyl imido complexes are relatively high and typical for high-density polyethylene (HDPE). The introduction of the Cp ligand should be effective for the suppression of branching in the polymer chain.

Polymerization catalyses of imidovanadium 2-methyl-8-quinolinolate complexes

### Syntheses of imidovanadium 2-methyl-8-quinolinolate complexes

Quinolinolate complexes of group 4 metals have been reported to show high activity for ethylene polymerization,[20] and this encouraged us to study quinolinolate complexes of vanadium. Imidovanadium trichlorides were synthesized through the reaction of VOCl$_3$ with RN=C=O (R = 2,6-^{i}Pr$_2$C$_6$H$_3^4$ or *n*-hexyl) in refluxing heptane. The reaction of these imido complexes with 2-methyl-8-quinolinol in hexane gave quinolinolate complexes, V(=NR)(O^N)Cl$_2$ [R = C$_6$H$_3^i$Pr$_2$-2,6 (**4**) or *n*-hexyl (**5**), O^N = 2-methyl-8-quinolinolato; Scheme 2]. These complexes were characterized with ^{1}H-NMR and elemental analysis.

Polymerization of ethylene with 2-methyl-8-quinolinolate complexes **4** and **5**

The catalyses of vanadium complexes **4** and **5** for the polymerization of ethylene were studied (Table IV). Without a cocatalyst, these complexes were inactive for ethylene polymerization. In the presence of MMAO as a cocatalyst, complex **4** showed moderate activity and produced PE with bimodal molecular weight distributions. This indicates that two or more kinds of active species were generated from the **4**/MMAO catalyst system. The *n*-hexylimino complex **5** showed lower polymerization activity than **4**, and the resulting polymer had a high molecular weight and a unimodal molecular weight distribution.

We investigated the effects of the cocatalyst and polymerization temperature on the polymerization of ethylene with complex **5** (Table IV). In the combination with MAO, complex **5** showed activities similar to
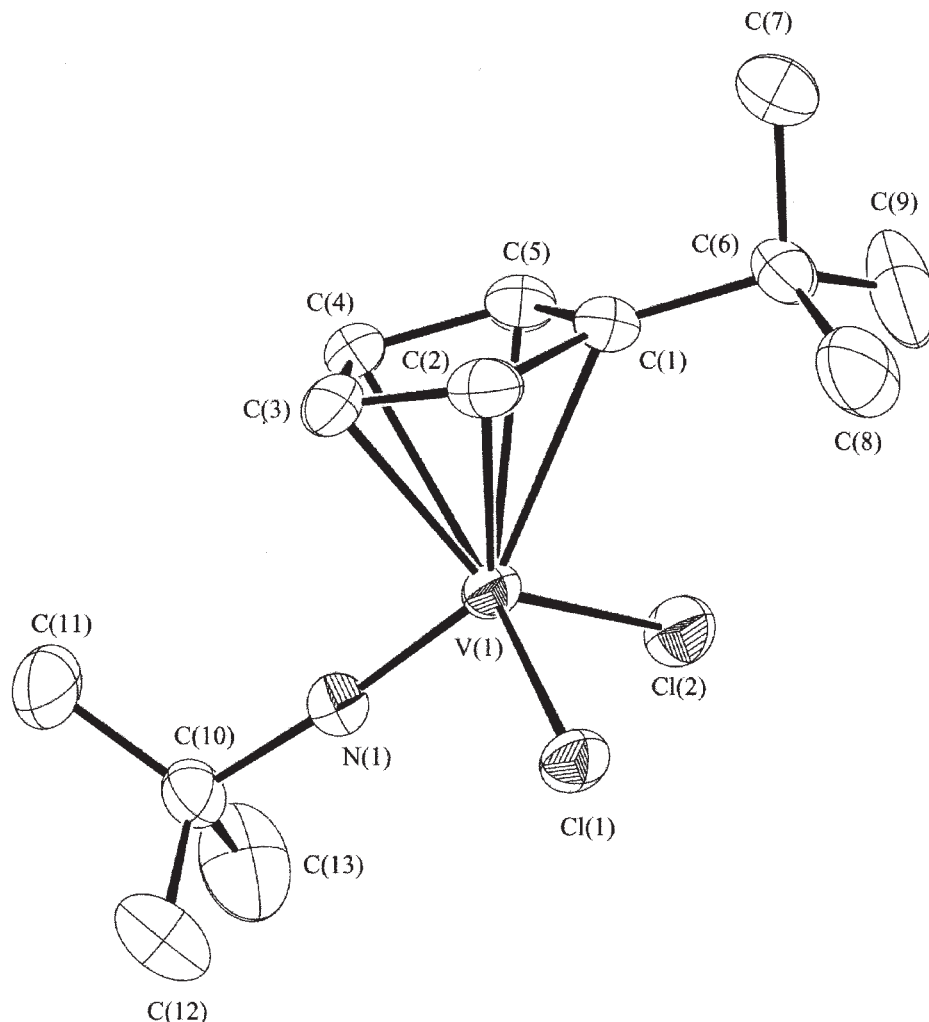
Figure 1 Molecular structure of complex **3**. The thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

those of the **4**/MMAO system. The polymerization of ethylene at 0°C with **5**/MAO ([Al]/[V] = 100) produced PE with a high molecular weight and relatively narrow molecular weight distributions. When the [Al]/[V] ratio was increased from 100 to 300 mol/mol, the molecular weight of the resulting PE was lowered and broadened because of frequent chain-transfer re-

TABLE II
Selected Bond Lengths (Å) and Angles (°) of Complex 3

Bond length		Bond angle	
V(1)—C(1)	2.472 (4)	Cl(1)—V(1)—Cl(2)	105.05 (5)
V(1)—C(2)	2.350 (4)	V(1)—N(1)—C(10)	175.6 (3)
V(1)—C(3)	2.206 (4)		
V(1)—C(4)	2.223 (4)		
V(1)—C(5)	2.343 (4)		
V(1)—N(1)	1.642 (3)		
V(1)—Cl(1)	2.243 (1)		
V(1)—Cl(2)	2.268 (1)		

actions to alkylaluminum. In combination with d-MAO, complex **5** showed higher activities than **5**/MAO. It is notable that a relatively low [Al]/[V] ratio of 50 was enough for the activation of **5** in the **5**/d-MAO system. With a high [Al]/[V] ratio ([Al]/[V] = 300), the resulting PE had bimodal molecular weight distributions, probably because of the multiplicity of the active species. Upon activation with $AlEt_2Cl$ or $AlMe_3$, complex **5** showed lower activities than the **5**/MAO system. Thus, d-MAO was found to be the most effective cocatalyst for the polymerization of ethylene with complex **5**. The activities of quinolinolate complexes **4** and **5** tended to be higher than those of monocyclopentadienyl-type complexes **1–3**. Thus, the quinolinolate ligand could be more effective for imidovanadium complexes than Cp-type ligands. On the other hand, a monodentate aryloxide complex system, $V(=NC_6H_3Me_2\text{-}2,6)(OC_6H_3{}^iPr_2\text{-}2,6)Cl_2$/d-MAO [120 kg of PE (mol of V)$^{-1}$ h^{-1} atm^{-1}],[7] was more active than **4**/d-MAO. The chelating coordination of

TABLE III
Ethylene Polymerization with Imidovanadium Complexes 1, 2, and 3 Activated with MAO

Complex	Temperature	Time (min)	Activity[a]	M_n ($\times 10^4$)[b]	M_w/M_n[b]	T_m (°C)[c]	X_c (%)[d]
1	RT	3	10.28	—[f]	—[f]	—[f]	—[f]
	0°C	5	2.15	1.0	57.0[e]	—[f]	—[f]
2	RT	5	3.35	—[f]	—[f]	—[f]	—[f]
	0°C	5	1.36	—[f]	—[f]	—[f]	—[f]
	0°C	360	0.32	55.73	13.9 (60%)	143.9	67.9
				0.17	9.2 (40%)		
3	RT	10	0.61	—[f]	—[f]	—[f]	—[f]
	0°C	10	0.61	—[f]	—[f]	—[f]	—[f]
	0°C	360	0.02	32.10	44.6 (80%)	143.4	73.5
				0.59	1.8 (20%)		

RT = room temperature.
Conditions: catalyst = 0.06 mmol; [Al]/[V] = 100; ethylene pressure = 1 atm; solvent volume = 30 mL of toluene.
[a] kg of PE (mol of V)$^{-1}$ h^{-1} atm^{-1}.
[b] Determined by GPC.
[c] Determined by DSC.
[d] Crystallinity determined by the equation X_c (%) = ($\Delta H_m/\Delta H_m^*$) × 100, where ΔH_m^* = 293 J/g for HDPE.
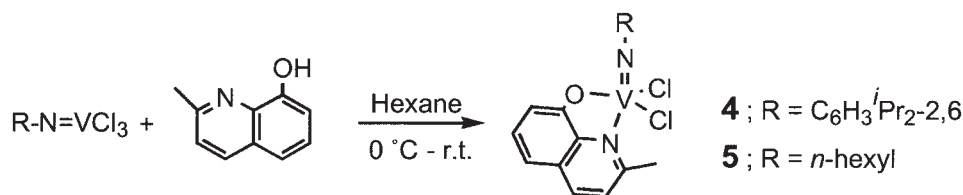[e] Bimodal peaks.
[f] Not measured.

the quinolinolate ligand could prevent accessibility of the monomer to the active metal center in comparison with monodentate aryloxide ligands. The T_m values of the resulting PEs were also quite high, ranging from 142 to 147°C and indicating the formation of highly linear PEs.

Polymerization of propylene with the 2-methyl-8-quinolinolate complex 5

To our knowledge, the polymerization of propylene by imidovanadium complexes has scarcely been reported. The *n*-hexylimido complex **5** showed catalytic activity for the polymerization of propylene, as summarized in Table V. MAO and d-MAO were effective cocatalysts for the activation of **5** in propylene polymerization, as observed in ethylene polymerization, whereas **5**/AlMe$_3$ and **5**/AlEt$_3$ showed no propylene polymerization activities. The activity of **5**/d-MAO was still lower than that of typical vanadium catalysts. This catalyst system showed the highest activity of 0.77 kg of PP (mol of V)$^{-1}$ h^{-1} atm^{-1} at 0°C, which is similar to that of the

Tp complex [1 kg of PP (mol of V)$^{-1}$ h^{-1} atm^{-1}].[5] Although the Tp complex produced oily PP with a low molecular weight [number-average molecular weight (M_n) = 3800], a quite high molecular weight PP was obtained with the complex **5** system (M_n = 187,000). The **5**/d-MAO system was also thermally unstable and gradually deactivated within 3 h at 0°C. The propylene polymerization by **5**/d-MAO ([Al]/[V] = 50) at room temperature produced polypropylenes with considerably narrow molecular weight distributions [weight-average molecular weight/number-average molecular weight (M_w/M_n) = 1.3–1.5], although the molecular weights of the resulting polypropylenes were not proportional to the polymer yield. Thus, 2-methyl-8-quinolinolate and *n*-hexylimido are effective ancillary ligands for the suppression of side reactions. At a higher [Al]/[V] ratio of 100, the activity and thermal stability of the catalyst system were improved, but it produced polymers with lower molecular weights and broader molecular weight distributions, probably because of the more frequent chain transfer to aluminum. In the combination of MAO, M_n's were

R-N=VCl$_3$ + [2-methyl-8-quinolinol] $\xrightarrow[\text{0 °C - r.t.}]{\text{Hexane}}$ [imidovanadium quinolinolate complex]

4 ; R = C$_6$H$_3^i$Pr$_2$-2,6
5 ; R = *n*-hexyl

Scheme 2

TABLE IV
Ethylene Polymerization with Imidovanadium 2-Methyl-8-quinolinolate Complexes 4 and 5

Catalyst	Cocatalyst	[Al]/[V] (mol/mol)	Temperature	Time (min)	Activity[a]	M_n ($\times 10^4$)[b]	M_w/M_n[b]	T_m (°C)[c]
4	MMAO	150	RT	5	21.2	1.2	96[d]	—[c]
5	MMAO	150	RT	5	7.3	17.1	11	—[e]
	MAO	100	RT	3	18.2	—[e]	—[e]	—[e]
				30	3.4	1.5	140	143
			0°C	3	11.2	63.3	4	147
				30	4.7	32.6	7	142
		300	0°C	10	6.6	3.3	42	142
	d-MAO	100	RT	10	12.4	1.4	76	—[e]
		50	0°C	10	17.1	4.7	36	142
		100			18.6	6.0	29	143
		300			11.3	1.0	140[d]	—[e]
	AlEt$_2$Cl	10	0°C	10	1.9	1.0	63	—[e]
		50			1.2	1.2	56	—[e]
	AlMe$_3$	100	0°C	10	1.3	1.6	94	—[e]

RT = room temperature.
Conditions: ethylene pressure = 1 atm; solvent volume = 30 mL of toluene.
[a] kg of PE (mol of V)$^{-1}$ h^{-1} atm^{-1}.
[b] Determined by GPC.
[c] Determined by DSC.
[d] Bimodal peaks.
[e] Not measured.

increasing even after 3 h, although the activities were lower than those of the **5**/d-MAO system. All the polypropylenes obtained with complex **5** were atactic and soluble in toluene and THF.

CONCLUSIONS

We prepared two series of imidovanadium complexes: monocyclopentadienyl complexes and 2-methyl-8-quinolinolate complexes. The addition of a bulky ^{t}Bu

group to the Cp ring of the former complexes tended to attenuate the polymerization activities. Upon activation with MAO, the latter complexes showed moderate activities for the polymerization of ethylene and produced polymers with relatively narrow molecular weight distributions at 0°C. In combination with d-MAO, the *n*-hexylimido complex showed higher activities than that of the MAO systems. The T_m values of the resulting PEs were quite high (~147°C) and indicated the formation of highly linear PE. The **5**/d-

TABLE V
Propylene Polymerization with *n*-Hexylimidovanadium Complex 5

Cocatalyst	[Al]/[V] (mol/mol)	Temperature	Time (h)	Activity[a]	M_n ($\times 10^4$)[b]	M_w/M_n[b]
d-MAO	50	0°C	1	0.77	11.6	2.8
			3	0.44	12.4	2.3
			6	0.21	18.7	1.4
	50	RT	1	0.24	17.2	1.4
			3	0.14	14.4	1.3
			6	0.09	14.5	1.5
	50	60°C	3	Trace	—[c]	—[c]
	100	RT	1	0.18	—[c]	—[c]
			2	0.26	7.1	2.7
			3	0.24	8.6	2.6
MAO	50	0°C	1	0.18	6.9	2.5
			2	0.14	8.9	2.4
			3	0.11	16.4	1.7

RT = room temperature.
Conditions: propylene pressure = 1 atm; solvent volume = 30 mL of toluene.
[a] kg of PP (mol of V)$^{-1}$ h^{-1} atm^{-1}.
[b] Determined by GPC.
[c] Not measured.

MAO system showed propylene polymerization activities that produced polymers with quite high molecular weights.

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