Vanadium(V) Complexes Containing Tetradentate Amine Trihydroxy Ligands as Catalysts for Copolymerization of Cyclic Olefins

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ABSTRACT: A series of vanadium(V) complexes bearing tetradentate amine trihydroxy ligands [NOOO], which differ in the steric and electronic properties, have been synthesized and characterized. Single crystal X-ray analysis showed that these complexes are five or six coordinated around the vanadium center in the solid state. Their coordination geometries are octahedral or trigonal bipyramidal. In the presence of Et_2AlCl, these complexes have been investigated as the efficient catalysts for ethylene polymerization and ethylene/norbornene copolymerization at elevated reaction temperature and produced the polymers with unimodal molecular weight distributions (MWDs), indicating the single site behaviors of these catalysts. Both the steric hindrance and electronic effect of the groups on the tetradentate ligands directly influenced catalytic activity and the molecular weights of the resultant (co)polymers. Other reaction parameters that influenced the polymerization behavior, such as reaction temperature, ethylene pressure, and comonomer concentration, are also examined in detail. Furthermore, high catalytic activities of up to 3.30 kg polymer/mmol$_V$·h were also observed when these complexes were applied to catalyze the copolymerization of ethylene and 5-norbornene-2-methanol, producing the high-molecular-weight copolymers (M_w = 157–400 kg/mol) with unimodal MWDs (M_w/M_n = 2.5–3.0) and high polar comonomer incorporations (up to 12.3 mol %). © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1122–1132, 2010

KEYWORDS: catalysts; functional polymers; homogeneous catalysis; polydentate ligands; polymerization; polyolefins; vanadium; Ziegler-Natta polymerization

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INTRODUCTION One of the most exciting objects in the field of transition metal catalysis, organometallic chemistry, and polymer science in recent years has been the intensive investigation of olefin polymerization catalysts.[1] Single-site and well-defined catalysts have been extensively explored during the last 2 decades to optimize polymer properties, resulting in the establishment of the relationship between the nature of catalysts and the features of the resultant polymers, and thereby providing various opportunities to adjust the polymer's architecture.[2] Among various classes of catalysts, vanadium catalysts have played a critically important role in producing high-molecular-weight polymers with narrow molecular weight distribution (MWD) as well as α-olefin or cycloolefin copolymers with high comonomer incorporations.[3] Nonetheless, the report on vanadium catalysts is limited owing to low activity, which is ascribed to their deactivation during the polymerization, especially at high polymerization temperature, due to reduction of catalytically active vanadium species to low valent, less active, or inactive species. In recent years, although a number of vanadium catalysts have been studied,[4–16] only a few reports regarding highly active and well-defined vanadium catalysts were published.[4(c),7,11(a,d,e),13] Gambarotta and coworkers reported that bis(imino)pyridine vanadium(III) complexes showed high catalytic activity toward ethylene polymerization, but produced bimodal MWD PEs.[7(b)] Gibson's group found that bis(benzimidazole)amine ligand can stabilize highly active vanadium(III) and vanadium(V) catalysts for olefin polymerization.[4(c)] Nomura et al. investigated (arylimido)vanadium(V) complexes containing aryloxide or phenoxyimine ligands as the efficient catalysts for olefin polymerization.[11] Redshaw et al. applied vanadium(V) complexes with calixarene ligands to catalyze ethylene (co)polymerization.[13(c)]

Despite the fact that some favorable vanadium catalysts have been reported for promoting olefin polymerization, the search for new vanadium catalysts that display excellent thermal stability and generate polyolefins with high molecular weight (MW) and relative narrow MWD remains of keen interest. It was proposed that ligand denticity played an important role in controlling the behavior of transition metal catalysis.[17–19] Previously, we found vanadium catalysts bearing tridentate Schiff base ligands showed better thermal stability than the corresponding bidentate ligands chelated

Additional Supporting Information may be found in the online version of this article. Correspondence to: Y.-S. Li (E-mail: ysli@ciac.jl.cn)
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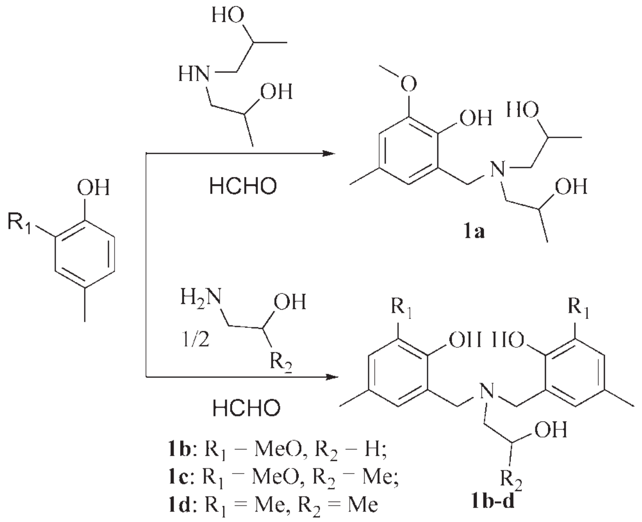


SCHEME 1 General synthetic route of the tetradentate ligands.

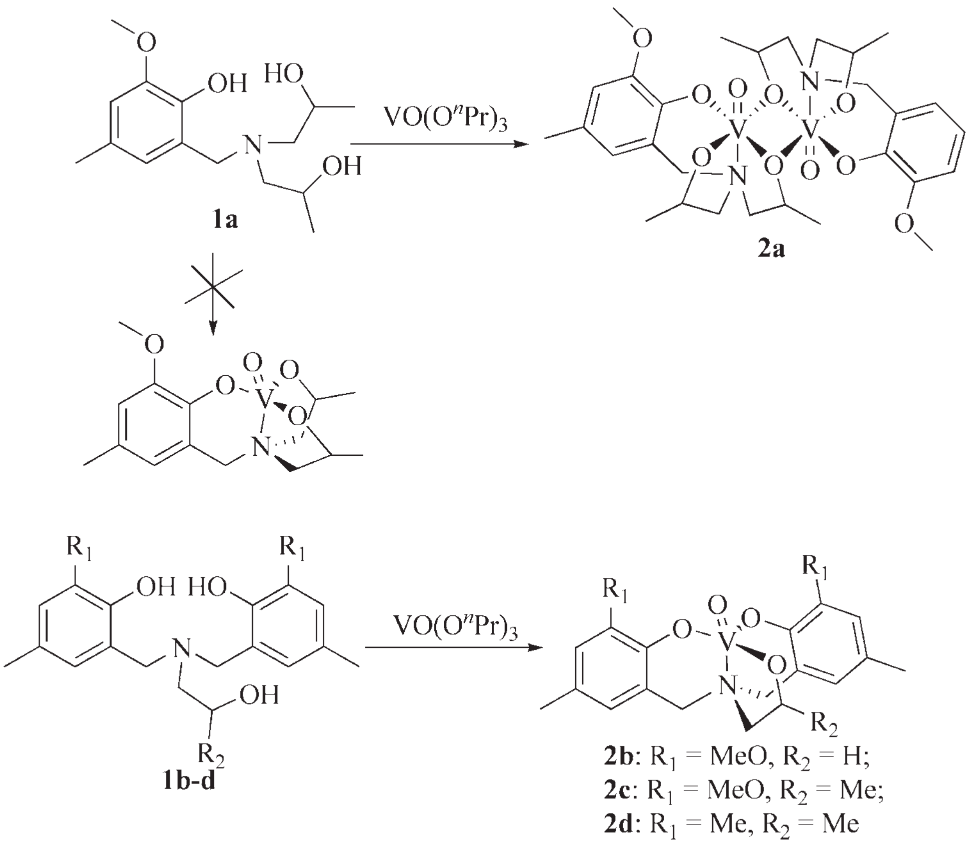
ones.[16(c)] We thus are interested in investigating the vanadium catalysts bearing polydentate ligand, which efficiently stabilize the active species and control over the MW and MWD of the resultant polymer. Herein, we report the investigation of versatile tetradentate amine trihydroxy ligands that afford highly active catalysts for ethylene polymerization, ethylene/norbornene, and ethylene/5-norbornene-2-methanol copolymerizations when bound to vanadium(V).

RESULTS AND DISCUSSION

Synthesis and Characterization of Oxovanadium(V) Complexes

The tetradentate amine trihydroxy ligands **1a–d** were prepared via literature procedures by using a Mannich condensation of the corresponding phenol with amine and formaldehyde (Scheme 1).[20] A general synthetic route of the new vanadium complexes used in this study is shown in Scheme 2. The reaction of ligands **1a–d** with VO(O^{n}Pr)$_3$ in dry CH_2Cl_2 under dry argon at room temperature yielded complexes **2a–d** as deep-red crystalline solids in high yields (76–98%). These complexes were identified by ^{1}H, ^{13}C, and ^{51}V NMR, FTIR, mass spectra, and elemental analysis.

The crystals suitable for crystallographic study were grown from the CH_2Cl_2–hexane mixture solution containing compounds **2a–d**, respectively, and their molecular structures were further confirmed by X-ray crystallographic analyses. The symmetry of **2a** was higher than expected (rhombohedral crystal system with *R*-3 space group). As shown in Figure 1, binuclear complex **2a** displayed a six-coordinate distorted octahedral geometry around each V center, which is surrounded by two ligands and is bound to each other by two bridging O atoms (the isopropoxides arm), possessing a dimeric structure. Attempt to isolate mononuclear species by changing the recrystallization solvent was not successful, probably because of the small steric hindrance of the two isopropoxide arms. The bond lengths (see Fig. S1 in Supporting Information) between vanadium and bridged oxygen



SCHEME 2 General synthetic route of the vanadium complexes used in this study.

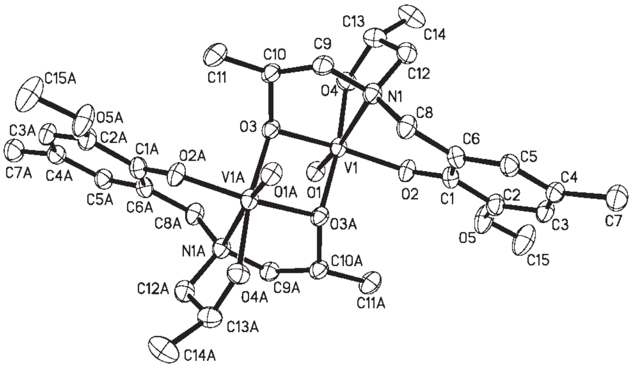


FIGURE 1 Molecular structure of complex **2a**. Thermal ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity.

(V(1)-O(3), 1.980(4) Å; V(1)-O(3A), 2.108(4) Å) are much longer than those between vanadium and nonbridged oxygen (V(1)-O(4), 1.846(4) Å). V(1)-N(1) bond distance of 2.335(5) Å is somewhat shorter than those in the literature documented vanadium(V) amine tris(phenolate) complexes (2.3765(14) and 2.4697(4) Å).[13(b),19(a)]

Pentacoordinate complexes **2b–d** display distorted trigonal bipyramidal geometry (Figs. 2 and S2–4 in Supporting Information, respectively), with the oxo function occupying the axial position, *trans* to the central nitrogen, as the evidence from the O—V—N bond angle (O(1)-V(1)-N(1): **2b**, 175.20(9)°) as well as the sum of bond angles around V (e.g., in **2b**: ca. 360°; O(2)-V(1)-O(3), 115.97(9)°; O(2)-V(1)-O(4), 119.13°; O(3)-V(1)-O(4), 117.37(9)°). A comparison of the V(1)-N(1) distances in the three structures shows that **2c** has shorter V(1)-N(1) bond distance (2.408(3) Å compared with 2.422(2) and 2.414(3) Å). The vanadyl V—O bond lengths in **2d** (1.595(3) and 1.606(3) Å) are longer than the corresponding bond length in **2c** (1.585(3) Å), highlighting the stronger electron donability of the OMe group in comparison with the Me group on the phenols. In addition, a careful examination of the X-ray structures of 2d reveals the presence of weak intermolecular π–π contacts between two phenol planes (Fig. S5). The planes defined by the benzene rings are 3.606 Å apart, with a centroid–centroid distance of 3.706 Å.

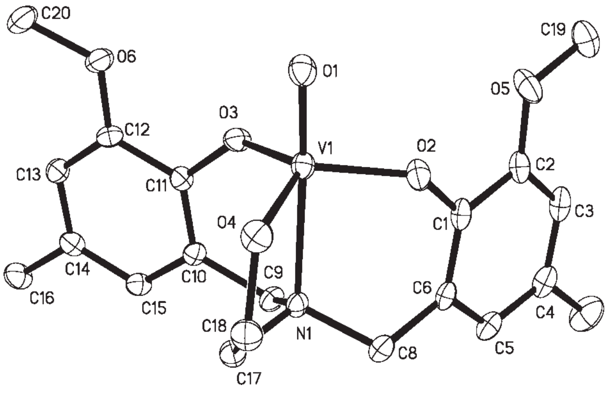
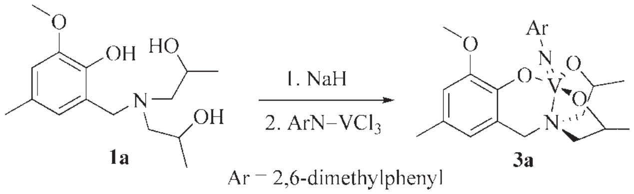


FIGURE 2 Molecular structure of complex **2b**. Thermal ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity.



SCHEME 3 General synthetic route of the vanadium complex used in this study.

Synthesis and Characterization of Imidovanadium(V) Complex

Tetradentate amine trihydroxy ligand **1a** was deprotonated by 3.0 equiv of NaH, followed by treating with 1.0 equiv of VCl$_3$(*N*-2,6-Me$_2$C$_6$H$_3$)[21] in Et$_2$O at −30 °C (Scheme 3). The reaction product was isolated by recrystallization from a mixture of Et$_2$O and *n*-hexane at −30 °C in glovebox. The X-ray crystal structure of **3a** was also determined. As shown in Figure 3, the geometries at vanadium are approximately trigonal bipyramidal with N-V-N as the axes. Noted that crystal of **3a** consists of two crystallographically different independent molecules in the unit cell (see Fig. S6 in Supporting Information), in one molecule the *N*-aryl plane was almost in parallel with the *O*-aryl plane in the tetradentate ligand, whereas in the other one the *N*-aryl plane was almost vertical to the *O*-aryl plane in the tetradentate ligand.

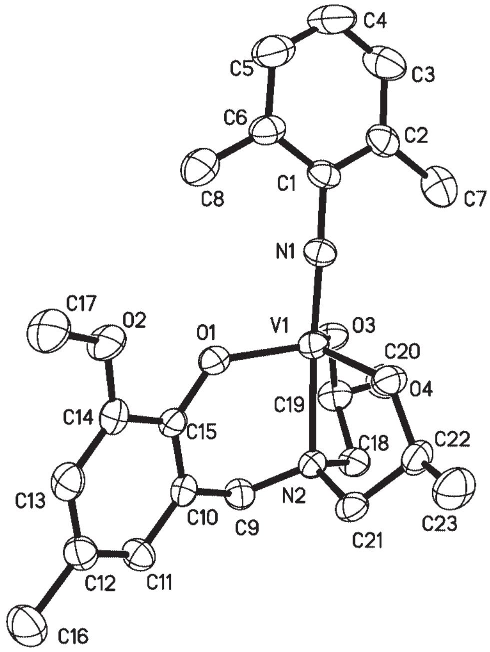


FIGURE 3 Molecular structure of complex **3a**. Thermal ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity.

TABLE 1 Ethylene Polymerization Catalyzed by **2a–d** and **3a**[a]

Entry	Catalyst (μmol)	T_p (°C)	Al/V (molar ratio)	p (C_2H_4) (bar)	Polymer (g)	Activity[b]	M_w[c] (kg/mol)	M_w/M_n[c]
1	**2a** (0.5)	50	4,000	4.0	0.25	6.00	167	2.4
2	**2b** (0.5)	50	4,000	4.0	0.56	13.44	52.1	2.6
3	**2c** (0.5)	25	4,000	4.0	0.51	12.24	650[d]	
4	**2c** (0.2)	50	4,000	2.0	0.14	8.40	305	2.7
5	**2c** (0.2)	50	4,000	4.0	0.45	27.00	323	3.0
6[e]	**2c** (0.2)	50	4,000	4.0	2.27	22.70	608[d]	
7	**2c** (0.2)	50	4,000	6.0	0.52	31.20	460[d]	
8	**2c** (0.5)	50	500	4.0	0.02	0.48	–[f]	–[f]
9	**2c** (0.5)	50	2,000	4.0	0.26	6.24	110	2.7
10	**2c** (0.5)	50	4,000	4.0	0.78	18.72	104	3.0
11	**2c** (0.5)	50	6,000	4.0	0.80	19.20	99.1	3.0
12	**2c** (0.5)	70	4,000	4.0	0.48	11.52	92.2	2.9
13	**2d** (0.5)	50	4,000	4.0	0.02	0.48	–[f]	–[f]
14	**3a** (0.5)	50	4,000	4.0	0.12	2.88	234	2.0

[a] Conditions: toluene = 50 mL, Al/V = 4000 (mol/mol), ETA/V = 300 (molar ratio), polymerization 5 min.

[b] Activity in kg polymer/(mmol$_V$·h).

[c] GPC data in 1,2,4-trichlorobenzene versus polystyrene standard.

[d] M_v was measured in decalin at 135 °C because polymer did not dissolve in 1,2,4-trichlorobenzene.

[e] Polymerization 30 min.

[f] Not determined.

Ethylene Polymerization

Oxovanadium(V) complexes **2a–d** and imidovanadium(V) complex **3a** have been investigated as the effective catalysts for ethylene polymerization in the presence of the cocatalyst Et_2AlCl and reactivating agent ethyl trichloroacetate (ETA). The typical results are summarized in Table 1. We found that ligand structure remarkably influenced catalytic activity and polymer property. Under the similar conditions, the higher activities were observed for complexes **2b** and **2c**, which contain two aryloxides and one alkoxide, whereas the lower activity was detected for complex **2a** presumably because of the higher electron-donating property of alkoxide than aryloxide and the steric bulk of the ancillary ligands in the oxo bridged structure. Higher MW polymers were produced by complex **2a**, but not by complexes **2b** and **2c**, indicating that chain transfer reactions were partly hindered in the more crowded structure **2a**. Compared with **2c**, complex **2d** exhibited much lower catalytic activity (0.48 kg PE/mmol$_V$·h), indicating that the *ortho* MeO group in the aryloxo in the ligand is indispensable for high activity in this type of catalyst. This result is different from the behavior of amine tris(3,5-dimethylphenolate) vanadium(V) catalyst, which displayed high activity toward ethylene polymerization in the presence of dimethylaluminum chloride and ETA.[13(b)]

Imidovanadium complex **3a** bearing the same trihydroxy ligand as oxovanadium complex **2a** was less productive, but produced polyethylenes with higher MW probably resulting from the steric hindrance of aryl group (2,6-dimethylphenyl) on the imido group. Similar result was reported in the O,N-chelating aminophenolate vanadium catalysts system.[8a] It should be noted that although the precursors are well defined, the active species or the alkylation's pass ways are obscure because paramagnetic derivatives formed simultaneously when the vanadium(V) complexes were combined with Et_2AlCl in the *in situ* NMR experiment.[13(b,c)]

We also observed a dependence of the catalytic activity of complex **2c** on the reaction parameters, such as reaction temperature, ethylene pressure, catalyst and cocatalyst concentrations. The increase of ethylene pressure is beneficial to productivities (entries 4, 5, and 7 in Table 1, from 8.40 to 31.2 kg PE/mmol$_V$·h when ethylene pressure increases from 2 to 6 atm), and the MW of the resultant polymer was also increased. The catalytic activity of **2c** is found to be sensitive to reaction temperature, with 50 °C being the optimum. However, the MW and MWD were only mildly influenced when reaction temperature was elevated from 50 to 70 °C, indicating high thermal stability of the catalyst. Compared with the Schiff base-chelated vanadium(III) previously reported,[16] catalyst **2c** produced much higher MW polymers at elevated reaction temperature. Both the catalytic activity and the MW of resultant PEs were influenced by catalyst concentration (entries 5 and 10). However, the MWDs of the resultant PEs were independent of the catalyst concentration used. Note that productivity was kept in high level (22.70 kg PE/mmol$_V$·h) in the 30-min polymerization at 50 °C, suggesting excellent thermal stability of the active species. As previously reported,[11(a,d,e),13(c,d),16] cocatalyst dosage also played an important role in the vanadium(V) catalytic systems studied. Although Al/V molar ratio remarkably influenced the catalytic activity of **2c** (entries 8–11 in Table 1), and the MW and MWD of the PEs only slightly changed, which indicates that the dominant chain transfer in this polymerization was not chain transfer to Al. The dependence of the MW and MWD of the PEs on monomer pressure (entries 4 and 5 in Table 1) also indicates that the main chain transfer is not to Al but to the monomer. This result was quite different from

TABLE 2 Copolymerization of Ethylene and Norbornene by **2a–d** and **3a**[a]

Entry	Cat. (μmol)	*T* (°C)	NBE (mol/L)	Polymer (g)	Activity[b]	NBE Content[c]	M_w[d] (kg/mol)	M_w/M_n[d]
1	**2a** (1.0)	50	0.5	0.30	1.80	15.1	210	2.1
2	**2b** (1.0)	50	0.5	2.32	13.9	17.9	235	2.8
3	**2c** (1.0)	50	0.1	1.43	8.58	5.50	132	3.0
4	**2c** (1.0)	50	0.3	2.08	12.5	10.5	301	2.8
5	**2c** (1.0)	50	0.5	2.73	16.4	15.7	341	2.5
6	**2c** (1.0)	50	0.7	2.27	13.6	20.4	248	2.0
7	**2c** (1.0)	50	0.9	1.51	9.06	22.3	207	1.7
8	**2c** (0.2)	50	0.9	0.42	12.6	22.9	183	1.8
9	**2c** (1.0)	25	0.5	0.52	3.12	9.78	396	9.5
10	**2c** (1.0)	70	0.5	1.88	11.3	17.8	93.8	2.3
11	**2d** (1.0)	50	0.5	0.02	0.12	–[e]	–[e]	–[e]
12	**3a** (1.0)	50	0.5	0.17	1.02	12.3	292	1.8

[a] Conditions: toluene + comonomer = 30 mL, ethylene = 4 bar, cocatalyst = Et_2AlCl, Al/V = 4000 (molar ratio), ETA/V = 300 (molar ratio), 10 min.

[b] Activity in kg polymer/($mmol_V$·h).

[c] NBE content (mol %) estimated by ^{13}C NMR spectra.

[d] GPC data in 1,2,4-trichlorobenzene versus polystyrene standard.

[e] Not determined.

the vanadium(III)/Et_2AlCl catalytic systems, which displayed obvious chain transfer to Al.[16] Other organoaluminum compounds such as modified MAO, dry MAO, $AlMe_3$, and $AlEt_3$ were also tested as the cocatalyst in combination with complex **2c**. Only **2c**/(modified MAO) system exhibited low activity (56 g PE/$mmol_V$·h), and trace or even no polymer was obtained using dry MAO, $AlMe_3$, or $AlEt_3$ as the cocatalyst.

Copolymerization of Ethylene with Norbornene

As tetradentate amine trihydroxy vanadium(V) complexes exhibited high catalytic activity for ethylene polymerization, the copolymerizations of ethylene with norbornene (NBE) by **2a–d** and **3a** were thus explored. The typical results are summarized in Table 2. As the ethylene polymerization, the data listed in entries 1, 2, 5, 11, and 12 indicate that ligand structure considerably affects the catalytic activity toward the copolymerization. Under the same conditions, complex **2c** showed the highest activity of 16.38 kg polymer/$mmol_V$·h, whereas complex **2d** revealed the lowest activity of 0.12 kg polymer/$mmol_V$·h. Imidovanadium complex **3a** displayed slightly low catalytic activity than oxovanadium complex **2a**, but the MW of the resultant copolymer produced by **3a** was higher than that obtained by **2a**, indicating that steric hindrance of aryl group (2,6-dimethylphenyl) on the imido partly restrained the chain transfer reactions. Introduction of an extra methyl group in the alkyloxide resulted in the increase of both catalytic activity and the MW of the copolymer produced, but a slight decrease of NBE incorporation (entry 2 vs. entry 5).

The effect of reaction conditions on the ethylene/NBE copolymerization was also investigated using catalyst **2c**. The data listed in Table 2 indicate that catalytic activity, the MWs, and MWDs of the resultant copolymers were directly influenced by NBE concentration. The highest activity and the highest MW copolymer appeared when 0.5 mol/L NBE was in feed, whereas the MWDs of the resultant copolymers decreased with the increase of NBE concentration. A steady increase of NBE incorporations was observed when more NBE was charged. Notably, there is a pronounced increase in catalytic activity with increasing temperature from 25 to 50 °C for catalytic system **2c**/Et_2AlCl, further elevating temperature to 70 °C leading to slightly losing productivity. Similar to the behavior of the tridentate Schiff base-chelated vanadium(III) catalysts, the MW of the resultant copolymers obtained by **2c** decreased with the elevation of reaction temperature. Nevertheless, at high reaction temperature, catalyst **2c** can produce much higher MW copolymers than vanadium (III) catalysts (e.g., at 50 °C, **2c**, MW = 341 kg/mol; $[OC_6H_4CH = NCH_2C_5H_4N]VCl_2(THF)$, MW = 164 kg/mol).[16(c)] The copolymer with broad MWD (M_w/M_n = 9.5) was obtained at 25 °C, but surprisingly the MWD narrowed with the increase of reaction temperature and unimodal MWD can be available at 50 or 70 °C (M_w/M_n = 2.5 and 2.3, respectively, GPC curves are listed as Fig. S7 in Supporting Information). Much more NBE monomers were incorporated into the polymer chain when the reaction temperature was elevated from 25 to 70 °C. The rational explanation is followed: One is the higher barrier of NBE insertion than that of ethylene insertion, and the another is that the copolymerization was conducted at constant pressure of ethylene; the increase of polymerization temperature caused the decrease of ethylene concentration in the solution due to the decrease in the partial pressure and the solubility of ethylene, which also caused the increase of NBE content.

The microstructures of the copolymers have been investigated by means of ^{13}C NMR techniques (Fig. 4). It is found that NBE was incorporated into polymer chains in an isolated or alternating manner with a mixture of iso- and syndiotactic NBE configurations, and no NBE dyads (no peaks at 33.5–35.0 ppm) were observed, which is similar to our previous results.[16(a,c)] In contrast to the copolymer with 5.5 mol % NBE incorporation, an increase of the alternating

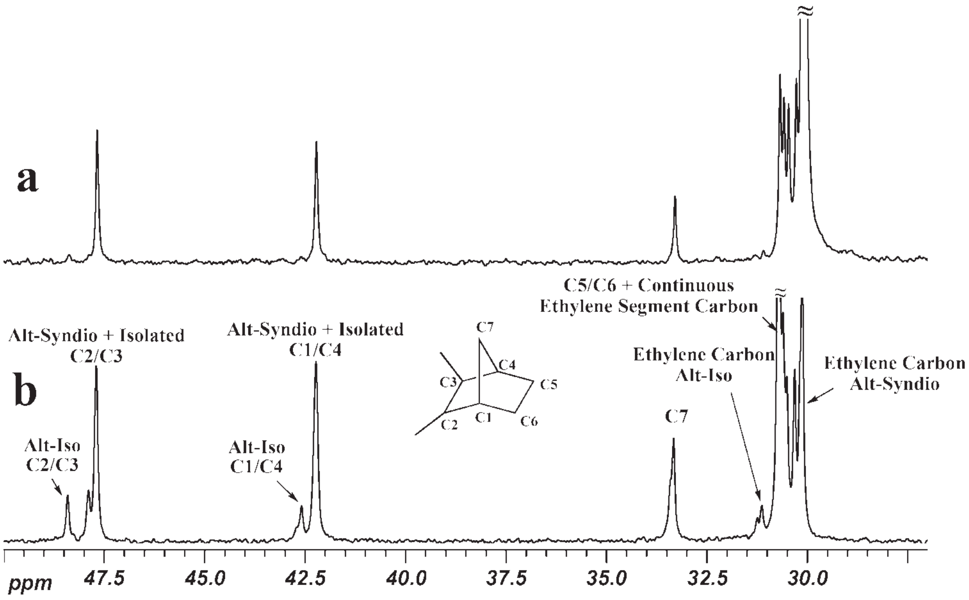


FIGURE 4 ^{13}C NMR of ethylene/NBE copolymer using catalyst **2c**: (a) 5.5 mol % (entry 3) and (b) 22.3 mol % (entry 7) in Table 2.

sequences was observed with the sample of 22.3 mol % NBE incorporated.

Copolymerization of Ethylene with 5-Norbornene-2-methanol

Polyolefins with polar functional groups possess not only modified surface properties, such as dyeability, adhesion, and wettability, but also unique bulk properties.[22] A number of late transition metal catalysts have shown great potential to catalyze the copolymerization of ethylene with polar comonomers and produce high MW functional polyolefins.[23,24] In contrast, reports on early transition metal catalysts are limited because they are typically oxophilic and thus are deactivated in the presence of polar monomers.[25] Considering vanadium possesses less oxophilic than group IV metals and can efficiently catalyze ethylene/norbornene copolymerization, we also explored the behaviors of the amine trihydroxy-ligated vanadium(V) complexes in catalyzing the copolymerization ethylene with polar norbornene derivative.

The steric protection of the functional group through alkylaluminum has been proved to be a successful method for the prevention of catalyst deactivation.[25] Herein, Et_2AlCl was chosen as both protecting agent and cocatalyst. The copolymerizations of ethylene with 5-norbornene-2-methanol (NB-CH_2OH) were carried out using vanadium(V) complexes **2a**–**c**, **3a**, and vanadium(III) complex **I** ([$OC_6H_4CH = NCH_2C_5H_4N$]VCl_2(THF)) as a comparison. The typical copolymerization results are summarized in Table 3. Under the same conditions, complex **2b** showed the highest activity (3.30 kg polymer/mmol$_V$·h) among the five complexes, whereas the much lower catalytic activities were observed when tetradentate phenol bialkanol amine ligand supported complexes **2a** and **3a** were applied. Note that the catalytic

TABLE 3 Copolymerization of Ethylene and 5-Norbornene-2-methanol (NB-CH_2OH) by **2a–d** and **3a**[a]

Entry	Cat.	*T* (°C)	NB-CH_2OH (mol/L)	Polymer (g)	Activity[b]	NB-CH_2OH Content[c]	M_w[d] (kg/mol)	M_w/M_n[d]	T_m[e] (°C)
1	**2a**	50	0.1	0.15	0.90	0.28	201	2.6	125.1
2	**2b**	50	0.1	0.55	3.30	2.29	214	2.6	124.3
3	**2c**	50	0.1	0.21	1.26	5.60	400	2.5	126.6
4	**2c**	70	0.1	0.10	0.60	7.50	157	2.4	125.0
5[f]	**2c**	50	0.3	0.25	1.50	9.86	289	2.7	118.9
6[g]	**2c**	50	0.5	0.28	1.68	12.3	214	3.0	117.6
7	**3a**	50	0.1	0.14	0.84	12.1	253	2.5	118.2
8	**I**[h]	50	0.1	0.49	2.94	0.60	69.5	3.0	128.6

[a] Conditions: toluene + comonomer = 30 mL, ethylene = 4 bar, catalyst = 1.0 μmol, cocatalyst Et_2AlCl = 7 mmol, ETA/V = 300 (molar ratio), 10 min, 50 °C.

[b] Activity in kg polymer/(mmol$_V$·h).

[c] NB-CH2OH content (mol %) estimated by ^{1}H NMR spectra.

[d] GPC data in 1,2,4-trichlorobenzene versus polystyrene standard.

[e] Determined by DSC.

[f] Et_2AlCl = 13 mmol.

[g] Et_2AlCl = 19 mmol.

[h] **I** = [$OC_6H_4CH{=}NCH_2C_5H_4N$]VCl_2(THF).[16(c)]

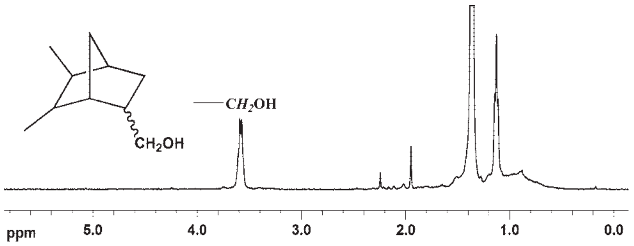


FIGURE 5 ^{1}H NMR spectrum for the copolymer formed with complex **2c** (entry 6 in Table 3).

activities toward ethylene/NB-CH$_2$OH copolymerization were much lower than those toward ethylene/norbornene copolymerization by complex **2c** under the similar conditions (e.g., entry 3 in Table 2 vs. entry 3 in Table 3), which presumably because of the steric hindrance of the protecting group on the NB-CH$_2$OH. The GPC analyses reveal that the obtained ethylene/NB-CH$_2$OH copolymers display both high MWs (M_w = 157–400 kg/mol) and unimodal MWDs (M_w/M_n = 2.5–3.0).

The data also show that the structure of the vanadium complex considerably affects both comonomer incorporation and the MW of the resultant copolymers. Much higher MW copolymers with more NB-CH$_2$OH incorporation were produced by complex **2c** over complex **2b**, indicating the influence of the methyl group on the alkoxide arm. A comparison of the copolymers obtained by different vanadium catalysts revealed that the copolymers produced by complex **3a** displayed not only higher MW but also much higher incorporation than those by complex **2a**, suggesting that the ancillary effect of imido group. Noticeably, although high catalytic activity toward the copolymerization was also observed by tridentate vanadium(III) catalyst [OC$_6$H$_4$CH = NCH$_2$C$_5$H$_4$N]VCl$_2$(THF) as reported previously[16(c)] (entry 8), the MW and the polar monomer content of the obtained copolymer were much lower than those produced by vanadium(V) complexes **2b**, **2c**, or **3a**, which indicates that the vanadium(V) complexes are the more attractive catalysts for the copolymerization of ethylene with functional norbornene.

Similar to the case of ethylene/norbornene copolymerization, increasing the amount of charged NB-CH$_2$OH resulted in the higher comonomer incorporation (entries 3, 5, and 6, 5.60–12.3 mol %), though the MW of the resultant copolymer decreased (M_w from 400 to 214 kg/mol) and the MWD slightly broadened (Fig. S8 in Supporting Information). In addition, the copolymerization was also sensitive to reaction temperature. The catalytic activity and the MW of the resultant copolymer decreased, but NB-CH$_2$OH incorporation increased when reaction temperature was elevated from 50 to 70 °C (entry 3 vs. entry 4).

The ethylene/NB-CH$_2$OH copolymers displayed melting temperature in the range of 117.6–126.6 °C, which was determined by means of DSC techniques at a heating rate of 10 °C/min. All copolymers produced displayed single melting temperature (see Supporting Information Figs. S9–11), indicating that the components of the copolymers are homogeneous. These copolymers differ from those obtained by metallocene/MAO catalytic systems, which exhibit two melting temperatures.[25(c)] The microstructures of the copolymers have been investigated using NMR techniques (Figs. 5 and 6). The peak presented at 3.56 ppm in ^{1}H NMR spectra is assigned to $-CH_2OH$, and the peaks at 67.37 and 64.84 ppm in ^{13}C NMR spectra indicate the exo and endo, respectively, with regard to the $-CH_2OH$ substituent at the norbornene backbone.[25(d)] These results represent the first examples of vanadium(V) catalysts, which exhibit attractive performance for the copolymerization of ethylene and functionalized norbornene.

CONCLUSIONS

We have synthesized and structurally characterized a series of vanadium(V) complexes bearing tetradentate trihydroxy amine ligands. The complexes displayed high catalytic activity toward ethylene polymerization in the presence of Et$_2$AlCl as a cocatalyst and Cl$_3$CCOOEt as a reactivating agent and produced high MW polyethylenes with unimodal MWD even at elevated reaction temperature. Catalyst structure plays an important role in tuning the catalytic activity and controlling the MW of the resulting polyethylenes. Further investigation shows that these complexes were also highly active catalysts for the copolymerization of ethylene with norbornene or 5-norbornene-2-methanol. Comonomer incorporation and polymer MW can be controlled in a wide range by the variation of catalyst structure and the reaction parameters. To the best of our knowledge, this is the first report

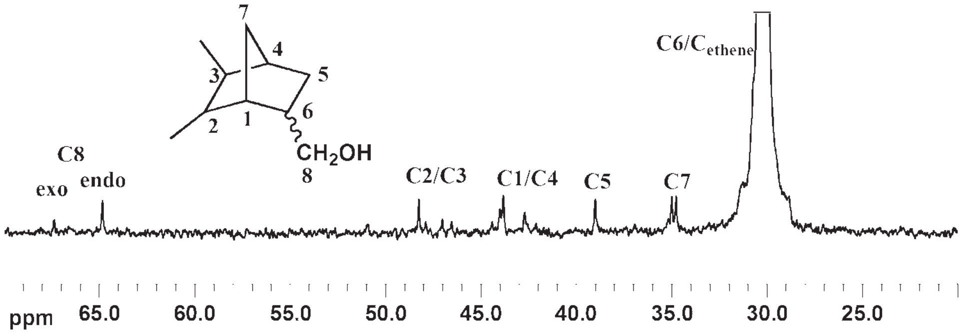


FIGURE 6 ^{13}C NMR spectrum for the copolymer formed with complex **2c** (entry 6 in Table 3).

on vanadium(V) complexes exhibiting high activity toward copolymerization of ethylene with polar norbornene derivative.

EXPERIMENTAL

General Procedures and Materials

All manipulation of air- and/or moisture-sensitive compounds was carried out under a dry argon atmosphere using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun SPS system. The NMR data of the ligand and vanadium complexes were obtained on a Bruker 300 MHz spectrometer at ambient temperature, with $CDCl_3$ as a solvent. ^{51}V NMR spectra were collected on a Bruker 78.92 MHz spectrometer and referenced to $VOCl_3$ ($\delta = 0$) as an external standard. The NMR data of polymers were obtained on a Varian Unity-400 MHz spectrometer at 135°C, with *o*-$C_6D_4Cl_2$ as a solvent. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific). The DSC measurements were performed on a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter at a rate of 10 °C/min. The weight-average MW (M_w) and the polydispersity index of polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene was used as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The intrinsic viscosity of the polymer sample was measured in decalin at 135 °C using an Ubbleohed viscometer, and the viscosity-average MW was calculated using the following equation.[26]

$$[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$$

Ethyl trichloroacetate (ETA) was purchased from Aldrich, dried over calcium hydride at room temperature, and then distilled. $VOCl_3$, $VO(O^nPr)_3$, phenol compounds, and amine compounds were purchased from Aldrich. Diethylaluminium chloride was obtained from Albemarle Corp. Literature procedures were used to synthesize amine trihydroxy ligands[27] and VCl_3(*N*-2,6-$Me_2C_6H_3$).[21]

Synthesis of Trihydroxy Amine Ligands (1a–d)

To a stirred solution of 2-methoxy-4-methylphenol (2.76 g, 20 mmol) in CH_3OH (25 mL) was added bis(2-hydroxypropyl)amine (2.66 g, 20 mmol) and paraformaldehyde (0.6 g, 20 mmol). After refluxing 72 h, the evaporation of the solvent under reduced pressure gave black oil, which was purified by column chromatography on silica gel using petroleum ether/methanol (5/1) as an eluent to give the product as white powder (4.25 g, 15 mmol) in 75% yield. Ligands **1b–d** were prepared analogously.

1a

^{1}H NMR ($CDCl_3$, 25 °C): δ 6.64 (s, 1H, Ar-*H*), 6.47 (s, 1H, Ar-*H*), 3.99 (sept, *J* = 6.0 Hz, 2H, C*H*), 3.81 (s, 3H, OC*H*$_3$), 3.79 (s, 2H, ArC*H*$_2$), 2.62 (d, *J* = 6.0 Hz, 4H, NC*H*$_2$), 2.25 (s, 3H, ArC*H*$_3$), 1.12 (d, *J* = 2.4 Hz, 6H, CHC*H*$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 147.92 (*C*), 143.97 (*C*), 128.80 (*C*), 123.22 (*C*), 122.44 (*C*H), 112.38 (*C*H), 66.64 (*C*H), 64.51 (*C*H), 63.80 (*C*H$_2$), 62.31 (*C*H$_2$), 59.43 (*C*H$_2$), 58.39 (*C*H$_3$), 56.21 (*C*H$_2$), 21.37 (*C*H$_3$), 21.10 (*C*H$_3$), 20.90 (*C*H$_3$). Anal. Calcd. for $C_{15}H_{25}NO_4$: C, 63.58; H, 8.89; N, 4.94. Found: C, 63.60; H, 8.94; N, 4.90.

1b

Yield 70%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.61 (s, 2H, Ar-*H*), 6.56 (s, 2H, Ar-*H*), 3.83 (s, 6H, OC*H*$_3$), 3.82 (s, 4H, ArC*H*$_2$), 3.79 (t, *J* = 3.0 Hz, 2H, OC*H*$_2$), 2.75 (t, *J* = 6.0 Hz, 4H, NC*H*$_2$), 2.25 (s, 6H, ArC*H*$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 147.46 (*C*), 143.35 (*C*), 129.12 (*C*), 122.97 (*C*), 122.08 (*C*H), 112.18 (*C*H), 60.40 (*C*H$_2$), 56.23 (*C*H$_2$), 55.74 (*C*H$_3$), 21.39 (*C*H$_3$). Anal. Calcd. for $C_{20}H_{27}NO_5$: C, 66.46; H, 7.53; N, 3.88. Found: C, 66.42; H, 7.55; N, 3.82.

1c

Yield 69%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.61 (s, 2H, Ar-*H*), 6.54 (s, 2H, Ar-*H*), 4.13 (sept, *J* = 6.0 Hz, 1H, C*H*CH$_3$), 3.85 (s, 6H, OC*H*$_3$), 3.78 (br, 4H, ArC*H*$_2$), 2.53 (m, 2H, NC*H*$_2$), 2.25 (s, 6H, ArC*H*$_3$), 1.08 (d, *J* = 6.0 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 147.47 (*C*), 143.34 (*C*), 128.93 (*C*), 122.92 (*C*), 122.71 (*C*H), 112.10 (*C*H), 65.59 (*C*H), 61.99 (*C*H$_2$), 56.73 (*C*H$_3$), 56.19 (*C*H$_2$), 21.38 (*C*H$_3$), 20.96 (*C*H$_3$). Anal. Calcd. for $C_{21}H_{29}NO_5$: C, 67.18; H, 7.79; N, 3.73. Found: C, 67.21; H, 7.73; N, 3.78.

1d

Yield 78%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.77 (s, 2H, Ar-*H*), 6.56 (s, 2H, Ar-*H*), 4.10 (sept, *J* = 6.0 Hz, 1H, C*H*CH$_3$), 3.65 (br, 4H, ArC*H*$_2$), 2.41 (m, 2H, NC*H*$_2$), 2.12 (s, 6H, ArC*H*$_3$), 2.10 (s, 6H, ArC*H*$_3$), 1.06 (d, *J* = 6.0 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.4 (*C*), 131.34 (*C*), 129.93 (*C*), 125.92 (*C*), 122.79 (*C*H), 114.16 (*C*H), 66.59 (*C*H), 61.57 (*C*H$_2$), 51.19 (*C*H$_2$), 24.38 (*C*H$_3$), 22.92 (*C*H$_3$), 14.58 (*C*H$_3$). Anal. Calcd. for $C_{21}H_{29}NO_3$: C, 73.44; H, 8.51; N, 4.08. Found: C, 73.50; H, 8.56; N, 4.03.

Synthesis of Oxovanadium(V) Complexes

To a stirred solution of $VO(O^nPr)_3$ (244 mg, 1.0 mmol) in dried CH_2Cl_2 (20 mL) was added slowly a solution of ligand **1a** (283 mg, 1.0 mmol) in CH_2Cl_2 (20 mL). After stirring for 4 h at room temperature, the red reaction mixture was concentrated to about 5 mL. Crystallization by diffusion of *n*-hexane (10 mL) into the clear solution yielded red black crystals of **2a** (264 mg, 76%). Compounds **2b–d** were prepared analogously.

2a

^{1}H NMR ($CDCl_3$, 25 °C): δ 6.68 (s, 2H, Ar-*H*), 6.65 (s, 2H, Ar-*H*), 6.53 (s, 2H, Ar-*H*), 6.49 (s, 2H, Ar-*H*), 5.03 (sept, *J* = 4.2 Hz, 2H, C*H*), 4.64 (sept, *J* = 4.2 Hz, 2H, C*H*), 3.88 (s, 6H, OC*H*$_3$), 3.74 (penta, *J* = 55.8 Hz, 4H, ArC*H*$_2$), 2.71 (d, *J* = 12.0 Hz, 4H, NC*H*$_2$), 2.51 (d, *J* = 12.0 Hz, 4H, NC*H*$_2$), 2.28 (s, 6H, ArC*H*$_3$), 1.22 (m, 12H, CHC*H*$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 156.28 (*C*), 145.96 (*C*), 133.05 (*C*), 126.03 (*C*), 122.37 (*C*H), 113.09 (*C*H), 82.86 (*C*H), 59.90 (*C*H), 56.68

(CH_2), 56.58 (CH_2), 56.39 (CH_3), 21.53 (CH_3). ^{51}V NMR (78.92 MHz, $CDCl_3$): δ −368. IR (KBr pellets): ν 2923, 2856, 1581, 1483, 1367, 1326, 1243, 1160, 1103, 967, 850, 643 cm^{-1}. EI-MS (70 ev): $m/z = 694$ [M^+]. Anal. Calcd. for $C_{30}H_{44}N_2O_{10}V_2$: C, 51.88; H, 6.93; N, 4.03. Found: C, 51.94; H, 6.95; N, 3.98.

2b

Yield 83%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.60 (s, 2H, Ar-*H*), 6.49 (s, 2H, Ar-*H*), 4.82 (br, 2H, OCH_2), 3.85 (s, 6H, OCH_3), 3.45 (br, 4H, $ArCH_2$), 2.72 (br, 2H, NCH_2), 2.26 (s, 6H, $ArCH_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 155.73 (*C*), 145.50 (*C*), 132.74 (*C*), 125.72 (*C*), 122.00 (*C*H), 112.54 (*C*H), 56.20 (CH_2), 55.75 (CH_2), 53.05 (CH_3), 21.19 (CH_3). ^{51}V NMR (78.92 MHz, $CDCl_3$): δ −364. IR (KBr pellets): ν 2919, 2850, 1602, 1581, 1462, 1366, 1322, 1242, 1160, 1100, 954, 857, 618, 540 cm^{-1}. EI-MS (70 ev): $m/z = 425$ [M^+]. Anal. Calcd. for $C_{20}H_{24}NO_6V$: C, 56.47; H, 5.69; N, 3.29. Found: C, 56.41; H, 5.66; N, 3.34.

2c

Yield 98%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.60 (s, 2H, Ar-*H*), 6.37 (s, 2H, Ar-*H*), 5.16 (sept, *J* = 6.0 Hz, 1H, $CHCH_3$), 3.85 (d, *J* = 6.0 Hz, 6H, OCH_3), 3.72 (br, 4H, $ArCH_2$), 2.52 (br, 2H, NCH_2), 2.26 (d, *J* = 12.0 Hz, 6H, $ArCH_3$), 1.16 (d, *J* = 6.0 Hz, 3H, $CHCH_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 156.13 (*C*), 146.44 (*C*), 133.23 (*C*), 125.80 (*C*), 123.05 (*C*H), 112.31 (*C*H), 84.54 (*C*H), 60.31 (*C*H), 56.78 (CH_2), 55.54 (CH_2), 55.35 (CH_3), 21.57 (CH_3). ^{51}V NMR (78.92 MHz, $CDCl_3$): δ −365. IR (KBr pellets): ν 2958, 2919, 2852, 1604, 1581, 1482, 1369, 1328, 1243, 1160, 1101, 1053, 964, 859, 643, 618 cm^{-1}. EI-MS (70 ev): $m/z = 439$ [M^+]. Anal. Calcd. for $C_{21}H_{26}NO_6V$: C, 57.41; H, 5.96; N, 3.19. Found: C, 57.51; H, 5.91; N, 3.14.

2d

Yield 88%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.88 (s, 2H, Ar-*H*), 6.64 (s, 2H, Ar-*H*), 5.19 (sept, *J* = 6.0 Hz, 1H, $CHCH_3$), 3.73 (br, 2H, $ArCH_2$), 2.51 (br, 2H, NCH_2), 2.34 (d, *J* = 12.0 Hz, 6H, $ArCH_3$), 2.23 (d, *J* = 12.0 Hz, 6H, $ArCH_3$), 1.18 (d, *J* = 6.0 Hz, 3H, $CHCH_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 159.20 (*C*), 148.23 (*C*), 133.55 (*C*), 126.60 (*C*), 124.45 (*C*H), 114.35 (*C*H), 86.62 (*C*H), 61.39 (*C*H), 56.97 (CH_2), 54.44 (CH_2), 23.35 (CH_3), 21.57 (CH_3), 14.57 (CH_3). ^{51}V NMR (78.92 MHz, $CDCl_3$): δ −364. IR (KBr pellets): ν 2977, 2918, 2851, 1605, 1472, 1449, 1371, 1239, 1218, 1159, 1077, 949, 862, 751, 641, 614 cm^{-1}. EI-MS (70 ev): $m/z = 407$ [M^+]. Anal. Calcd. for $C_{21}H_{26}NO_4V$: C, 61.91; H, 6.43; N, 3.44. Found: C, 61.82; H, 6.38; N, 3.39.

Synthesis of (Arylimido)vanadium(V) Complex 3a

To a slurry of NaH (26.4 mg, 1.1 mmol) in Et_2O (10 mL) was added to a solution of ligand **1a** (283 mg, 1.0 mmol) in Et_2O (10 mL) at −30 °C. The resulting suspension was warmed to room temperature and stirred for 4 h. Then, the white mixture was slowly transferred to an Et_2O solution (20 mL) containing $VCl_3(N\text{-}2,6\text{-}Me_2C_6H_3)$ (276 mg, 1.0 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature (25 °C), and the mixture was stirred over night. The reaction mixture was condensed and filtered to remove NaCl and the excess NaH. The filtrate was concentrated and recrystallized in Et_2O/*n*-hexane yielded 157 mg of the pure complex as red crystal (35%).

^{1}H NMR ($CDCl_3$, 25 °C): δ 6.64–6.81 (m, 3H, Ar-*H*), 6.65 (s, 1H, Ar-*H*), 6.59 (s, 1H, Ar-*H*), 6.41 (s, 1H, Ar-*H*), 5.03 (sept, *J* = 4.2 Hz, 1H, C*H*), 4.90 (sept, *J* = 4.2 Hz, 1H, C*H*), 3.74 (s, 3H, OCH_3), 3.72 (br flat, 2H, $ArCH_2$), 2.71 (d, *J* = 12.0 Hz, 2H, NCH_2), 2.74 (s, 6H, $ArCH_3$), 2.51 (m, 4H, NCH_2), 2.21 (s, 3H, $ArCH_3$), 1.22 (d, *J* = 3.0 Hz, 3H, $CHCH_3$), 1.01 (d, *J* = 3.0 Hz, 3H, $CHCH_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 159.92 (*C*), 147.97 (*C*), 134.75 (*C*), 128.87 (*C*H), 128.23 (*C*H), 126.75 (*C*),126.69 (*C*H), 125.88 (*C*), 122.06 (*C*H), 113.69 (*C*H), 81.58 (*C*H), 78.41 (*C*H), 61.13 (CH_2), 59.71 (CH_2), 59.43 (CH_2), 56.48 (CH_3), 55.63 (CH_2), 21.64 (CH_3), 20.82 (CH_3), 18.40 (CH_3). ^{51}V NMR (78.92 MHz, $CDCl_3$): δ −249. IR (KBr pellets): ν 2961, 2919, 2851, 1579, 1484, 1314, 1250, 1160, 1125, 1104, 1070, 990, 955, 842, 669, 641 cm^{-1}. EI-MS (70ev): $m/z = 450$ [M^+]. Anal. Calcd. for $C_{23}H_{31}N_2O_4V$: C, 61.33; H, 6.94; N, 6.22. Found: C, 61.18; H, 6.90; N, 6.27.

General Procedure for Ethylene (Co)Polymerization

Ethylene polymerizations were conducted in toluene by using a 100-mL scale autoclave. Toluene, Et_2AlCl, ETA, and comonomer were charged into the autoclave in sequence in the drybox. The autoclave was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution containing a prescribed amount of catalyst via a syringe, the reactor was sealed and pressurized to the desired level, and then the stirring motor was engaged. After the prescribed reaction time, the stirring motor was stopped and the reactor was vented, and the resulted mixture was added to acidic ethanol. The solid polymer was isolated by filtration, washed with ethanol, and dried at 60 °C for 12 h *in vacuo*.

Crystallographic Studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystallographic data, collection parameters, and refinement parameters are listed in Supporting Information (Table S1). The crystals were manipulated in a glovebox. The intensity data were collected with the ω scan mode (186K) on a Bruker Smart APEX diffractometer with CCD detector using Mo Kα radiation ($\lambda = 0.71073$Å). Lorentz, polarization factors were made for the intensity data, and absorption corrections were performed using SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

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