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Olefin Polymerization and Ring-Opening Metathesis Polymerization of Norbornene by (Arylimido)(aryloxo)vanadium(V) Complexes of the Type $VX_2(NAr)(OAr')$. Remarkable Effect of Aluminum Cocatalyst for the Coordination and Insertion and Ring-Opening Metathesis Polymerization

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ABSTRACT: Various (arylimido)(aryloxo)vanadium(V) complexes of the type $VCl_2(NAr)(OAr')$ [NAr = N-2,6-$Me_2C_6H_3$ (**2**), N-2,6-$^iPr_2C_6H_3$ (**3**); OAr′ = O-2,6-$Me_2C_6H_3$ (**a**), O-2,6-$^iPr_2C_6H_3$ (**b**), O-2,6-$^tBu_2$-4-MeC_6H_2 (**c**)] have been prepared in high yields from $VCl_3(NAr)$ with Ar′OH in *n*-hexane. **2b** exhibited remarkable catalytic activity for ethylene polymerization in the presence of methylaluminoxane (MAO), affording high molecular weight polymer with unimodal molecular weight distribution ($M_w = 2.92 \times 10^6$, $M_w/M_n = 2.88$). $V(CH_2Ph)_2$(N-2,6-$Me_2C_6H_3$)(O-2,6-$^iPr_2C_6H_3$) (**4**) initiated ring-opening metathesis polymerization (ROMP) of norbornene without cocatalyst, affording high molecular weight polymer with unimodal molecular weight distribution ($M_w = 4.69 \times 10^6$, $M_w/M_n = 1.93$). The ROMP also proceeded efficiently if **2b** or **2c** was treated with $AlMe_3$ (5−10 equiv) in toluene, and high stereoregularity (trans/cis = 91/9) in the olefinic double bond for the resultant polymer was observed by **2b**. On the other hand, remarkable catalytic activities by **2b** (3700−8300 kg of PE/mol of V h) have also been observed for ethylene polymerization in the presence of Et_2AlCl, which was an ineffective cocatalyst for the above ROMP.

Introduction

Olefin polymerization by homogeneous transition-metal catalysis attracts particular attention not only in the field of organometallic chemistry and catalysis but also in the field of polymer chemistry.[1] Although the classical Ziegler−Natta vanadium catalyst systems have displayed a number of interesting characteristics[2−5] such as (a) synthesis of high molecular weight polymers with narrow polydispersity,[3] (b) synthesis of ethylene/α-olefin copolymer with high α-olefin content,[4] and (c) others,[5] examples with vanadium complexes as the olefin polymerization catalysts have been limited so far.[6,7]

We reported that *nonbridged* (cyclopentadienyl)(aryloxo)titanium(IV) complexes of the type $Cp'TiCl_2(OAr)$ [Cp′ = C_5Me_5, 1,3-$Me_2C_5H_3$, etc.; OAr = O-2,6-$^iPr_2C_6H_3$, etc.] exhibited remarkable catalytic activity not only for ethylene polymerization but also for ethylene/α-olefin copolymerization.[8] Moreover, these complexes also exhibited notable catalytic activity for styrene polymerization, and efficient ethylene/styrene copolymerization could be accomplished by (1,3-$Me_2C_5H_3$)$TiCl_2$(O-2,6-$^iPr_2C_6H_3$), affording poly(ethylene-*co*-styrene) exclusively with efficient styrene incorporation.[9] Since we would like to expand our titanium chemistry for finding a new type of catalyst with the other transition metals, also since the classical vanadium catalysts displayed interesting characteristics as described above, we thus had an interest to explore the possibility for designing new type of vanadium catalyst for precise olefin polymerization.

We focused on vanadium(V) complexes containing an arylimido ligand, because syntheses of a series of the (arylimido)vanadium(V) complexes have already been established by several researchers[10] and also because this ligand moiety should be relatively stable at high temperature.[10c] In addition, we also focused on the synthesis of a 14e vanadium(V) complex which should have the same electron count as our original half-metallocene type titanium catalyst.[8,9]

We reported as our preliminary communication that (arylimido)(aryloxo)vanadium(V) complexes of the type VCl_2(N-2,6-$Me_2C_6H_3$)(OAr) [OAr = O-2,6-$^iPr_2C_6H_3$ (**2b**), O-2,6-$^tBu_2$-4-MeC_6H_2 (**2c**)] exhibited remarkable catalytic activities for ethylene polymerization in the presence of methylaluminoxane (MAO) and that $V(CH_2Ph)_2$(N-2,6-$Me_2C_6H_3$)(O-2,6-$^iPr_2C_6H_3$) (**4**) initiated ring-opening metathesis polymerization (ROMP) of norbornene.[11] Since we assumed that both cationic vanadium(V)−alkyl and vanadium(V)−alkylidene species would play important key roles in these polymerizations also since moderate catalytic activity for olefin polymerization was observed in the presence of an alkylaluminum cocatalyst in Ziegler type vanadium catalysts,[2−5] we thus explored the possibility for finding more efficient catalyst systems. In the present paper, we wish to introduce more details concerning olefin polymerization with (arylimido)(aryloxo)vanadium(V) complexes (Chart 1); we especially wish to introduce a notable effect of alkylaluminum not only for ethylene addition (coordination and insertion) polymerization but also for the ring-opening metathesis polymerization (ROMP) of norbornene.[12,13]

Results and Discussion

1. Synthesis of (Arylimido)(aryloxo)vanadium(V) Complexes. $VCl_3(NAr)$ (NAr = 2,6-$Me_2C_6H_3$, N-2,6-$^iPr_2C_6H_3$) complexes could be prepared in high yields (90−95%) from $VOCl_3$ with ArNCO in octane (reflux for

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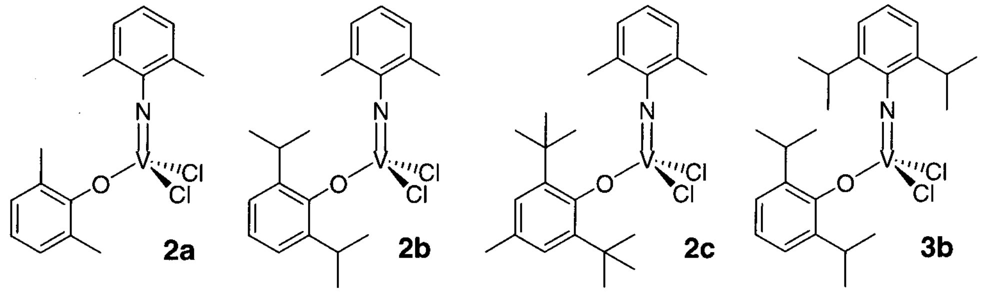
Chart 1



Scheme 1

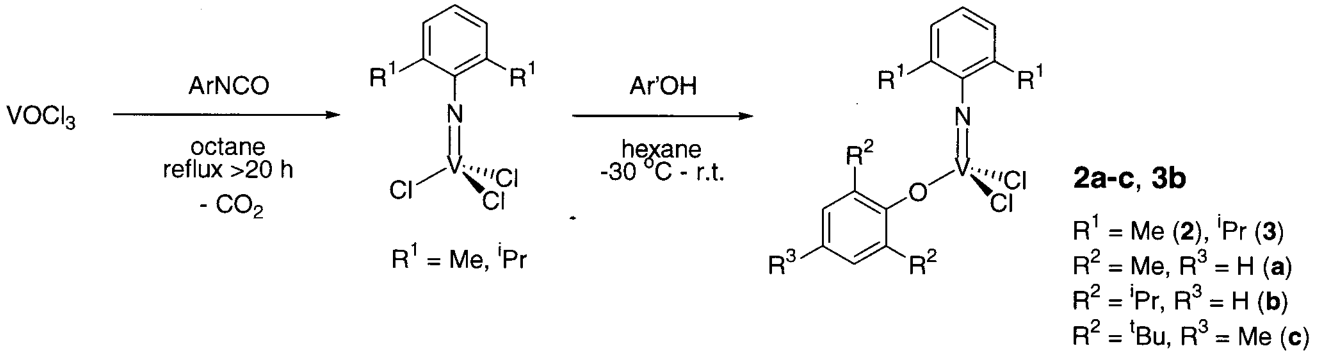


Table 1. Ethylene Polymerization Catalyzed by $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ [OAr = $O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (2b), O-2,6-*tert*-Bu_2-4-MeC_6H_2 (2c)]−Cocatalyst System[a]

run no.	catalyst (μmol)	cocatalyst (Al/V)[b]	solvent	temp/°C	time/min	yield/mg	activity[c]	M_w[d]/×10^{-4}	M_w/M_n[d]
1	**2b** (5.0)	d-MAO (1000)	toluene	0	10	480	576	609	2.61
2	**2b** (5.0)	d-MAO (1000)	toluene	0	10	449	539	600	2.69
3	**2b** (5.0)	d-MAO (1000)	toluene	25	10	802	962	292	2.88
4	**2b** (5.0)	d-MAO (1000)	toluene	25	10	806	967	203	2.73
5	**2b** (5.0)	d-MAO (1000)	toluene	40	10	290	348		
6	**2b** (5.0)	MMAO (1000)	*n*-hexane	25	10	173	208		
7	**2b** (5.0)	Al^iBu_3/B (500/1.5)[e]	toluene	25	10	80	95.4		
8	**2c** (5.0)	d-MAO (1000)	toluene	25	10	202	242		
9	**2c** (2.0)	d-MAO (2500)	toluene	60	10	162	486	78.4	2.07
10	**2c** (2.0)	d-MAO (2500)	toluene	60	10	154	462		
11	**2c** (2.0)	d-MAO (2500)	toluene	80	10	67.0	201		
12	**2c** (5.0)	MMAO (1000)	*n*-hexane	25	10	121	145		
13	**2c** (2.0)	MMAO (2500)	*n*-hexane	25	60	447	224	65.9	5.61

[a] Reaction conditions: toluene or *n*-hexane 30 mL, ethylene 8 atm, 10 min, 100 mL scale autoclave, d-MAO (prepared by removing $AlMe_3$ and toluene from commercially available MAO) or MMAO (methylisobutylaluminoxane, 5.8 wt % Al in hexane). [b] Molar ratio of Al/V. [c] Activity = kg of PE/(mol of V h). [d] GPC data in *o*-dichlorobenzene vs polystyrene standard. [e] $Al^iBu_3/Ph_3CB(C_6F_5)_4/V = 500/1.5/1.0$ (molar ratio).

20 h), and this should be an established procedure for preparing a series of (arylimido)vanadium(V) complexes.[10] The desired complexes could be isolated as the pure needles from the chilled *n*-hexane solution (−30 °C).

It was revealed that (arylimido)(aryloxo)vanadium(V) complexes of the type $VCl_2(NAr)(OAr')$ [NAr = 2,6-$Me_2C_6H_3$ (**2**), N-2,6-$^iPr_2C_6H_3$ (**3**); OAr′ = O-2,6-$Me_2C_6H_3$ (**a**), O-2,6-$^iPr_2C_6H_3$ (**b**), O-2,6-$^tBu_2$-4-MeC_6H_2 (**c**)] have been prepared in high yields from $VCl_3(NAr)$ (**1**) by treating with 1.0 equiv of the corresponding phenol in *n*-hexane (Scheme 1). These complexes could also be prepared by adding the corresponding lithium phenoxide in place of phenol in Et_2O. The products isolated were deep purple microcrystals and could be identified by ^1H, ^{13}C NMR, and repeated elemental analysis runs.

2. Olefin Polymerization Catalyzed by 2−MAO, MMAO Catalyst Systems. 2.1. Ethylene Polymerization. Ethylene polymerizations by **2b**,**c** were conducted in toluene or in *n*-hexane using a 100 mL scale autoclave and a d-MAO white solid prepared by removing toluene and an excess amount of $AlMe_3$ from commercially available MAO (PMAO-S, Tosoh Finechem Co.) or MMAO (methylisobutylaluminoxane, Tosoh Finechem Co.) was used as the cocatalyst. The results are summarized in Table 1.

It turned out that **2b** exhibited significant catalytic activity for ethylene polymerization in the presence of d-MAO, and the use of d-MAO was more effective than MMAO or $Al^iBu_3-Ph_3CB(C_6F_5)_4$ under the optimized conditions (runs 3−4, 6−7). The activity by **2b** decreased if the polymerization was performed at 0 or 40 °C. We assume that the decrease in the activity at 40 °C would be due to partial decomposition of the catalytically active species as also observed in the ethylene polymerization with different cocatalyst mentioned below. The catalytic activity by **2c** in the presence of d-MAO at 25 °C was somewhat lower than that by **2b**, but the activity increased at higher temperature of 60 °C (runs 8−10). In addition, interestingly, the catalytic activity by **2c** did not decrease after 60 min if MMAO was used in *n*-hexane (runs 12−13). These results suggest that effect

Table 2. Polymerization of Propylene by the 2b−d-MAO Catalyst System[a]

run no.	propylene/ atm	temp/ °C	time/ min	activity[b]	M_w[c]/×10^{-4}	M_w/M_n[c]
14	8	0	60	14.2	38.6	2.00
15	6	0	60	13.6		
16	6	25	60	4.02	24.5	2.01
17	6	40	60	3.72	21.7	1.85

[a] Conditions: **2b** 5.0 μmol, toluene 30 mL, d-MAO (prepared by removing $AlMe_3$ and toluene from commercially available MAO), Al/V = 1000 (molar ratio), 100 mL scale autoclave. [b] Activity = kg of PP/(mol of V h). [c] GPC data in *o*-dichlorobenzene vs polystyrene standard.

of steric bulk plays a role for the activity. We expect that the reason for the higher activity than those previously reported using a series of (arylimido)vanadium(V) complexes[7] would be due to the low-coordinate (14e) vanadium species as the starting catalyst precursor.

The resultant polymer by **2b** was linear, which was confirmed by NMR spectroscopy, and possessed exceptionally high molecular weight with unimodal molecular weight distribution ($M_w = 2.92 \times 10^6$, $M_w/M_n = 2.88$, run 3), and the M_w value increased if the polymerization was performed at 0 °C ($M_w = 6.09 \times 10^6$, $M_w/M_n = 2.61$, run 1). The polydispersity by **2c** was narrow even at 60 °C if d-MAO was used as the cocatalyst in toluene ($M_w/M_n = 2.07$, run 9), but the M_w/M_n value became broad even at 25 °C if MMAO was used as the cocatalyst in *n*-hexane ($M_w/M_n = 5.61$, run 13).

2.2. Polymerization of Propylene, 1-Hexene by 2b−MAO Catalyst System. Table 2 summarizes results for propylene polymerization with the **2b**−d-MAO catalyst in toluene. The catalytic activities by **2b** were significantly lower than those in ethylene polymerization, and the activity increased at lower temperature. The resultant polymers possessed relatively high molecular weights with unimodal molecular weight distributions ($M_w/M_n = 1.85-2.01$) in all cases, which might suggest that the polymerization would proceed with single-site nature in all cases. However, ^{13}C 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).

Polymerization of 1-hexene by the **2b**−d-MAO catalyst system was also conducted at 25 °C (conditions: **2b** 5.0 μmol, d-MAO with Al/V molar ratio = 1000, 1-hexene 5.0 g, 9 h). The observed catalytic activity was lower than those in both ethylene and propylene polymerizations (2.03 kg of PH/mol of V h), although the resultant polymer possessed unimodal molecular weight distribution ($M_w = 8.11 \times 10^4$, $M_w/M_n = 1.69$). As expected from the propylene polymerization results, the resultant polymer had no stereoregularity and contained both 1,2- and 2,1-inserted units. One probable assumption for the observed lower catalytic activities for these polymerizations (propylene, 1-hexene) compared to those for ethylene polymerization would be due to the steric hindrance between the metal center coordinated with the arylimido and aryloxo ligands and the methyl or *n*-butyl group attached to the olefinic double bond especially in 2,1-insertion.

3. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene with $V(CH_2Ph)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (4). As introduced in our preliminary communication,[11] attempts to isolate the above dibenzyl complex **4** from **2b** by treating with $PhCH_2MgCl$ or $Mg(CH_2Ph)_2(THF)_n$ was not successful, probably due to the difficulty for isolation of **4** from the reaction mixture. However, the desired complex $V(CH_2Ph)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**4**) could be synthesized from its tribenzyl analogue, $V(CH_2Ph)_3(N\text{-}2,6\text{-}Me_2C_6H_3)$,[14] by treating with 1.0 equiv of $2,6\text{-}{}^iPr_2C_6H_3OH$ in dichloromethane.

It should be noted that ring-opened poly(norbornene), which could be identified by ^1H and ^{13}C NMR spectra as the mixture of cis/trans olefinic double bonds, could be isolated if norbornene and **2** were dissolved in toluene. In addition, interestingly, the resultant polymer possessed high molecular weight with unimodal molecular weight distribution ($M_w = 4.69 \times 10^6$, $M_w/M_n = 1.93$). This is, as far as we know, the first example of a vanadium complex initiating ring-opening metathesis polymerization (ROMP) without a cocatalyst. In addition, this is also the rare example affording exceptionally high molecular weight polymer with unimodal molecular weight distribution.[15] Since the polymerization should proceed via metathesis mechanism, we assumed that the vanadium(V)−alkylidene complex would play an essential role in this catalysis (Scheme 2).[16]

4. Ring-Opening Metathesis Polymerization of Norbornene with $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ (2)−Cocatalyst System. Ziegler-type vanadium catalyst systems (e.g., $VCl_4/AlEt_3$, VCl_4/Et_2Mg, VCl_4/Et_3Ga, etc.) have been known to be active in cyclobutene addition polymerization, although the ring-opened polymer was prepared with the $VCl_4/{}^nBuLi$ catalyst.[17] Furthermore, polymerization of cyclopentene with $VCl_4/AlEt_3$, $VOCl_3/Et_2AlCl$, or $V(acac)_3/Et_2AlCl$ was known to give a mixture of metathesis and addition polymerization products, but the catalytic activities observed were extremely low.[18] Therefore, the descriptions concerning metathesis polymerization with vanadium have been limited so far.[17−19] One description could be found concerning ROMP of norbornene with vanadium catalysts.[19] Since a lot of studies have been devoted concerning $Cp_2Ti{=}CH_2$ chemistry[20,21] (derived from so-called Tebbe reagent[20]) including ROMP,[21d] we explored the possibility of vanadium as the initiator for ROMP of norbornene by the similar approach of titanium.[20d,22]

As shown in Tables 3−5, polymerization of norbornene took place if **2b** or **2c** was treated with $AlMe_3$ in toluene. The catalytic activities were improved significantly, especially compared to the above example using **4**, although the resultant polymer possessed relatively low molecular weight compared to the former case (Table 5).

Figures 1 and 2 show typical ^1H and ^{13}C NMR spectra for the resultant poly(norbornene) prepared by the **2b**−$AlMe_3$ system (run 43, Table 5). ^1H NMR showed the broad resonances at 5.2−5.4 ppm and between 1 and 1.9 ppm in addition to 2.4 and 2.8 ppm. Four resonances were observed in the ^{13}C NMR spectrum. Comparison of these spectral data with those reported previously[20d,22,23] shows that these resonances are characteristic of ring-opened polymer of this general type. The result thus indicates that the polymerization by **2b**−$AlMe_3$ took place in a ring-opened metathesis fashion without accompanying addition polymerization. Moreover, based on the ^1H NMR spectral data with those previously reported,[20d,22,23] high trans-stereoregularity (trans/cis = 91/9) was observed for the resultant ROMP polymers. The results are reproducible in this catalysis, although the observed stereoselectivity was somewhat

Scheme 2

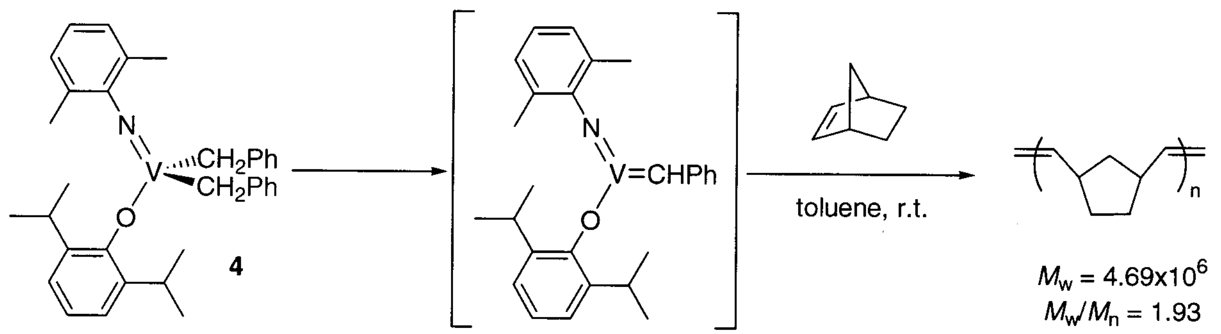


Table 3. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene with the $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (2b)−Cocatalyst Systems;[a] Effect of Cocatalyst

run no.	complex (μmol)	cocatalyst (equiv)[b]	time/ min	polymer yield/mg	TON[c]
18	**2b** (10)	$AlMe_3$ (5)	30	29.0	31
19	**2b** (20)	$AlMe_3$ (5)	20	28.2	15
20	**2b** (20)	$AlEt_3$ (2)	60	5.1	2.7
21	**2b** (20)	$AlEt_3$ (5)	60	4.3	2.3
22	**2b** (20)	$AlEt_3$ (10)	60	trace	
23	**2b** (10)	$SnMe_4$ (10)	60		
24	**2b** (10)	Et_2AlCl 10)			
25	Cp_2ZrCl_2 (10)	$AlMe_3$ (5)	60		
26	Cp_2ZrCl_2 (10)	$AlMe_3$ (10)	75	trace	
27	Cp_2TiCl_2 (10)	$AlMe_3$ (10)	60		

[a] Conditions: toluene 2.43 mL (2.1 g), norbornene 100 mg, −30 to 25 °C. [b] Molar ratio based on vanadium ($AlMe_3$, $AlEt_3$, and Et_2AlCl were used as 1 M *n*-hexane solution). [c] TON (turnover number) = norbornene consumed (mmol)/V(mmol).

Table 4. ROMP of Norbornene with the 2b−$AlMe_3$ Catalyst System[a]

run no.	**2b**/μmol	Al/V[b]	time/min	polymer yield/mg	TON[c]
28	10	2	10	15.3	16
29	10	2	20	26.3	28
30	10	2	20	27.4	29
31	10	5	10	21.0	22
18	10	5	30	29.0	31
19	20	5	20	28.2	15
32	20	5	60	42.6	23
33	20	10	15	24.9	13
34	20	10	30	31.0	16
35	20	10	60	49.4	26

[a] Conditions: toluene 2.43 mL (2.1 g), norbornene 100 mg, −30 to 25 °C. [b] Molar ratio based on vanadium ($AlMe_3$ was used as 1.0 M *n*-hexane solution). [c] TON (turnover number) = norbornene consumed (mmol)/V(mmol).

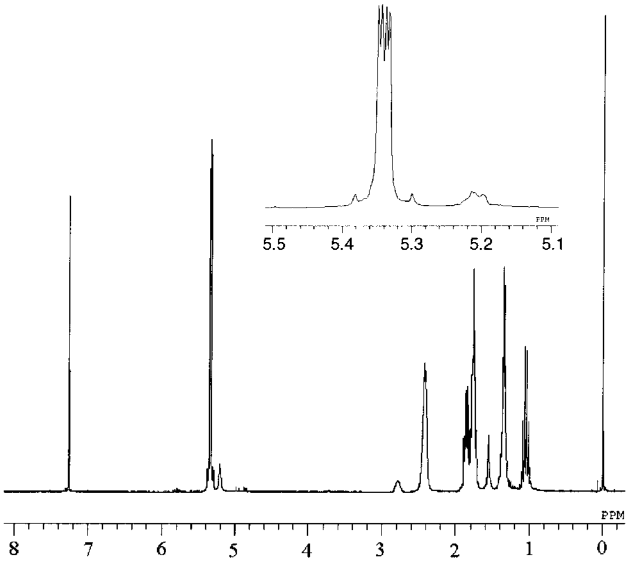


Figure 1. ^1H NMR spectra ($CDCl_3$) for ring-opened poly(norbornene) prepared by the **2b**−$AlMe_3$ catalyst system (run 43, Table 5).

different from that by **4**. We assume that the reason for the observed high stereospecifity would be explained similarly by those reported for the ROMP by half-metallocene type tantalum−carbene complexes or by well-defined molybdenum−alkylidene complexes,[24,25] where rotation of alkylidene and/or coordination of norbornene would be controlled by bulky arylimido and aryloxo ligands.

The use of $SnMe_4$ or Et_2AlCl in place of $AlMe_3$ did not initiate the ROMP under the same conditions, and a trace amount of polymer could be collected if $AlEt_3$ was used in place of $AlMe_3$ (Table 3). We assumed that the observed difference would be due to the efficiency for generating metal−alkylidene species. In addition, the catalytic activities with Cp_2TiCl_2 or Cp_2ZrCl_2 in place of **2a** were extremely low under the same reaction

Table 5. ROMP of Norbornene with the $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ [OAr = $O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (2b), O-2,6-*tert*-Bu_2-4-MeC_6H_2 (2c)]−$AlMe_3$ Catalyst[a]

run no.	V complex (μmol)	Al/V[b]	monomer conc[c]	time/min	polymer yield/mg	TON[d]	$M_n{}^e/\times10^{-4}$	$M_w/M_n{}^e$
36	**2c** (20)	10	0.44	30	54.1	29	8.5	2.0
37	**2c** (20)	10	0.44	120	89.7[f]	48	6.8	1.9
38	**2b** (10)	5	0.23	30	13.9	15	4.03	1.97
39	**2b** (10)	5	0.46	10	16.6	18		
40	**2b** (10)	5	0.46	30	20.3	22	4.96	2.04
41	**2b** (10)	5	0.46	60	26.5	28		
42	**2b** (10)	5	0.92	30	21.5	23	4.04	2.23
43	**2b** (20)	5	0.92	30	65.2	35	1.70	2.27

[a] Conditions: in toluene (runs 36−37, 2.43 mL; runs 38−43, 2.31 mL) at 25 °C (runs 36−37, −30−25 °C), norbornene 100 mg (run 38, 50 mg; runs 42−43, 200 mg). [b] Molar ratio based on vanadium ($AlMe_3$ was used as ca. 1.0 M *n*-hexane solution). [c] Monomer concentration in mmol/mL. [d] TON (turnover number) = norbornene consumed (mmol)/V (mmol). [e] GPC data in THF vs polystyrene standard. [f] Ca. 90% *isolated* yield.

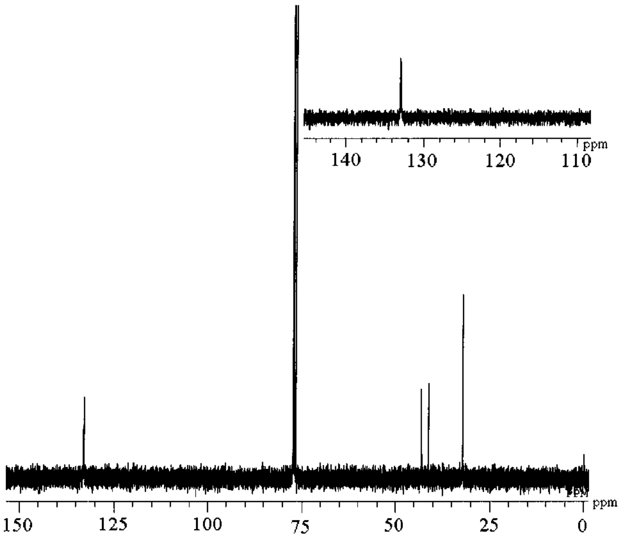


Figure 2. ^{13}C NMR spectrum ($CDCl_3$) for ring-opened poly(norbornene) prepared by the **2b**−$AlMe_3$ catalyst system (run 43, Tale 5).

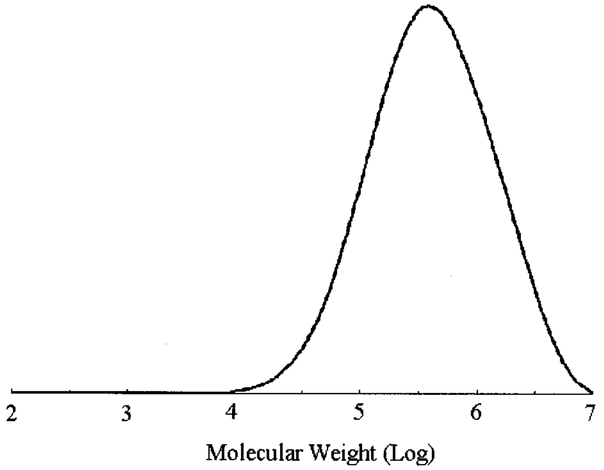


Figure 3. GPC trace (in *o*-dichlorobenzene at 140 °C) for polyethylene prepared by the **2b**−Et_2AlCl catalyst system [run 49 ($M_w = 7.22 \times 10^5$, $M_w/M_n = 3.90$), Table 6].

conditions, although titanacyclobutane derivative prepared from so-called Tebbe reagent, $Cp_2TiCH_2{\cdot}AlClMe_2$, with norbornene initiates the ROMP in a living manner at 65 °C. One plausible explanation concerning the fact would be due to the different reactivity toward olefinic double bond of norbornene among these metal−alkylidene species in the presence of aluminum compounds.

As shown in Table 4, the catalytic activity was affected by $AlMe_3$/V molar ratios, and the ratio of 5−10 was found to be preferred. The activity decreased although the polymer yield increased over time. The isolated yield of ca. 90% could be attained if the polymerization by **2c** was performed for 2 h (Table 5, run 37). The catalytic activity was also affected by the monomer concentration (Table 5, runs 38 vs 40), but the activity did not change at higher concentration region. This might be an interesting contrast to the fact that zero-order dependence of polymerization rates on the monomer concentration was observed for the ROMP with titanium catalyst.[21d] The resultant ring-opened polymer possessed unimodal polydispersity in all cases ($M_w/M_n = 1.97{-}2.23$), but the molecular weights were lower ($M_n = (4.03{-}4.96) \times 10^4$ by **2b**) than those obtained by the dibenzyl analogue, **4**. The M_n value increased if **2c** was used in place of **2b**, suggesting that the steric bulk might control the degree of chain-transfer reaction by alkylaluminum cocatalyst.

5. Ethylene Polymerization with the $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ (2)−Et_2AlCl Catalyst System.[26−28] Since Et_2AlCl was not an effective cocatalyst for the ROMP of norbornene, we thus had an interest to explore the possibility for using this compound as the cocatalyst in ethylene polymerization because the possibility of generating other species like cationic vanadium(V)−alkyl species would be considered.[26,27] Table 6 summarizes results for ethylene polymerization by **2b** in the presence of alkylaluminum cocatalysts.

It is important to note that *remarkably high catalytic activities for ethylene polymerization were observed if **2a** was treated with Et_2AlCl* (Table 6, 3740−8300 kg of PE/(mol of V h)).[28] The low catalytic activity was observed if $AlMe_3$ was used in place of Et_2AlCl (26 kg of PE/(mol of V h)) although the use of $AlMe_3$ as cocatalyst was effective for the ROMP. We believe that the results observed here would be an interesting contrast among these polymerizations.

The catalytic activity increased at lower polymerization temperature (runs 49−56, Table 6), and the trend was different from that in the presence of MAO as the cocatalyst (runs 1−4, Table 1). The activity was also affected by Al/V molar ratios (runs 51−52). The resultant polyethylene was linear, and the M_w values were somewhat lower than those with MAO cocatalyst. One plausible explanation for the difference (M_w value) would be that the degree of chain-transfer reaction by aluminum species increased by using a smaller cocatalyst of Et_2AlCl than methylaluminoxane. The activity of 8300 kg of PE/(mol of V h) could be attained, and, we believe this should be an interesting example as one of the highest catalytic activity with a simple, *inexpensive* cocatalyst.

As shown in Table 7, the observed catalytic activities were not strongly affected by the ethylene pressure (at the same temperature, runs 53−54 vs runs 57−58), and the activities were rather affected by the polymerization temperature (runs 49−50 vs runs 53−54 and/or run 51). On the other hand, however, under the optimized conditions, the activity seemed dependent upon ethylene pressure [runs 49−50 (ethylene 8 atm), run 59 (6 atm), run 62 (4 atm)], and this would suggest that the part of catalytically active species might be decomposed due to the significant exotherm because of the extremely high catalytic activity especially during the polymerization at 8 atm. This is also a plausible explanation of relatively broad molecular weight distribution as well as the difference in M_w value for polyethylene under the same conditions. We are examining in more detail the ligand effect for the catalytic activity and the copolymerization with α-olefin. These will be introduced in the near future.

We have shown an interesting example that *the choice of aluminum promoters directly controls olefin coordination insertion or metathesis pathway exclusively* (Scheme 3). In addition, the possibility for preparing high molecular weight ROMP polymer could be presented by choosing vanadium initiator without cocatalyst, although the example for ROMP with this metal had been limited so far. Moreover, unexpected notable catalytic activity for ethylene polymerization by **2b** could be attained with use of a simple, inexpensive cocatalyst. We thus believe that these findings presented here

Table 6. Ethylene Polymerization by the $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)-Et_2AlCl$ System;[a] Effect of Cocatalyst and Temperature at Ethylene 8 atm

run no.	**2b**/μmol	cocatalyst	Al/V^b	temp/°C	polymer yield/ mg	activity^c	$M_w{}^d/\times10^{-4}$	$M_w/M_n{}^d$
2	5.0	MAO^f	1000	0	449	539	600	2.69
3	5.0	MAO^f	1000	25	802	962	292	2.88
44	5.0	$AlMe_3$	10	25	21	26		
45	5.0	Et_2AlCl	10	25	>1440^e	>1730		
46	1.0	Et_2AlCl	10	25	103	620		
47	1.0	Et_2AlCl	20	25	143	860		
48	1.0	Et_2AlCl	50	25	>1370^e	>8220		
49	0.5	Et_2AlCl	100	−20	692	8300	72.2	3.90
50	0.5	Et_2AlCl	100	−20	679	8140	24.8	3.14
51	0.5	Et_2AlCl	100	0	479	5740		
52	0.5	Et_2AlCl	50	0	592	7100		
53	0.5	Et_2AlCl	100	25	332	3980	48.0	3.75
54	0.5	Et_2AlCl	100	25	311	3740	82.0	4.51
55	0.5	Et_2AlCl	100	40	51.1	613	50.6	8.25
56	0.5	Et_2AlCl	100	40	54.3	652	39.6	6.45

[a] Reaction conditions: toluene 30 mL, ethylene 8 atm, 10 min, 100 mL scale autoclave. [b] Molar ratio of Al/V. [c] Polymerization activity (kg of PE/(mol of Ti h)). [d] GPC data in *o*-dichlorobenzene vs polystyrene standard. [e] The polymerization terminated at the beginning due to the high exotherm. [f] d-MAO (prepared by removing $AlMe_3$ and toluene from ordinary MAO), and data cited from Table 1.

Scheme 3

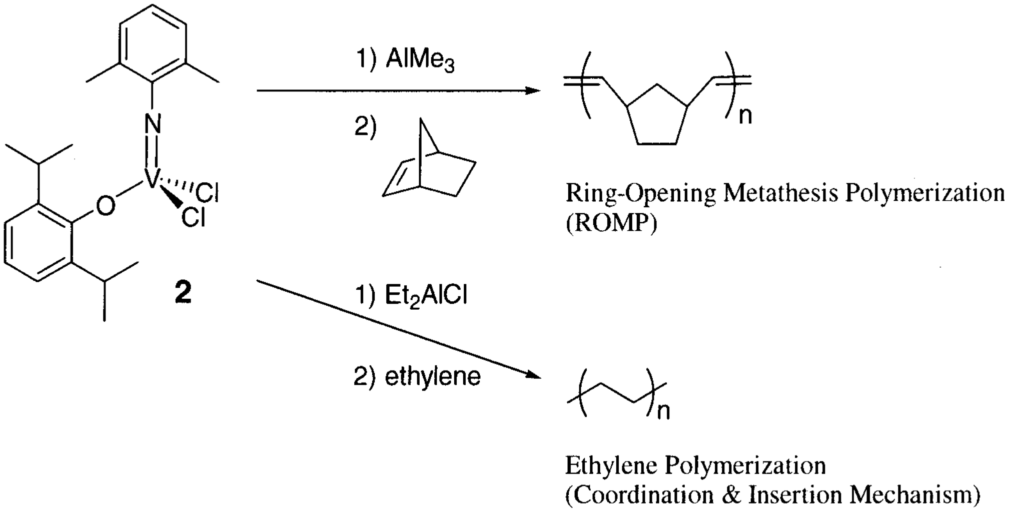


Table 7. Ethylene Polymerization by the $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (2b)$-Et_2AlCl$ System;[a] Effect of Ethylene Pressure

run no.	Al/V^b	ethylene/ atm	temp/ °C	polymer yield/ mg	activity^c	$M_w{}^d/\times10^{-4}$	$M_w/M_n{}^d$
49	100	8	−20	692	8300	72.2	3.90
50	100	8	−20	679	8140	24.8	3.14
53	100	8	25	332	3980	48.0	3.75
54	100	8	25	311	3740	82.0	4.51
57	100	6	25	334	4000	64.9	4.14
58	100	6	25	336	4030	52.8	3.81
52	50	8	0	592	7100		
51	100	8	0	479	5740		
59	100	6	0	494	5930		
60	200	6	0	475	5700	26.5	4.41
61	200	6	0	446	5350	65.8	4.10
62	100	4	0	360	4320		

[a] Reaction conditions: **2b** 0.5 μmol, toluene 30 mL, 10 min, 100 mL scale autoclave. [b] Molar ratio of Al/V. [c] Polymerization activity (kg of PE/(mol of Ti h)). [d] GPC data in *o*-dichlorobenzene vs polystyrene standard.

should be potentially important for studying more efficient catalyst for precise olefin polymerization.

Experimental Section

General Procedure. All synthetic experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Toluene for the polymerization was distilled over sodium and benzophenone under a nitrogen atmosphere and was stored in a Schlenk tube in the drybox in the presence of molecular sieves (mixture of 3A and 4A 1/16 and 13X). Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd.) and was used as received. Propylene for polymerization was of polymerization grade (purity >99.9%, Takachiho Chem. Co. Ltd.) and was used as received. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed and dried in vacuo in the drybox and used as the white solid. MMAO [MMAO-3A, 5.8 wt % (Al) in hexane, Tosoh Finechem Co.] was used as received. $Ph_3CB(C_6F_5)_4$ was purchased from Asahi Glass Chemical Co. and was used as received.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H; 100.40 MHz, ^{13}C). All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves in the drybox. The ^{13}C NMR spectrum for resultant polyethylene was obtained by using a JEOL LA400 spectrometer (*o*-dichlorobenzene-d_4) with proton decoupling at 130 °C. The spectrum for resultant polypropylene (at 25 °C) was obtained in CDCl$_3$ at 60 °C. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 10 000. The ^{1}H NMR spectrum for the polyethylene was measured in the same manner (*o*-dichlorobenzene-*d*$_4$) at 130 °C. The polymer solutions were prepared by dissolving polymers in solvent up to 10 wt %.

Molecular weight and molecular weight distribution of the resultant polyethylene were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH$_{HR}$-H HT × 2) at 140 °C using *o*-dichlorobenzene containing 0.05% (w/v) 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. Molecular weights and molecular weight distributions for resultant ring-opened poly(norbornene)s and polypropylene and poly(1-hexene) were measured by GPC (Shimazu SCL-10A with RID-10A detector, column: ShimPAC GPC-806, 804, and 802) in THF vs polystyrene standard.

Synthesis of VCl$_2$(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (2b). Method 1 (with ArOH). Into an *n*-hexane solution (30 mL) containing VCl$_3$(N-2,6-Me$_2$C$_6$H$_3$) (1.30 g, 4.70 mmol), 2,6-^{i}Pr$_2$C$_6$H$_3$OH (838 mg, 4.70 mmol) was added in a dropwise manner at −30 °C; the reaction mixture was warmed slowly to room temperature, and then the mixture was stirred for 10 h. The solution was removed in vacuo, and the resultant deep brown tan residue was layered by *n*-hexane (ca. 5 mL) at −30 °C. The chilled solution gave a deep brown solid and was washed quickly with a small amount of cold hexane and dried in vacuo. Yield 1.82 g (93%). ^{1}H NMR (CDCl$_3$): δ 1.13 (d, 12H, *J* = 6.8 Hz, (C*H*$_3$)$_2$CH−), 2.38 (s, 6H, CH$_3$), 3.24 (m, 2H, Me$_2$C*H*−), 6.82 (m, 3H), 7.10 (m, 3H). ^{13}C NMR (CDCl$_3$): δ 18.3, 23.2, 27.1, 123.3, 126.2, 127.3, 129.6, 136.2, 138.9, 166.5. Anal. Calcd for C$_{20}$H$_{26}$Cl$_2$NOV: C, 57.43; H, 6.27; N, 3.35. Found (1): C, 57.46; H, 6.42; N, 3.22%. Found (2): C, 57.42; H, 6.40; N, 3.28%.

Method 2 (with LiOAr). Into a Et$_2$O solution (5 mL) containing V(N-2,6-Me$_2$C$_6$H$_3$)Cl$_3$ (152 mg, 0.550 mmol), 2,6-^{i}Pr$_2$C$_6$H$_3$OLi (101 mg, 0.548 mmol) was added at −30 °C; the reaction mixture was warmed slowly to room temperature, and then the mixture was stirred for 10 h. The solution was removed in vacuo, and the resultant deep brown tan residue was extracted with *n*-hexane (ca. 10 mL). The *n*-hexane was then removed in vacuo, and the resultant deep brown tan residue was layered by *n*-hexane (ca. 1 mL) at −30 °C. The chilled solution gave a deep brown solid. Yield 215 mg (first and second crops, 93%).

Synthesis of VCl$_2$(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-Me$_2$C$_6$H$_3$) (2a). Synthesis of **2a** was carried out by the same procedure as that in **2b** (method 1) except that VCl$_3$(N-2,6-Me$_2$C$_6$H$_3$) (1.664 g, 6.02 mmol) and 2,6-^{i}Pr$_2$C$_6$H$_3$OH (735 mg, 6.02 mmol) were used. Yield 1.90 g (87%). ^{1}H NMR (CDCl$_3$): δ 2.24 (s, 6H), 2.38 (s, 6H), 6.84 (m, 3H), 6.92 (m, 1H), 7.02 (m, 2H). ^{13}C NMR (CDCl$_3$): δ 16.9, 18.2, 125.5, 125.8, 127.4, 128.5, 129.7, 139.2, 168.8. Anal. Calcd for C$_{16}$H$_{18}$Cl$_2$NOV: C, 53.06; H, 5.01; N, 3.87%. Found (1): C, 53.58; H, 5.11; N, 3.89%. Found (2): C, 53.76; H, 5.11; N, 3.95%.

Synthesis of VCl$_2$(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$) (2c). Synthesis of **2c** was carried out by the same procedure as that in **2b** (method 1) except that 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$OH was used in place of 2,6-Me$_2$C$_6$H$_3$OH. Yield 94%. ^{1}H NMR (CDCl$_3$): δ 0.97 (s, 18H), 1.93 (s, 3H), 2.07 (s, 6H), 6.42 (m, 3H), 6.64 (s, 1H), 6.82 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 21.5, 22.7, 31.9, 35.5, 125.5, 126.0, 127.3, 129.9, 134.4, 139.0, 139.1, 168.6 ppm. Anal. Calcd for C$_{23}$H$_{32}$Cl$_2$NOV: C, 60.01; H, 7.01; N, 3.04%. Found (1): C, 59.86; H, 7.13; N, 2.80%. Found (2): C, 60.05; H, 7.24; N, 2.91%.

Synthesis of VCl$_2$(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (3b). Synthesis of **3b** was carried out by the same procedure as that in **2b** (method 1) except that VCl$_3$(N-2,6-^{i}Pr$_2$C$_6$H$_3$) (1.16 g, 3.49 mmol) and 2,6-^{i}Pr$_2$C$_6$H$_3$OH (623 mg, 3.49 mmol) were used. After the reaction, the mixture was filtered through Celite pad, and the solvent was removed in vacuo. The resultant tan residue was placed in the freezer (−30 °C) for several hours and then covered with cold *n*-hexane with a minimum amount. Yield 1.13 g (first crop only, yield 68%). Completion for the crystallization took more than ca. 3−5 days in the freezer due to the slow crystallization in organic solvent. ^{1}H NMR (CDCl$_3$): δ 1.08 (d, 12H, *J* = 6.8 Hz, (C*H*$_3$)$_2$CH−), 1.14 (d, 12H, *J* = 6.8 Hz, (C*H*$_3$)$_2$CH−), 3.25 (m, 2H, Me$_2$C*H*−), 3.69 (m, 2H, Me$_2$C*H*−), 6.93 (br m), 6.95 (br s), 6.98−7.12 (m), 7.13 (br s), 7.09−7.15 (m). ^{13}C NMR (CDCl$_3$): δ 22.6, 23.5, 24.3, 27.3, 27.5, 28.7, 29.2, 122.2, 122.7, 123.2, 123.7, 125.9, 126.4, 130.1, 130.6, 136.5, 149.8 ppm.

Synthesis of V(CH$_2$Ph)$_3$(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (4). Into a cold CH$_2$Cl$_2$ solution (25 mL, −30 °C) dissolved in V(CH$_2$Ph)$_3$(N-2,6-Me$_2$C$_6$H$_3$) (1.0 g, 2.25 mmol), 2,6-diisopropylphenol was added in several portions, and the mixture was stirred for 40 h at room temperature. The reaction mixture was filtered through a Celite pad, the solvent was removed in vacuo, and the resultant solid was dissolved in a small amount of hexane. The chilled solution gave deep brown microcrystals. Yield 75%. For **4**, ^{1}H NMR(CDCl$_3$): δ 1.32 (d, 12H), 2.97 (d, 10H), 3.20 (m, 2H), 7.23 (m, 16H). ^{13}C NMR (CDCl$_3$): δ 22.7, 27.1, 37.8, 37.9, 77.2, 120.6, 123.4, 125.9, 128.3, 128.4, 133.6, 141.8, 150.0.

ROMP of Norbornene with 4. Into a round-bottom flask (10 mL scale) containing norbornene (235 mg) dissolved in toluene (2.9 g), a toluene solution (1.0 g) containing **4** (13.2 mg, 25 μmol) was added in one portion at room temperature. The mixture was stirred for 11 h, and the solution was poured into methanol (200 mL). The resultant solid was collected by filtration, washed with methanol, and then dried in vacuo. Yield 87 mg (37%). ^{1}H NMR (CDCl$_3$): δ 5.22 and 5.35 (br m, 2H olefinic), 2.80 and 2.37 (br s, 2H), 1.85 and 1.08 (m, 2H), 1.81 and 1.36 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 134.0, 133.9, 133.8, 133.7, and 133.1, 133.0, and 132.8 (olefinic), 68.0, 50.8, 43.4, 43.2, 42.7, 42.1, 41.3, 38.6, 38.4, 33.1, 32.9, 32.3, 32.2, 25.6, 21.3.

Polymerization of Ethylene, Propylene, and 1-Hexene. Ethylene and propylene polymerizations were conducted in a 100 mL scale stainless steel autoclave. The typical reaction procedure (run 3, Table 1) is as follows. Toluene (29 mL) and MAO solid (290 mg, prepared from ordinary MAO (Tosoh Finechem Co. PMAO-S) by removing toluene and AlMe$_3$) were added into the autoclave in the drybox. The reaction apparatus was then filled with ethylene (1 atm), **2b** (5.0 μmol) in toluene (1.0 mL) was then added into the autoclave, the reaction apparatus was then immediately pressurized to 7 atm, and the mixture was magnetically stirred for 10 min. After the above procedure, ethylene remained was purged, and the mixture was then poured into EtOH (100 mL) containing HCl (5 mL). The resultant polymer (white precipitate) was collected on a filter paper by filtration, adequately washed with EtOH and water, and then dried in vacuo at 50 °C for several hours. Polymerization of propylene was conducted according to the same procedure except that propylene was used in place of ethylene. Ethylene polymerization with Et$_2$AlCl was also performed in the same manner except that Et$_2$AlCl was used in place of MAO. In the case of ethylene polymerization by the **2b**−Et$_2$AlCl catalyst system, the reproducibility for the polymerization result would be improved if **2b** was pretreated with ca. 2.0 equiv of Et$_2$AlCl in toluene at 0 °C for 5 min.

1-Hexene polymerization was performed using a round-bottom flask equipped with three-way valve under a nitrogen atmosphere. MAO and 1-hexene were added in a round-bottom flask (25 mL), and the polymerization was started by adding a toluene solution (1.0 mL) containing **2b** (5.0 μmol). The resultant polymer was isolated according to the established procedure described in our previous paper.[8d]

ROMP with 2b−AlMe$_3$ Catalyst System. The basic reaction procedure was the same as that in the ROMP with **4** except that AlMe$_3$ (*n*-hexane solution) was added into a toluene solution (2.43 mL for Table 3) containing **2b** (10 or 20 μmol) and norbornene (100 mg for Tables 4 and 5) at −30 °C. In the case of run 43, propionaldehyde was used in place of benzaldehyde. The detailed conditions were described in Tables 3−5. Typical ^{1}H and ^{13}C NMR spectra are shown in Figures 1 and 2.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for polypropylene prepared by the **2b**−MAO catalyst system. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) This complex has been prepared according to the analogous procedure for synthesis of $V(CH_2Ph)_3(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)$: Murphy, M. J.; Turner, H. *Organometallics* **1997**, *16*, 2495. $V(CH_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ had also been prepared from the tribenzyl complex by treating with the corresponding phenol in CH_2Cl_2.

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(26) Recent example for ethylene polymerization with vanadium−$MgCl_2$−$AlEt_3$ catalyst system: (a) Sobota, P.; Ejfler, J.; Szafert, S.; Glowiak, T.; Fritzky, I. O.; Szczegot, K. *J. Chem. Soc., Dalton Trans.* **1995**, 1727. (b) Janas, Z.; Jerzykiewicz, L. B.; Richards, R. L.; Sobota, P. *Chem. Commun.* **1999**, 1105.

(27) Ethylene polymerization and ethylene/propylene copolymerizaton by $(R_2N)_2VCl_2$−alkylaluminum cocatalyst system: Desmangles, N.; Gambarotta, S.; Bensimon, C.; Davis, S.; Zahalka, H. *J. Organomet. Chem.* **1998**, *562*, 53. In this report, the activities with 265 and 860 kg of PE/(mol of V h) were observed in ethylene homopolymerization and ethylene/propylene copolymerization, respectively.

(28) Recently, Gambarotta et al. also presented independently in a symposium that remarkable catalytic activity for ethylene polymerization as well as ethylene/propylene copolymerization was observed, if vanadium(III) complexes containing chelate bis(amido)amine ligand, $\{[(Me_3SiNCH_2CH_2)_2NSiMe_3]VCl\}_2$, was treated with Me_2AlCl or Et_2AlCl.[13d]

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