Inorganic Chemistry

Article

pubs.acs.org/IC

Synthesis and Structural Analysis of (Imido)Vanadium(V) Complexes Containing Chelate (Anilido)Methyl-imine Ligands: Ligand Effect in Ethylene Dimerization

Kotohiro Nomura,*[†] Atsushi Igarashi,[†] Shohei Katao,[‡] Wenjuan Zhang,[§] and Wen-Hua Sun[§]

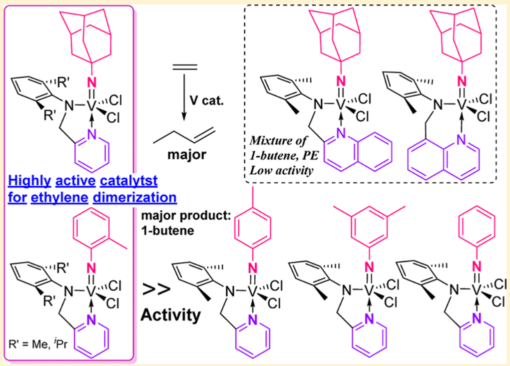
[†]Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan

[‡]Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

[§]Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Beijing 100190, People's Republic of China

Supporting Information

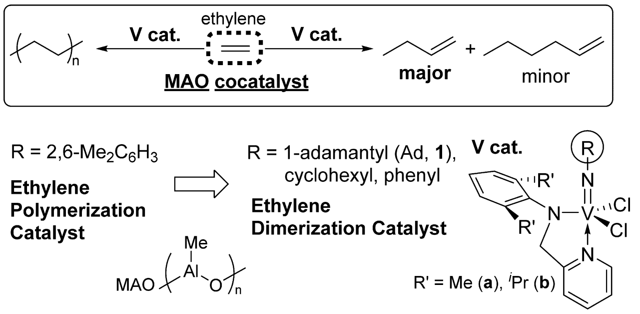
ABSTRACT: A series of (imido)vanadium dichlorido complexes containing chelate anionic donor ligands of the type, $VCl_2(L)(NR)$ [R = 1-adamantyl (Ad), L = 2-(2,6-$Me_2C_6H_3$)$NCH_2(C_9H_6N)$ (**2**), 8-(2,6-$Me_2C_6H_3$)$NCH_2(C_9H_6N)$ (**3**); L = 2-(2,6-$R'_2C_6H_3$)$NCH_2(C_5H_4N)$, R = 2-MeC_6H_4, R′ = Me (**4a**), ^{i}Pr (**4b**); L = 2-(2,6-$Me_2C_6H_3$)$NCH_2(C_5H_4N)$, R = 4-MeC_6H_4 (**5**), 3,5-$Me_2C_6H_3$ (**6**)], have been prepared and identified. The reactions with ethylene by **2**,**3** in the presence of methylaluminoxane (MAO) afforded a mixture of high molecular weight polyethylene and oligomers. Reactions with ethylene by VCl_2[2-(2,6-$R'_2C_6H_3$)-$NCH_2(C_5H_4N)$](NAd) (**1a**,**b**), **4**−**6** afforded 1-butene with high selectivities (>92%), and the activities by **4a**,**b** are at the same level as those in **1a**,**b**. The activities by **5**,**6** were lower than **4a**,**b** and were at the same level of that by VCl_2[2-(2,6-$Me_2C_6H_3$)$NCH_2(C_5H_4N)$](NPh). These results thus suggest that both the chelate anionic donor and the imido ligands play a role for both the activity and the selectivity.



INTRODUCTION

Since the classical Ziegler-type vanadium catalyst systems [$V(acac)_3$, $VOCl_3$, etc. and Et_2AlCl, $EtAlCl_2$, ^{n}BuLi, etc.] display unique high reactivity toward olefins in olefin coordination/insertion polymerization,[1−5] the design and synthesis of efficient vanadium complex catalysts for olefin coordination insertion polymerization/oligomerization thus attract considerable attention in the field of catalysis, organometallic chemistry, as well as of polymer chemistry.[5] Our group focuses on (imido)vanadium(V) complexes containing anionic donor ligands of the type, $VCl_2(Y)(NR)$ [Y = aryloxo, ketimide, phenoxyimine, etc.],[6,7] and demonstrated that these complexes, exemplified as VCl_2(O-2,6-$Me_2C_6H_3$)(N-2,6-$Me_2C_6H_3$), exhibited remarkable catalytic activities for ethylene (co)-polymerization in the presence of aluminum cocatalysts.[5c−e,6] More recently, we demonstrated that the (imido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligand, VCl_2[2-$ArNCH_2(C_5H_4N)$](NR) [Ar = 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$; R = 1-adamantyl (Ad, **1**), cyclohexyl, phenyl], efficiently dimerize ethylene with both notable catalytic activities and high selectivities in the presence of methylaluminoxane (MAO) cocatalyst (Scheme 1),[5e,7,8] whereas the 2,6-dimethylphenylimido analogue, VCl_2[2-$ArNCH_2(C_5H_4N)$](N-2,6-$Me_2C_6H_3$), showed moderate catalytic activity for ethylene polymerization.[6e] Through these facts, we thus assumed that (i) steric bulk of the imido ligand *directly* affects the reactivity (dimerization vs polymerization), and that (ii) the electronic factor also plays a role toward the activity (in dimerization).[7a] Moreover, on the basis of both the electron spin resonance (ESR) spectra and the ^{51}V NMR spectra, it was suggested that the chelate anionic donor ligand plays an important role for stabilization of the oxidation state in the catalyst solution even containing aluminum alkyls in excess amount.[7b]

Scheme 1

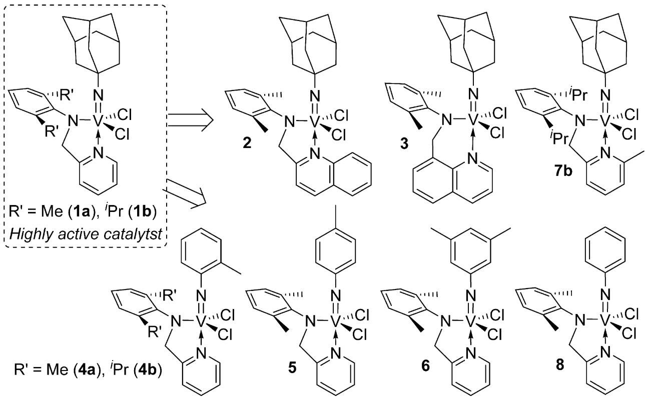


Received: December 1, 2012
Published: February 18, 2013

dx.doi.org/10.1021/ic302633y | Inorg. Chem. 2013, 52, 2607−2614

To explore the ligand effect toward both the activity and the selectivity in detail, we thus prepared a series of (imido)vanadium(V) dichlorido complexes containing chelate anionic donor ligands (shown in Scheme 2) of the type, $VCl_2(L)(NR)$ [R = Ad, L = 2-(2,6-$Me_2C_6H_3$)NCH_2(C_9H_6N) (**2**), 8-(2,6-$Me_2C_6H_3$)NCH_2(C_9H_6N) (**3**); L = 2-(2,6-$R'_2C_6H_3$)-NCH_2(C_5H_4N), R = 2-MeC_6H_4 {R′ = Me (**4a**), ^{i}Pr (**4b**)}; L = 2-(2,6-$Me_2C_6H_3$)NCH_2(C_5H_4N), R = 4-MeC_6H_4 (**5**), 3,5-$Me_2C_6H_3$ (**6**)], and conducted the reaction with ethylene in the presence of MAO cocatalyst. Through this study, we wish to present that the ligand modifications (both the imido and the chelate anionic donor ligands) play an important role for exhibiting both high activity and selectivity.[9]

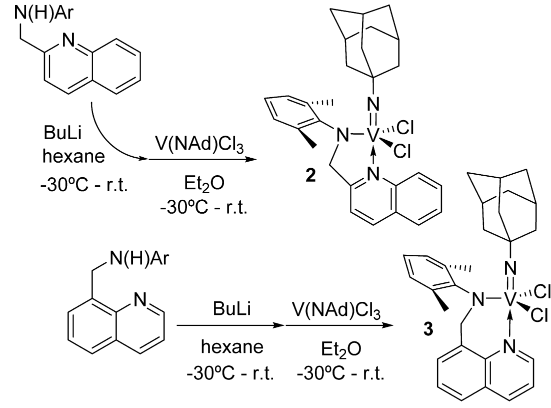
Scheme 2



■ RESULTS AND DISCUSSION

1. Synthesis and Structural Analysis of $VCl_2(L)(NR)$ [R = 1-adamantyl (Ad), 2-MeC_6H_4, 4-MeC_6H_4, 3,5-$Me_2C_6H_3$; L = 2-(2,6-$Me_2C_6H_3$)NCH_2(C_9H_6N), 8-(2,6-$Me_2C_6H_3$)-NCH_2(C_9H_6N), 2-(2,6-$R'_2C_6H_3$)NCH_2(C_5H_4N)]. (1-Adamantlyimido)vanadium(V) dichlorido complexes containing 2- or 8-(anilidomethyl)quinoline ligands, $VCl_2(L)(NAd)$ [L = 2-(2,6-$Me_2C_6H_3$)NCH_2(C_9H_6N) (**2**), 8-(2,6-$Me_2C_6H_3$)-NCH_2(C_9H_6N) (**3**); Ad = 1-adamantyl], were prepared in Et_2O by reacting the trichlorido analogue, $VCl_3(NAd)$, with the lithium salts that were prepared in situ by treating 2- or 8-(2,6-$Me_2C_6H_3$)N(H)CH_2(C_9H_6N)[10] with 1 equiv of BuLi in hexane at −30 °C (Scheme 3). These are analogous procedures for synthesis of VCl_2[2-(2,6-$R'_2C_6H_3$)NCH_2(C_5H_4N)](NAd) [R′ = Me (**1a**), ^{i}Pr (**1b**)],[7a] VCl_2[2-(2,6-$R'_2C_6H_3$)NCH_2(C_5H_4N)](N-2,6-$Me_2C_6H_3$),[6e] reported previously. The resultant complexes were identified by NMR spectra (^{1}H, ^{13}C, ^{51}V) and elemental analyses, and their structures were determined by X-ray crystallography (Figure 1, shown below).[11]

Scheme 3



In contrast, attempted reactions of VCl_3(N-2-MeC_6H_4)[12] with Li[2-(2,6-$R'_2C_6H_3$)NCH_2(C_5H_4N)] afforded the desired complexes, VCl_2[2-(2,6-$R'_2C_6H_3$)NCH_2(C_5H_4N)](N-2-MeC_6H_4) [R′ = Me (**4a**), ^{i}Pr (**4b**)], in extremely low or negligible yields (described in the Supporting Information). The dichlorido complexes (**4a**,**b**) could be isolated in moderate yields, if the reactions of VCl_3(N-2-MeC_6H_4) with (2-anilidomethyl)pyridine, 2-(2,6-$R'_2C_6H_3$)N(H)CH_2(C_5H_4N), were conducted in toluene in the presence of NEt_3 (Scheme 4). The other (arylimido)vanadium(V) dichlorido complexes containing (2-anilidomethyl)pyridine ligand, VCl_2[2-(2,6-$Me_2C_6H_3$)NCH_2(C_5H_4N)](NR) [R = 4-MeC_6H_4 (**5**), 3,5-$Me_2C_6H_3$ (**6**)] could also be prepared similarly from VCl_3(N-4-MeC_6H_4) or VCl_3(N-3,5-$Me_2C_6H_3$), prepared from $VOCl_3$ by treating with the corresponding isocyanate (Scheme 4).[12] The resultant complexes were identified by NMR spectra (^{1}H, ^{13}C, ^{51}V) and elemental analyses, and the structures of **4a**,**b** were determined by X-ray crystallography (Figure 2, shown below).

2. Structural Analysis of $VCl_2(L)(NAd)$ [L = 2-(2,6-$Me_2C_6H_3$)NCH_2(C_9H_6N) (2), 8-(2,6-$Me_2C_6H_3$)NCH_2-(C_9H_6N) (3)], and VCl_2[2-(2,6-$R'_2C_6H_3$)NCH_2(C_5H_4N)](N-2-MeC_6H_4) [R′ = Me (4a), ^{i}Pr (4b)]. Structures of $VCl_2(L)(NAd)$ [L = 2-(2,6-$Me_2C_6H_3$)NCH_2(C_9H_6N) (**2**), 8-(2,6-$Me_2C_6H_3$)-NCH_2(C_9H_6N) (**3**)] determined by X-ray crystallographic analysis are shown in Figure 1, and selected bond distances and angles are summarized in Table 1.[11] The structures indicate that these complexes fold a distorted trigonal bipyramidal geometry around vanadium consisting of two nitrogen atoms in the quinoline, and the imido ligands axis and an equatorial plane consisted of two chlorine atoms and the nitrogen in the anilide ligand, as observed in **1a**,[7a] reported previously [N(1)−V−N(2): 173.09(6)° in **2**, 173.35(9)° in **3**; total bond angles of Cl(1)−V−Cl(2), Cl(1)−V−N(3), Cl(2)−V−N(3) = 356.822° in **2**, 356.272° in **3**]. The nitrogen atom in the quinoline is located *trans* to the imido ligand. The bond distances in V−N(1) and V−N(2) are similar to those in **1a**, and bond angles in Cl(1)−V−Cl(2), Cl(1)−V−N(3), Cl(2)−V−N(3) are slightly larger than those in **1a**. A V−Cl bond distance in **3** [2.3054(6) Å] is longer than the others [2.2630(5)−2.2792(5) Å] probably because of steric bulk [forms 6 membered ring in **3** vs 5 membered ring in **1a** and **2**]. It might be interesting to note that the bond distances between vanadium and nitrogen in the imino ligand in **2**,**3** [2.2911(14) Å, 2.3338(18) Å, in **2**,**3**, respectively] are apparently longer than that in **1a** [2.2241(11) Å]. These bond distances are also longer than those in VCl_2[2-(2,6-^{i}$Pr_2C_6H_3$)NCH_2(C_5H_4N)](NAd) [**1b**, 2.225(2) Å],[7a] VCl_2[2-(2,6-^{i}$Pr_2C_6H_3$)NCH_2(C_5H_4N)](NCy) [2.221(2) Å],[7a] and VCl_2[2-(2,6-^{i}$Pr_2C_6H_3$)NCH_2(C_5H_4N)](N-2,6-$Me_2C_6H_3$) [2.211(2) Å].[6e] Moreover, these bond distances are also longer than those between vanadium and nitrogen in the phenoxyimine ligand of VCl_2[O-2-R″-6-{(2,6-^{i}$Pr_2C_6H_3$)N=CH}C_6H_3]-(N-2,6-$Me_2C_6H_3$) [2.216(4)-2.203(2) Å; R″ = H, Me, ^{t}Bu], reported previously.[6d] It thus seems likely that these (rather long bond distances) might be due to the use of the (anilidomethyl)quinoline ligand in place of the (anilidomethyl)pyridine ligand.

The structures of VCl_2[2-(2,6-$R'_2C_6H_3$)NCH_2(C_5H_4N)](N-2-MeC_6H_4) [R′ = Me (**4a**), ^{i}Pr (**4b**)] are shown in Figure 2,

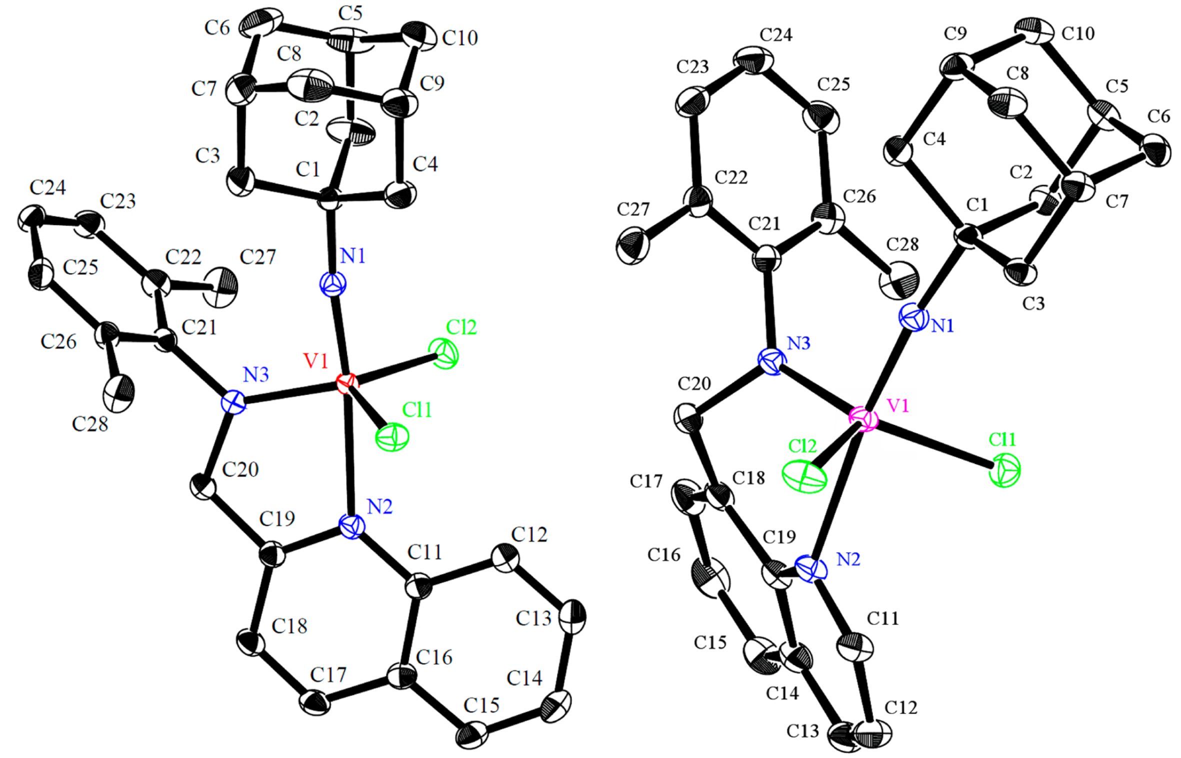
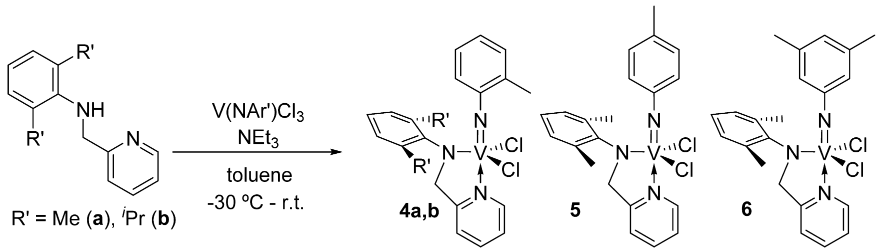


Figure 1. ORTEP drawings for $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](N\text{-}1\text{-adamantyl})$ (**2**), and $VCl_2[8\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](N\text{-}1\text{-adamantyl})$ (**3**). Thermal ellipsoids are drawn at 50% probability level, and H atoms were omitted for clarity.[11].

Scheme 4



and selected bond distances and angles are summarized in Table 1. Similarly to **2**,**3**, the structures indicate that these complexes fold a distorted trigonal bipyramidal geometry around vanadium consisting of two nitrogen atoms in the pyridine, and the imido ligands axis and an equatorial plane consisted of two chlorine atoms and the nitrogen in the anilide ligand [N(1)−V−N(2) = 173.65(7)° in **4a**, 173.26(16)° in **4b**; total bond angles of Cl(1)−V−Cl(2), Cl(1)−V−N(3), Cl(2)−V−N(3): 354.98° in **4a**, 355.17° in **4b**]. The nitrogen atom in the pyridine locates at the *trans*-position of the imido ligand. The vanadium−nitrogen bond distances in the imido and the anilido ligands as well as the V−Cl bond distances are close to those in **1a**: the bond angles in Cl(1)−V−Cl(2), Cl(1)−V−N(3), Cl(2)−V−N(3) are slight larger than those in **1a**, but are similar to those in **2**,**3**. The vanadium−nitrogen bond distances in the pyridine ligand are 2.1790(19) Å (**4a**), 2.1976(17) Å (**4b**), respectively, which are rather shorter than those in **1a**,**b** [2.2241(11), 2.225(2) Å, respectively][7a] and $VCl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}2,6\text{-}Me_2C_6H_3)$ [2.211(2) Å].[6e]

3. Reaction with Ethylene by $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)(NAd)]$ (2), $VCl_2[8\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](NAd)$ (3), and $VCl_2[2\text{-}(2,6\text{-}R'_2C_6H_3)NCH_2(C_5H_4N)](NR)$ [R = 2-MeC_6H_4 (4a,b), 4-MeC_6H_4 (5), 3,5-$Me_2C_6H_3$ (6)]−MAO Catalyst Systems. Reactions with ethylene in the presence of $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](NAd)$ (**2**), $VCl_2[8\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](NAd)$ (**3**) in the presence of MAO (methylaluminoxane) were conducted in toluene, and the results are summarized in Table 2. The results using $VCl_2[2\text{-}(2,6\text{-}R'_2C_6H_3)NCH_2(C_5H_4N)](NAd)$ [R′ = Me (**1a**), ^{i}Pr (**1b**)], and $VCl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2\text{-}6\text{-}Me(C_5H_3N)](NAd)$ (**7b**) are also shown for comparison.[7a] We recently demonstrated that **1a**,**b** showed the significant catalytic activities affording 1-butene exclusively in the presence of MAO (runs 1,2):[7a] the activity was affected by the aluminum/vanadium molar ratios and ethylene pressure without significant changes in the selectivity of 1-butene.[7b] In contrast, we also demonstrated that attempts at using the complex containing methyl group in the *ortho* position (**7b**) in place of **1b** showed low activities affording a mixture of 1-butene and high molecular weight polyethylene (runs 8,9).[7a]

Unfortunately, the catalytic activities by **2**,**3** were apparently lower than **1a**,**b**: the activities by **2**,**3** under the optimized aluminum/vanadium molar ratios (runs 5, 7) were lower than that by **7b** (run 9). Moreover, the resultant products by the

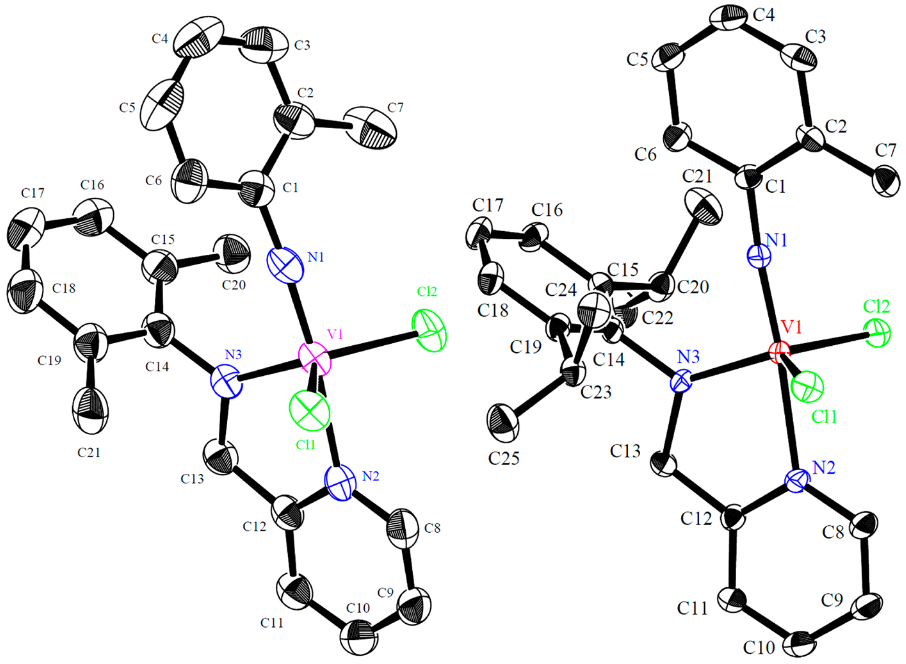


Figure 2. ORTEP drawings for $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}2\text{-}MeC_6H_4)$ (**4a**), and $VCl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)(N\text{-}2\text{-}MeC_6H_4)]$ (**4b**). Thermal ellipsoids are drawn at 50% probability level, and H atoms were omitted for clarity.[11].

Table 1. Selected Bond Distances and Angles for $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](NAd)$ (2), $VCl_2[8\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](NAd)$ (3), $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}2\text{-}MeC_6H_4)$ (4a), and $VCl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)(N\text{-}2\text{-}MeC_6H_4)]$ (4b)

	1a[a]	2	3	4a	4b	$VCl_2(L)(N\text{-}2,6\text{-}Me_2C_6H_3)$[b]
			Bond Distances (Å)			
V−N(1)	1.6517(12)	1.6502(14)	1.6503(18)	1.6697(19)	1.640(18)	1.679(2)
V−N(2)	2.2241(11)	2.2911(14)	2.3338(18)	2.1790(19)	2.1976(17)	2.211(2)
V−N(3)	1.8580(12)	1.8567(12)	1.844(3)	1.8524(18)	1.8526(17)	1.850(2)
V−Cl(1)	2.2677(3)	2.2792(5)	2.3054(6)	2.2776(7)	2.2645(8)	2.2645(10)
V−Cl(2)	2.2709(4)	2.2630(5)	2.2752(7)	2.2695(7)	2.2642(7)	2.2868(9)
			Bond Angles (deg)			
Cl(1)−V−Cl(2)	119.953(16)	121.512(17)	126.02(3)	125.45(3)	122.42(3)	121.87(3)
N(1)−V−N(2)	174.90(4)	173.09(6)	173.35(9)	173.47(9)	175.65(7)	175.93(10)
V−N(1)−C(1)	170.94(10)	172.15(11)	172.2(2)	176.42(17)	173.26(19)	176.2(2)
Cl(1)−V−N(3)	98.90(3)	119.12(5)	114.50(6)	115.31(6)	118.12(7)	114.55(7)
Cl(2)−V−N(3)	96.02(4)	115.64(5)	115.81(6)	114.22(6)	114.63(7)	116.98(8)

[a]Cited from reference 7a. [b]$VCl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}2,6\text{-}Me_2C_6H_3)$ cited from reference 6e.

(anilidomethyl)quinoline analogues (**2**,**3**) were a mixture of oligomer (1-butene as the major product) and polyethylene for which the molecular weight (and the distribution) could not be measured by ordinary GPC analysis (in *o*-dichlorobenzene at 140 °C, suggesting formation of ultrahigh molecular weight polymers[6c,7b]). The facts observed here might suggest that there are several (at least two) catalytically active species generated in the reaction mixture from **2**,**3** in the presence of MAO under these conditions. One probable speculation we may consider is that these might be because complexes **2** and **3** possess rather long vanadium−nitrogen bond distances in the imine ligand [expressed as V−N(2)] compared to those in **1a**,**4a** and the others, and these might lead a partial dissociation of the vanadium−nitrogen bond in the reaction mixture upon addition of MAO in excess amount.

The results in ethylene dimerization using $VCl_2[2\text{-}(2,6\text{-}R'_2C_6H_3)NCH_2(C_5H_4N)](NR)$ [R = $2\text{-}MeC_6H_4$ (**4a**,**b**), $4\text{-}MeC_6H_4$ (**5**), $3,5\text{-}Me_2C_6H_3$ (**6**)] in the presence of MAO are summarized in Table 3. The results using the adamantylimido analogues (R = Ad; **1a**,**b**) and the phenylimido analogue, $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)](NPh)$ (**8**),[7a] are also shown for comparison.

It should be noted that the 2-methylphenylimido analogues (**4a**,**b**) exhibited remarkable catalytic activities affording 1-butene as the major product. Moreover, the observed activities by **4a**,**b** are the same level as those in **1a**,**b** [ex. TOF 1760000 h^{-1} (run 14) by **4a** vs 2060000 (run 1) by **1a**; 1450000 (run 17) by **4b** vs 1280000 (run 2) by **1b**]. The activity by the 2-methylphenyl analogue (**4a**) under the optimized conditions was much higher than that by the phenylimido analogue (**8**, run 31). As reported previously by **1a**,**b**,[7a] the activities were dependent upon the aluminum/vanadium molar ratios employed, whereas the selectivity in 1-butene were not affected by the ratio because the initial product was 1-butene, and 1-hexene was formed from 1-butene that accumulated in the mixture.[7a]

Table 2. Reactions with Ethylene by $VCl_2(L)(NAd)$ [L = 2-(2,6-$R'_2C_6H_3$)$NCH_2(C_5H_4N)$ {R′ = Me (1a), ^{i}Pr (1b)}, 2-(2,6-$Me_2C_6H_3$)$NCH_2(C_9H_6N)$ (2), 8-(2,6-$Me_2C_6H_3$)$NCH_2(C_9H_6N)$ (3), 2-(2,6-^{i}$Pr_2C_6H_3$)NCH_2-6-MeC_5H_3N (7b)]−MAO Catalyst Systems[a]

				oligomer[d]/ %		polyethylene (PE)	
	complex (μmol)	Al/V[b]	activity[c]	C_4'	C_6'	yield/ mg	activity[e]
1	**1a** (0.2)[f]	500	57800	96.8	3.2	none	
2	**1b** (0.5)[f]	1000	35700	92.1	7.9	none	
3	**2** (2.0)	200	103	90.2	9.8	16[g]	47
4	**2** (2.0)	1000	201	92.4	7.6	10[g]	30
5	**2** (2.0)	1500	249	92.0	8.0	15[g]	45
6	**3** (5.0)	200	trace			13[g]	16
7	**3** (5.0)	1000	43	71.6	28.4	44[g]	53
8	**7b** (0.5)[f]	1000	510	>99[h]	trace	[h]	
9	**7b** (0.5)[f]	2000	2100	95.9[h]	4.1	[h]	

[a] Conditions: toluene 30 mL, ethylene 8 atm, 25 °C, 10 min. [b] Molar ratio of aluminum/vanadium. [c] Activity in kg-ethylene reacted/mol-V·h. [d] Determined by GC. [e] Activity in kg-PE/mol-V·h. [f] Data cited from reference 7a. [g] Insoluble for ordinary GPC measurement (in o-dichlorobenzene at 140 °C). [h] Small amount of PE was obtained, [$M_w = 2.55 \times 10^6$, $M_w/M_n = 1.9$ (run 8); $M_w = 2.93 \times 10^6$, $M_w/M_n = 2.6$ (run 9)].[7a]

Table 3. Ethylene Dimerization by VCl_2[2-(2,6-$R'_2C_6H_3$)$NCH_2(C_5H_4N)$](NR) [R = 2-MeC_6H_4, R′ = Me (4a), ^{i}Pr (4b); R′ = Me, R = 4-MeC_6H_4 (5), 3,5-$Me_2C_6H_3$ (6), Ph (8)]−MAO Catalyst Systems (Ethylene 8 atm in Toluene at 25 °C for 10 min)[a]

run	complex (μmol)	Al/V[b]	activity[c]	TOF[d]	C_4'/%[e]	C_6'/%[e]
10[f]	**1a** (0.5)	500	51100	1830000	92.5	7.5
1[f]	**1a** (0.2)	500	57800	2060000	96.8	3.2
2[f]	**1b** (0.5)	1000	35700	1280000	92.1	7.9
11	**4a** (0.2)	200	20500	718000	98.6	1.4
12	**4a** (0.2)	400	44400	1560000	97.5	2.5
13	**4a** (0.2)	500	41400	1450000	94.7	5.3
14	**4a** (0.2)	600	50300	1760000	95.2	4.8
15	**4a** (0.2)	1000	34000	1190000	96.0	4.0
16	**4b** (0.2)	500	27000	946000	97.4	2.6
17	**4b** (0.2)	700	41500	1450000	97.1	2.9
18	**4b** (0.2)	1000	28000	980000	95.6	4.4
19	**5** (0.5)	100	13800	483000	93.1	6.9
20	**5** (0.5)	200	15100	529000	94.0	6.0
21	**5** (0.5)	500	14000	490000	95.3	4.7
22	**5** (0.5)	750	8680	304000	96.4	3.6
23	**5** (0.5)	1000	11200	393000	94.5	5.5
24	**5** (0.5)	1500	2040	71600	96.6	3.4
25	**6** (0.5)	200	5800	203000	95.6	4.4
26	**6** (0.5)	500	13400	470000	95.0	5.0
27	**6** (0.5)	750	14200	497000	94.6	5.4
28	**6** (0.5)	1000	2710	95000	95.4	4.6
29	**6** (0.5)	1500	1300	45700	97.2	2.8
30	**6** (0.2)	1250	14200	499000	96.7	3.3
31[f]	**8** (0.5)	500	18300	654000	95.1	4.9

[a] Conditions: toluene 30 mL, d-MAO white solid [methylaluminoxane prepared by removing $AlMe_3$, toluene from PMAO-S], 25 °C. [b] Aluminum/vanadium molar ratio. [c] Activity in kg-ethylene reacted/mol-V·h. [d] TOF (turnover frequency) = (molar amount of ethylene reacted)/mol-V·h. [e] By GC analysis vs internal standard. [f] Cited from reference 7a.

The 4-methylphenylimido analogue (**5**) also showed high catalytic activities affording 1-butene as the major product (runs 19−24), but the activities were apparently lower that those the 2-methylphenyl analogue (**4a**), suggesting that the placement of the methyl group in the *ortho* position plays a role for exhibiting high activity. Moreover, the 3,5-dimethylphenylimido analogue (**6**) also showed high catalytic activities affording 1-butene as the major product (runs 25−30). These results are, we believe, a unique contrast to those by the 2,6-dimethylphenylimido analogue, VCl_2[2-(2,6-$Me_2C_6H_3$)-$NCH_2(C_5H_4N)$](N-2,6-$Me_2C_6H_3$),[6e] which afforded ultrahigh molecular weight polyethylene with moderate (rather low) catalytic activity under the same conditions [activity 78 kg-PE/mol-V·h, $M_w = 2.98 \times 10^6$, $M_w/M_n = 2.0$].[6e]

We previously demonstrated that the activities by VCl_2[2-(2,6-$Me_2C_6H_3$)$NCH_2(C_5H_4N)$](NR) increased in the order: R = 1-adamantyl (**1a**) > cyclohexyl > phenyl, and assumed that the activities are affected by an electronic nature of the imido ligand employed.[7a] As described above, the results by **4a,b** also suggest that the *ortho* substituent in the phenyl imido ligand plays an important role toward the activity, although we do not have clear explanation of the observed unique ligand effect.

Taking into account the facts summarized above, we can at least say it is clear that *fine-tuning* of substituents in both the imido ligand and the chelate anionic donor ligand plays an essential key role for the remarkable activity with high selectivity. We highly believe that such information is potentially important for designing efficient molecular catalysis with vanadium for precise olefin polymerization as well as oligomerization.

■ EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Anhydrous grade toluene, *n*-hexane (Kanto Kagaku Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under nitrogen stream, and were passed through an alumina short column under N_2 stream prior to use. $VCl_3(NAd)$[13] (Ad = 1-adamantyl), VCl_2[2-(2,6-$R'_2C_6H_3$)-$NCH_2(C_5H_4N)$](NAd) [R′ = Me (**1a**), ^{i}Pr (**1b**)], Li[2-(2,6-$Me_2C_6H_3$)$NCH_2(C_5H_4N)$], Li[2-(2,6-^{i}$Pr_2C_6H_3$)$NCH_2(C_5H_4N)$] were prepared according to our previous reports.[6e,7a] *o*-Tolyl isocyanate, 3,5-dimethylphenylisocyanate, triethylamine (TCI Co., Ltd.), and $VOCl_3$ (Sigma-Aldrich Co.) were used as received. Polymerization grade ethylene (purity >99.9%, Sumitomo Seika Co. Ltd.) 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 under reduced pressure (at ca. 50 °C for removing toluene, $AlMe_3$, and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. GC analysis was performed with a SHIMADZU GC-2025AF gas chromatograph (Shimadzu Co. Ltd.) equipped with a flame ionization detector.

Elemental analyses were performed by using EAI CE-440 CHN/O/S Elemental Analyzer (Exeter Analytical, Inc.). All ^{1}H, ^{13}C and ^{51}V NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C and 131.55 MHz for ^{51}V). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in parts per million (ppm) and are referenced to $SiMe_4$ (δ 0.00 ppm, ^{1}H, ^{13}C) and $VOCl_3$ (δ 0.00, ^{51}V). Coupling constants and half-width values, $\Delta\nu_{1/2}$, are given in hertz (Hz).

Synthesis of $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](N\text{-}1\text{-}adamantyl)$ (2). Into a toluene solution (15.0 mL) containing 2-(2,6-$Me_2C_6H_3$)$NHCH_2(C_9H_6N)$ (300 mg, 1.15 mmol) was added *n*-BuLi (0.75 mL, 1.18 mmol, *n*-hexane solution) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was then stirred for 3 h. The resultant solid (lithium salt) was collected on a glass filter and was washed with *n*-hexane. The solid was then dried in vacuo to yield green solid (266 mg). Into a Et_2O solution (15.0 mL) containing $VCl_3(NAd)$ (304 mg, 0.992 mmol) was added the above green solid (266 mg) at −30 °C. The reaction mixture was then warmed slowly to room temperature, and the solution was then stirred overnight. The resultant solution was passed through a Celite pad, and the filtercake was washed with hot toluene. The combined filtrate and the wash were placed in a rotary evaporator to remove the volatiles. The resultant solid was dissolved in a minimum amount of CH_2Cl_2, and was then layered with *n*-hexane. The chilled solution placed in the freezer (−30 °C) afforded orange crystals (216 mg, 0.406 mmol). Yield: 40.9% [based on $VCl_3(NAd)$]. ^1H NMR ($CDCl_3$): δ 8.67 (d, 1H, *J* = 8.75, quino-*H*), 8.34 (d, 1H, *J* = 8.50, quino-*H*), 7.90 (d, 1H, *J* = 7.95, quino -*H*), 7.81−7.78 (m, 1H, quino-*H*), 7.63 (t, 1H, *J* = 7.33, quino-*H*), 7.46 (d, 1H, *J* = 8.45, quino-*H*), 7.18−7.13 (m,3H, Ar-*H*), 5.31 (s, 2H, NCH_2) 2.30 (s, 6H, $ArCH_3$), 1.92 (s, 3H, Ad-*H*), 1.81 (d, 6H, Ad-*H*), 1.47 (t, 6H, Ad-*H*). ^{13}C NMR ($CDCl_3$): δ 163.5, 158.2, 144.7, 139.3, 130.2, 129.2, 129.0, 128.5, 128.4, 128.1, 127.3, 127.1, 117.6, 70.9, 41.1, 35.7, 35.7, 28.8, 18.5. ^{51}V NMR ($CDCl_3$): δ −119.3 ($\Delta\nu_{1/2}$ = 1973 Hz). Anal. Calcd. for $C_{28}H_{32}Cl_2N_3V$: C, 63.16 (60.91+VC, vanadium carbide); H, 6.06; N, 7.89. Found (1): C, 61.52; H, 5.97; N, 7.58. Found (2): C, 61.90; H, 6.00; N, 7.66. Found (3): C, 61.81; H, 5.84; N, 7.66. In spite of several independent analysis runs (with different samples), the observed C values were somewhat low because of incomplete combustion (by production of vanadium carbide), whereas both H and N observed values were close to the calculated values. NMR spectra for **2** are shown in the Supporting Information.

Synthesis of $VCl_2[8\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](N\text{-}1\text{-}adamantyl)$ (3). Into a toluene solution (15.0 mL) containing 8-(2,6-$Me_2C_6H_3$)$N(H)CH_2(C_9H_6N)$ (300 mg, 1.15 mmol) was added *n*-BuLi (0.75 mL, 1.18 mmol, *n*-hexane solution) at −30 °C. The reaction mixture was then warmed slowly to room temperature, and the mixture was stirred for 3 h. The resultant solid (lithium salt) was collected on a glass filter and was washed with *n*-hexane. The solid was then dried in vacuo to yield yellow powder (296 mg). Into a Et_2O solution (15.0 mL) containing $VCl_3(NAd)$ (332 mg, 1.10 mmol) was added the above yellow powder (296 mg) at −30 °C. The reaction mixture was then warmed slowly to room temperature, and the mixture was then stirred overnight. The resultant solution was passed through a Celite pad, and the filtercake was washed with hot toluene. The combined filtrate and the wash were placed in a rotary evaporator to remove the volatiles. The solid was then dissolved in a minimum amount of CH_2Cl_2, and was layered with *n*-hexane. The chilled solution placed in the freezer (−30 °C) afforded red microcrystals (145 mg, 0.272 mmol). Yield: 25.1% [based on $VCl_3(NAd)$]. ^1H NMR ($CDCl_3$): δ 9.48−9.47 (m, 1H, quino-*H*), 8.45−8.43 (m, 1H, quino-*H*), 7.94−7.92 (m, 1H, quino-*H*), 7.71−7.68 (m, 1H, quino-*H*), 7.57−7.24 (m, 2H, quino-*H*), 7.18−7.08 (m, 3H, Ar-*H*), 5.29 (s, 2H, NCH_2), 2.21 (s, 6H, $ArCH_3$), 1.88 (s, 3H, Ad-*H*), 1.74−1.73 (d, 6H, Ad-*H*), 1.46−1.41 (m, 6H, Ad-*H*). ^{13}C NMR ($CDCl_3$): δ 168.8, 153.8, 145.7, 139.7, 135.7, 129.5, 128.8, 128.8, 128.6, 128.5, 127.3, 126.8, 122.2, 67.3, 53.6, 41.2, 35.8, 29.0, 19.5. ^{51}V NMR ($CDCl_3$): δ −106.4 ($\Delta\nu_{1/2}$ = 1776 Hz). Anal. Calcd. for $C_{28}H_{32}Cl_2N_3V$ CH_2Cl_2: C, 56.42; H, 5.55; N, 6.81. Found: C, 56.40; H, 5.49; N, 6.73.

Synthesis of $VCl_3(N\text{-}2\text{-}MeC_6H_4)$. Into a sealed Schlenk glass tube, *n*-octane (50 mL) and *o*-tolyl isocyanate (5.13 g, 38.5 mmol) were added sequentially in the drybox, and $VOCl_3$ (11.1 g, 64.6 mmol) was then added to the mixture. The wall of the tube was washed with *n*-octane (5 mL), and the mixture was placed in an oil bath that had been preheated at 140 °C, and was stirred overnight (17 h). The tube was connected to a nitrogen line, and evolved CO_2 was carefully removed several times from the mixture. After the reaction, the cooled mixture was filtered through a Celite pad, and the filtercake was washed with *n*-hexane several times to extract $VCl_3(N\text{-}2\text{-}MeC_6H_4)$. The combined filtrate and the wash were added toluene and were placed to dry under reduced pressure to remove solvent (octane, *n*-hexane and toluene). The resultant solid was dissolved in a minimum amount of CH_2Cl_2, and a deep brown solid (7.80 g, 29.7 mmol) was obtained at room temperature. Yield: 77.1% (based on *o*-tolyl isocyanate). ^1H NMR ($CDCl_3$): δ 7.61 (d, 1H, *J* = 7.85, Ar-*H*), 7.21 (m, 3H, Ar-*H*), 2.85 (s, 3H, $ArCH_3$). ^{13}C NMR ($CDCl_3$): δ 138.3, 132.3, 130.2, 128.8, 126.2, 18.5. ^{51}V NMR ($CDCl_3$): δ 296.7 ($\Delta\nu_{1/2}$ = 349 Hz).

Synthesis of $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}2\text{-}MeC_6H_4)$ (4a). Into a toluene solution (60.0 mL) containing $VCl_3(N\text{-}2\text{-}MeC_6H_4)$ (524 mg, 2.00 mmol) was added a toluene solution (20.0 mL) containing 2-(2,6-$Me_2C_6H_3$)$NHCH_2(C_5H_4N)$ (427 mg, 2.01 mmol) and triethylamine (223 mg, 2.20 mmol) at −30 °C. The reaction mixture was then warmed slowly to room temperature, and the mixture was then stirred overnight. The solution was passed through a Celite pad, and the filtercake was washed with hot toluene. The combined filtrate and the wash were placed in a rotary evaporator to remove the volatiles. The resultant solid was dissolved in a minimum amount of hot toluene. The chilled solution placed in the freezer (−30 °C) afforded red microcrystals (589 mg, 1.34 mmol). Yield: 67.3%. ^1H NMR ($CDCl_3$): δ 9.04 (d, 1H, *J* = 5.50, Py-*H*), 7.99 (dt, 1H, *J* = 7.73 and 1.20, Py-*H*), 7.60 (t, 1H, *J* = 6.48, Py-*H*), 7.53 (d, 1H, *J* = 7.90, Py-*H*), 6.98 (d, 2H, *J* = 7.50, Ar-*H*), 6.93−6.89 (m, 2H, Ar-*H*), 6.87−6.83 (m, 3H, Ar-*H*), 5.32 (s, 2H, NCH_2), 2.62 (s, 3H, $ArCH_3$), 2.20 (s, 6H, $ArCH_3$). ^{13}C NMR ($CDCl_3$): δ 161.6, 157.4, 149.7, 139.8, 138.4, 131.0, 129.5, 129.2, 128.3, 128.3, 127.8, 127.0, 125.4, 123.8, 120.3, 72.0, 18.6, 18.3. ^{51}V NMR ($CDCl_3$): δ 35.4 ($\Delta\nu_{1/2}$ = 1380 Hz). Anal. Calcd. for $C_{21}H_{22}Cl_2N_3V$: C, 57.55; H, 5.06; N, 9.59. Found: C, 57.51; H, 5.06; N, 9.45. The attempted synthesis of **4a** by treatment with Li[2-(2,6-$Me_2C_6H_3$)$NCH_2(C_5H_4N)$] is shown in the Supporting Information.

Synthesis of $VCl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}2\text{-}MeC_6H_4)$ (4b). Into a toluene solution (12.0 mL) containing $VCl_3(N\text{-}2\text{-}MeC_6H_4)$ (782 mg, 2.98 mmol) was added a toluene solution (2.0 mL) containing 2-(2,6-$^iPr_2C_6H_3$)$NHCH_2(C_5H_4N)$ (800 mg, 2.98 mmol) and triethylamine (336 mg, 3.32 mmol) at −30 °C. The reaction mixture was then warmed slowly to room temperature, and the mixture was then stirred overnight. The solution was passed through a Celite pad, and the filtercake was washed with hot toluene. The combined filtrate and the wash were placed in a rotary evaporator to remove the volatiles. The resultant solid was dissolved in minimum amount of hot toluene. The chilled solution placed in the freezer (−30 °C) afforded dark yellow microcrystals (432 mg, 0.874 mmol). Yield: 29.3%. ^1H NMR ($CDCl_3$): δ 8.99 (d, 1H, *J* = 5.35, Py-*H*), 7.99 (dt, 1H, *J* = 7.70 and 1.28, Py-*H*), 7.60 (t, 1H, *J* = 6.48, Py-*H*), 7.53 (d, 1H, *J* = 7.90, Py-*H*), 7.37 (t, 1H, *J* = 7.70, Ar-*H*), 7.27 (d, 2H, Ar-*H*), 7.02 (d, 1H, *J* = 7.55, Ar-*H*), 6.83 (t, 1H, *J* = 7.45, Ar-*H*), 6.67 (t, 1H, *J* = 7.62, Ar-*H*), 5.46 (d, 1H, *J* = 8.00, Ar-*H*), 5.33 (s, 2H, NCH_2), 2.93−2.88 (m, 5H, $ArCH_3$ and $-CH(CH_3)_2$), 1.17 (d, 6H, *J* = 6.95, $-CH(CH_3)_2$), 1.12 (d, 6H, *J* = 6.65, $-CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ160.2, 157.2, 149.7, 141.3, 139.2, 138.5, 129.8, 128.3, 127.8, 125.1, 124.7, 123.9, 120.2, 74.4, 28.2, 25.2, 24.4, 19.6. ^{51}V NMR ($CDCl_3$): δ 79.7 ($\Delta\nu_{1/2}$ = 2049.5 Hz). Anal. Calcd. for $C_{25}H_{30}Cl_2N_3V$: C, 60.73 (58.31+VC, vanadium carbide); H, 6.13; N, 8.50. Found: C, 59.50; H, 6.22; N, 8.37. Attempted synthesis of **4b** by treatment with Li[2-(2,6-$^iPr_2C_6H_3$)$NCH_2(C_5H_4N)$] is shown in the Supporting Information.

Synthesis of $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)(N\text{-}4\text{-}MeC_6H_4)]$ (5). Into a toluene solution (60.0 mL) containing $VCl_3(N\text{-}4\text{-}MeC_6H_4)$ (525 mg, 2.00 mmol) was added a toluene solution (20.0 mL) containing 2-(2,6-$Me_2C_6H_3$)$NHCH_2(C_5H_4N)$ (425 mg, 2.00 mmol) and triethylamine (226 mg, 2.23 mmol) at −30 °C. The reaction mixture was then warmed slowly to room temperature, and the mixture was then stirred overnight. The solution was passed through a Celite pad, and the filtercake was washed with hot toluene. The combined filtrate and the wash were placed in a rotary evaporator to remove the volatiles. The solid was dissolved in a minimum amount of CH_2Cl_2 and was layered with *n*-hexane. The chilled solution placed in the freezer (−30 °C) afforded red microcrystals (387 mg, 0.833

Table 4. Crystal Data and Collection Parameters of $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](NAd)$ (2), $VCl_2[8\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_9H_6N)](NAd)$ (3), $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}2\text{-}MeC_6H_4)$ (4a), and $VCl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}2\text{-}MeC_6H_4)$ (4b)[a]

	2	3[b]	4a	4b[c]
formula	$C_{28}H_{32}Cl_2N_3V$	$C_{29}H_{34}Cl_4N_3V$	$C_{21}H_{22}Cl_2N_3V$	$C_{51}H_{62}Cl_6N_6V_2$
formula weight	532.43	617.36	438.27	1073.69
crystal color, habit	yellow, platelet	orange, platelet	orange, platelet	yellow, platelet
crystal size (mm)	0.210 × 0.180 × 0.030	0.200 × 0.180 × 0.070	0.240 × 0.170 × 0.010	0.120 × 0.080 × 0.020
crystal system	monoclinic	triclinic	orthorhombic	triclinic
space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	*Pbca* (#61)	$P\bar{1}$ (#2)
a (Å)	16.4655(3)	8.9224(2)	7.7648(2)	9.4747(2)
b (Å)	14.5364(2)	10.1100(3)	14.4294(3)	17.3921(4)
c (Å)	10.7782(1	16.7358(5)	36.7708(8)	17.9733(4)
α (deg)		77.7248(7)		68.8893(7)
β (deg)	99.4194	85.5932(7)		74.8665(7)
γ (deg)		74.3597(7)		80.4037(7)
V (Å^3)	2544.96(7)	1420.22(6)	4119.9(2)	2658.4(1)
Z value	4	2	8	2
D_{calcd} (g/cm^3)	1.389	1.444	1.413	1.341
F_{000}	1112.00	640.00	1808.00	1116.00
temp (K)	123	123	123	123
μ (MoKα) (cm^{-1})	6.214	7.492	7.509	6.923
no. of reflections measured (R_{int})	total: 25020 unique: 5821 (0.0296)	total: 14238 unique: 6483 (0.0169)	total: 66707 unique: 4720 (0.0585)	total: 26683 unique: 12147 (0.0379)
$2\theta_{max}$ (deg)	54.9	54.9	55.0	55.0
no. of observations [$I > 2.00\sigma(I)$]	5821	6483	4720	12147
no. of variables	309	336	247	596
R1 [$I > 2.00\sigma(I)$]	0.0334	0.0529	0.0412	0.0407
wR2 [$I > 2.00\sigma(I)$]	0.0901	0.1554	0.1220	0.0969
goodness of fit	1.137	1.096	1.082	1.046

[a] Detailed structural data are shown in the Supporting Information. [b] Complex **3** contains CH_2Cl_2 in the crystal. [c] Structure for **4b** was solved as two crystals containing CH_2Cl_2.

mmol). Yield: 44.2%. ^{1}H NMR ($CDCl_3$): δ 9.02 (d, 1H, *J* = 5.35, Py-*H*), 7.99−7.96 (m, 1H, Py-*H*), 7.59 (t, 1H, *J* = 6.43, Py-*H*), 7.52 (d, 1H, *J* = 7.90, Py-*H*), 7.03 (d, 2H, *J* = 7.40, Ar-*H*), 6.98−6.95 (m, 1H, Ar-*H*), 6.84−6.80 (m, 4H, Ar-*H*), 5.30 (s, 2H, NC*H*$_2$), 2.31 (s, 3H, ArC*H*$_3$), 2.17 (s, 6H, ArC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 162.1, 157.6, 149.6, 138.7, 138.5, 128.5, 128.5, 128.3, 128.0, 127.0, 123.8, 71.8, 21.7, 18.3. ^{51}V NMR ($CDCl_3$): δ 31.3 ($\Delta\nu_{1/2}$ = 1868 Hz). Anal. Calcd. for $C_{21}H_{22}Cl_2N_3V$: C, 57.55; H, 5.06; N, 9.59. Found: C, 57.52; H, 5.07; N, 9.72.

Synthesis of $VCl_3(N\text{-}3,5\text{-}Me_2C_6H_3)$. Into a sealed Schlenk glass tube, *n*-octane (20 mL) and 3,5-dimethylphenylisocyanate (2.5 g, 17.0 mmol) were added sequentially in the drybox, and $VOCl_3$ (4.98 g, 28.8 mmol) was then added to the mixture. The wall of the reactor was washed with *n*-octane (5 mL), and the mixture was placed in an oil bath that had been preheated at 140 °C, and was stirred overnight (24 h). The tube was connected to a nitrogen line, and CO_2 evolved was carefully released several times from the mixture. After the reaction, the cooled mixture was filtered through a Celite pad, and the filtercake was washed with *n*-hexane and toluene several times to extract $VCl_3(N\text{-}3,5\text{-}Me_2C_6H_3)$. The combined filtrate and the wash were placed into dryness under reduced pressure to remove solvent (octane, *n*-hexane, and toluene). The resultant residue was dissolved in a minimum amount of hot toluene. A black solid (2.79 g, 10.1 mmol) was collected from the chilled solution (placed in the freezer at −30 °C). Yield: 59.3% (based on 3,5-dimethylphenylisocyanate). $VCl_3(N\text{-}3,5\text{-}Me_2C_6H_3)$, yield 2.79 g, 10.1 mmol, 59.3% ^{1}H NMR ($CDCl_3$): δ 7.19 (2, 2H, Ar-*H*), 6.98 (s, 1H, Ar-*H*), 2.32 (s, 6H, ArC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 138.6, 134.7, 124.0, 21.2. ^{51}V NMR ($CDCl_3$): δ 280.3 ($\Delta\nu_{1/2}$ = 506 Hz). Anal. Calcd for $C_8H_9Cl_3NV$: C, 34.76; H, 3.28; N, 5.07. Found: C, 34.82; H, 3.29; N, 4.79.

Synthesis of $VCl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)](N\text{-}3,5\text{-}Me_2C_6H_3)$ (6). Into a toluene solution (70.0 mL) containing $VCl_3(N\text{-}3,5\text{-}Me_2C_6H_3)$ (631 mg, 2.28 mmol) was added a toluene solution (20.0 mL) containing $2\text{-}(2,6\text{-}Me_2C_6H_3)NHCH_2(C_5H_4N)$ (484 mg, 2.28 mmol) and triethylamine (253 mg, 2.51 mmol) at −30 °C. The reaction mixture was then warmed slowly to room temperature, and the mixture was then stirred overnight. The solution was passed through a Celite pad, and the filtercake was washed with hot toluene. The combined filtrate and the wash were placed in a rotary evaporator to remove the volatiles. The solid was dissolved in a minimum amount of CH_2Cl_2 and was layered with *n*-hexane. The chilled solution placed in the freezer (−30 °C) afforded red microcrystals (400 mg, 0.884 mmol). Yield: 38.8%. ^{1}H NMR ($CDCl_3$): δ 9.02 (d, 1H, *J* = 5.40, Py-*H*), 8.00−7.96 (m, 1H, Py-*H*), 7.60 (t, 1H, *J* = 6.43, Py-*H*), 7.52 (d, 1H, *J* = 7.90, Py-*H*), 7.06 (d, 2H, *J* = 7.35, Ar-*H*), 7.02−6.99 (m, 1H, Ar-*H*), 6.65 (s, 1H, Ar-*H*), 6.47 (s, 2H, Ar-*H*), 5.31 (s, 2H, NC*H*$_2$), 2.17 (s, 6H, ArC*H*$_3$), 2.09 (s, 6H, ArC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 162.4, 157.6, 149.7, 138.5, 137.4, 130.5, 128.7, 128.3, 127.0, 125.4, 123.9, 120.3, 71.8, 21.1, 18.4. ^{51}V NMR ($CDCl_3$): δ 24.9 ($\Delta\nu_{1/2}$ = 1973 Hz). Anal. Calcd. for $C_{22}H_{24}Cl_2N_3V$: C, 58.42; H, 5.35; N, 9.29. Found: C, 58.40; H, 5.35; N, 9.55.

Oligomerization/Polymerization of Ethylene. Ethylene oligomerizations were conducted in a 100 mL scale stainless steel autoclave. The typical reaction procedure is as follows. Toluene (29 mL) and prescribed amount of MAO were added into the autoclave in the drybox. The reaction apparatus was then filled with ethylene (1 atm), and the prescribed amount of complexes in toluene (1.0 mL) was then added into the autoclave, the reaction apparatus was then immediately pressurized to 7 atm (total 8 atm), and the mixture was magnetically stirred for 10 min. After the above procedure, the remaining ethylene was purged at −30 °C, and 0.5 g of heptane was added as an internal standard. The solution was then analyzed by GC to determinate the activity and the product distribution. Ethylene polymerizations were also conducted similarly. After oligomerization, the chilled remaining mixture in the autoclave was then poured into MeOH containing HCl. The resultant polymer (white precipitate) was collected on a filter paper by filtration and was adequately washed with MeOH. The resultant polymer was then dried in vacuo at 60 °C for 2 h.

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo−Kα radiation. The crystal collection parameters are listed below (Table 4). All structures were solved by direct methods and expanded using Fourier techniques,[14] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Crystal Structure[15] crystallographic software package except for refinement, which was performed using SHELXL-97.[16]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for syntheses of 2-ArN(H)-CH$_2$(C$_9$H$_6$N) and 8-ArN(H)CH$_2$(C$_9$H$_6$N) (Ar = 2,6-Me$_2$C$_6$H$_3$). Attempted syntheses of VCl$_2$[2-(2,6-Me$_2$C$_6$H$_3$)-NCH$_2$(C$_5$H$_4$N)](N-2-MeC$_6$H$_4$) (**4a**), and VCl$_2$[2-(2,6-^{i}Pr$_2$C$_6$H$_3$)NCH$_2$(C$_5$H$_4$N)](N-2-MeC$_6$H$_4$) (**4b**) by another method via treatment of VCl$_3$(N-2-MeC$_6$H$_4$) with the lithium salts, Li[2-(2,6-R′$_2$C$_6$H$_3$)NCH$_2$(C$_5$H$_4$N)]. ^{1}H NMR spectra for V(NAd)Cl$_2$[2-(2,6-Me$_2$C$_6$H$_3$)NCH$_2$(C$_9$H$_6$N)] (**2**), V(NAd)Cl$_2$[8-(2,6-Me$_2$C$_6$H$_3$)NCH$_2$(C$_9$H$_6$N)] (**3**), and V(N-2-MeC$_6$H$_4$)Cl$_2$[2-(2,6-^{i}Pr$_2$C$_6$H$_3$)NCH$_2$(C$_5$H$_4$N)] (**4b**). Structural reports including CIF files for VCl$_2$[2-(2,6-Me$_2$C$_6$H$_3$)-NCH$_2$(C$_9$H$_6$N)](NAd) (**2**), VCl$_2$[8-(2,6-Me$_2$C$_6$H$_3$)-NCH$_2$(C$_9$H$_6$N)](NAd) (**3**), VCl$_2$[2-(2,6-Me$_2$C$_6$H$_3$)-NCH$_2$(C$_5$H$_4$N)](N-2-MeC$_6$H$_4$) (**4a**), and VCl$_2$[2-(2,6-^{i}Pr$_2$C$_6$H$_3$)NCH$_2$(C$_5$H$_4$N)](N-2-MeC$_6$H$_4$) (**4b**). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +81-42-677-2547. Fax: +81-42-677-2547. E-mail: ktnomura@tmu.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was partly supported by Bilateral Joint Projects between Japan Society of Promotion of Sciences (JSPS) and National Natural Science Foundation of China (NSFC). K.N. and A.I. express their heartfelt thanks to Tosoh Finechem Co. for donating MAO. This project by W.Z. and W.S. was also supported partly by NSFC (No. 21011140068).

■ REFERENCES

(1) (a) Carrick, W. L. *J. Am. Chem. Soc.* **1958**, *80*, 6455. (b) Carrick, W. L.; Kluiber, R. W.; Bonner, E. F.; Wartman, L. H.; Rugg, F. M.; Smyth, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 3883. (c) Phillips, G. W.; Carrick, W. L. *J. Polym. Sci.* **1962**, *59*, 401.

(2) (a) Junghanns, E.; Gumboldt, O.; Bier, G. *Makromol. Chem.* **1962**, *58*, 18. (b) Natta, G.; Mazzanti, G.; Valvassori, A.; Sartori, G.; Fiumani, D. *J. Polym. Sci.* **1961**, *51*, 411.

(3) For example Christman, D. L.; Keim, G. I. *Macromolecules* **1968**, *1*, 358.

(4) (a) Doi, Y.; Ueki, S.; Keii, T. *Macromolecules* **1978**, *12*, 814. (b) Doi, Y.; Koyama, T.; Soga, K. *Makromol. Chem.* **1985**, *186*, 11.

(5) For recent reviews (vanadium catalysts), see: (a) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357. (b) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229. (c) Nomura, K.; Zhang, W. *Chem. Sci.* **2010**, *1*, 161. (d) Redshaw, C. *Dalton Trans.* **2010**, *39*, 5595. (e) Nomura, K.; Zhang, S. *Chem. Rev.* **2011**, *111*, 2342 ; related references are cited therein.

(6) (a) Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, *35*, 1583. (b) Wang, W.; Nomura, K. *Macromolecules* **2005**, *38*, 5905. (c) Wang, W.; Nomura, K. *Adv. Synth. Catal.* **2006**, *348*, 743. (d) Onishi, Y.; Katao, S.; Fujiki, M.; Nomura, K. *Organometallics* **2008**, *27*, 2590. (e) Zhang, S.; Katao, S.; Sun, W,-H.; Nomura, K. *Organometallics* **2009**, *28*, 5925.

(7) (a) Zhang, S.; Nomura, K. *J. Am. Chem. Soc.* **2010**, *132*, 4960. (b) Igarashi, A.; Zhang, S.; Nomura, K. *Organometallics* **2012**, *31*, 3575.

(8) V complex catalysts, see: (a) Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2000**, 497. (b) Schmidt, R.; Welch, M. B.; Knudsen, R. D.; Gottfried, S.; Alt, H. G. *J. Mol. Catal. A* **2004**, *222*, 17. (c) Hanton, M. J.; Tenza, K. *Organometallics* **2008**, *27*, 5712. ; Vanadium complexes containing chelate bis(imino)pyridine ligands yielded polymers/oligomers with Schultz−Flory distribution.[8b,c]

(9) These results were partly introduced by K.N. at the *Chemelot International Polyolefins Symposium 2012 (CIPS2012)*, Maastricht, The Netherlands, October, 2012.

(10) Syntheses of 2-(2,6-Me$_2$C$_6$H$_3$)N(H)CH$_2$(C$_9$H$_6$N), 8-(2,6-Me$_2$C$_6$H$_3$)N(H)CH$_2$(C$_9$H$_6$N) are described in the Supporting Information.

(11) Structural reports including CIF files for VCl$_2$[2-(2,6-Me$_2$C$_6$H$_3$)NCH$_2$(C$_9$H$_6$N)](NAd) (**2**), VCl$_2$[8-(2,6-Me$_2$C$_6$H$_3$)NCH$_2$(C$_9$H$_6$N)](NAd) (**3**), VCl$_2$[2-(2,6-Me$_2$C$_6$H$_3$)NCH$_2$(C$_5$H$_4$N)](N-2-MeC$_6$H$_4$) (**4a**), and VCl$_2$[2-(2,6-^{i}Pr$_2$C$_6$H$_3$)NCH$_2$(C$_5$H$_4$N)](N-2-MeC$_6$H$_4$) (**4b**) are provided in the Supporting Information.

(12) Syntheses of VCl$_3$(N-2-MeC$_6$H$_4$) and VCl$_3$(N-3,5-Me$_2$C$_6$H$_3$) were performed under the same conditions for that in V(N-4-MeC$_6$H$_4$)Cl$_3$, reported previously, as described in the Experimental Section. (a) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maata, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408. Analogous synthesis of the THF adduct of VCl$_3$(THF)(N-3,5-Me$_2$C$_6$H$_3$) (b) Nomura, K.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1996**, *35*, 3695.

(13) Zhang, W.; Nomura, K. *Inorg. Chem.* **2008**, *47*, 6482.

(14) SIR2008: Burla, M. C.; Calandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Siliqi, D.; Spagna, R. *J. Appl. Crystallogr.* **2007**, *40*, 609.

(15) *Crystal Structure* 4.0, Crystal Structure Analysis Package; Rigaku and Rigaku Americas: Tokyo, Japan, 2000−2010; pp 196−8666.

(16) SHELX97: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.