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Highly Efficient Dimerization of Ethylene by (Imido)vanadium Complexes Containing (2-Anilidomethyl)pyridine Ligands: Notable Ligand Effect toward Activity and Selectivity

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Abstract: (Imido)vanadium(V) complexes containing the (2-anilidomethyl)pyridine ligand, V(NR)Cl$_2$[2-ArNCH$_2$(C$_5$H$_4$N)] (R = 1-adamantyl (Ad), cyclohexyl (Cy), phenyl), exhibit remarkably high catalytic activities (e.g. TOF = 2 730 000 h^{-1} (758 s^{-1}) by V(NAd)Cl$_2$[2-(2,6-Me$_2$C$_6$H$_3$)NCH$_2$(C$_5$H$_4$N)) for ethylene dimerization in the presence of MAO, affording 1-butene exclusively (selectivity 90.4 to >99%). The steric bulk of the imido ligand plays an important role in the selectivity (polymerization vs dimerization), and the electronic nature directly affects the catalytic activity (activity: R = Ad > Cy > Ph).

Introduction

Liner α-olefins are important intermediates for a variety of products (such as detergents, polymers, lubricants, surfactants, etc.)[1] and are largely produced by ethylene oligomerization,[2,3] as exemplified by the Shell Higher Olefin Process (SHOP) using a Ni complex catalyst containing a chelate P−O ligand.[2] Although recent examples of ethylene oligomerization, especially using Ni[4] and Fe complexes,[5] or ethylene trimerization, especially using Cr complex catalysts,[6,7] have been known, the examples using group 4 (Ti, Zr)[8] and group 5 (V, Ta)[9,10] catalysts have been limited. In particular, reports of efficient complex catalysts with notable catalytic activity have not been reported so far.

Designing vanadium complex catalysts should be promising for the target, because the classical Ziegler-type catalyst systems (V(acac)$_3$, VOCl$_3$, etc. and Et$_2$AlCl, EtAlCl$_2$, ^{n}BuLi, etc.) display uniquely high reactivity toward olefins in olefin coordination/insertion polymerization.[11] We previously reported that (arylimido)vanadium(V) complexes containing anionic ancillary donor ligands of the type V(N-2,6-Me$_2$C$_6$H$_3$)Cl$_2$(X) (X = aryloxo,[12a−c] ketimide,[12d] phenoxyimine,[12e] (2-anilidomethyl)pyridine[12f])

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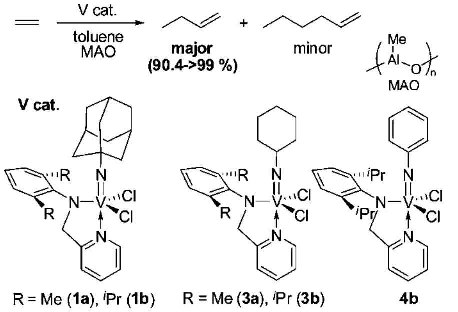
Scheme 1



Scheme 2

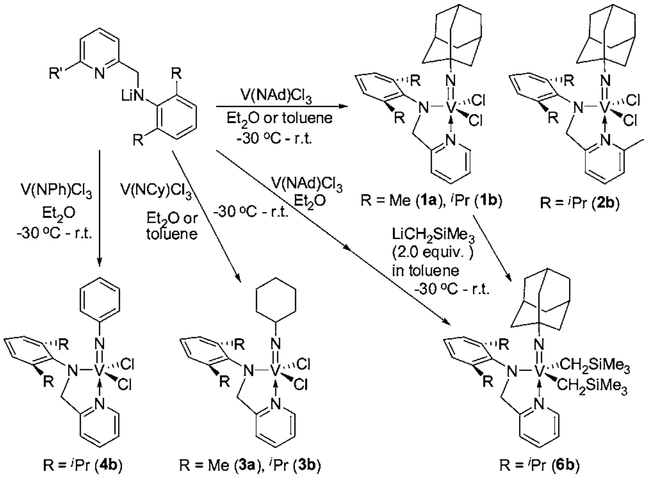


Table 1. Selected Bond Lengths and Angles for $V(NAd)Cl_2[2\text{-}(2,6\text{-}R_2C_6H_3)NCH_2(C_5H_4N)]$ (R = Me (**1a**), ^{i}Pr (**1b**)) and $V(NCy)Cl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (**3b**)[a]

	1a	1b	3b
	Bond Distances (Å)		
V1−N1	2.2241(11)	2.225(2)	2.221(2)
V1−N2	1.8580(12)	1.8607(18)	1.854(2)
V1−N3	1.6517(12)	1.654(2)	1.648(2)
V1−Cl1	2.2677(3)	2.2743(6)	2.2652(12)
V1−Cl2	2.2709(4)	2.2680(6)	2.2705(7)
	Bond Angles (deg)		
N1−V1−N2	78.20(4)	77.96(8)	78.14(9)
N1−V1−N3	174.90(4)	176.95(8)	175.63(13)
N1−V1−Cl1	85.49(3)	83.85(5)	84.08(8)
N1−V1−Cl2	83.93(3)	85.53(5)	84.37(5)
N2−V1−N3	97.41(5)	99.05(9)	97.53(12)
N2−V1−Cl1	116.92(4)	119.71(6)	114.38(8)
N2−V1−Cl2	118.18(3)	114.68(6)	118.36(9)
N3−V1−Cl1	98.90(3)	97.19(7)	98.33(13)
N3−V1−Cl2	96.02(4)	96.36(7)	97.35(8)
Cl1−V1−Cl2	119.953(16)	120.53(2)	121.90(3),
V1−N3−C19(C25)	170.94(10)	170.20(16)	165.8(4), 158.6(5)

[a] Detailed structural analysis data, including CIF files for complexes **1a**,**b** and **3b**, are given in the Supporting Information.

showed remarkable catalytic activities for ethylene polymerization in the presence of Al cocatalysts (methylaluminoxane (MAO), Et_2AlCl, etc.) and the aryloxo analogues showed notable catalytic activity and comonomer incorporation in ethylene/norbornene copolymerization.[12b,c] We also reported that (1-adamantylimido)vanadium(V) complexes containing aryloxo and ketimide ligands, $V(NAd)Cl_2(X)$ (Ad = 1-adamantyl), showed moderate catalytic activities for ethylene polymerization in the presence of MAO.[13] In this paper, we wish to report that (imido)vanadium(V) complexes containing (2-anilidomethyl)pyridine of the type $V(NR)Cl_2[2\text{-}ArNCH_2(C_5H_4N)]$ (R = Ad, cyclohexyl (Cy), phenyl; Ar = $2,6\text{-}Me_2C_6H_3$ (**a**), $2,6\text{-}{}^iPr_2C_6H_3$ (**b**)) efficiently dimerize ethylene with both remarkably high catalytic activities and high selectivity (Scheme 1).

Results and Discussion

1. Synthesis of (Imido)vanadium(V) Complexes Containing (2-Anilidomethyl)pyridine Ligands. A series of (imido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligands, $V(NR)Cl_2[2\text{-}ArNCH_2(C_5H_4N)]$ (R = Ad (**1**), Cy (**3**); Ar = $2,6\text{-}Me_2C_6H_3$ (**a**), $2,6\text{-}{}^iPr_2C_6H_3$ (**b**)), $V(NAd)Cl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2\text{-}6\text{-}MeC_5H_3N]$ (**2b**), and $V(NPh)Cl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (**4b**), were prepared by reacting the corresponding (imido)vanadium(V) trichloride analogues $V(NR)Cl_3$ with $Li[2\text{-}ArNCH_2(C_5H_4N)]$ (prepared by treating $2\text{-}Ar'N(H)CH_2(C_5H_4N)$ with 1 equiv of ^{n}BuLi in *n*-hexane at −30 °C)[12f] in Et_2O or toluene (Scheme 2). These procedures are analogous to those for the synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (**5b**), reported previously.[12f] The resultant complexes were identified by NMR spectra (^1H, ^{13}C, ^{51}V) and elemental analyses, and structures of some complexes (**1a**,**b**, **3b**) were determined by X-ray crystallography (Figure 1).[14] The reaction of **1b** with 2.0 equiv of $LiCH_2SiMe_3$ in toluene afforded the dialkyl complex $V(NAd)(CH_2SiMe_3)_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (**6b**) in moderate yield (87%). Complex **6b** was identified on the basis of NMR spectra (^1H, ^{13}C, ^{51}V) and elemental analysis.

The structures of **1a**,**b** and **3b** indicate that these complexes fold a distorted-trigonal-bipyramidal geometry around vanadium with two nitrogen atoms from the pyridine and the imido ligands at the axial positions and an equatorial plane consisting of two chlorine atoms and the nitrogen in the anilide ligand. Selected bond distances and angles are summarized in Table 1. The nitrogen atom in the pyridine is located trans to the imido ligand. The V═N(3) bond lengths in the alkylimido complexes (**1a**,**b**, **3b**, 1.648−1.654 Å) are relatively shorter than that in the arylimido complex (**5b**, 1.679 Å), probably due to the electronic donation from the alkyl substituents.

2. Ethylene Dimerization Using $V(NR)Cl_2[2\text{-}ArNCH_2(C_5H_4N)]$−MAO Catalysts. It should be noted that the adamantylimido analogues (**1a**,**b**) exhibit remarkable catalytic activities for ethylene dimerization in the presence of MAO, affording 1-butene with high selectivities (Table 2). The activity was affected by the Al/V molar ratios, ethylene pressure without significant changes in the selectivity of 1-butene. The activity was also affected by the reaction temperature, and the activity decreased at 0 °C as well as at 50 °C (runs 4, 9, and 10). Since the selectivity of 1-butene seems to decreasing (or that of 1-hexene increases) for prolonged times as well as upon an increase of 1-butene accumulated in the reaction mixture, it is thus assumed that 1-hexene would be produced by the reaction

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(14) Detailed structural analysis data, including CIF files, for complexes **1a**,**b** and **3b** are given in the Supporting Information. Carbon atoms in the cyclohexyl group in **3b** could not be defined, probably due to their flexible structure (observed as a mixture of two structures).

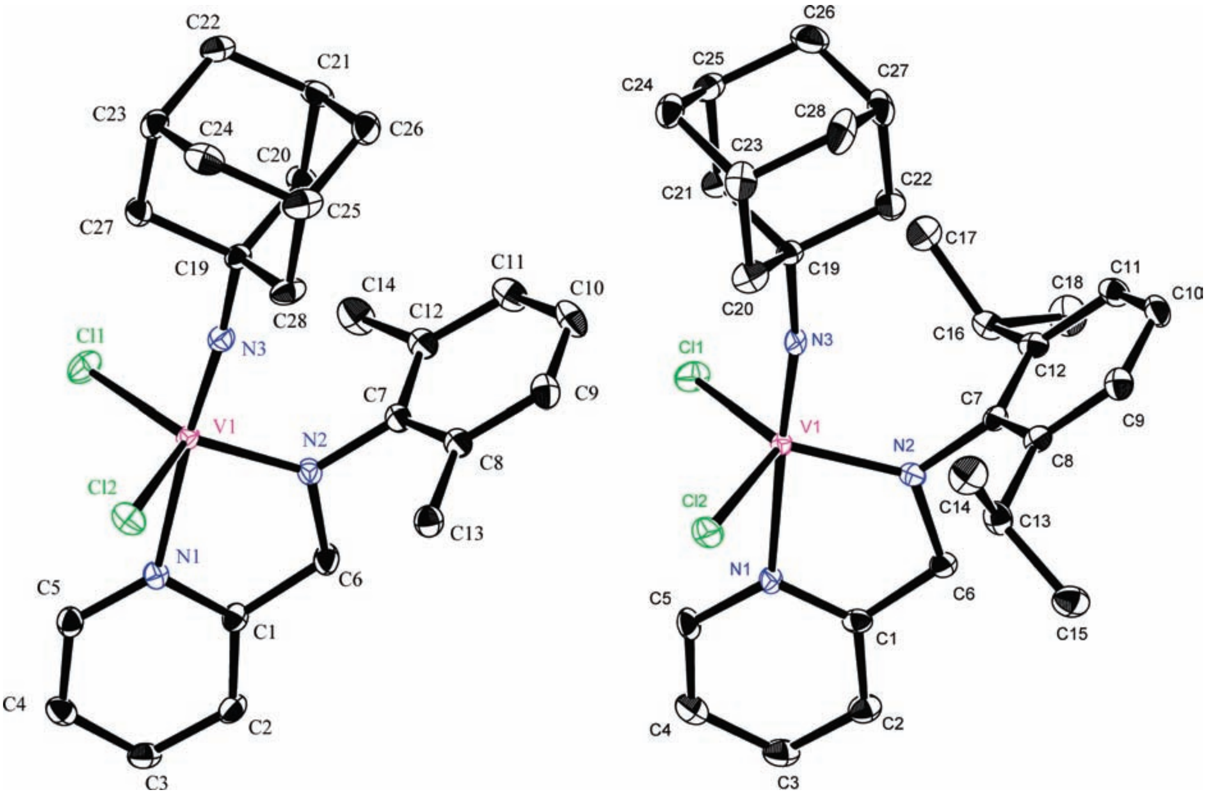

Figure 1. ORTEP drawings of **1a** (left) and **1b** (right). Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Details are given in the Supporting Information.[14]

Table 2. Ethylene Dimerization by $\mathrm{V(NAd)X_2[2\text{-}ArNCH_2(C_5H_4N)]}$ (**1a**,**b**, **6b**)− and $\mathrm{V(NAd)Cl_2[2\text{-}(2,6\text{-}{}^{i}Pr_2C_6H_3)NCH_2\text{-}6\text{-}MeC_5H_3N]}$ (**2b**)−MAO Catalyst Systems (X = Cl and Ar = $\mathrm{2,6\text{-}Me_2C_6H_3}$ (**1a**), $\mathrm{2,6\text{-}{}^{i}Pr_2C_6H_3}$ (**1b**); X = $\mathrm{CH_2SiMe_3}$ and Ar = $\mathrm{2,6\text{-}{}^{i}Pr_2C_6H_3}$ (**6b**))[a]

run	complex (amt/μmol)	Al/V[b]	ethylene/atm	temp/°C	time/min	activity[c]	TOF[d]	C_4'/%[e]	C_6'/%[e]
1	**1a** (0.5)	100	8	25	10	1 350	48 200	94.0	6.0
2	**1a** (0.5)	200	8	25	10	50 600	1 810 000	94.9	5.1
3	**1a** (0.5)	500	8	25	5	35 400	1 260 000	96.7	3.3
4	**1a** (0.5)	500	8	25	10	51 100	1 830 000	92.5	7.5
5	**1a** (0.5)	500	4	25	10	25 500	911 000	92.2	7.8
6	**1a** (0.5)	500	8	25	20	50 300	1 800 000	90.4	9.6
7	**1a** (0.5)	1 000	8	25	10	40 400	1 440 000	95.5	4.5
8	**1a** (0.5)	2 000	8	25	10	6 780	242 000	95.0	5.0
9	**1a** (0.5)	500	8	50	10	8 160	291 000	95.2	4.8
10	**1a** (0.5)	500	8	0	10	17 500	625 000	97.9	2.1
11	**1a** (0.2)	500	8	25	10	57 800	2 060 000	96.8	3.2
12	**1a** (0.1)	1 000	8	25	10	45 800	1 640 000	98.0	2.0
13	**1a** (0.1)	1 500	8	25	10	76 500	2 730 000	97.0	3.0
14	**1a** (0.1)	1 500	8	25	60	74 800	2 670 000	92.1	7.9
15	**1a** (0.1)	2 000	8	25	10	42 900	1 530 000	98.2	1.8
16	**1b** (0.5)	500	8	25	10	20 200	721 000	95.0	5.0
17	**1b** (0.5)	1 000	8	25	10	35 700	1 280 000	92.1	7.9
18	**1b** (0.5)	1 000	8	0	10	23 800	850 000	95.2	4.8
19	**1b** (0.5)	2 000	8	25	10	32 300	1 150 000	92.7	7.3
20	**1b** (0.5)	3 000	8	25	10	15 600	557 000	94.1	5.9
21	**1b** (0.5)	1000[f]	8	25	10	17 900	639 000	94.0	6.0
22	**6b** (0.5)	1 000	8	25	10	16 600	593 000	95.6	4.4
23	**2b** (2.0)	1 000	8	25	10	510	18 000	>99[g]	
24	**2b** (2.0)	2 000	8	25	10	2 100	75 000	95.9[g]	4.1

[a] Conditions: toluene 30 mL, ethylene 4 or 8 atm, d-MAO white solid (prepared by removing $\mathrm{AlMe_3}$, toluene from PMAO-S (commercial sample)). [b] Al/V molar ratio. [c] Activity in (kg of ethylene)/((mol of V) h). [d] TOF (turnover frequency) = (molar amount of ethylene reacted)/((mol of V) h). [e] By GC analysis vs internal standard. [f] d-MMAO (prepared by removing $\mathrm{AlMe_3}$, $\mathrm{Al{}^{i}Bu_3}$, and hexane from a modified methylaluminoxane (methylisobutylaluminoxane), MMAO-BH (molar ratio $\mathrm{Me/{}^{i}Bu}$ 3.54)) was used in place of d-MAO. [g] A small amount of polyethylene (PE) was also collected (ca. 70 mg).

Table 3. Ethylene Dimerization by $\mathrm{V(NR)Cl_2[2\text{-}ArNCH_2(C_5H_4N)]}$ (**1a**,**b**, **3a**,**b**, **4b**, **5b**)−MAO Catalyst Systems[a]

run	complex (ant/μmol)	R	Al/V[b]	activity[c]	TOF[d]	C_4'/%[e]	C_6'/%[e]
4	**1a** (0.5)	Ad	500	51 100	1 830 000	92.5	7.5
13	**1a** (0.1)	Ad	1 500	76 500	2 730 000	97.0	3.0
17	**1b** (0.5)	Ad	1 000	35 700	1 280 000	92.1	7.9
25	**3a** (0.5)	Cy	100	15 300	546 000	97.1	2.9
26	**3a** (0.5)	Cy	200	28 200	1 010 000	93.2	6.8
27	**3a** (0.5)	Cy	500	6 400	229 000	98.4	1.6
28	**3a** (0.5)	Cy	1 000	940	34 000	>99	
29	**3a** (0.5)	Cy	2 000	500	18 000	>99	
30	**3b** (0.5)	Cy	50	1 100	39 000	>99	
31	**3b** (0.5)	Cy	100	13 200	471 000	97.8	2.2
32	**3b** (0.5)	Cy	200	32 300	1 150 000	95.9	4.1
33	**3b** (0.5)	Cy	500	13 100	468 000	96.5	3.5
34	**4b** (0.5)	Ph	200	trace			
35	**4b** (0.5)	Ph	500	18 300	654 000	95.1	4.9
36	**4b** (0.5)	Ph	750	9 600	343 000	97.2	2.8
37	**4b** (0.5)	Ph	1 000	5 500	196 000	>99	
38	**5b** (2.0)	$\mathrm{2,6\text{-}Me_2C_6H_3}$	200	39	1 390	PE	
39	**5b** (2.0)	$\mathrm{2,6\text{-}Me_2C_6H_3}$	500	42	1 500	PE	
40	**5b** (2.0)	$\mathrm{2,6\text{-}Me_2C_6H_3}$	1 000	66	2 350	PE[f]	
41	**5b** (2.0)	$\mathrm{2,6\text{-}Me_2C_6H_3}$	3 000	189	6 740	PE[f]	

[a] Conditions: toluene 30 mL, ethylene 8 atm, 25 °C, 10 min, d-MAO white solid. [b] Al/V molar ratio. [c] Activity in (kg of ethylene)/((mol of V) h). [d] TOF (turnover frequency) = (molar amount of ethylene reacted)/((mol of V) h). [e] By GC analysis vs internal standard. [f] Polyethylene (PE) was obtained[12f] ($M_w = 2.55 \times 10^6$, $M_w/M_n = 1.9$ (run 40); $M_w = 2.93 \times 10^6$, $M_w/M_n = 2.6$ (run 41)).

of preformed 1-butene[12a] with ethylene (runs 3, 4, 6, and run 4 vs runs 12−15). A TOF of 2 730 000 h^{-1} (758 s^{-1}) with 97.0% selectivity of 1-butene has been achieved under the optimized conditions (run 13), and the activity (TOF values) did not change even after 60 min (run 14).

The activities by **1a** (Ar = 2,6-$Me_2C_6H_3$) were slightly higher than those by **1b** (Ar = 2,6-$^iPr_2C_6H_3$), but no apparent differences were seen under the same conditions. Use of MMAO (modified methylaluminoxane (methylisobutylaluminoxane)) in place of MAO was also effective in enhancing both the high catalytic activity and the selectivity (run 21, by **1b**). The dialkyl complex **6b** also showed catalytic activity, affording 1-butene with high selectivity (run 22). The fact thus suggests that similar catalytically active species are present in this catalysis.

In contrast, attempts using the complex containing a methyl group in the ortho position (**2b**) in place of **1b** afforded products in trace amounts under the same conditions (**2b**, 0.5 μmol of ethylene, 8 atm, 10 min at 25 °C, Al/V = 100, 500, 1000, 2000, same conditions as in runs 1, 3, 5, 7, and 8). A mixture of 1-butene and polyethylene was collected when the reactions by **2b** were conducted at higher catalyst concentration (runs 23 and 24). This fact thus clearly suggests that the steric bulk of the (2-anilidomethyl)pyridine ligand plays a key role in the selectivity as well as the activity.

Reactions with ethylene using the other (imido)vanadium(V) complexes $V(NR)Cl_2[2\text{-}ArNCH_2(C_5H_4N)]$ (R = Cy (**3a**,**b**), Ph (**4b**)) were conducted under the same conditions (Table 3). Note that the cyclohexylimido analogues (**3a**,**b**) also showed high activities, affording 1-butene with high selectivities under the optimized conditions (Al/V molar ratios, e.g. runs 26 and 32). Moreover, the phenylimido analogue **4b** also afforded 1-butene as the major product under the same conditions (runs 35−37), whereas, as reported recently,[12f] the 2,6-dimethylphenylimido analogue **5b** afforded polyethylene (runs 38−41). These results thus clearly indicate that the steric bulk of the imido substituent plays an essential role in the selectivity in this catalysis. These results also indicate that the activity was affected by the electronic nature of the imido ligand, because the activities (under the optimized Al/V molar ratios) by **1b** and **3b** were higher than those by **4b**.

In summary, we have shown that the (imido)vanadium(V) complexes showed significant catalytic activities (TOF of 2 730 000 h^{-1} (758 s^{-1}), run 13) for ethylene dimerization, affording 1-butene exclusively (selectivity >97.0−98.2%, runs 11−13 and 15). We are now exploring more details, including the effects of ligand substituents, cocatalysts, or codimerization with α-olefins in this catalysis.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Anhydrous grade toluene, *n*-hexane, diethyl ether, and dichloromethane (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 N_2, and were passed through an alumina short column under an N_2 stream prior to use. 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 and $AlMe_3$ and then heated to >100 °C for 1 h for completion) in the drybox to give a white solid. MMAO-3BH (Me/^{i}Bu = 3.54) was also supplied from Tosoh Finechem Co. and was used as a white solid after removing *n*-hexane, $AlMe_3$, and Al^iBu_3 in vacuo according to a procedure analogous to that for PMAO-S, except that the resultant solid was redissolved in *n*-hexane and the solvent then removed in vacuo to remove Al^iBu_3 completely.

GC analysis was performed with a Shimadzu GC-17A gas chromatograph (Shimadzu Co. Ltd.) equipped with a flame ionization detector. Elemental analyses were performed by using a PE2400II Series instrument (Perkin-Elmer Co.). All ^1H, ^{13}C, and ^{51}V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^1H, 100.40 MHz for ^{13}C, and 105.31 MHz for ^{51}V). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00; ^1H, ^{13}C), and $VOCl_3$ (δ 0.00; ^{51}V). Coupling constants and half-width values, $\Delta\nu_{1/2}$, are given in Hz.

Synthesis of $V(NAd)Cl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)]$ (1a). To a Et_2O solution containing $V(NAd)Cl_3$ (1160 mg, 3.78 mmol) was added $Li[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)]$ (824 mg, 3.78 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was then stirred overnight. The solvent was then removed in vacuo, and the resultant deep red-tan residue was extracted with toluene. The solvent was removed in vacuo, and the solid was dissolved in a minimum amount of CH_2Cl_2. The CH_2Cl_2 solution was layered with *n*-hexane, and orange crystals were obtained at room temperature upon standing. Yield: 536 mg (29%). ^1H NMR ($CDCl_3$): δ 8.87 (d, 1H, J = 4.40, Py-H), 7.89 (t, 1H, J = 7.60, Py-H), 7.51 (t, 1H, J = 6.40, Py-H), 7.40 (d, 1H, J = 7.60, Py-H), 7.14−7.07 (m, 3H, Ar-H), 5.12 (s, 2H, NCH_2), 2.21 (s, 6H, $ArCH_3$), 1.87 (s, 3H, Ad-H), 1.72 (s, 6H, Ad-H), 1.43 (s, 6H, Ad-H). ^{13}C NMR ($CDCl_3$): δ 163.6, 157.0, 148.9, 137.8, 128.7, 128.2, 127.7, 127.5, 127.3, 126.6, 123.4, 119.8, 81.7, 70.4, 40.8, 35.3, 28.5, 18.1. ^{51}V NMR ($CDCl_3$): δ −97.3 ($\Delta\nu_{1/2}$ = 2498 Hz). Anal. Calcd for $C_{24}H_{30}Cl_2N_3V\cdot0.1$(toluene): C, 60.35; H, 6.32; N, 8.55. Found: C, 60.67; H, 6.31; N, 8.50.

Synthesis of $V(NAd)Cl_2[2\text{-}(2,6\text{-}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (1b). The synthetic procedure of **1b** was similar to that for **1a**, except that $Li[2\text{-}(2,6\text{-}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (738 mg, 2.69 mmol) was used in place of $Li[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)]$. Orange microcrystals of **1b** were collected in a yield of 50% (824 mg). ^1H NMR ($CDCl_3$): δ 8.94 (d, 1H, J = 4.40, Py-H), 7.96 (t, 1H, J = 7.40, Py-H), 7.58 (t, 1H, J = 7.20, Py-H), 7.48 (d, 1H, J = 7.20, Py-H), 7.32−7.22 (m, 4H, Ar-H), 5.23 (s, 2H, NCH_2), 2.95 (m, 2H, $CH(CH_3)_2$), 2.41 (s, toluene), 1.97 (s, 3H, Ad-H), 1.90 (s, 6H, Ad-H), 1.51 (s, 6H, Ad-H), 1.46 (d, 6H, J = 6.80, $CH(CH_3)_2$), 1.20 (d, 6H, J = 6.80, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 159.6, 156.9, 149.3, 139.2, 137.9, 137.8, 128.9, 128.1, 127.7, 125.2, 124.0, 123.6, 119.8, 82.4, 72.9, 40.9, 35.6, 28.8, 27.6, 25.7, 24.2, 21.4. ^{51}V NMR ($CDCl_3$): δ −78.4 ($\Delta\nu_{1/2}$ = 3044 Hz). Anal. Calcd for $C_{28}H_{38}Cl_2N_3V\cdot0.8$(toluene): C, 65.92; H, 7.31; N, 6.86. Found: C, 65.87; H, 7.52; N, 6.91.

Synthesis of $V(NAd)Cl_2[2\text{-}(2,6\text{-}^iPr_2C_6H_3)NCH_2\text{-}6\text{-}MeC_5H_3N)]$ (2b). To a toluene solution containing $V(NAd)Cl_3$ (404 mg, 1.32 mmol) was added $Li[2\text{-}(2,6\text{-}^iPr_2C_6H_3)NCH_2(2\text{-}MeC_5H_3N)]$ (380 mg, 1.32 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was then stirred overnight. The resultant solution was filtrated through a Celite pad, and the filter cake was washed with toluene. The solvent was then removed in vacuo, and the solid was dissolved in a minimum amount of CH_2Cl_2 (ca. 1 mL). The CH_2Cl_2 solution was then layered with *n*-hexane, and orange crystals were obtained at room temperature upon standing. Yield: 310 mg (41%). ^1H NMR ($CDCl_3$): δ 7.76 (t, 1H, J = 7.80, Py-H), 7.30−7.16 (m, 5H, Py-H and Ar-H), 5.16 (s, 2H, NCH_2), 2.97 (m, 2H, $CH(CH_3)_2$), 2.88 (s, 3H, $PyCH_3$), 1.89 (s, 3H, Ad-H), 1.83 (s, 6H, Ad-H), 1.44 (s, 6H, Ad-H), 1.41 (d, 6H, J = 6.40, $CH(CH_3)_2$), 1.12 (d, 6H, J = 7.20, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ158.4, 158.0, 155.3, 138.2, 137.1, 136.8, 127.9, 127.1, 126.8, 124.2, 124.0, 123.0, 122.4, 116.9, 81.7, 71.4, 39.9, 34.6, 27.8, 26.5, 24.8, 23.1, 22.8. ^{51}V NMR ($CDCl_3$): δ −97.9 ($\Delta\nu_{1/2}$ = 2423 Hz). Anal. Calcd for $C_{29}H_{40}Cl_2N_3V\cdot0.2$(toluene): C, 63.95; H, 7.34; N, 7.36. Found: C, 63.94; H, 7.62; N, 7.17.

Synthesis of $V(NCy)Cl_3$. The synthetic procedure for $V(NCy)Cl_3$ is analoguos to that for $V(2,6\text{-}Me_2C_6H_3)Cl_3$ reported previously.[15]

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(15) Buijink, J.-K. F.; Teubin, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922.

Into a sealed glass Schlenk tube, *n*-octane (20 mL) and $VOCl_3$ (6.92 g, 40 mmol) were added sequentially in the drybox, and cyclohexanyl isocyanate (3.75 g, 30 mmol) was then added to the mixture. The wall of the reactor was washed with *n*-octane (30 mL), and the mixture was placed into an oil bath that had been preheated at 125 °C. The solution was then stirred overnight (>12 h). The tube was connected to a nitrogen line, and the CO_2 that evolved was released, removed from the mixture by opening the cap during the reaction. After the reaction, the cooled mixture was filtered through a Celite pad, and the filter cake was washed with hexane several times to extract $V(NCy)Cl_3$. The combined wash and the filtrate were brought to dryness under reduced pressure to remove solvent (octane and hexane). The resultant tan residue was dissolved in a minimum amount of hot *n*-hexane. Green microcrystals were collected from the chilled solution (placed in the freezer at −30 °C). Yield: 37% (2.81 g). ^{1}H NMR ($CDCl_3$): δ 4.74 (br, 1H, Cy-*H*), 2.15−2.10 (m, 4H, Cy-*H*), 1.98−1.92 (m, 2H, Cy-*H*), 1.50−1.38 (m, 4H, Cy-*H*). ^{13}C NMR ($CDCl_3$): δ 97.2 (br), 33.2, 25.1, 23.8. ^{51}V NMR ($CDCl_3$): δ 37.1 ($\Delta\nu_{1/2}$ = 373 Hz). Anal. Calcd for $C_6H_{11}Cl_3V$: C, 28.32; H, 4.36; N, 5.50. Found: C, 28.50; H, 4.46; N, 5.46.

Synthesis of $V(NCy)Cl_2[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)]$ (3a). To a toluene solution containing $V(NCy)Cl_3$ (255 mg, 1.0 mmol) was added $Li[2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)]$ (218 mg, 1.0 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was then stirred for 6 h. Then the solution was filtered through a Celite pad and the filter cake was washed with toluene. The combined filtrate and wash was concentrated in vacuo and layered with *n*-hexane. Yellow microcrystals were obtained from the chilled solution (−30 °C). Yield: 151 mg (35%). ^{1}H NMR ($CDCl_3$): δ 8.91 (d, 1H, J = 5.20, Py-*H*), 7.91 (t, 1H, J = 7.40, Py-*H*), 7.53 (t, 1H, J = 6.40, Py-*H*), 7.44 (d, 1H, J = 8.40, Py-*H*), 7.16−7.07 (m, 3H, Ar-*H*), 5.18 (s, 2H, NC*H*$_2$), 3.41 (m, Cy-*H*), 2.19 (s, 6H, Ar−C*H*$_3$), 1.80−1.76 (m, 2H, Cy-*H*), 1.51−1.48 (m, 4H, Cy-*H*), 1.30−1.25 (m, 2H, Cy-*H*), 1.11−1.05 (m, 2H, Cy-*H*). ^{13}C NMR ($CDCl_3$): δ 162.0, 157.4, 149.5, 138.3, 128.7, 128.3, 127.0, 123.8, 120.2, 80.9, 71.2, 32.0, 25.5, 23.9, 18.3. ^{51}V NMR ($CDCl_3$): δ −115 ($\Delta\nu_{1/2}$ = 1876 Hz). Anal. Calcd for $C_{20}H_{26}Cl_2N_3V\cdot 0.3$(toluene): C, 57.96; H, 6.25; N, 9.18. Found: C, 57.99; H, 6.06; N, 9.34.

Synthesis of $V(NCy)Cl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (3b). To a Et_2O solution containing $V(NCy)Cl_3$ (255 mg, 1.0 mmol) was added $Li[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (274 mg, 1.0 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was then stirred overnight. The solvent was removed in vacuo, and the resultant deep red tan residue was extracted with toluene. This solvent was then removed in vacuo, and the resultant solid was dissolved in a minimum amount of CH_2Cl_2 (ca. 1 mL). The CH_2Cl_2 solution was layered with *n*-hexane, and orange microcrystals were obtained from the chilled solution (−30 °C). Yield: 98 mg (20%). ^{1}H NMR ($CDCl_3$): δ 8.91 (d, 1H, J = 5.20, Py-*H*), 7.91 (t, 1H, J = 6.80, Py-*H*), 7.53 (t, 1H, J = 6.20, Py-*H*), 7.44 (d, 1H, J = 7.60, Py-*H*), 7.28−7.18 (m, 3H, Ar-*H*), 5.20 (s, 2H, NC*H*$_2$), 3.59 (m, Cy-*H*), 2.83 (m, 2H, C*H*(CH$_3$)$_2$), 1.80−1.75 (m, 2H, Cy-*H*), 1.59−1.55 (m, 4H, Cy-*H*), 1.31 (d, 6H, J = 6.80, CH(C*H*$_3$)$_2$), 1.21−1.17 (m, 2H, Cy-*H*), 1.12 (d, 6H, J = 6.80, CH(C*H*$_3$)$_2$), 1.06−1.03 (m, 2H, Cy-*H*). ^{13}C NMR ($CDCl_3$): δ 158.8, 157.0, 149.4, 138.9, 138.1, 127.6, 123.7, 123.6, 120.0, 81.4, 73.2, 31.9, 27.6, 25.8, 25.3, 24.0, 23.9. ^{51}V NMR ($CDCl_3$): δ −97.8 ($\Delta\nu_{1/2}$ = 2427 Hz). Anal. Calcd for $C_{24}H_{34}Cl_2N_3V$: C, 59.26; H, 7.05; N, 8.64. Found: C, 59.16; H, 7.32; N, 8.53.

Synthesis of $V(NPh)Cl_3$. The synthesis of $V(NPh)Cl_3$ was similar to that for $V(NCy)Cl_3$, except that phenyl isocyanate (3.57 g, 30 mmol) was used in place of cyclohexanyl isocyanate. Red microcrystals of $V(NPh)Cl_3$ were collected. Yield: 6.28 g (84%). ^{1}H NMR ($CDCl_3$): δ 7.56 (d, 2H, J = 8.0, Ph-*H*), 7.42 (t, 2H, J = 7.8, Ph-*H*), 7.33 (d, 1H, J = 7.4, Ph-*H*). ^{13}C NMR ($CDCl_3$): δ 132.7, 129.0, 126.8. ^{51}V NMR ($CDCl_3$): δ 251.7 ($\Delta\nu_{1/2}$ = 322 Hz).

Synthesis of $V(N\text{-}Ph)Cl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (4b). To a Et_2O solution containing $V(NPh)Cl_3$ (82 mg, 0.3 mmol) was added $Li[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (75 mg, 0.3 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was then stirred overnight. The solvent was removed in vacuo, and the resultant deep red-tan residue was extracted with toluene. The solution was concentrated and layered with *n*-hexane. Red microcrystals were obtained from the chilled solution (−30 °C). Yield: 27 mg (19%). ^{1}H NMR ($CDCl_3$): δ 8.99 (d, 1H, J = 5.60, Py-*H*), 7.98 (t, 1H, J = 7.20, Py-*H*), 7.60 (t, 1H, J = 6.20, Py-*H*), 7.53 (d, 1H, J = 8.00, Py-*H*), 7.32 (t, 1H, J = 7.90, Ar-*H*), 7.22−7.15 (m, 2H, Ar-*H*), 7.06−6.98 (m, 3H, Ar-*H*), 6.70 (d, 2H, J = 7.80, Ar-*H*), 5.30 (s, 2H, NC*H*$_2$), 2.85 (m, 2H, C*H*(CH$_3$)$_2$), 1.14 (d, 6H, J = 6.80, CH(C*H*$_3$)$_2$), 1.09 (d, 6H, J = 6.40, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ 160.3, 157.4, 149.6, 139.0, 138.5, 128.2, 128.1, 128.0, 127.9, 124.4, 123.9, 120.3, 74.0, 28.0, 25.3, 24.2. ^{51}V NMR ($CDCl_3$): δ 40.2 ($\Delta\nu_{1/2}$ = 2087 Hz). Anal. Calcd for $C_{24}H_{28}Cl_2N_3V$: C, 60.01; H, 5.88; N, 8.75. Found: C, 60.18; H, 5.97; N, 8.63.

Synthesis of $V(NAd)(CH_2SiMe_3)_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (6b). (i) Method 1 from $V(NAd)Cl_3$. To a Et_2O solution (20 mL) containing the lithium salt $Li[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (445 mg, 1.62 mmol) was added $VCl_3(NAd)$ (495 mg, 1.62 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 12 h. The solvent was then removed in vacuo, and the orange solid was washed with hexane. Toluene was added to the mixture, and the solution was cooled to −30 °C. $LiCH_2SiMe_3$ (304 mg, 3.24 mmol) was then added to the solution, and the reaction mixture was warmed slowly to room temperature and was stirred overnight. The solvent was then removed in vacuo, and the resulting residue was extracted with *n*-hexane. The *n*-hexane solution was then concentrated in vacuo, and the concentrated *n*-hexane solution was placed in the freezer (−30 °C). Brown microcrystals (310 g, 0.48 mmol) were obtained from the chilled solution in the yield of 30%.

(ii) Method 2 from 1b. To a toluene solution (20 mL) containing **1b** (291 mg, 0.54 mmol) was added $LiCH_2SiMe_3$ (102 mg, 1.08 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 6 h. The solvent was then removed in vacuo, and the resultant residue was extracted with *n*-hexane. After the *n*-hexane was removed, the resultant tan residue was dissolved in a minimum amount of *n*-hexane. The chilled solution (−30 °C) gave brown microcrystals (303 mg, 0.47 mmol) in a yield of 87%. ^{1}H NMR (C_6D_6): δ 9.05 (d, 1H, J = 5.60, Py-*H*), 7.19−7.14 (m, 3H, Ar-*H*), 6.98 (t, 1H, J = 8.00, Py-*H*), 6.80 (t, 1H, J = 6.80, Py-*H*), 6.61 (d, 1H, J = 8.00, Py-*H*), 4.85 (s, 2H, NC*H*$_2$), 3.19 (m, 2H, C*H*(CH$_3$)$_2$), 2.65 (d, 2H, J = 8.00, C*H*$_2$SiMe$_3$), 2.16 (s, 6H, Ad-*H*), 1.96 (s, 3H, Ad-*H*), 1.59−1.45 (m, 12H, CH(C*H*$_3$)$_2$ and Ad-*H*), 1.16 (d, 6H, J = 6.80, CH(C*H*$_3$)$_2$), 0.71 (d, 2H, J = 9.60, C*H*$_2$SiMe$_3$), 0.12 (s, 18H, CH$_2$Si*Me*$_3$). ^{13}C NMR (C_6D_6): δ 162.1, 158.7, 148.1, 142.3, 136.8, 125.6, 124.0, 122.5, 120.6, 69.4, 43.6, 36.6, 31.9, 29.8, 27.1, 27.0, 24.6, 23.0, 14.3, 3.4. ^{51}V NMR (C_6D_6): δ 237.9 ($\Delta\nu_{1/2}$ = 1303 Hz). Anal. Calcd for $C_{36}H_{60}N_3Si_2V$: C, 67.35; H, 9.42; N, 6.55. Found: C, 67.38; H, 9.63; N,6.62.

Oligomerization of Ethylene. Ethylene oligomerizations were conducted in a 100 mL stainless steel autoclave. The typical reaction procedure is as follows. Toluene (29 mL) and a prescribed amount of MAO solid (prepared from ordinary MAO by removing toluene and $AlMe_3$) were added into the autoclave in the drybox. The reaction apparatus was then filled with ethylene (1 atm), and the complex (0.5 μmol) 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 −78 °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.

Table 4. Crystal Data and Collection Parameters of $V(NAd)Cl_2[2\text{-}(2,6\text{-}R_2C_6H_3)NCH_2(C_5H_4N)]$ (R = Me (**1a**), ^{i}Pr (**1b**)) and $V(NCy)Cl_2[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3)NCH_2(C_5H_4N)]$ (**3b**)

	1a	**1b**	**3b**
formula	$C_{24}H_{30}Cl_2N_3V$	$C_{28}H_{38}N_3Cl_2V$	$C_{24}H_{23}N_3Cl_2V$
formula wt	482.37	538.48	475.31
cryst color, habit	orange, block	orange, block	red, block
cryst size (mm)	0.40 × 0.24 × 0.20	0.60 × 0.56× 0.30	0.26 × 0.20× 0.15
cryst syst	orthorhombic	triclinic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	12.0709(4)	10.0663(18)	17.3177(5)
b (Å)	12.5390(5)	10.537(2)	19.4500(5)
c (Å)	15.2621(5)	13.172(3)	20.2626(6)
α (deg)		96.887(5)	
β (deg)		96.829(6)	132.7575(8)
γ (deg)		91.582(5)	
V (Å^3)	2310.02(14)	1375.9(5)	5011.2(2)
Z	4	2	8
D_{calcd} (g/cm^3)	1.387	1.300	1.260
$F(000)$	1008.00	568.00	1960.00
temp (K)	113	103	153
μ(Mo Kα) (cm^{-1})	6.764	5.752	6.229
no. of rflns measd			
total	18 728	11 086	40 757
unique	4198	4996	9113
no. of observns ($I > 2.00\sigma(I)$)	4080	4577	9113
no. of variables	302	345	600
R1 ($I > 2.00\sigma(I)$)	0.0169	0.0343	0.0448
wR2 ($I > 2.00\sigma(I)$)	0.0519	0.0925	0.1323
goodness of fit	1.032	1.000	1.072

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. The selected bond lengths and bond angles as well as crystal collection parameters are given in Table 4. All structures were solved by direct methods and expanded using Fourier techniques,[16] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **1a**,**b** were performed using the Crystal Structure[17,18] crystallographic software package. All calculations for analysis of **3b** were performed using the Crystal Structure[17,18] crystallographic software package except for refinement, which was performed using SHELXL-97.[19]

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Supporting Information Available: Text, tables, figures, and CIF files giving structural analysis data for complexes **1a**,**b** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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