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Article

Synthesis of (1-Adamantylimido)vanadium(V) Complexes Containing Aryloxo, Ketimide Ligands: Effect of Ligand Substituents in Olefin Insertion/Metathesis Polymerization

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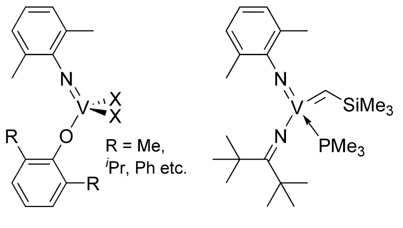
A series of (1-adamantylimido)vanadium(V) complexes containing anionic donor ligands of the type, V(NAd)Cl_2(L) [Ad = 1-adamantyl; L = O-2,6-$Me_2C_6H_3$ (**2**), O-2,6-$^iPr_2C_6H_3$ (**3**), N=C$^tBu_2$ (**5**), N=C(^{t}Bu)CH_2SiMe_3 (**6**), N=C(^{t}Bu)Ph (**7**), N=CPh_2 (**8**)], have been prepared from V(NAd)Cl_3, which was in turn prepared from $VOCl_3$ by treatment with 1-adamantylisocyanate in octane, by treatment with the corresponding lithium salts (lithium phenoxides, lithium ketimides) in Et_2O. These complexes (**2**, **3**, **5**−**8**) were identified by NMR spectroscopy and elemental analysis, and the structures for **2** and **5** were determined by X-ray crystallography. The reaction of V(NAd)Cl_3 with 2,6-dimethylphenol in *n*-hexane afforded the tris(aryloxo) analogue V(NAd)(O-2,6-$Me_2C_6H_3$)$_3$ (**4**), the structure of which was determined by X-ray crystallography. **8** gradually decomposed in toluene to give a dimeric species, $[N(Ad)H_3]^+[V_2(\mu_2\text{-}Cl)_3Cl_2(NAd)_2(N{=}CPh_2)_2]^-$ (**10**), but **8** was stabilized as a PMe_3 coordinated species, V(NAd)Cl_2(N=CPh_2)(PMe_3)$_2$ (**9**): the structures for **9** and **10** were determined by X-ray crystallography. These complexes were evaluated as catalyst precursors for ethylene polymerization in the presence of MAO. The ketimide analogues, especially **5**, exhibited moderate catalytic activity, and the activity with a series of V(NAd)Cl_2(L)−MAO catalyst systems increased in the order: L = N=C$^tBu_2$ (**5**, 516 kg-PE/mol·V·h) > N=C(^{t}Bu)Ph (**7**, 300) > N=CPh_2 (**8**, 105) > N=C(^{t}Bu)CH_2SiMe_3 (**6**, 70.8). These complexes (**2**, **3**, **5**, **6**) were found to be effective as catalyst precursors for the ring-opening metathesis polymerization (ROMP) of norbornene (NBE) in the presence of MeMgBr and PMe_3.

Introduction

Classical Ziegler-type vanadium catalyst systems show promising characteristics[1,2] due to their high reactivity toward olefins in olefin coordination insertion polymerization. Therefore, the design and synthesis of new vanadium complex catalysts for controlled polymerization has attracted considerable attention.[1,3–5] This is because the design and synthesis of efficient transition-metal complex catalysts are important for the development of new polyolefin materials with unique properties.[1,6,7] Although there have been many reports on olefin polymerization,[3–5,7] especially with vanadium(III) and vanadium(IV) complexes,[1d,e,3] we focused on high oxidation state (arylimido)vanadium(V) complexes that contained an anionic donor ligand as promising candidates.[4,7]

Chart 1



Effective catalyst precursor for ethylene (co)polymerization

Effective catalyst for ring-opening metathesis polymerization (ROMP)

We recently reported that (arylimido)vanadium(V) complexes containing aryloxo ligands of the type, V(N-2,6-$Me_2C_6H_3$)Cl_2(OAr) (Ar = 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, 2,6-$Ph_2C_6H_3$, Chart 1), exhibited high catalytic activities in ethylene polymerization,[4a–e] and their activities in the presence of halogenated aluminum alkyls were higher than those in the presence of MAO (methylaluminoxane).[4b,d,e] The

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arylimido−ketimide analogues $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[N{=}C(R^1)^tBu]$ ($R^1 = {}^tBu$, CH_2SiMe_3) also showed moderate catalytic activities for ethylene polymerization in the presence of MAO,[4f] but remarkable enhancements in the activities were not seen in the presence of Et_2AlCl.

In contrast to the examples of olefin polymerization using vanadium complex catalysts as well as Ziegler-type vanadium catalysts, there have been few examples of olefin metathesis with vanadium. We previously showed that generation of the favored catalytically active species for olefin coordination insertion or ring-opening metathesis polymerization (ROMP) using $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(OAr)$ could be *directly* controlled by choosing suitable aluminum promoters ($AlMe_3$ or Et_2AlCl).[4b] Later, the isolated vanadium(V)-alkylidene, $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CHSiMe_3)(N{=}C^tBu_2)(PMe_3)$ (Chart 1), was shown to exhibit remarkable catalytic activity for the ROMP of norbornene (NBE) for the first time, and the activity increased at higher temperature: high molecular weight ring-opened polymers with uniform molecular weight distributions were obtained in this catalysis.[8,9] More recently, *olefin-metathesis active* vanadium−alkylidene species have been efficiently prepared from $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(N = C^tBu_2)$ by the addition of MeMgBr and PMe_3, and the ROMP of NBE proceeded with both high catalyst efficiency and high catalytic activity to give high molecular weight ring-opened poly(NBE)s with unimodal molecular weight distributions.[10]

In the above polymerization systems (olefin insertion and metathesis polymerization), both imido and anionic donor ligands should play essential key roles in stabilizing the catalytically active species and/or controlling the electronic/steric environment during the catalytic reactions, which should strongly affect the catalytic activity as well as monomer reactivity. Molybdenum-alkyidenes that contain an adamantylimido ligand often show unique characteristics in olefin metathesis,[9a,11,12] especially in the polymerization of acetylene[11c] as well as ring-closing metathesis,[11d] and the metal−imido group has been shown to promote high-oxidation-state coordination and organometallic chemistry as a spectator or supporting ligand through modification of the N substituent.[7] Thus, we are interested in admantylimido chemistry, because the ligand should be better able to access as a σ donor than the arylimido analogues, which would stabilize the catalytically active species and lead to higher activity in olefin polymerization. However, there are few examples of syntheses of $V(NAd)Cl_3(dme)$ (Ad = 1-adamantyl, dme = 1,2-dimethoxy ethane), $V(NAd)[S_2C(X^iPr_2)]_3$ (X = O, S), and $V(NAd)[S\text{-}2,6\text{-}(SiMe_3)_2C_6H_3]$.[13,14] Because we recently prepared adduct-free (1-adamantylimido)vanadium(V) trichloride as a starting compound, $V(NAd)Cl_3$, we

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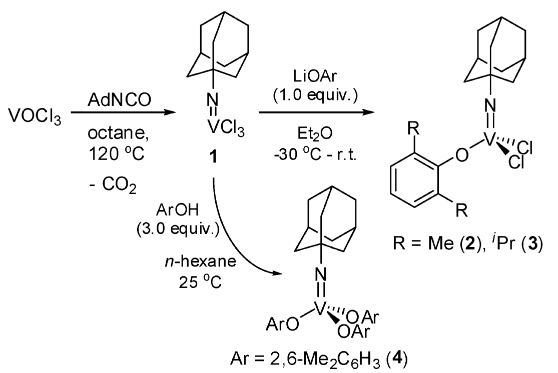
Scheme 1



explored studies concerning the synthesis and structural analysis of a series of (1-adamantylimido)vanadium(V) complexes containing anionic donor ligands of the type, $V(NAd)Cl_2(L)[L{=}O\text{-}2,6\text{-}Me_2C_6H_3, O\text{-}2,6\text{-}{}^iPr_2C_6H_3, N{=}C{}^tBu_2, N{=}C({}^tBu)CH_2SiMe_3, N{=}C({}^tBu)Ph, N{=}CPh_2]$.[15] We also explored the possibility of their uses as catalyst precursors for both ethylene polymerization and ROMP of NBE to evaluate the effects of the adamantylimido ligand in these polymerizations.

Results and Discussion

1. Synthesis and Structure Analysis of Various (1-Adamantylimido)vanadium(V) Complexes Containing Anionic Donor Ligands. The starting trichloride complex, $V(NAd)Cl_3$ (**1**, Ad = 1-adamantyl), was prepared from $VOCl_3$ by treatment with 1-adamantylisocyanate according to the analogous method reported previously.[13,16] The reaction of **1** with 1.0 equiv of LiOAr in Et_2O gave $V(NAd)Cl_2(OAr)$ [Ar = $2,6\text{-}Me_2C_6H_3$ (**2**), $2,6\text{-}{}^iPr_2C_6H_3$ (**3**)] (Scheme 1). The reaction of **1** with 3.0 equiv of $2,6\text{-}Me_2C_6H_3OH$ in n-hexane in the presence of NEt_3 gave $V(NAd)(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ (**4**) in high yield (72.9%). These complexes were identified by ^1H, ^{13}C, and ^{51}V NMR spectroscopy and elemental analysis. The structures of **2** and **4** were determined by X-ray crystallography (Figures 1 and 2), and selected bond distances and angles are summarized in Table 1. Two resonances were observed in the ^{51}V NMR spectrum for **4**, whereas resonances in the ^1H and ^{13}C NMR spectra seemed to be one set: the result in the crystallographic analysis indicates that **4** is a mixture of two isomers (detailed analysis result was shown in the Supporting Information).

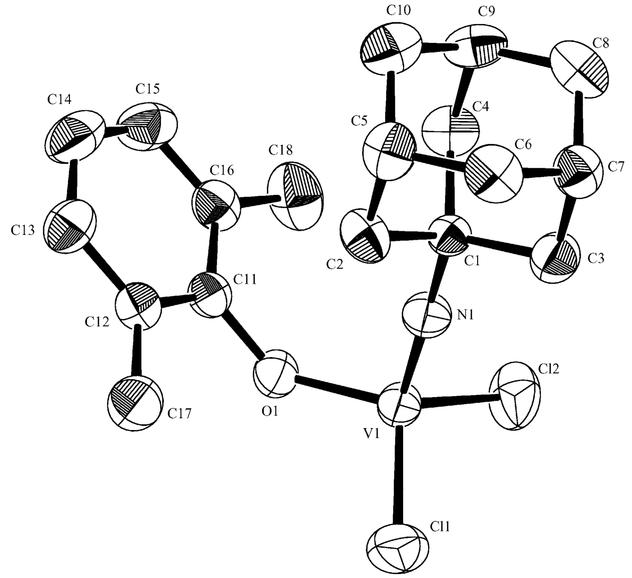


Figure 1. ORTEP drawings for $V(NAd)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2**). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

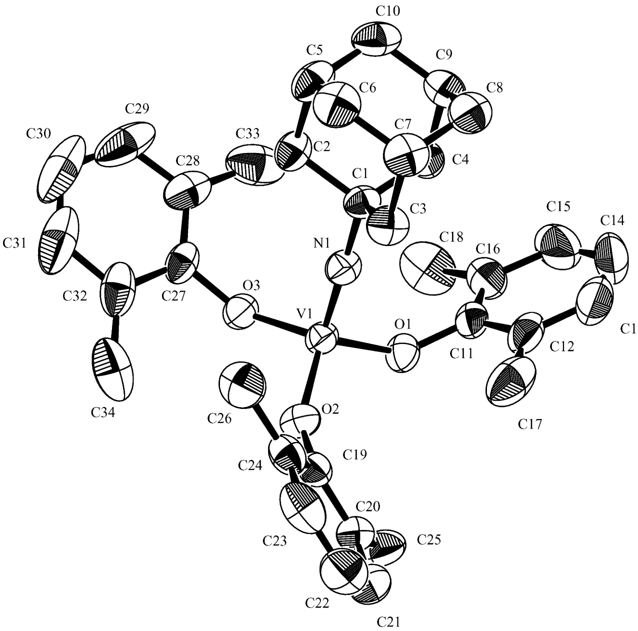


Figure 2. ORTEP drawings for $V(NAd)(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ (**4**). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

The structure for **2** indicates that **2** folds in a distorted tetrahedral geometry around vanadium, and the V−N−C bond angle is 179.10(18)°, which suggests that not only the σ donation but also a stronger π donation from the nitrogen to vanadium can be seen.[7] **4** also shows a distorted tetrahedral geometry around vanadium: the V−N−C bond angle 176.4(2)° is similar to that in **2**. In contrast, one of the V−O−C bond angles [150.4(2)°] is larger than that in **2** [132.64(16)°], probably due to the steric bulk of three aryloxo ligands. The V−O bond distance [1.7633(17) Å] is slightly longer than that in $V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(CH_2Ph)_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [1.746(2) Å],[17] and the V−O bond distances in **4** (1.783−1.799 Å) are slightly longer than that in **2** [1.7633(17) Å] probably due to reflecting the V−O π donation.

The adamantylimido-ketimide analogues $V(NAd)Cl_2(L)$ [L = $N{=}C{}^tBu_2$ (**5**), $N{=}C({}^tBu)CH_2SiMe_3$ (**6**), $N{=}C({}^tBu)Ph$ (**7**), $N{=}CPh_2$ (**8**)] were prepared by treating of $V(NAd)Cl_3$ with 1 equiv of the corresponding lithium salt in Et_2O (Scheme

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[15] Some of these results were presented at the *XVIIth International Symposium on Olefin Mmetathesis (ISOMXVII)*, July 2007, Pasadena, CA, USA.

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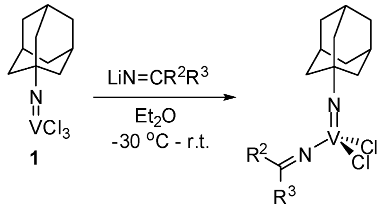
Table 1. Selected Bond Distances and Angles for V(NAd)Cl_2(O-2,6-$Me_2C_6H_3$) (**2**), V(NAd)(O-2,6-$Me_2C_6H_3$)$_3$ (**4**), V(NAd)Cl_2(N=C^tBu_2) (**5**)[a]

2		4		5	
		Bond Distances (Angstroms)			
V(1)−Cl(1)	2.1901(8)	V(1)−O(1)	1.793(3)	V(1)−Cl(1)	2.2272(3)
V(1)−Cl(2)	2.1933(9)	V(1)−O(2)	1.783(2)	V(1)−Cl(2)	2.2263(3)
V(1)−O(1)	1.7633(17)	V(1)−O(3)	1.799(2)	V(1)−N(1)	1.6276(9)
V(1)−N(1)	1.623(2)	V(1)−N(1)	1.635(2)	V(1)−N(2)	1.7855(11)
O(1)−C(11)	1.370(2)			N(1)−C(1)	1.4359(13)
N(1)−C(1)	1.438(3)			N(2)−C(11)	1.2601(17)
		Bond Angles (Degrees)			
Cl(1)−V(1)−Cl(2)	115.33(3)	O(1)−V(1)−O(2)	110.27(11)	Cl(1)−V(1)−Cl(2)	114.508(16)
Cl(1)−V(1)−O(1)	111.24(6)	O(1)−V(1)−O(3)	112.35(11)	Cl(1)−V(1)−N(1)	109.59(4)
Cl(1)−V(1)−N(1)	106.27(8)	O(2)−V(1)−O(3)	108.58(11)	Cl(1)−V(1)−N(2)	112.34(3)
Cl(2)−V(1)−O(1)	111.34(7)	O(2)−V(1)−N(1)	112.48(14)	Cl(2)−V(1)−N(1)	110.02(3)
Cl(2)−V(1)−N(1)	106.90(8)	O(1)−V(1)−N(1)	105.55(15)	Cl(2)−V(1)−N(2)	108.37(3)
O(1)−V(1)−N(1)	105.00(8)	V(1)−O(3)−C(27)	135.9(2)	N(1)−V(1)−N(2)	101.19(5)
V(1)−O(1)−C(11)	132.64(16)	V(1)−O(2)−C(19)	150.4(2)	V(1)−N(1)−C(1)	177.96(10)
V(1)−N(1)−C(1)	179.10(18)	V(1)−N(1)−C(1)	176.4(2)	V(1)−N(2)−C(11)	172.34(7)

[a] Detailed analysis conditions, see the Supporting Information.

Scheme 2



R^2;R^3 = ^{t}Bu;^{t}Bu (**5**), ^{t}Bu, CH_2SiMe_3 (**6**), ^{t}Bu;Ph (**7**), Ph;Ph (**8**),

2). These complexes could be isolated and identified based on their ^1H, ^{13}C, and ^{51}V NMR spectra and elemental analyses. The structure for **5** could be determined by X-ray crystallography (Figure 3). The fact that these (1-adamantylimido)vanadium(V) complexes (**7** and **8**) could be isolated in pure form is interesting because attempts to isolate (arylimido)vanadium(V) complexes containing those ketimide ligands were unsuccessful.

Selected bond distances and angles for **5** as determined by crystallographic analysis are summarized in Table 1. The structure for **5** revealed that it folds in a distorted tetrahedral geometry around the vanadium metal center, as expected from the other results. The V−N(imido) bond distance [1.6276(9) Å] is shorter than that in the arylimido analogue V(N-2,6-$Me_2C_6H_3$)Cl_2(N=C^tBu_2), [1.660(2) Å], whereas the V−N(C^tBu_2) bond length [1.7855(11) Å] is close to that in the arylimino analogue [1.787(1) Å].[8] The V−Cl bond distances [2.2272(3), 2.2263(3) Å] are somewhat shorter than those in the arylimido analogue [2.2338(5), 2.2710(5) Å].[8] These findings might be due to the influence of the adamantylimido ligand. The V−N(imido)−C bond angle is 177.96(10)°, and this value is close to that in the above arylimido analogue [179.0(1)°] as well as that in **2**.

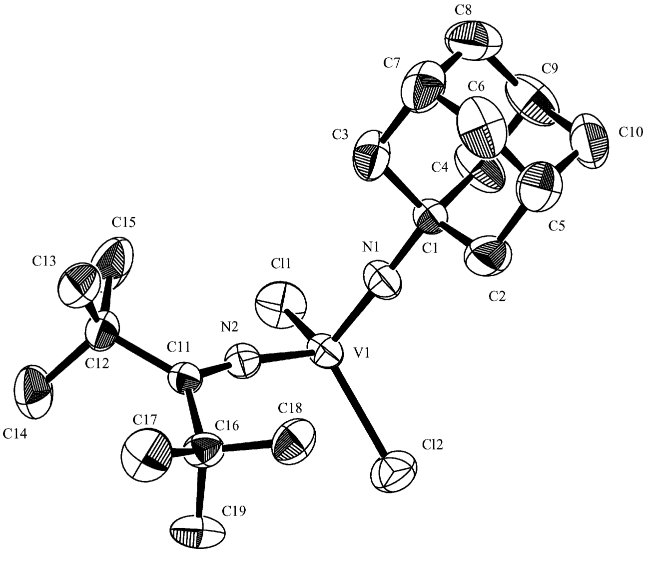
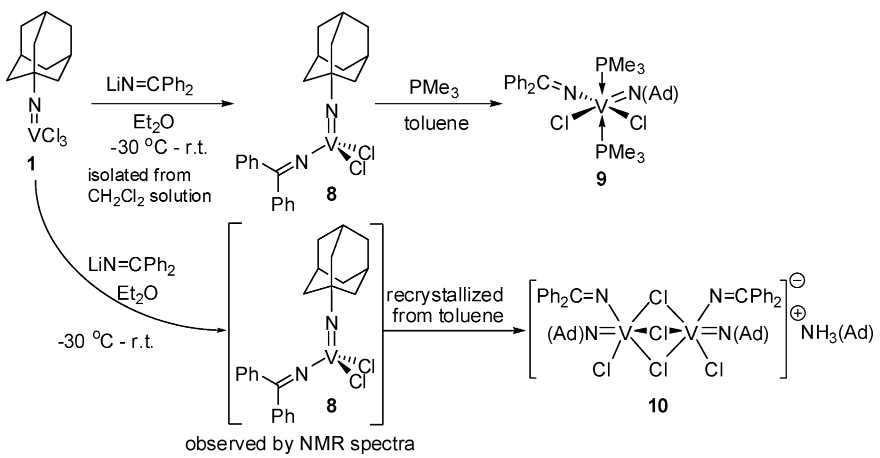


Figure 3. ORTEP drawings for V(NAd)Cl_2(N=C^tBu_2)(**5**). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

Analytically, pure **8** could only be obtained by the separation of **8** with LiCl after the mixture was dissolved with a minimum amount of dichloromethane because, as shown in Scheme 3, gradual decomposition of **8** in toluene gave the dimeric species $[N(Ad)H_3]^+[V_2(\mu_2\text{-}Cl)_3Cl_2(NAd)_2(N{=}CPh_2)_2]^-$ (**10**). Complex **10** could be identified based on NMR spectra and an elemental analysis, and the structure was determined by X-ray crystallography (Figure 4, right). However, we have no appropriate explanation how **10** was formed from **8**. Complex **8** is a 14e unsaturated species and could thus be stabilized by addition of PMe_3 even in toluene (Scheme 3); the adduct VCl_2(NAd)(N=CPh_2)(PMe_3)$_2$ (**9**) was isolated as a yellow precipitate from the chilled toluene solution covered with *n*-hexane (−30 °C). The complex was identified based on NMR spectra and elemental analysis, and the structure was determined by X-ray crystallography (Figure 4, left).

Selected bond distances and angles for **9** are summarized in Table 2. The crystallographic analysis (Figure 4, left) for **9** revealed that **9** folds in a rather distorted octahedral geometry around vanadium, consisting of a P−V−P axis [P(1)−V(1)−P(2) 162.06(5)°] and a distorted plane formed by two nitrogen and two chlorine atoms [total 360.01°]. The V−Cl bond distances in **9** [2.4954(12), 2.4382(12) Å] are longer than those in **2** [2.1901(8), 2.1933(9) Å], as well as those in **5** [2.2272(3), 2.2263(3) Å], and the V−N(imido) bond distance [1.666(3) Å] is longer than those in **2** [1.623(2) Å] and **5** [1.6276(9) Å]. These observations are probably

Scheme 3



due to the influence of the electron donation of PMe_3 to the vanadium metal center. The V−N(ketimide) bond length [1.836(3) Å] is also longer than that in **5** [1.7855(11) Å].

Selected bond distances and angles for **10** are also summarized in Table 2. A dimeric structure bridged by three chlorine atoms was determined, and one chlorine atom is coordinated to vanadium as a monodentate ligand. Thus, significant differences in the V−Cl bond distances are seen between the bridged [2.4541(16)−2.6342(16) Å] and monodendate [2.3765(16), 2.3769(17) Å] ligands. In particular, both V(1)−Cl(2) and V(2)−Cl(2) distances [2.6342(16), 2.6074(16) Å] are longer than the others [2.4541(16)−2.5101(16) Å], which suggests that Cl(2) weakly coordinates to two vanadium atoms and plays a role as a counteranion to the ammonium salt, $N(Ad)H_3^+$. The bond distances for V−N(imido) [1.635(4), 1.627(4) Å] are shorter than that in **9** [1.666(3) Å] but close to those in **5** [1.6276(9) Å]. The decomposition pathway to afford **10** is presently unclear.

2. Ethylene Polymerization by $V(NAd)Cl_2(L)$ (L: Aryloxo, Ketimide) − MAO Catalyst Systems. Ethylene polymerizations by $V(NAd)Cl_2(L)$ [L = O-2,6-$Me_2C_6H_3$ (**2**), O-2,6-${}^iPr_2C_6H_3$ (**3**), N=C^tBu_2 (**5**), N=$C(^tBu)CH_2SiMe_3$ (**6**), N=$C(^tBu)Ph$ (**7**), N=CPh_2 (**8**)] were conducted in toluene at 25 °C in the presence of d-MAO white solid (prepared by removing toluene and an excess amount of $AlMe_3$ from commercially available MAO) (Scheme 4). Polymerizations with the (arylimido)vanadium(V) analogues [V(N-2,6-$Me_2C_6H_3$)-Cl_2(L), L = O-2,6-$Me_2C_6H_3$ (**2***), N=C^tBu_2 (**5***)][4b,c,f] were also conducted for comparison. The results are summarized in Table 3.

The adamantyl-aryloxo analogues (**2**, **3**) showed moderate catalytic activities for ethylene polymerization, and the activity was dependent upon the aluminum/vanadium molar ratios used (runs 1−5). However, the observed activities were lower than those by the arylimido−aryloxo analogue (**2***, runs 20, 21) reported previously.[4c] The resultant polymers, especially by the **3**-MAO catalyst, possessed bimodal molecular weight distributions, and the results were different from those prepared by the **2***-MAO catalyst (run 21).[4c−e]

The adamantyl−ketimide analogues, especially **5**,**7**-MAO catalyst systems, exhibited moderate catalytic activities, and the activity by **5** was similar to that by the arylimido−ketimide

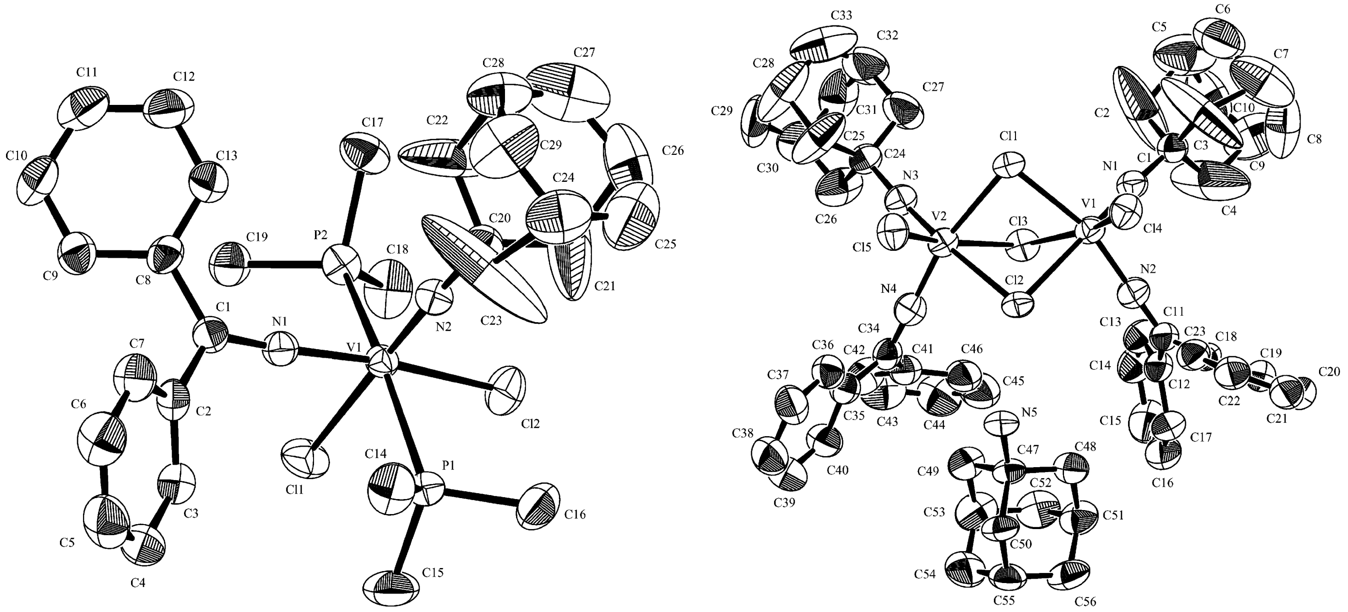


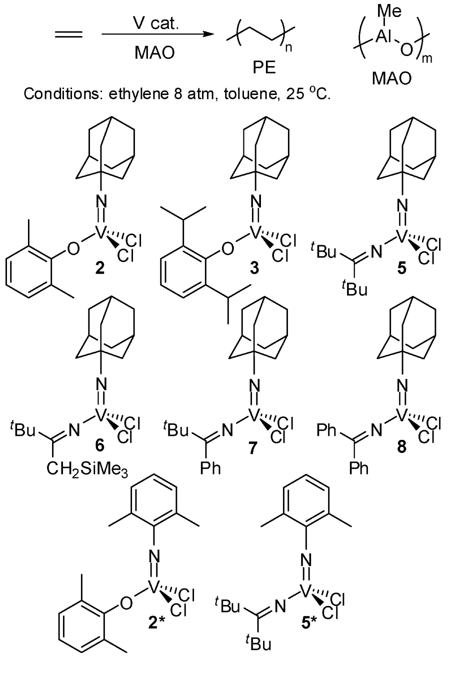
Figure 4. ORTEP drawings for $V(NAd)Cl_2(N{=}CPh_2)(PMe_3)_2$ (**9**, left) and $[N(Ad)H_3]^+[V_2(\mu_2\text{-}Cl)_3Cl_2(NAd)_2(N{=}CPh_2)_2]^-$ (**10**, right). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances and Angles for $V(NAd)Cl_2(N{=}CPh_2)(PMe_3)_2$ (**9**), $[N(Ad)H_3]^+[V_2(\mu_2\text{-}Cl)_3Cl_2(NAd)_2(N{=}CPh_2)_2]^-$ (**10**)[a]

		9			
		Bond Distances (Angstroms)			
V(1)−Cl(1)	2.4954(12)	V(1)−Cl(2)	2.4382 (12)	V(1)−P(1)	2.5096(13)
V(1)−P(2)	2.5346(13)	V(1)−N(1)	1.836(3)	V(1)−N(2)	1.666(3)
P(2)−C(17)	1.821(5)	P(2)−C(18)	1.806(6)		
		Bond Angles (Degrees)			
Cl(1)−V(1)−Cl(2)	86.58(4)	Cl(1)−V(1)−P(1)	86.85(4)	Cl(1)−V(1)−P(2)	78.28 (4)
Cl(1)−V(1)−N(1)	84.80(10)	Cl(1)−V(1)−N(2)	179.30(12)	Cl(2)−V(1)−P(1)	84.47(4)
Cl(2)−V(1)−P(2)	84.68(4)	Cl(2)−V(1)−N(1)	171.33(11)	Cl(2)−V(1)−N(2)	92.89(11)
P(1)−V(1)−P(2)	162.06(5)	P(1)−V(1)−N(1)	95.91(11)	P(1)−V(1)−N(2)	92.64(11)
P(2)−V(1)−N(1)	92.70(11)	P(2)−V(1)−N(2)	102.14(12)	N(1)−V(1)−N(2)	95.74(15)
V(1)−P(1)−C(14)	113.91(19)	V(1)−P(1)−C(16)	116.39(19)	V(1)−P(1)−C(15)	117.1 (2)
		10			
		Bond Distances (Angstroms)			
V(1)−Cl(1)	2.4887(16)	V(1)−Cl(2)	2.6342(16)	V(1)−Cl(3)	2.4614(17)
V(1)−Cl(4)	2.3769(17)	V(1)−N(1)	1.635(4)	V(1)−N(2)	1.814(4)
V(2)−Cl(1)	2.5101(16)	V(2)−Cl(2)	2.6074(16)	V(2)−Cl(3)	2.4541(16)
V(2)−Cl(5)	2.3765(16)	V(2)−N(3)	1.627(4)	V(2)−N(4)	1.826(4)
		Bond Angles (Degrees)			
Cl(1)−V(1)−Cl(2)	80.10(4)	Cl(1)−V(1)−Cl(3)	77.61(5)	Cl(1)−V(1)−Cl(4)	86.49(5)
Cl(1)−V(1)−N(1)	100.07(15)	Cl(1)−V(1)−N(2)	163.76(16)	Cl(2)−V(1)−Cl(3)	78.65(5)
Cl(2)−V(1)−Cl(4)	88.57(5)	Cl(2)−V(1)−N(1)	175.17(16)	Cl(2)−V(1)−N(2)	84.16(15)
Cl(3)−V(1)−Cl(4)	161.04(6)	Cl(3)−V(1)−N(1)	96.64(17)	Cl(3)−V(1)−N(2)	95.44(15)
Cl(4)−V(1)−N(1)	96.26(16)	Cl(4)−V(1)−N(2)	97.15(15)	N(1)−V(1)−N(2)	95.3(2)
Cl(1)−V(2)−Cl(2)	80.10(4)	Cl(1)−V(2)−Cl(3)	77.61(5)	Cl(1)−V(2)−Cl(5)	86.40(5)
Cl(2)−V(2)−Cl(3)	79.31(5)	Cl(3)−V(2)−Cl(5)	160.43(6)		

[a] Detailed analysis conditions, see the Supporting Information.

Scheme 4



analogue (**5***, runs 11, 12, and 22). The catalytic activity in toluene at 25 °C with a series of $V(NAd)Cl_2(L)$ [L = $N{=}C^tBu_2$ (**5**), $N{=}C(^tBu)CH_2SiMe_3$ (**6**), $N{=}C(^tBu)Ph$ (**7**), $N{=}CPh_2$ (**8**)] − MAO catalyst systems under the optimized conditions increased in the order: L = $N{=}C^tBu_2$ (**5**, 516 kg·PE/mol·V·h) > $N{=}C(^tBu)Ph$ (**7**, 300) > $N{=}CPh_2$ (**8**, 105) > $N{=}C(^tBu)CH_2SiMe_3$ (**6**, 70.8). These results suggest that electronic factors in the ketimide ligand would play a role in the activity (**5** > **7** > **8**), and the low activity by the **6**-MAO catalyst system might be due to stability in the reaction mixture as assumed previously.[4f] The resultant polymers possessed bimodal molecular weight distributions (runs 14−18) or rather large M_w/M_n values (runs 10−12). No remarkable improvements in the catalytic activities were seen by adopting the adamantylimido analogues from the arylimido analogues, although we expected that adamantyl imido would act as a better electron donor than the arylimido analogue, which may help to stabilize the catalytically active species. These results indicate that the nature of the imido ligand strongly affects the catalytic activity.

3. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE) Catalyzed by $V(NAd)Cl_2(L)$ (L: aryloxo, ketimide) − $MeMgBr{-}PMe_3$ Catalyst Systems. We previously reported that catalyst systems consisting of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(L)$ [L = $O\text{-}2,6\text{-}Me_2C_6H_3$ (**2***), $N{=}C^tBu_2$ (**5***)], MeMgBr, and PMe_3 exhibited remarkable catalytic activities for the ROMP of NBE,[10] and the activities increased at higher temperature; the observed trend concerning the effect of an anionic donor ligand on the activity was somewhat similar to that observed in ethylene polymerization using $V(NAr)Cl_2(L)$-MAO catalyst systems.[4c] Therefore, ROMPs of NBE were conducted by using a series of $V(NAd)Cl_2(L)$ [L = $O\text{-}2,6\text{-}Me_2C_6H_3$ (**2**), $O\text{-}2,6\text{-}^iPr_2C_6H_3$ (**3**), $N{=}C^tBu_2$ (**5**), $N{=}C(^tBu)CH_2SiMe_3$ (**6**)] in the presence of $MeMgBr{-}PMe_3$ (Scheme 5). Polymerizations by $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(L)$ [L = $O\text{-}2,6\text{-}Me_2C_6H_3$ (**2***), $O\text{-}2,6\text{-}^iPr_2C_6H_3$ (**3***), $N{=}C^tBu_2$ (**5***), $N{=}C(^tBu)CH_2SiMe_3$ (**6***)] were also examined for comparison.[10] The results are summarized in Table 4.

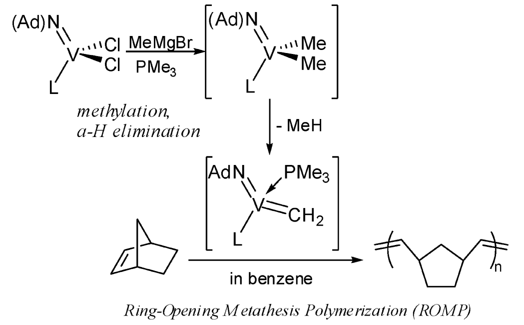
The dimethylphenoxy analogue (**2**) showed much higher catalytic activity than the diisopropylphenyl analogue (**3**); the observed trend was the same as that seen in ROMP using arylimido analogues.[10] The resultant polymers prepared by **2** possessed a ring-opened structure confirmed by ^1H and ^{13}C NMR spectra, and the M_n values (M_n = 6.0−11.0 ×

Table 3. Ethylene Polymerization by $V(NAd)Cl_2(L)$ [L = O-2,6-$Me_2C_6H_3$(**2**), O-2,6-$^iPr_2C_6H_3$ (**3**), $N{=}C^tBu_2$ (**5**), $N{=}C(^tBu)CH_2SiMe_3$ (**6**), $N{=}C(^tBu)Ph$ (**7**), $N{=}CPh_2$ (**8**)] − MAO Catalyst Systems[a]

run	complex, L (μmol)	d-MAO/ mmol (Al/V)	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]
1	O-2,6-$Me_2C_6H_3$, **2** (10)	1.0 (100)	118	1.35	6.18
2	O-2,6-$Me_2C_6H_3$, **2** (10)	3.0 (300)	95.4		
3	O-2,6-$^iPr_2C_6H_3$, **3** (10)	1.0 (100)	149	134 (1.67)[d]	2.55 (4.37)[d]
4	O-2,6-$^iPr_2C_6H_3$, **3** (10)	2.0 (200)	113		
5	O-2,6-$^iPr_2C_6H_3$, **3** (10)	3.0 (300)	94.2	1.97	5.08
6[e]	O-2,6-$^iPr_2C_6H_3$, **3** (10)	1.0 (100)	51.0	81.5 (0.96)[d]	2.71 (4.48)[d]
7	$N{=}C^tBu_2$, **5** (5.0)	1.0 (200)	311		
8	$N{=}C^tBu_2$, **5** (5.0)	3.0 (600)	376		
9	$N{=}C^tBu_2$, **5** (2.5)	1.0 (400)	391		
10	$N{=}C^tBu_2$, **5** (2.5)	3.0 (1200)	432	7.46	7.87
11	$N{=}C^tBu_2$, **5** (1.0)	1.0 (1000)	450	11.0	6.31
12	$N{=}C^tBu_2$, **5** (1.0)	3.0 (3000)	516	8.67	8.34
13	$N{=}C(^tBu)CH_2SiMe_3$, **6** (10)	1.0 (100)	12.0		
14	$N{=}C(^tBu)CH_2SiMe_3$, **6** (10)	3.0 (300)	70.8	17.3 (0.12)[d]	6.82 (1.41)[d]
15	$N{=}C(^tBu)Ph$, **7** (5.0)	1.0 (200)	286	15.4 (0.16)[d]	8.75 (1.61)[d]
16	$N{=}C(^tBu)Ph$, **7** (5.0)	3.0 (600)	269	9.3 (0.14)[d]	6.1 (1.69)[d]
17	$N{=}C(^tBu)Ph$, **7** (2.5)	1.0 (400)	300	20.7 (0.16)[d]	7.12 (1.97)[d]
18	$N{=}CPh_2$, **8** (10)	1.0 (100)	105	8.8 (0.14)[d]	6.77 (1.81)[d]
19	$N{=}CPh_2$, **8** (10)	3.0 (300)	95.4		
20	NAr, O-2,6-$Me_2C_6H_3$, **2*** (10)	1.0 (100)	362		
21[f]	NAr, O-2,6-$Me_2C_6H_3$, **2*** (1.0)	2.5 (2500)	2980	167	1.71
22	NAr, $N = C^tBu_2$, **5*** (1.0)	1.0 (1000)	432		
23	NAr, $N = C^tBu_2$, **5*** (1.0)	3.0 (3000)	270		

[a] Reaction conditions: toluene 30 mL, ethylene 8 atm, 100 mL scale autoclave, d-MAO (prepared by removing $AlMe_3$ and toluene from commercially available MAO). [b] Activity = kg•PE/mol•V•h. [c] GPC data in *o*-dichlorobenzene versus polystyrene standards. [d] Bimodal molecular weight distribution. [e] Polymerization at 50 °C. [f] Data cited from ref 4c.

Scheme 5



10^4, runs 24−25) were somewhat lower than that with the arylimido analogue **2*** (M_n = 1.54 × 10^6, run 26). The activity by **2** was not affected by the polymerization temperature (runs 24, 25).

ROMP of NBE proceeded at remarkable rates when the ketimide analogues (**5**, **6**) were employed as catalyst precursors. Note that the catalytic activity at 50 °C by $V(NAd)Cl_2[N{=}C(^tBu)CH_2SiMe_3]$ (**6**) was higher than that by $V(NAd)Cl_2(N{=}C^tBu_2)$ (**5**) [TON = 4361 by **6** (run 35) vs 1541 by **5** (run 31)], and this trend is in interesting contrast to that seen in ROMP using the arylimido analogues because the activity by **5*** was much higher than that by **6*** (runs 32 vs 36). The M_n values for resultant ROMP polymers prepared by the adamantyl−ketimde analogues (**5**, **6**) were lower than those prepared by the arylimido analogues (**5***, **6***), and the trend observed here seems to be similar to that seen in the ROMP using the aryloxo analogues. Thus, the results suggest that the nature of the imido ligand affected the M_n value in the resultant polymers.

Concluding Remarks. A series of (1-adamantylimido)vanadium(V) complexes containing an anionic donor ligand of type, $V(NAd)Cl_2(L)$ [L = O-2,6-$Me_2C_6H_3$ (**2**), O-2,6-$^iPr_2C_6H_3$ (**3**), $N{=}C^tBu_2$ (**5**), $N{=}C(^tBu)CH_2SiMe_3$ (**6**), $N{=}C(^tBu)Ph$ (**7**), $N{=}CPh_2$ (**8**)], have been prepared and identified by NMR spectra, elemental analysis (Schemes 1 and 2), and the structures for **2** and **5** were determined by X-ray crystallography. Isolation of **7** and **8** should be an interesting contrast because attempts to isolate the arylimido analogues under the same conditions were unsuccessful due to their subsequent decomposition.[18] These complexes exhibited catalytic activities for ethylene polymerization in the presence of MAO (Scheme 4, Table 3), and the activities by the adamantylimido−aryloxo analogues (**2**, **3**) were lower than those by the arylimido−aryloxo analogue (**2***) under the same conditions. The ketimide analogues, especially **5**, exhibited moderate catalytic activities, and the activity with a series of $V(NAd)Cl_2(L)$−MAO catalyst systems increased in the order: *L* = $N{=}C^tBu_2$ (**5**, 516 kg•PE/mol•V•h) > $N{=}C(^tBu)Ph$ (**7**, 300) > $N{=}CPh_2$ (**8**, 105) > $N{=}C(^tBu)CH_2SiMe_3$ (**6**, 70.8). These complexes (**2**, **3**, **5**, and **6**) were found to be effective as catalyst precursors for the ring-opening metathesis polymerization (ROMP) of norbornene (NBE) in the presence of MeMgBr and PMe_3 (Scheme 5, Table 4); **6** showed notable catalytic activity, and the trend observed here was different from that seen in the ROMP using arylimido analogues.[10] The present results clearly indicate that the nature of the imido ligands should affect the catalytic activity for both ethylene (insertion) polymerization and the ROMP of norbornene. We are exploring the possibility of isolating vanadium−alkyl and vanadium−alkylidene complexes containing adamantylimido ligands.

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(18) Yamada, J. unpublished results. The results were presented in part at the *International Symposium on Catalysis and Fine Chemicals 2004 (C&FC2004)*, December 2004, Hong Kong, and the *15th International Symposium on Olefin Metathesis and Related Chemistry (ISOMXV)*, July 2003, Kyoto, Japan.

Table 4. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE) by $V(NAd)Cl_2(L)$ [L= O-2,6-$Me_2C_6H_3$ (**2**), O-2,6-$^iPr_2C_6H_3$ (**3**), $N{=}C^tBu_2$ (**5**), $N{=}C(^tBu)CH_2SiMe_3$ (**6**)] in the presence of MeMgBr and PMe_3[a]

run	complex (μmol)	temp/ °C	time/ min	yield/ mg	TON[b]	M_n[c] × 10^{-4}	M_w/M_n[c]
24	O-2,6-$Me_2C_6H_3$, **2** (1.0)	25	40	58.2	619	11.0	1.88
25	O-2,6-$Me_2C_6H_3$, **2** (1.0)	50	40	65.7	699	6.0	1.85
26[d]	NAr, O-2,6-$Me_2C_6H_3$, **2*** (0.2)	50	40	140	7440	154	1.46
27	O-2,6-$^iPr_2C_6H_3$, **3** (1.0)	25	40	1.0	10		
28[e]	O-2,6-$^iPr_2C_6H_3$, **3** (1.0)	50	40	3.0	30	81.3	1.53
29[d]	NAr, O-2,6-$^iPr_2C_6H_3$, **3*** (1.0)	50	40	37	390	35	2.25
30	$N{=}C^tBu_2$, **5** (1.0)	25	40	1.1	11		
31	$N{=}C^tBu_2$, **5** (1.0)	50	25	144.9	1541	7.5	2.77
32[d]	NAr, $N{=}C^tBu_2$, **5*** (0.2)	50	40	166	8820	67	2.13
33	$N{=}C(^tBu)CH_2SiMe_3$, **6** (1.0)	25	40	trace			
34	$N{=}C(^tBu)CH_2SiMe_3$, **6** (1.0)	50	15	115.4	1223	13.0	3.03
35	$N{=}C(^tBu)CH_2SiMe_3$, **6** (0.2)	50	10	82.0	4361	17.2	3.57
36[d]	NAr, $N{=}C(^tBu)CH_2SiMe_3$, **6*** (1.0)	50	10	31	330	69	1.83

[a] Conditions: benzene 5.0 mL, NBE 200 mg, PMe_3/MgBr/V = 1.0:2.1:1.0 (molar ratio). [b] TON (turnover number) = NBE consumed (mmol)/ mmol·V. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Polymerization results by the (arlyimido)vanadium analogues cited from ref . [e] GPC data in THF vs polystyrene standards.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. All chemicals used were of reagent grade and purified by standard purification procedures. Anhydrous-grade toluene and *n*-hexane (Kanto Kagaku Co., Ltd.) were transferred to 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 then passed through an alumina short column before use. Anhydrous-grade dichloromethane was 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. Polymerization grade ethylene (purity > 99.9%, Sumitomo Seika Co. Ltd.) was used as received. Toluene and $AlMe_3$ in commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C to remove toluene and $AlMe_3$, and then at >100 °C for 1 h for completion) in the drybox to give white solids (d-MAO).

The molecular weights and molecular weight distributions of the polyethylene were measured at 145 °C by gel permeation chromatography (Waters 150 CV) using *o*-dichlorobenzene as the solvent and calibration with standard polystyrene samples (measured in Sumitomo Chemical Co., Ltd.). The molecular weight and molecular weight distribution of the resultant poly(norbornene) were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMHHR-H HT × 2) at 140 °C using *o*-dichlorobenzene containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol as an eluent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

All ^1H, ^{13}C, and ^{51}V NMR spectra were recorded on a JEOL JNMLA 400 spectrometer (399.65 MHz, 1H). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere in the drybox, and all chemical shifts are given in ppm and are referenced to Me_4Si. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted, and s $LiN{=}C^tBu_2$, $LiN{=}C^tBu(CH_2SiMe_3)$, $LiN{=}CPh_2$, and $LiN{=}C(Ph)^tBu$ were prepared according to the reported procedure.[19]

Synthesis of $V(NAd)Cl_3$ (1). $V(NAd)Cl_3$ (**1**) was prepared according to a procedure analogous to that reported previously.[13,16] Into a sealed Schlenk glass tube, *n*-octane (40 mL) and $VOCl_3$ (5.80 g, 33.5 mmol) were added sequentially in the drybox, and 1-adamantylisocyanate (2.0 g, 11.3 mmol) was then added to the mixture. The wall of the reactor was washed with *n*-octane (10 mL), and the mixture was placed in an oil bath that had been preheated at 120 °C, and was stirred overnight (>12 h). The tube was connected to a nitrogen line, and CO_2 evolved was released, removed from the mixture by opening the cap. After the reaction, the cooled mixture was filtered through a Celite pad, and the filter cake was washed with hexane several times to extract **1**. The combined filtrate and the wash were placed into 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 (3.14 g, 10.2 mmol) were collected from the chilled solution (placed in the freezer at −30 °C). Yield: 90.8% (based on 1-adamantylisocyanate). ^1H NMR ($CDCl_3$): δ 2.27 (s, 6H, Ad-*H*), 2.20 (s, 3H, Ad-*H*), 1.64 (s, 6H, Ad-*H*). ^{13}C NMR ($CDCl_3$): δ 98.5, 41.9, 35.1, 29.3. ^{13}C NMR (C_6D_6): δ 98.7, 41.8, 35.0, 29.7. ^{51}V NMR ($CDCl_3$): δ 41.5 ($\Delta\nu_{1/2}$ = 442.3 Hz). Anal. Calcd for $C_{10}H_{15}NCl_3V$: C, 39.18; H, 4.93; N, 4.57%. Found: C, 39.26; H, 5.03; N, 4.50%.

Synthesis of $V(NAd)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (2). To an Et_2O solution (20 mL) containing $V(NAd)Cl_3$ (0.5 g, 1.63 mmol) was added $Li(O\text{-}2,6\text{-}Me_2C_6H_3)$ (0.209 g, 1.63 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and stirred overnight (>12 h). Solvent in the mixture was then removed in vacuo, and the resultant brown tan residue was extracted with hot hexane. The extracts were filtered through a Celite pad. Reddish-brown microcrystals (0.328 g, 0.84 mmol) were obtained by recrystallization from the hot *n*-hexane solution upon cooling. (Yield: 51.3%). Samples for the crystallographic analysis were obtained by recrystallization from the chilled *n*-hexane solution at −30 °C. ^1H NMR ($CDCl_3$): δ 7.08 (d, 2H, *J* = 4.12, Ph-*H*), 6.96 (t, 1H, *J* = 4.24, Ph-*H*), 2.25 (s, 6H, Ad-*H*), 1.98 (s, 3H, Ad-*H*), 1.75 (s, 6H, C*H*$_3$), 1.45 (m, 6H, Ad-*H*). ^{13}C NMR ($CDCl_3$): δ 169.0, 128.2, 125.4, 124.1, 93.6, 42.0, 35.1, 29.0, 17.1. ^{51}V NMR ($CDCl_3$): δ −169.2 ($\Delta\nu_{1/2}$ = 413.3 Hz). Anal. Calcd for $C_{18}H_{24}Cl_2NOV$: C, 55.12; H, 6.17; N, 3.57%. Found: C, 55.08; H, 6.17; N, 3.38%.

Synthesis of $V(NAd)Cl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (3). Into a Et_2O solution (20 mL) containing $V(NAd)Cl_3$ (0.514 g, 1.67 mmol), LiO-2,6-$^iPr_2C_6H_3$ (0.309 g, 1.67 mmol) was added at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred overnight (>12 h). Et_2O was removed in vacuo, and the resultant brown-tan residue was extracted with hot *n*-hexane and filtrated through a Celite pad. The filtercake was washed with hot *n*-hexane, and the combined filtrate and the wash were concentrated and placed in the freezer (−30 °C). Red-brown microcrystals (0.361 g, 0.8 mmol) were collected from chilled *n*-hexane solution (Yield: 48.0%). ^1H NMR ($CDCl_3$): δ 7.12 (m,

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(19) (a) Zhang, S.; Piers, W. E.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **2000**, *122*, 5499–5509. (b) Zhang, S.; Piers, W. E. *Organometallics* **2001**, *20*, 2088–2092.

3H, Ph-*H*), 3.19 (m, 2H, C*H*(CH$_3$)$_2$), 1.95 (s, 3H, Ad-*H*), 1.76 (s, 6H, Ad-*H*), 1.44 (m, 6H, Ad-H), 1.20 (d, 12H, $J = 6.96$, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ 166.6, 134.9, 125.7, 123.2, 93.8, 42.2, 35.2, 29.1, 27.0, 23.3, 23.0. ^{51}V NMR (CDCl$_3$): δ 174.8 ($\Delta\nu_{1/2} = 412.1$ Hz). Anal. Calcd for $C_{22}H_{32}Cl_2NOV$: 58.94; H, 7.19; N, 3.12% Found: C, 59.21; H, 6.96; N, 2.82%

Synthesis of V(NAd)(O-2,6-Me$_2$C$_6$H$_3$)$_3$ (4). 2,6-Me$_2$C$_6$H$_3$OH (0.478 g, 3.90 mmol) was added into a stirred *n*-hexane (30 mL) solution containing V(NAd)Cl$_3$ (0.400 g, 1.30 mmol) and Et$_3$N (0.50 g). The mixture was stirred overnight (> 12 h) at room temperature, and the resultant mixture was passed through Celite pad to remove white precipitates (ammonium salts). The filtrate was concentrated in vacuo, and the resultant residue was dissolved in a minimum amount of *n*-hexane. Orange microcrystals (0.536 g, 0.95mmol) were grown from the chilled *n*-hexane solution (−30 °C, Yield: 72.9%). ^{1}H NMR (C$_6$D$_6$): δ 7.01 (d, 6H, $J = 7.96$, Ph-*H*), 6.85 (t, 3H, $J = 7.96$, Ph-*H*), 2.50 (s, 18H, -C*H*$_3$), 1.46 (s, 9H, Ad-*H*), 1.05 (s, 6H, Ad-*H*). ^{13}C NMR: δ 166.8, 128.7, 126.3, 122.5, 42.8, 35.4, 29.3, 17.8. 128.7, 126.3, 122.5, 42.8, 35.4, 29.3, 17.8. The resonance ascribed to the *tert*-carbon in the adamantyl group [N−*C*(CH$_2$−)$_3$] was not seen (probably due to the tiny intensity). ^{51}V NMR: δ −527.3 ($\Delta\nu_{1/2} = 378.36$ Hz). −513.5 (sharp peak). Anal. Calcd for $C_{34}H_{42}NO_3V$: C, 72.45; H, 7.51; N, 2.49%. Found: C, 72.53.; H, 7.21; N, 2.27%. Two resonances were observed in the ^{51}V NMR spectrum, and the result in the crystallographic analysis indicates that (similar) two structures were determined. (These results suggest that the compound is a mixture of two isomers.)

Synthesis of V(NAd)Cl$_2$(N=C^{t}Bu$_2$) (5). Into a Et$_2$O solution (20 mL) containing V(NAd)Cl$_3$ (0.5 g, 1.63 mmol), LiN=C^{t}Bu$_2$ (0.24 g, 1.63 mmol) was added at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred overnight. Et$_2$O was removed in vacuo, and the resultant brown tan residue was extracted with hot *n*-hexane and filtrated through a Celite pad. The filtercake was then washed with hot *n*-hexane. Red-brown microcrystals (0.424 g, 1.03 mmol) were obtained from chilled concentrated solution (Yield: 63.2%). ^{1}H NMR (CDCl$_3$): δ 2.13 (s, 6H, Ad-*H*), 2.09 (s, 3H, Ad-*H*), 1.59 (s, 6H, Ad-*H*), 1.30 [s, 18H, (C*H*$_3$)$_3$]. ^{13}C NMR (CDCl$_3$): δ 89.9, 46.4, 43.1, 35.6, 31.4, 30.1, 29.3, 22.5, 14.0. The resonance ascribed to the imino carbon (*N* = C^{t}Bu$_2$) was not seen (due to the broad, tiny intensity). ^{51}V NMR (CDCl$_3$): δ −103.7 ($\Delta\nu_{1/2} = 270.5$ Hz). Anal. Calcd for $C_{19}H_{33}N_2Cl_2V$: C, 55.48; H, 8.09; N, 6.81%. Found: C, 55.00; H, 8.54; N, 6.55%.

Synthesis of V(NAd)Cl$_2$[N=C(^{t}Bu)CH$_2$SiMe$_3$] (6). Synthesis of **6** was performed in the analogous procedure for preparation of **5** except, that a Et$_2$O solution (50 mL) containing V(NAd)Cl$_3$ (0.920 g, 3.00 mmol), LiN=C(^{t}Bu)CH$_2$SiMe$_3$ (0.532 g, 3.00 mmol) was added at −30 °C. Brown microcrystals (0.811 g, 1.43 mmol) were obtained from the chilled *n*-hexane solution (Yield: 61.2%). ^{1}H NMR(CDCl$_3$): δ 2.13 (s, 6H, Ad-*H*), 2.09 (s, 3H, Ad-*H*), 2.04 (s, 2H, C*H*$_2$SiMe$_3$), 1.59 (s, 6H, Ad-*H*), 1.18 [s, 9H, C(C*H*$_3$)$_3$], 0.19 [s, 9H, Si(C*H*$_3$)$_3$]. ^{13}C NMR (CDCl$_3$): δ 45.4, 43.5, 35.8, 29.6, 28.5, 28.3, 0.4. The resonances ascribed to both the *tert*-carbon in the adamantyl group [N−C(CH$_2$−)$_3$] and the imino carbon [N=C(^{t}Bu)-CH$_2$SiMe$_3$] were not seen (probably due to the tiny intensity). ^{51}V NMR (CDCl$_3$): δ −136.0 ($\Delta\nu_{1/2} = 310.5$ Hz). Anal. Calcd for $C_{19}H_{35}Cl_2N_2SiV$: C, 51.70; H, 7.99; N, 6.35%. Found: C, 51.54; H, 8.04; N, 6.14%.

Synthesis of VCl$_2$(NAd)[N=C(^{t}Bu)Ph] (7). Into a Et$_2$O solution (20 mL) containing V(NAd)Cl$_3$ (0.245 g, 0.80 mmol), LiN=C(^{t}Bu)Ph (0.134 g, 0.80 mmol) was added at −30 °C. The reaction mixture was warmed slowly to room temperature and the mixture was stirred overnight. The solvent was then removed in vacuo, and the resultant brown powder was extracted with hot toluene and was filtrated through the Celite pad. The filtercake was also washed with toluene several times. The obtained solution was concentrated in vacuo, and covered with *n*-hexane. Orange powder (0.174 g, 0.40 mmol) was obtained (Yield: 50.0%). ^{1}H NMR (CDCl$_3$): δ 7.24−7.47 (m, 5H, Ph-*H*), 2.15 (s, 6H, Ad-*H*), 2.10 (s, 3H, Ad-*H*), 1.60 (s, 6H, Ad-*H*), 1.36 (s, 9H, Me-*H*). ^{13}C NMR (CDCl$_3$): δ 165.6, 135.7, 130.4, 128.5, 127.4, 45.1, 43.1, 35.6, 29.4, 29.3. The resonance ascribed to the *tert*-carbon in the adamantyl group [N−C(CH$_2$−)$_3$] was not seen (probably due to the tiny intensity). ^{51}V NMR (CDCl$_3$): δ −154.9 ($\Delta\nu_{1/2} = 315.9$ Hz). Anal. Calcd for $C_{22}H_{32}Cl_2NOV \cdot 0.2$(*n*-hexane): C, 59.44; H, 7.15; N, 6.25%. Found: C, 59.38; H, 7.41; N, 6.16%.

Synthesis of VCl$_2$(NAd)(N=CPh$_2$) (8). Into a Et$_2$O solution (20 mL) containing V(NAd)Cl$_3$ (0.516 g, 1.68 mmol), LiN=CPh$_2$ (0.315 g, 1.68 mmol) was added at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for overnight (> 12 h). During the reaction, first the mixture became a clear-orange solution, and then many orange precipitates were observed. The precipitates were collected and were dried for a long time. Then it was dissolved in little amount dichloromethane and filtrated at −30 °C through a Celite pad. All of the solvent was removed, and orange powder (0.328 g, 0.687 mmol) was collected and in yield (43.1%). ^{1}H NMR (CDCl$_3$): δ 7.63−7.44(m, 10H, Ph-*H*), 2.14(s, 6 H, Ad-*H*), 2.06(s, 3H, Ad-*H*), 1.56(s, 6H, Ad-*H*). ^{13}C NMR (CDCl$_3$): δ 134.8, 132.2, 130.0, 128.8, 43.2, 35.5, 29.4. The resonances ascribed to both the *tert*-carbon in the adamantyl group [N−C(CH$_2$−)$_3$] and the imino carbon [N=CPh$_2$] were not seen (probably due to the tiny intensity). ^{51}V NMR (CDCl$_3$): δ −199.0 ($\Delta\nu_{1/2} = 294.8$ Hz). Anal. Calcd for $C_{23}H_{25}Cl_2N_2V$: C, 61.21; H, 5.58; N, 6.21%. Found: C, 61.51; H, 5.71; N, 6.17%

Synthesis of VCl$_2$(NAd)(N=CPh$_2$)(PMe$_3$)$_2$ (9). Into a Et$_2$O solution containing V(NAd)Cl$_3$ (0.448 g, 1.46 mmol), LiN=CPh$_2$ (0.274 g, 1.46 mmol) and PMe$_3$(0.333 g, 4.38 mmol) was added at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for overnight (> 12 h). Solvent in the mixture was then removed in vacuo, and then the resultant residue was then extracted with hot toluene and the extracts were filtered through a Celite pad. The solution was concentrated and covered with *n*-hexane at −30 °C, then yellow precipitate was obtained in yield (49.0%). Samples for the crystallographic analysis were obtained by recrystallization from toluene solution covered with hexane at room temperature. ^{1}H NMR (CDCl$_3$): δ 7.64 (t, 4H, $J = 5.52$, Ph-*H*), 7.38−7.43 (m, 6H, Ph-*H*), 2.07 (s, 9H, Ad-*H*), 1.59 (s, 6H, Ad-*H*), 1.32 (s, 18H, P(C*H*$_3$)$_3$). ^{51}V NMR (CDCl$_3$): δ −646.3 ($\Delta\nu_{1/2} = 641.9$ Hz). ^{13}C NMR (CDCl$_3$): δ 137.4, 130.0, 129.3, 128.1, 44.2, 35.7, 29.0, 16.8, 16.7, 16.6. The resonances ascribed to both the *tert*-carbon in the adamantyl group [N−C(CH$_2$−)$_3$] and the imino carbon [N=CPh$_2$] were not seen (probably due to the tiny intensity). ^{31}P NMR: broad resonance at ca. 1.8, 9.9. Anal. Calcd for $C_{29}H_{43}Cl_2N_2P_2V \cdot$(0.5 toluene): C, 60.0; H, 7.23; N, 4.31%. Found: C, 59.92; H, 7.50; N, 4.21%. Broad resonance in^{31}P NMR spectrum would be due to the equilibrium between phosphine coordinated and (partially) dissociated species in the solution.

Synthesis of [N(Ad)H$_3$]$^+$[V$_2$(μ_2-Cl)$_3$Cl$_2$(NAd)$_2$(N=CPh$_2$)$_2$]$^-$ (10). Into a Et$_2$O solution (20 mL) containing V(NAd)Cl$_3$ (0.3 g, 0.98 mmol), LiN=CPh$_2$ (0.18 g, 0.98 mmol) was added at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for overnight (> 12 h). During the reaction, first the mixture became clear solution and

Table 5. Crystal Data and Crystallographic Parameters for $V(NAd)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2**), $V(NAd)(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ (**4**), $V(NAd)Cl_2(N{=}C^tBu_2)$ (**5**), $V(NAd)Cl_2(N{=}CPh_2)(PMe_3)_2$ (**9**), $[N(Ad)H_3]^+[V_2(\mu_2\text{-}Cl)_3Cl_2(NAd)_2(N{=}CPh_2)_2]^-$ (**10**) [a]

	2	4	5	9	10
empirical formula	$C_{18}H_{24}Cl_2NOV$	$C_{34}H_{42}NO_3V$	$C_{19}H_{33}Cl_2N_2V$	$C_{33}H_{43}Cl_2N_2P_2V$	$C_{63}H_{76}Cl_5N_5V_2$
fw	392.24	563.65	411.33	651.51	1182.47
cryst color, habit	brown, block	orange, block	red, block	orange, block	orange, block
cryst dimens(mm)	0.80 × 0.40 × 0.40	0.60 × 0.50 × 0.30	0.34 × 0.28 × 0.14	0.40 × 0.30 × 0.20	0.26 × 0.14 × 0.12
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
lattice params					
a (Å)	14.7201(10)	31.0043(14)	7.0301(3)	16.9138(6)	17.0144(7)
b (Å)	13.3386(11)	10.5248(4)	12.3507(6)	10.7352(5)	20.9148(8)
c (Å)	20.2542(15)	20.6197(10)	13.6085(6)	20.4484(7)	18.0351(8)
β (°)	107.885(2)	112.8303(16)	77.7759(16)	112.7838(8)	101.7723(13)
α (°)			74.152(2)		
γ (°)			75.7851(17)		
V (Å^3)	3784.6(5)	6201.4(5)	1088.52(9)	3423.2(2)	6281.7(4)
space group	$C2/c$ (#15)	$P2_1/c$ (#14)	$P1$ (#2)	$P2_1/c$ (#14)	$P2_1/n$(#14)
Z value	8	8	2	4	4
D_{calcd} (g/cm^3)	1.377	1.207	1.255	1.264	1.250
F000	1632.00	2400.00	436.00	1368.00	2480.00
μ(Mo Kα)(cm^{-1})	8.089	3.525	7.039	5.630	5.510
2θmax (°)	54.8	50.7	54.9	50.0	54.8
no. of reflns measd	total: 17 994 unique: 4266 ($R_{int} = 0.026$)	total: 46 107 unique: 11 282 ($R_{int} = 0.038$)	total: 10 766 unique: 4915 ($R_{int} = 0.018$)	total: 25 883 unique: 6002 ($R_{int} = 0.024$)	total: 56 942 unique: 14 046 ($R_{int} = 0.065$)
no. of observations ($I > 2.00(I)$)	3452	7026	3652	4663	5689
no. of variables	232	787	250	404	764
residuals: R; Rw($I > 2.00(I)$)	0.0444; 0.1549	0.0564; 0.1678	0.0389; 0.0350	0.0597; 0.1049	0.0609; 0.0687
GOF	1.006	1.004	0.928	1.001	1.078

[a] Diffractometer: Rigaku RAXIS-RAPID imaging plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Radiation: Mo Kα (λ = 0.71075 Å) graphite monochromated.

then an abundant orange precipitate was observed. Solvent in the mixture was then removed in vacuo, and the resultant residue was extracted with hot toluene and the extracts were filtered through a Celite pad. The solution was concentrated and covered with *n*-hexane at −30 °C, and then orange crystals (0.314 g, 0.26 mmol) were obtained in yield (54.1% based on vanadium). Samples for the crystallographic analysis were obtained by recrystallization from toluene solution covered with hexane at room temperature. ^1H NMR($CDCl_3$): δ 7.77−7.63 (m, 8H, Ph-*H*), 7.44−7.36 (m, 12H, Ph-*H*), 2.12−1.95 (m, 27H, Ad-*H*), 1.62−1.54 (m, 18H, Ad-*H*). ^{13}C NMR ($CDCl_3$): δ 137.4, 137.3, 137.2, 130.0, 129.3, 128.4, 83.9, 44.2, 35.7, 29.0, 16.8, 16.7, 16.6. The resonance ascribed to the imino carbon [$N{=}CPh_2$] was not seen (probably due to the tiny intensity). ^{51}V NMR ($CDCl_3$): −202.6 ($\Delta\nu_{1/2} = 462.4$ Hz). Anal. Calcd for $C_{58}H_{73}Cl_5N_5V_2\cdot(0.3$ toluene): C, 62.79; H, 6.54; N, 6.12%. Found: C, 62.76; H, 6.44; N, 5.99%.

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and expanded using Fourier techniques,[20] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **2**, **4**, **5**, **9**, **10** were performed using the *Crystal Structure* crystallographic software package.[21] Selected crystal collection parameters are summarized in Tables 5.

Polymerization of Ethylene. Ethylene polymerization was conducted in toluene by using a 100 mL scale autoclave. Solvent (29.0 mL) and a prescribed amount of d-MAO were added to the autoclave in the drybox, and the apparatus was placed under an ethylene atmosphere (1 atm). After the addition of toluene solution (1.0 mL) containing complex (1 μmol) via a syringe, the reaction apparatus was pressurized to 8 atm, and the mixture was stirred magnetically for 10 min. Next, ethylene was purged off and the mixture was then poured into EtOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration, adequately washed with EtOH and dried in vacuo.

ROMP of Norbornene by an $AdNVCl_2(L)$-MeMgBr-PMe_3 System. The general procedure for the ROMP of NBE using a $V(NAd)Cl_2(L)$ (**2**, **3**, **5**, **6**)-MeMgBr-PMe_3 catalyst system is as fellows: Benzene (4.5 mL), norbornene (2.12 mmol, 200 mg), and MeMgBr in dilute Et_2O (0.020 μmol) were added into a sealed Schlenk tube. Premixed catalyst solution was independently prepared by adding complex (20 μmol) and MeMgBr to Et_2O (40 μmol, 2.0 equiv.), followed by the addition of PMe_3 (20 μmol, 1.0 equiv) at room temperature. The mixture was stirred for 5 min before the addition of MeMgBr and PMe_3, respectively. A prescribed amount of the prepared catalyst solution was then added to the sealed Schlenk tube and magnetically stirred for a prescribed time at a prescribed temperature. The polymerization was then quenched by the addition of excess PhCHO, and the solution was stirred for an additional 1 h at room temperature for completion. The mixture was then poured into MeOH (ca. 100 mL). The resultant polymer was collected on filter paper, adequately washed with MeOH, and dried in vacuo for several hours.

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Supporting Information Available: Crystal structure determinations, reports for V(NAd)Cl_2(O-2,6-$Me_2C_6H_3$) (**2**), V(NAd)(O-2,6-$Me_2C_6H_3$)$_3$ (**4**), V(NAd)Cl_2(N=C^tBu_2) (**5**), V(NAd)Cl_2(N=CPh_2)(PMe_3)$_2$ (**9**), and [N(Ad)H_3]$^+$[V_2(μ_2-Cl)$_3$$Cl_2(NAd)_2$(N=$CPh_2$)$_2$]$^-$ (**10**); the crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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