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Synthesis and Structural Analysis of (Imido)vanadium(V) Dichloride Complexes Containing Imidazolin-2-iminato- and Imidazolidin-2-iminato Ligands, and their Use as Catalyst Precursors for Ethylene (Co)polymerization

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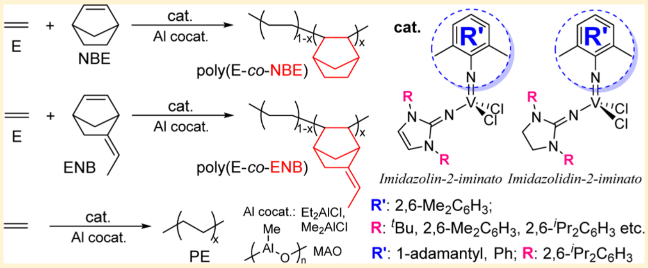
Supporting Information



ABSTRACT: A series of (imido)vanadium(V) dichloride complexes containing 1,3-imidazolin-2-iminato or 1,3-imidazolidin-2-iminato ligands of the type, $V(NR')Cl_2(L)$ [R′ = 2,6-$Me_2C_6H_3$, L = 1,3-$R_2(CHN)_2C{=}N$ (**1a−c,e**) or 1,3-$R_2(CH_2N)_2C{=}N$ (**2a−d**), R = ^{t}Bu (**a**), 2,6-$Me_2C_6H_3$ (**b**), 2,6-$^i Pr_2C_6H_3$ (**c**), C_6H_5 (**d**), 2,6-$(Ph_2CH)_2$-4-MeC_6H_2 (**e**); L = 1,3-(2,6-$^i Pr_2C_6H_3)_2(CHN)_2C{=}N$, R′ = 1-adamantyl (Ad, **3c**), C_6H_5 (**4c**); L = 1,3-(2,6-$^i Pr_2C_6H_3)_2(CH_2N)_2C{=}N$, R′ = Ad (**5c**)], were prepared and characterized. The molecular structures of **1a**, **2a**,**c**,**d**, **3c**, **4c**, and **5c** were determined by X-ray crystallography. All complexes showed high catalytic activity for ethylene polymerization especially in the presence of Et_2AlCl cocatalyst; the 2,6-$R_2C_6H_3$ analogues (R = Me, ^{i}Pr; **1b**,**c**, **2b**,**c**) exhibited higher catalytic activities than the ^{t}Bu analogues (**1a**, **2a**), which display rather unique (small) V—N—C(imido) bond angles in the solid state. A good correlation between the activity and the ^{51}V NMR chemical shift was found for the (arylimido)vanadium precatalysts (**1a−c,e**, **2a−d**, and **4c**). These complexes showed high catalytic activity for the copolymerization of ethylene with norbornene (NBE), affording ultrahigh molecular weight copolymers with uniform molecular weight distributions. The activities were affected by the imido ligand as well as by the substituents in the anionic ligand, and the 2,6-$^i Pr_2C_6H_3$ analogues (especially **2c** and **4c**) showed the higher activities. The complexes **2c** and **4c** also showed high activities with efficient comonomer incorporation for the ethylene copolymerization with 5-ethylidene-2-norbornene (ENB) in the presence of Et_2AlCl; both the comonomer incorporation and the molecular weight in the resulting polymers were affected by the comonomer employed (NBE vs ENB).

■ INTRODUCTION

The classical Ziegler-type vanadium catalyst systems [e.g., consisting of $V(acac)_3$, $VOCl_3$, etc. and Et_2AlCl, $EtAlCl_2$, ^{n}BuLi, etc.] are known to display uniquely high reactivity toward olefins in olefin coordination/insertion polymerization.[1−5] The design and synthesis of efficient vanadium precatalysts for olefin coordination insertion polymerization has thus attracted considerable attention in the fields of catalysis, organometallic chemistry, and polymer chemistry.[5−7] Our group has focused on (imido)vanadium(V) complexes containing anionic donor ligands of the type, $VCl_2(Y)(NR)$ (Y = aryloxo, ketimide, phenoxyimine, etc.),[5c,e,6,8] and has demonstrated that these complexes, exemplified by $V(N$-2,6-$Me_2C_6H_3)Cl_2(O$-2,6-$Me_2C_6H_3)$ (**A** in Scheme 1),[6a−d] exhibit remarkable catalytic activities not only for ethylene polymerization but also for ethylene copolymerization with norbonene (NBE) in the presence of aluminum cocatalysts.[6a−d] Moreover, we also reported that (2-anilidomethyl)pyridine-supported (imido)vanadium(V) complexes of the type, $V(NR')Cl_2[2\text{-}ArNCH_2(C_5H_4N)]$ [Ar = 2,6-$Me_2C_6H_3$, etc.; R′ = 1-adamantyl (Ad), cyclohexyl, *o*-tolyl, phenyl, etc.], efficiently dimerize ethylene with both notable catalytic activity and high selectivity in the presence of methylaluminoxane (MAO),[8] whereas the resulting products were polyethylene with ultrahigh molecular weight when the reactions were conducted in the presence of Et_2AlCl or Me_2AlCl.[8b,d]

Half-titanocenes containing imidazolin-2-iminato ligands as an anionic donor ligand (Y) were also introduced as promising catalyst precursors for olefin polymerization, and complexes of this type, exemplified by $CpTiCl_2[1,3\text{-}^tBu_2(CHN)_2{=}N]$ (**B** in Scheme 1), exhibit high catalytic activities for ethylene

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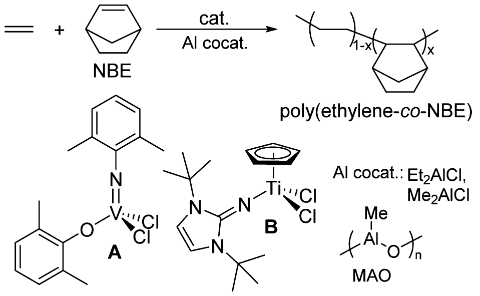
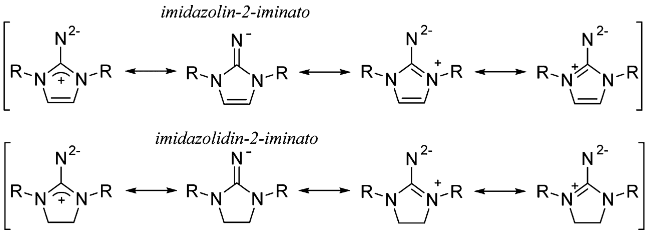
Scheme 1. Recently Reported Complexes as Effective Precatalysts for Ethylene/Norbornene Copolymerization



polymerization in the presence of MAO,[9] affording ultrahigh molecular weight polymers.[9b] Furthermore, these complexes show notable catalytic activities for copolymerization of ethylene with α-olefins (1-hexene, 1-dodecene) and superior catalyst performance in the (living) copolymerization of ethylene with styrene.[9d] More recently, an efficient synthesis of high molecular weight poly(ethylene-*co*-NBE)s with high NBE contents (affording high T_g values) was achieved by use of complex **B** for ethylene/NBE copolymerization (Scheme 1).[9e] Certain cyclic olefin copolymers (COCs) are amorphous materials with a promising combination of high transparency in the UV−vis region along with humidity- and heat-resistance (high glass transition temperature, T_g),[10] and these polymers have been commercialized (as TOPAS) by using metallocene catalysts as ultrapure (applicable to advanced pharma packaging, food contact films), crystal-clear (glass clear, amorphous), high barrier (resistant to moisture, alcohols, acids) materials.[11] Similar to imidazolin-2-iminato ligands, which have been extensively used for the preparation of early transition metal complexes,[12] their 4,5-dihydro congeners are also suitable ancillary ligands, and thus, the corresponding half-titanocenes containing imidazolidin-2-iminato ligands also exhibit unique characteristics for ethylene (co)polymerization.[13] For both ligand systems, a similar stabilization by the zwitterionic resonance structures shown in Scheme 2 can be considered, affording strong basic nitrogen donor ligands with a high π-electron release capability toward early transition metals and/or metals in a higher oxidation state.[9,12,13]

Scheme 2. Resonance Structures for Imidazolin-2-iminato (top) and Imidazolidin-2-iminato (bottom) Ligands



In this paper, we report the synthesis of (imido)vanadium(V) dichloride complexes containing both imidazolin-2-iminato and imidazolidin-2-iminato ligands (Chart 1) and their use as catalyst precursors for ethylene polymerization and ethylene copolymerization with the cyclic olefins [norbornene (NBE), ethylidene-2-norbornene (ENB)]. In particular, we wish to demonstrate that these complexes are promising candidates as catalyst precursors for the efficient synthesis of high molecular weight poly(ethylene-*co*-NBE)s.

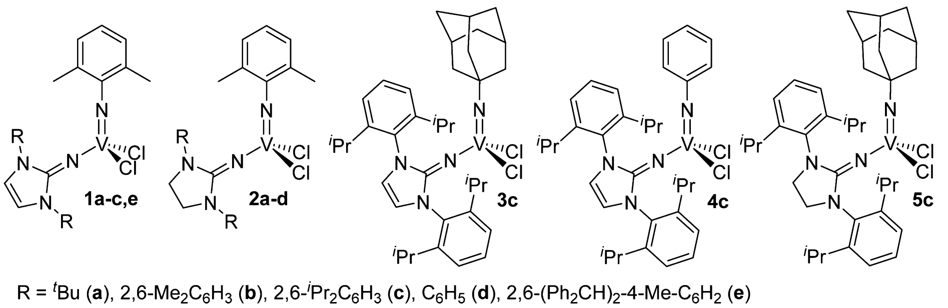
■ RESULTS AND DISCUSSION

1. Synthesis and Structural Characterization of (Imido)-vanadium(V) Dichloride Complexes Containing Imidazolin-2-iminato, and Imidazolidin-2-iminato Ligands. A series of (arylimido)vanadium(V) dichloride complexes containing imidazolin-2-iminato ligands of type V(NAr)Cl$_2$(L1) [Ar = 2,6-Me$_2$C$_6$H$_3$; L1 = 1,3-R$_2$(CHN)$_2$C=N, R = ^{t}Bu (**1a**), 2,6-Me$_2$C$_6$H$_3$ (**1b**), 2,6-(Ph$_2$CH)$_2$4-MeC$_6$H$_2$ (**1e**)] were prepared according to a published procedure[12n] for the synthesis of V(NAr)Cl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N] (**1c**) by reacting V(NAr)Cl$_3$[14] with **L1-SiMe$_3$** in toluene (Scheme 3); this protocol is also similar to that for the preparation of the corresponding CpTiCl$_2$(L1) complexes.[9b] Complexes **1a,b,e** were identified by ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy and elemental analysis, and the molecular structure of **1a** was determined by X-ray diffraction analysis (described below, see Figure 1). Similarly, the reactions of V(NAd)Cl$_3$ (Ad = 1-adamantyl)[15] or V(NPh)Cl$_3$[8a] with **L1-SiMe$_3$** (R = 2,6-^{i}Pr$_2$C$_6$H$_3$) in toluene afforded the corresponding V(NR′)Cl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N] [R′ = Ad (**3c**), Ph (**4c**)], and both compounds were fully characterized by NMR spectroscopy and elemental analyses, and their molecular structures were determined by X-ray diffraction analysis (described below, see Figure 1).

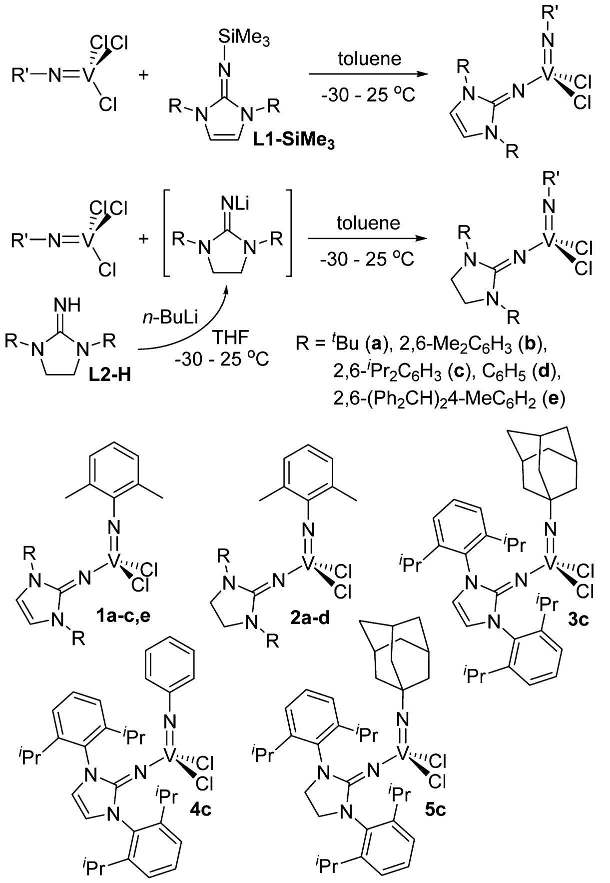
A related series of (arylimido)vanadium(V) dichloride complexes containing imidazolidin-2-iminato ligands of the type, V(NAr)Cl$_2$(L2) [L2 = 1,3-R$_2$(CH$_2$N)$_2$C=N, R = ^{t}Bu (**2a**), 2,6-Me$_2$C$_6$H$_3$ (**2b**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2c**), Ph (**2d**)], were prepared by reacting V(NAr)Cl$_3$[14] with **L2-Li** in toluene, with the lithium reagents obtained by treatment of **L2-H**[13,16] with *n*-BuLi (1 equiv) in THF; it should be noted that the corresponding CpTiCl$_2$(L2) complexes had been prepared in a similar fashion.[13] The analogous reaction of V(NAd)Cl$_3$ with **L2c-Li** (R = 2,6-^{i}Pr$_2$C$_6$H$_3$) in toluene afforded V(NAd)Cl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CH$_2$N)$_2$C=N] (**5c**). Complexes **2a−d** and **5c** were identified by ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy and elemental analysis, and the molecular structure of each complexes except for **2b** were determined by X-ray diffraction analysis (described below, see Figure 2).

Figure 1 shows structures for V(NAr)Cl$_2$[1,3-^{t}Bu$_2$(CHN)$_2$C=N] (**1a**), V(NAd)Cl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N] (**3c**), and V(NPh)Cl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N] (**4c**), and selected bond distances and angles are summarized in Table 1.[17] As expected from the previously reported structure of **1c**[12n] and from that of the ketimide analogue, V(NAr)Cl$_2$(N=C^{t}Bu$_2$),[18] these complexes display distorted tetrahedral geometries around the vanadium atoms. The V—Cl bond distances in **1a** [2.2462(8), 2.2514(7) Å] are longer than those in the 2,6-^{i}Pr$_2$C$_6$H$_3$ analogues (**1c**,[12n] **3c**, **4c**) [2.2120(10)−2.2386(7) Å] but somewhat shorter than that in V(NAr)Cl$_2$(N=C^{t}Bu$_2$) [2.2710(5), 2.2338(5) Å].[18] The V—N(1) imido bond length in **3c** [1.638(2) Å] is apparently shorter than those in the other imidazolin-2-iminato analogues [1.664(3)−1.6689(15) Å]. The Cl(1)—V—Cl(2) angles in **3c** and **4c** [112.66(3), 112.66(4)°] are just slightly smaller than that in **1a** [113.00(3)°] but are slightly larger than that in **1c** [111.45(2)°];[12n] however, these angles are smaller than that in V(NAr)Cl$_2$(N=C^{t}Bu$_2$) [118.87(2)°],[18] which might be ascribed to the presence of the sterically more demanding imidaozolin-2-iminato ligands. Moreover, the imidazolin-2-iminato V—N—C bond angle in **3c** [158.07(15)°] is apparently smaller than those in the other complexes [163.92(10)−164.58(18)°], which corresponds to

Chart 1



Scheme 3. Synthesis of (Imido)vanadium Dichloride Complexes Containing Imidazolin-2-iminato and Imidazolidin-2-iminato Ligands



the fact that the V—N(2) bond distance in **3c** [1.7466(18) Å] is longer than those in the other systems [1.7256(15)−1.7308(11) Å]. It might be interesting to note that the V—N(1)—C in the imido ligand [163.45(13)°] angle in **1a** is smaller than the others [171.14(17)−171.25(18)°], whereas the corresponding V—N(1) distance in **1a** [1.6689(15) Å] is close to those in the others [1.664(3)−1.6684(13) Å], except **3c** [1.638(2) Å].

Figure 2 shows molecular structures of V(N-2,6-$Me_2C_6H_3$)-Cl_2[1,3-$R_2(CH_2N)_2C{=}N$] [R = ^{t}Bu (**2a**), 2,6-$^iPr_2C_6H_3$ (**2c**), Ph (**2d**)], and V(NAd)Cl_2[1,3-(2,6-$^iPr_2C_6H_3)_2(CH_2N)_2C{=}N$] (**5c**), and their selected bond distances and angles are summarized in Table 1.[17] Likewise, these complexes display distorted tetrahedral geometries around the vanadium atoms. The V—Cl bond distances in these complexes [2.2222(4)−2.248(3) Å] fall in the same range as found for the imidazolin-2-iminato analogues (**1a**,**c**, **3c**, **4c**) [2.2120(10)−2.2514(7) Å]. The V—N(1) imido bond length in **2a** [1.620(13) Å] is shorter than those in the other complexes [1.645(3)−1.6635(12) Å], whereas the V—N(1)—C angle [157.3(11)°] in **2a** is smaller than the others [167.96(11)—179.20(11)°]: the angle in **2c** [167.96(11)°] is smaller than those in **2d** and **5c** [179.20(11), 174.5(2)°, respectively]. Moreover, the imidazolidin-2-iminato V—N—C bond angle is affected by the ligand substituents, and accordingly, the bond angles in V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-$R_2(CH_2N)_2C{=}N$] [R = ^{t}Bu (**2a**), 2,6-$^iPr_2C_6H_3$ (**2c**), Ph (**2d**)] increase in the order: 150.06(12)° (**2d**) < 157.9(4)° (**2a**) < 174.79(11)° (**2c**). In contrast, the corresponding vanadium−nitrogen bond distance in **2d** [1.7538(13) Å] is longer than those in **2a** [1.736(5) Å] and **2c** [1.7383(13) Å]. The Cl(1)—V—Cl(2) bond angle in **2a** [111.71(9)°] is smaller than those in **2c** and **2d** [113.006(15), 113.164(15)°, respectively] but close to that in **5c** [111.23(4)°].

Overall, all complexes display the expected tetrahedral geometry around vanadium atom, and the structural parameters along the V—N—C axes of the anionic donor ligands (imidazolin-2-iminato or imidazolidin-2-iminato) are clearly affected by the substituents of the respective *N*-heterocycle. In particular, the complexes containing *tert*-butyl substituents (**1a**, **2a**) possess rather unique V—N—C bond angles in both arylimido and the anionic donor ligands, probably due to a steric bulk of the *tert*-butyl groups.

2. Ethylene Polymerization Using (Imido)vanadium(V) Dichloride Complexes Containing Imidazolin-2-iminato and Imidazolidin-2-iminato Ligands in the Presence of Al Cocatalysts. Table 2 summarizes the results for ethylene polymerization using the imidazolin-2-iminato precatalysts, V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-$R_2(CHN)_2C{=}N$] [R = ^{t}Bu (**1a**), 2,6-$Me_2C_6H_3$ (**1b**), 2,6-$^iPr_2C_6H_3$ (**1c**), 2,6-$(Ph_2CH)_2$-4-MeC_6H_2 (**1e**)] and V(NR′)Cl_2[1,3-(2,6-$^iPr_2C_6H_3)_2(CHN)_2C{=}N$] [R′ = 1-adamantyl (**3c**), C_6H_5 (**4c**)], in the presence of Al cocatalysts (in toluene, ethylene 8 atm, 10 min). As additionally illustrated by Figure 3 (left), the catalytic activity, on the basis of polymer yield, was affected by the Al/V molar ratio and by the nature of the Al cocatalyst; the activities in the presence of methylaluminoxane (MAO) cocatalyst were lower than those in the presence of $EtAlCl_2$. Moreover, the activity in ethylene polymerization in the presence of Et_2AlCl cocatalyst at 25 °C became low compared to that conducted at 0 °C. The observed trends are similar to those found for ethylene polymerization using the aryloxo substituted (arylimido)vanadium dichloride complexes, Al cocatalyst systems.[6b−d] The resulting polymers are linear polyethylene that are not sufficiently soluble in hot *o*-dichlorobenzene (140 °C) required for a GPC analysis. Because the poly(ethylene-*co*-norbornene)s obtained below possessed uniform molecular weight distributions, it is highly

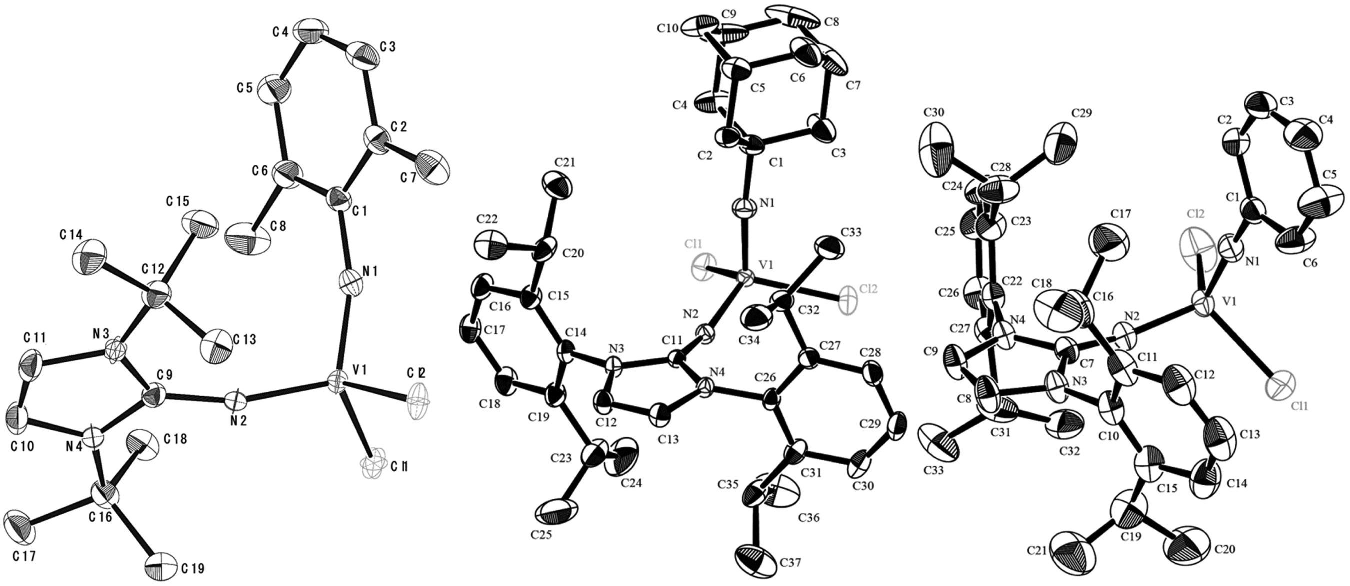


Figure 1. ORTEP drawings for V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-$^tBu_2$$(CHN)_2C{=}N$] (**1a**, left), V(NAd)$Cl_2$[1,3-(2,6-$^iPr_2C_6H_3$)$_2$$(CHN)_2C{=}N$] (**3c**, middle), and V(NPh)Cl_2[1,3-(2,6-$^iPr_2C_6H_3$)$_2$$(CHN)_2C{=}N$] (**4c**, right). Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity. Details are given in the Supporting Information.[17]

assumed that ultrahigh molecular weight polyethylene has formed in this catalysis as previously reported for the polymerization in the presence of the aryloxo modified (arylimido)vanadium catalysts (exemplified as complex **A** in Scheme 1).[6b−d]

The activity of the imidazolin-2-iminato analogues (with optimized Al/V molar ratio) in the presence of the Et_2AlCl cocatalyst increased in the order (in toluene, ethylene 8 atm, 0 °C, 10 min): 6300 kg-PE/mol-V·h (**1a**) < 8220 (**3c**) < 26 700 (**1e**) < 34 700 (**1c**) < 38 300 (**1b**) < 42 900 (**4c**). Among the arylimido congeners (**1a**−**c**,**e**), the complexes with aryl substituents (**1b**,**c**,**e**) in the imidazolin-2-iminato ligand showed higher activity than the *tert*-butyl analogue (**1a**), suggesting that the electronic nature of the substituent has an impact on the activity. Further increase of steric bulk in the 1,3-position upon going from **1b** to **1c** and **1e** led to a decrease in activity, suggesting that the activity is also influenced by the steric bulk requirements of the ancillary ligands. Moreover, the activity of V(NR′)Cl_2[1,3-(2,6-$^iPr_2C_6H_3$)$_2$$(CHN)_2C{=}N$] [R′ = 2,6-$Me_2C_6H_3$ (**2c**), 1-adamantyl (**3c**), C_6H_5 (**4c**)] increased in the order: 8220 (**3c**) ≪ 34 700 (**1c**) < 42 900 (**4c**).

Table 3 summarizes the results for ethylene polymerization using the imidazolidin-2-iminato precatalysts, V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-$R_2$$(CH_2N)_2C{=}N$] [R = ^{t}Bu (**2a**), 2,6-$Me_2C_6H_3$ (**2b**), 2,6-$^iPr_2C_6H_3$ (**2c**), C_6H_5 (**2d**)], and V(NAd)-Cl_2[1,3-(2,6-$^iPr_2C_6H_3$)$_2$$(CHN)_2C{=}N$] (**5c**), in the presence of Al cocatalysts (in toluene, ethylene 8 atm, 10 min). As also shown in Figure 3 (right), the catalytic activity was affected by the Al/V molar ratio employed, and similar trends with regard to the effect of the Al cocatalyst and the temperature were observed as described above for the polymerization in the presence of the imidazolin-2-iminato analogues. The activity (with the optimized Al/V molar ratio) in the presence of Et_2AlCl cocatalyst increased in the order (in toluene, ethylene 8 atm, 0 °C, 10 min): 9420 kg-PE/mol-V·h (**5c**) < 13 200 (**2a**) < 26 700 (**2d**) < 29 000 (**2c**) < 32 000 (**2b**). The catalytic activity of the arylimido derivatives (**2a**−**d**) was higher than the adamantylimido analogue (**5c**), in agreement with the findings found for the imidazolin-2-iminato catalyst systems. The arylimido complexes with aryl substituents in 1,3-positions of the imidazolidin-2-iminato ligand (*N*-heterocycle **2b**,**c**) showed higher activity than the *tert*-butyl analogue (**2a**), suggesting again that the electronic nature of the substituent affects the activity. The observed trend was similar to that described above for ethylene polymerization using the imidazolin-2-iminato (imido)vanadium complexes.

Table 4 summarizes the selected results for ethylene polymerization using the imidazolin-2-iminato (**1a**−**c**,**e**, **3c**, **4c**) and the imidazolidin-2-iminato (**2a**−**d**, **5c**) complexes under the optimized conditions. In both cases, the 2,6-dimethylphenyl (**1b**, **2b**) and the 2,6-diisopropylphenyl analogues (**1c**, **2c**) exhibited higher catalytic activities than the *tert*-butyl analogues (**1a**, **2a**). The low activities displayed by **1a** and **2a** containing *tert*-butyl substituents may be ascribed to the fact that these complexes (**1a**, **2a**) possess rather unique V—N—C bond angles within the arylimido as well as within the anionic ancillary donor ligands. The adamantylimido complexes (**3c**, **5c**) showed low activities, suggesting that an electronic nature of the imido ligand might play a role. Moreover, the imidazolin-2-iminato analogues exhibited higher activities than the imidazolidin-2-iminato analogues in the ethylene polymerization using the (arylimido)vanadium(V) dichloride complexes Et_2AlCl systems.

Figure 4 shows plots of catalytic activity against the chemical shifts (δ in ppm) in the ^{51}V NMR spectra in $CDCl_3$ (at 25 °C). It might be interesting to note that a good relationship between the activity and the chemical shift was observed for the (arylimido)vanadium complexes (**1a**−**c**,**e**, **2a**−**d**, **4c**), this fact might suggest that a certain degree of electron donation through the imidazolin-2-iminato or imidazolidin-2-iminato ligands plays a role toward the catalytic activity. One simple assumption that one might take into consideration for an explanation based on the results reported for the half-metallocenes such as Cp′Ti(OMe)$_3$ in the syndiospecific styrene polymerization[19] or Cp′$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) in ethylene polymerization[20] could be that a stabilization of the

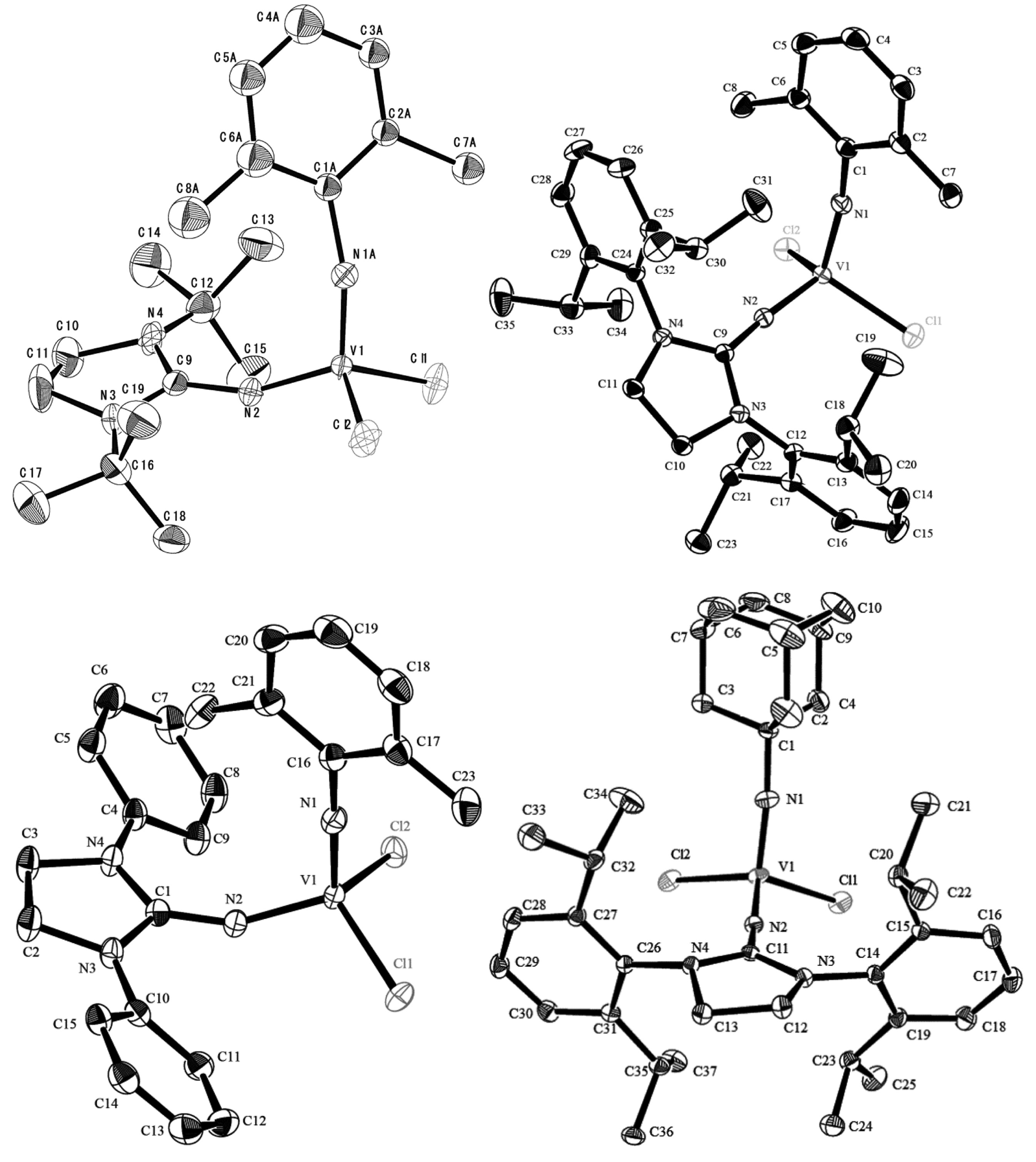


Figure 2. ORTEP drawings for V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-${}^tBu_2(CH_2N)_2C{=}N$] (**2a**, top left), V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-(2,6-${}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N$] (**2c**, top right), V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-$Ph_2(CH_2N)_2C{=}N$] (**2d**, bottom left), and V(NAd)Cl_2[1,3-(2,6-${}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N$] (**5c**, bottom right). Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity. Details are given in the Supporting Information.[17]

active site by more electron-donating substituents is important for the observation of high activity.[21]

3. Copolymerization of Ethylene with Norbornene (NBE) Using (Imido)vanadium(V) Dichloride Complexes Containing Imidazolin-2-iminato and Imidazolidin-2-iminato Ligands in the Presence of Al Cocatalysts. Table 5 summarizes the results for the copolymerization of ethylene with norbornene (NBE) using the imidazolin-2-iminato derivatives, V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-$R_2(CHN)_2$-C=N] [R = ^{t}Bu (**1a**), 2,6-$Me_2C_6H_3$ (**1b**), 2,6-${}^iPr_2C_6H_3$ (**1c**), 2,6-$(Ph_2CH)_2$-4-MeC_6H_2 (**1e**)] or V(NR′)Cl_2[1,3-(2,6-${}^iPr_2C_6H_3)_2(CHN)_2C{=}N$] [R′ = 1-adamantyl (**3c**), C_6H_5 (**4c**)], in the presence of Al cocatalysts (in toluene, ethylene 8 atm, 10 min).[22]

Table 1. Selected Bond Distances and Angles for V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-R_2(CHN)$_2$C=N] [R = ^{t}Bu (1a), 2,6-^{i}$Pr_2C_6H_3$ (1c)], V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-R_2(CH_2N)$_2$C=N] [R = 2,6-^{i}$Pr_2C_6H_3$ (2c), C_6H_5 (2d)], V(NR′)Cl_2[1,3-(2,6-^{i}$Pr_2C_6H_3$)$_2$(CHN)$_2$C=N] [R′ = 1-adamantyl (Ad, 3c), C_6H_5 (4c)], and V(NAd)Cl_2[1,3-(2,6-^{i}$Pr_2C_6H_3$)$_2$(CH_2N)$_2$C=N] (5c)[a]

	1c[b]	2c	3c	4c	5c	1a	2a	2d
V(1)—Cl(1)	2.2314(4)	2.2378(4)	2.2386(7)	2.2342(9)	2.2427(10)	2.2514(7)	2.236(3)	2.2354(3)
V(1)—Cl(2)	2.2251(6)	2.2262(4)	2.2375(7)	2.2120(10)	2. 2368(10)	2.2462(8)	2.248(3)	2.2222(4)
V(1)—N(1)	1.6684(13)	1.6635(12)	1.638(2)	1.664(3)	1.645(3)	1.6689(15)	1.620(13)	1.6578(14)
V(1)—N(2)	1.7308(11)	1.7383(13)	1.7466(18)	1.728(2)	1.749(2)	1.7256(15)	1.736(5)	1.7538(13)
Cl(1)—V(1)—Cl(2)	111.45(2)	113.006(15)	112.66(3)	112.66(4)	111.23(4)	113.00(3)	111.71(9)	113.164(15)
Cl(1)—V(1)—N(1)	107.21(4)	106.80(5)	106.53(7)	103.84(8)	107.01(11)	107.15(6)	109.6(5)	107.25(4)
Cl(1)—V(1)—N(2)	110.17(4)	106.80(4)	111.43(6)	109.61(7)	110.85(8)	109.62(5)	108.90(17)	110.64(3)
Cl(2)—V(1)—N(1)	105.45(5)	106.14(5)	102.69(7)	107.51(8)	105.09(10)	107.20(6)	103.8(5)	106.39(4)
Cl(2)—V(1)—N(2)	109.62(4)	111.97(4)	110.03(6)	110.57(7)	111.12(9)	108.15(6)	109.49(13)	110.00(4)
N(1)—V(1)—N(2)	112.87(5)	112.10(6)	113.20(9)	112.51(10)	111.32(12)	111.74(7)	113.4(5)	109.21(6)
V(1)—N(1)—C(1)imido	171.18(10) V(1)—N(1)—C(16)	167.96(11)	171.14(17)	171.25(18)	174.5(2)	163.45(13)	157.3(11)	179.20(11) V(1)—N(1)—C(16)
V(1)—N(2)—C(imine)	163.92(10) V(1)—N(2)—C(1)	174.79(11) V(1)—N(2)—C(9)	158.07(15) V(1)—N(2)—C(11)	164.58(18) V(1)—N(2)—C(7)	169.5(2) V(1)—N(2)—C(11)	164.42(12) V(1)—N(2)—C(9)	157.9(4) V(1)—N(2)—C(9)	150.06(12) V(1)—N(2)—C(1)

[a] Detailed structural data are given in the Supporting Information.[17] [b] Cited from reference 12n.

Table 2. Ethylene Polymerization by V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-R_2(CHN)$_2$C=N] [R = ^{t}Bu (1a), 2,6-$Me_2C_6H_3$ (1b), 2,6-^{i}$Pr_2C_6H_3$ (1c), 2,6-(Ph_2CH)$_2$-4-MeC_6H_2 (1e)], V(NR′)Cl_2[1,3-(2,6-^{i}$Pr_2C_6H_3$)$_2$(CHN)$_2$C=N] [R′ = 1-adamantyl (Ad, 3c), C_6H_5 (4c)] Cocatalyst Systems[a]

complex (μmol)	Al cocatalyst	Al/V[b]	temperature (°C)	yield (mg)	activity[c]
1a (0.04)	Et_2AlCl	500	0	23	3450
1a (0.04)	Et_2AlCl	1000	0	42	6300
1a (0.04)	Et_2AlCl	1500	0	33	4950
1b (0.04)	Et_2AlCl	500	0	67	10100
1b (0.04)	Et_2AlCl	1000	0	150	22500
1b(0.04)	Et_2AlCl	1500	0	182	27300
1b (0.04)	Et_2AlCl	2000	0	255	38300
1b (0.04)	Et_2AlCl	2500	0	116	17400
1b (0.04)	Et_2AlCl	2000	25	51	7650
1b (2.0)	MAO	500	25	142	426
1b (2.0)	MAO	1000	25	169	507
1c (0.04)	Et_2AlCl	200	0	62	9300
1c (0.04)	Et_2AlCl	500	0	231	34700
1c (0.04)	Et_2AlCl	1000	0	126	18900
1c (0.04)	Et_2AlCl	1500	0	62	9300
1e (0.04)	Et_2AlCl	100	0	trace	
1e (0.04)	Et_2AlCl	200	0	178	26700
1e (0.04)	Et_2AlCl	500	0	159	23900
1e (0.04)	Et_2AlCl	1000	0	102	15300
1e (0.02)	Et_2AlCl	500	0	111	33300
3c (0.10)	Et_2AlCl	500	0	120	7200
3c (0.10)	Et_2AlCl	1000	0	131	7860
3c (0.10)	Et_2AlCl	1500	0	137	8220
3c (0.10)	Et_2AlCl	2000	0	122	7320
4c (0.04)	Et_2AlCl	250	0	48	7200
4c (0.04)	Et_2AlCl	500	0	286	42900
4c (0.04)	Et_2AlCl	1000	0	205	30800
4c (0.04)	Et_2AlCl	1500	0	171	25600
4c (0.04)	Et_2AlCl	2000	0	118	17700

[a] Conditions: toluene 30 mL, ethylene 8 atm, 10 min, Et_2AlCl or d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO). [b] Molar ratio of Al/V. [c] Activity in kg-PE/mol-V·h.

Although the activities observed for **1a–c** were lower than those found in ethylene homopolymerization, the copolymerization proceeded with moderate catalytic activities, affording ultrahigh molecular weight polymers with uniform molecular weight distributions (runs 1–14). The activities of the 2,6-dimethylphenylimido analogues (**1a–c**) Et_2AlCl catalyst systems under the same conditions (ethylene 8 atm, NBE 0.50 mmol/mL, under optimized A/V molar ratio) increased in the order: **1a** (102 kg-polymer/mol-V·h) < **1b** (1920) < **1c** (4830). The activity of the **1c** Et_2AlCl catalyst system decreased upon increasing the NBE concentrations (0.50 M → 0.90M), and the activity also decreased upon increasing the polymerization temperature (run 9 vs run 6). In contrast, the activity in the presence of MAO cocatalyst increased at 25 °C (runs 11–12), although these values were low even under the optimized conditions.

The activity in the copolymerization by V(NR′)Cl_2[1,3-(2,6-^{i}$Pr_2C_6H_3$)$_2$(CHN)$_2$C=N] [R′ = 2,6-$Me_2C_6H_3$ (**1c**), 1-adamantyl (**3c**), C_6H_5 (**4c**)] Et_2AlCl catalyst systems under optimized Al/V molar ratios (ethylene 8 atm, NBE 0.50 mmol/mL) increased in the order: **3c** (R′ = Ad, activity =2850 kg-polymer/mol-V·h, run 16) < **1c** (R′ = 2,6-$Me_2C_6H_3$, 4830, run 6) < **4c** (R′ = Ph, 7080, run 24). The same order was observed, when these

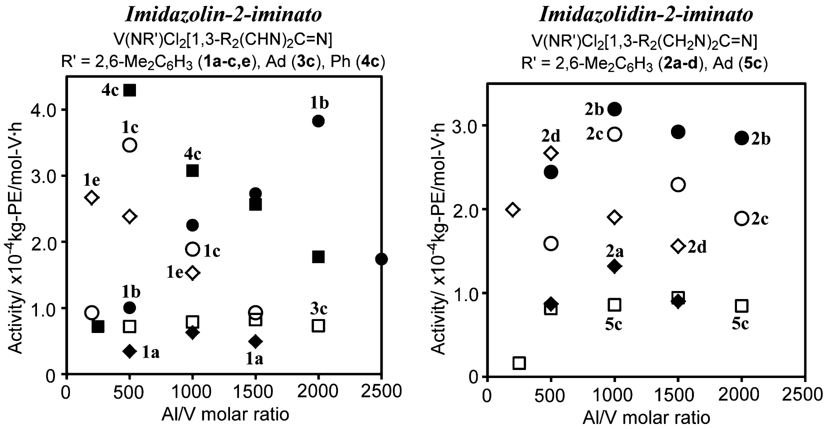


Figure 3. Plots of catalytic activity (kg-PE/mol-V·h) vs Al/V molar ratios in ethylene polymerization using (imido)vanadium complexes containing imidazolin-2-iminato and imidazolidin-2-iminato ligands (on the basis of data in Tables 2 and 3). Left: complexes **1a** (◆), **1b** (●), **1c** (○), **1e** (◇), **3c** (□), and **4c** (■). Right: complexes **2a** (◆), **2b** (●), **2c** (○), **2d** (◇), and **5c** (□). V(NR′)Cl$_2$[1,3-R$_2$(CHN)$_2$C=N] [R′ = 2,6-Me$_2$C$_6$H$_3$ (**1a**,**c**,**e**), Ad (**3c**), Ph (**4c**), shown left]; V(NR′)Cl$_2$[1,3-R$_2$(CH$_2$N)$_2$C=N] [R′ = 2,6-Me$_2$C$_6$H$_3$ (**2a**-**d**), Ad (**5c**), shown right]; R = ^{t}Bu (**a**), 2,6-Me$_2$C$_6$H$_3$ (**b**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**c**), 2,6-Ph$_2$C$_6$H$_3$ (**d**), 2,6-(Ph$_2$CH)$_2$-4-MeC$_6$H$_2$ (**e**).

Table 3. Ethylene Polymerization by V(N-2,6-Me$_2$C$_6$H$_3$)Cl$_2$[1,3-R$_2$(CH$_2$N)$_2$C=N] [R = ^{t}Bu (2a), 2,6-Me$_2$C$_6$H$_3$ (2b), 2,6-^{i}Pr$_2$C$_6$H$_3$ (2c), C$_6$H$_5$ (2d)], and V(NAd)Cl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CH$_2$N)$_2$C=N] (5c) Cocatalyst Systems[a]

complex (μmol)	Al cocatalyst	Al/V[b]	temperature (°C)	yield (mg)	activity[c]
2a (0.04)	Et$_2$AlCl	500	0	58	8700
2a (0.04)	Et$_2$AlCl	1000	0	88	13200
2a (0.04)	Et$_2$AlCl	1500	0	60	9000
2b (0.04)	Et$_2$AlCl	500	0	163	24500
2b (0.04)	Et$_2$AlCl	1000	0	213	32000
2b (0.04)	Et$_2$AlCl	1500	0	195	29300
2b (0.04)	Et$_2$AlCl	2000	0	190	28500
2b (0.04)	Et$_2$AlCl	1000	25	40	6000
2b (2.0)	MAO	500	25	167	501
2b (2.0)	MAO	1000	25	209	627
2c (0.04)	Et$_2$AlCl	500	0	106	15900
2c (0.04)	Et$_2$AlCl	1000	0	193	29000
2c (0.04)	Et$_2$AlCl	1500	0	153	23000
2c (0.04)	Et$_2$AlCl	2000	0	126	18900
2c (2.0)	MAO	1000	25	151	453
2d (0.04)	Et$_2$AlCl	200	0	133	20000
2d (0.04)	Et$_2$AlCl	500	0	178	26700
2d (0.04)	Et$_2$AlCl	1000	0	127	19100
2d (0.04)	Et$_2$AlCl	1500	0	104	15600
5c (0.10)	Et$_2$AlCl	250	0	27	1620
5c (0.10)	Et$_2$AlCl	500	0	136	8160
5c (0.10)	Et$_2$AlCl	1000	0	143	8580
5c (0.10)	Et$_2$AlCl	1500	0	157	9420
5c (0.10)	Et$_2$AlCl	2000	0	141	8460

[a] Conditions: toluene 30 mL, ethylene 8 atm, 10 min, Et$_2$AlCl or d-MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO). [b] Molar ratio of Al/V. [c] Activity in kg-PE/mol-V·h.

Table 4. Selected Data for Ethylene Polymerization by V(N-2,6-Me$_2$C$_6$H$_3$)Cl$_2$[1,3-R$_2$(CHN)$_2$C=N] [R = ^{t}Bu (1a), 2,6-Me$_2$C$_6$H$_3$ (1b), 2,6-^{i}Pr$_2$C$_6$H$_3$ (1c), 2,6-(Ph$_2$CH)$_2$-4-MeC$_6$H$_2$ (1e)], V(N-2,6-Me$_2$C$_6$H$_3$)Cl$_2$[1,3-R$_2$(CH$_2$N)$_2$C=N] [R = ^{t}Bu (2a), 2,6-Me$_2$C$_6$H$_3$ (2b), 2,6-^{i}Pr$_2$C$_6$H$_3$ (2c), C$_6$H$_5$ (2d)], V(NR′)Cl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N] [R′ = Ad (3c), C$_6$H$_5$ (4c)], V(NAd)Cl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CH$_2$N)$_2$C=N] (5c) Et$_2$AlCl Catalyst Systems[a]

R′; R	complex (μmol)	Al cocatalyst	Al/V[b]	activity[c]	δ (ppm) ^{51}V NMR[d]
	imidazolin-2-iminato				
2,6-Me$_2$C$_6$H$_3$; ^{t}Bu	**1a** (0.04)	Et$_2$AlCl	1000	6300	−85
2,6-Me$_2$C$_6$H$_3$; 2,6-Me$_2$C$_6$H$_3$	**1b** (0.04)	Et$_2$AlCl	2000	38300	−148
2,6-Me$_2$C$_6$H$_3$; 2,6-^{i}Pr$_2$C$_6$H$_3$	**1c** (0.04)	Et$_2$AlCl	500	34700	−147
2,6-Me$_2$C$_6$H$_3$; 2,6-(Ph$_2$CH)$_2$-4-MeC$_6$H$_2$	**1e** (0.04)	Et$_2$AlCl	200	26700	−107
1-adamantyl (Ad); 2,6-^{i}Pr$_2$C$_6$H$_3$	**3c** (0.10)	Et$_2$AlCl	1500	8220	−257
C$_6$H$_5$; 2,6-^{i}Pr$_2$C$_6$H$_3$	**4c** (0.04)	Et$_2$AlCl	500	42900	−180
	imidazolidin-2-iminato				
2,6-Me$_2$C$_6$H$_3$; ^{t}Bu	**2a** (0.04)	Et$_2$AlCl	1000	13200	−77
2,6-Me$_2$C$_6$H$_3$; 2,6-Me$_2$C$_6$H$_3$	**2b** (0.04)	Et$_2$AlCl	1000	32000	−158
2,6-Me$_2$C$_6$H$_3$; 2,6-^{i}Pr$_2$C$_6$H$_3$	**2c** (0.04)	Et$_2$AlCl	1000	29000	−140
2,6-Me$_2$C$_6$H$_3$; 2,6-C$_6$H$_5$	**2d** (0.04)	Et$_2$AlCl	500	26700	−99
1-adamantyl (Ad); 2,6-^{i}Pr$_2$C$_6$H$_3$	**5c** (0.10)	Et$_2$AlCl	1500	9420	−251

[a] Conditions: toluene 30 mL, ethylene 8 atm, 0 °C, 10 min, Et$_2$AlCl cocatalyst. [b] Molar ratio of Al/V. [c] Activity in kg-PE/mol-V·h. [d] In CDCl$_3$ at 25 °C.

copolymerizations were conducted at rather higher NBE concentrations (0.50 M → 0.90M), although the activities of **3c** (run 19) and **4c** (run 27) became low as observed for **1c** (run 10). The resulting polymers were poly(ethylene-*co*-NBE)s with ultrahigh molecular weights with uniform molecular weight distributions. These results suggest that the copolymerization proceeded with uniform catalytically active species.

The NBE contents in the resulting copolymers prepared by **1c**, **3c**, and **4c** Et$_2$AlCl catalyst systems increased upon increasing the NBE concentration from 0.50 to 0.90 M [**1c**, 15.3 mol % (run 6) → 23.2 mol % (run 10); **3c**, 14.9 mol % (run 16) → 19.4 mol % (run 19); **4c**, 14.5 mol % (run 24) → 21.9 mol % (run 27)]. Significant differences were not observed in terms of NBE incorporation by **1c**, **3c**, and **4c** under these

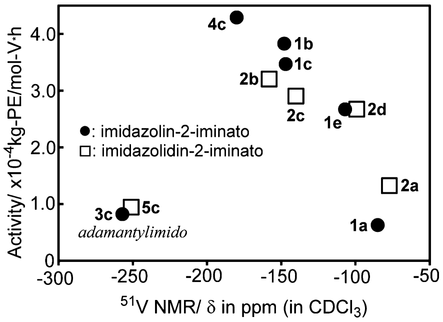


Figure 4. Plots of catalytic activity (kg-PE/mol-V·h) vs chemical shifts (*δ* in ppm) of the vanadium complexes (based on data in Table 4).

conditions, although, as described above, the activities were affected by the nature of the imido ligand employed. Moreover, it is interesting to note that the NBE contents (in the copolymers by **1c**, **3c**, **4c** Et_2AlCl catalyst systems) did not increase upon further increasing of the NBE concentration (0.90 M → 2.50M), although the observed activities became low under high NBE concentration conditions. It might also be interesting to note that the NBE content in the resulting copolymers was not affected by the Al cocatalyst employed (Et_2AlCl, d-MAO, Me_2AlCl), despite a rather strong impact Al cocatalyst on the activities. The observed facts are in interesting contrast to what had been observed for the copolymerization using V(N-2,6-$Me_2C_6H_3$)Cl_2(O-2,6-$Me_2C_6H_3$) Al cocatalyst systems in which both the activity and the NBE incorporations were affected by the Al cocatalyst and the solvent employed.[6c,d]

Table 6 summarizes the results of the copolymerization of ethylene with norbornene (NBE) using the imidazolidin-2-iminato derivatives, V(NR′)Cl_2[1,3-(2,6-^{i}$Pr_2C_6H_3$)$_2$(CH_2N)$_2$C═N] [R′ = 2,6-$Me_2C_6H_3$ (**2c**), 1-adamantyl (Ad, **5c**)], in the presence of Al cocatalysts (in toluene, 10 min).[22]

The activities of the arylimido complex **2c** were generally higher than those of its adamantylimido congener **5c**, and the activities decreased upon increasing the NBE concentration charged: the activities were low when these copolymerizations were conducted at 60 °C (runs 35, 43), probably because of deactivation of the catalytically active species. The resulting polymers were poly(ethylene-*co*-NBE)s possessing ultrahigh molecular weights with uniform molecular weight distributions. These results also suggest that the copolymerizations proceed with uniform catalytically active species. The NBE contents in the resultant copolymers prepared by **2c**, **5c** Et_2AlCl catalyst systems increased upon increasing the NBE concentration from 0.50 to 0.90 M, but the NBE contents did not increase upon further increase of the NBE concentration (0.90 → 2.50 M),

Table 5. Copolymerization of Ethylene with Norbornene (NBE) by V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-R_2(CHN)$_2$C═N] [R = ^{t}Bu (1a), 2,6-$Me_2C_6H_3$ (1b), 2,6-^{i}$Pr_2C_6H_3$ (1c), 2,6-(Ph_2CH)$_2$-4-MeC_6H_2 (1e)], V(NR′)Cl_2[1,3-(2,6-^{i}$Pr_2C_6H_3$)$_2$(CHN)$_2$C═N] [R′ = 1-adamantyl (Ad, 3c), C_6H_5 (4c)] Cocatalyst Systems[a]

run	complex(μmol)	Al cocatalyst	Al/V[b]	NBE (mol/L)[c]	temperature (°C)	yield (mg)	activity[d]	$M_n \times 10^{-5}$[e]	M_w/M_n[e]	NBE (mol %)[f]
1	**1a** (2.0)	Et_2AlCl	500	0.50	0	34	102	18.1	1.8	16.5
2	**1a** (2.0)	Et_2AlCl	1000	0.50	0	14	42	19.5	2.2	
3	**1b** (0.2)	Et_2AlCl	500	0.50	0	64	1920	27.1	1.7	13.4
4	**1b** (0.2)	Et_2AlCl	1000	0.50	0	36	1080	25.8	2.0	
5	**1c** (0.2)	Et_2AlCl	250	0.50	0	20	600	23.1	2.1	
6	**1c** (0.2)	Et_2AlCl	500	0.50	0	161	4830	22.5	1.9	15.3
7	**1c** (0.2)	Et_2AlCl	1000	0.50	0	72	2160	19.4	1.8	14.8
8	**1c** (0.2)	Et_2AlCl	1500	0.50	0	68	2040	16.7	2.3	
9	**1c** (0.4)	Et_2AlCl	500	0.50	25	48	720	17.2	2.4	
10	**1c** (0.2)	Et_2AlCl	500	0.90	0	75	2250	18.5	2.4	23.2
11	**1c** (2.0)	d-MAO	500	0.90	25	43	129	10.4	1.7	34.1
12	**1c** (2.0)	d-MAO	1000	0.90	0	31	93	16.2	1.9	26.1
13[g]	**1c** (1.2)	Et_2AlCl	500	2.50	0	53	265	10.1	2.0	24.5
14[g]	**1c** (1.2)	Me_2AlCl	500	2.50	0	61	305	9.6	2.3	26.3
15	**3c** (0.2)	Et_2AlCl	250	0.50	0	27	810	17.1	2.3	
16	**3c** (0.2)	Et_2AlCl	500	0.50	0	95	2850	16.5	2.6	14.9
17	**3c** (0.2)	Et_2AlCl	1000	0.50	0	78	2340	13.8	2.5	
18	**3c** (0.2)	Et_2AlCl	500	0.50	25	37	1100	12.4	2.8	
19	**3c** (0.2)	Et_2AlCl	500	0.90	0	57	1710	10.7	2.1	19.4
20	**3c** (0.2)	Me_2AlCl	500	0.90	0	120	3600	12.2	2.3	20.8
21[g]	**3c** (1.2)	Et_2AlCl	500	2.50	0	32	160	4.8	2.5	26.2
22	**4c**(0.2)	Et_2AlCl	250	0.50	0	59	1770	19.8	1.8	14.2
23	**4c**(0.2)	Et_2AlCl	500	0.50	0	217	6510	19.1	2.1	
24	**4c**(0.1)	Et_2AlCl	500	0.50	0	118	7080	18.8	2.4	14.5
25	**4c**(0.2)	Et_2AlCl	1000	0.50	0	164	4920	16.9	2.0	
26	**4c**(0.2)	Et_2AlCl	1500	0.50	0	132	3960	13.3	2.5	
27	**4c**(0.2)	Et_2AlCl	500	0.90	0	157	4710	12.8	2.1	21.9
28[g]	**4c**(1.2)	Et_2AlCl	500	2.50	0	84	420	7.8	2.2	24.8
29[g]	**4c**(1.2)	Me_2AlCl	500	2.50	0	97	485	6.4	2.5	25.2

[a] Conditions: toluene 30 mL, ethylene 8 atm, 10 min, Et_2AlCl, Me_2AlCl or d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO) cocatalyst. [b] Molar ratio of Al/V. [c] Norbornene (NBE) concentration charged (mol/L). [d] Activity in kg-polymer/mol-V·h. [e] GPC data in *o*-dichlorobenzene vs polystyrene standards. [f] Comonomer content estimated by ^{13}C NMR spectra. [g] Toluene 10 mL.

Table 6. Copolymerization of Ethylene with Norbornene (NBE) by $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}R_2(CH_2N)_2C{=}N]$ [R = ^{t}Bu (2a), $2,6\text{-}Me_2C_6H_3$ (2b), $2,6\text{-}{}^iPr_2C_6H_3$ (2c), C_6H_5 (2d)] and $V(NAd)Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N]$ (5c) Cocatalyst Systems[a]

run	complex (μmol)	Al cocatalyst	Al/V[b]	NBE (mol/L)[c]	temperature (°C)	ethylene (atm)	yield (mg)	activity[d]	$M_n \times 10^{-5e}$	M_w/M_n[e]	NBE (mol %)[f]
30	**2c** (0.2)	Et_2AlCl	125	0.50	0	8	98	2940	25.1	1.8	
31	**2c** (0.2)	Et_2AlCl	250	0.50	0	8	173	5190	24.4	1.9	
32	**2c** (0.2)	Et_2AlCl	500	0.50	0	8	157	4710	23.9	2.1	11.3
33	**2c** (0.2)	Et_2AlCl	1000	0.50	0	8	112	3360	19.8	2.0	
34	**2c** (0.2)	Et_2AlCl	250	0.90	0	8	102	3060	17.5	2.4	24.0
35	**2c** (1.2)	Et_2AlCl	250	0.90	60	8	10	50	11.4	3.5	
36[g]	**2c** (0.2)	Et_2AlCl	250	2.50	0	8	29	870	10.2	2.6	26.1
37[g]	**2c** (0.2)	Me_2AlCl	250	2.50	0	8	59	1770	11.8	2.4	27.0
38[g]	**2c** (1.2)	Me_2AlCl	250	2.50	0	4	53	265	7.6	2.3	32.8
39	**5c** (0.2)	Et_2AlCl	250	0.50	0	8	74	2220	17.4	1.9	
40	**5c** (0.2)	Et_2AlCl	500	0.50	0	8	115	3450	15.9	2.0	10.0
41	**5c** (0.2)	Et_2AlCl	1000	0.50	0	8	96	2880	13.7	2.3	11.3
42	**5c** (0.2)	Et_2AlCl	500	0.90	0	8	64	1920	9.6	2.5	17.7
43	**5c** (1.2)	Et_2AlCl	500	0.90	60	8	29	145	5.4	2.7	
44[g]	**5c** (1.2)	Et_2AlCl	500	2.50	0	8	44	220	5.7	2.4	23.1
45[g]	**5c** (1.2)	Me_2AlCl	500	2.50	0	8	69	345	6.1	2.2	24.7
46[g]	**5c** (2.0)	Me_2AlCl	500	2.50	0	4	63	189	2.8	2.6	29.6
47[g]	**5c** (2).0	Me_2AlCl	500	2.50	0	2	27	81	1.3	3.2	37.3

[a] Conditions: toluene 30 mL, 10 min. [b] Molar ratio of Al/V. [c] Norbornene concentration charged (mol/L). [d] Activity in kg-polymer/mol-V·h. [e] GPC data in *o*-dichlorobenzene vs polystyrene standards. [f] Comonomer content estimated by ^{13}C NMR spectra. [g] Toluene 10 mL.

Table 7. Selected Data for Copolymerization of Ethylene with Norbornene (NBE) by $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}R_2(CHN)_2C{=}N]$ [R = ^{t}Bu (1a), $2,6\text{-}Me_2C_6H_3$ (1b), $2,6\text{-}{}^iPr_2C_6H_3$ (1c)], $V(NR')Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)_2(CHN)_2C{=}N]$ [R′ = Ad (3c), C_6H_5 (4c)], $V(NR')Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N]$ [R′ = $2,6\text{-}Me_2C_6H_3$ (2c), Ad (5c)] Et_2AlCl Catalyst Systems[a]

run	complex $V(NR')Cl_2(L)$			Al/V[b]	NBE (mol/L)[c]	activity[d]	$M_n \times 10^{-5e}$	M_w/M_n[e]	NBE (mol %)[f]
	R′	R	(μmol)						
1	$2,6\text{-}Me_2C_6H_3$	^{t}Bu	**1a** (2.0)	500	0.50	102	18.1	1.8	16.5
3	$2,6\text{-}Me_2C_6H_3$	$2,6\text{-}Me_2C_6H_3$	**1b** (0.2)	500	0.50	1920	27.1	1.7	13.4
6	$2,6\text{-}Me_2C_6H_3$	$2,6\text{-}{}^iPr_2C_6H_3$	**1c** (0.2)	500	0.50	4830	22.5	1.9	15.3
31	$2,6\text{-}Me_2C_6H_3$	$2,6\text{-}{}^iPr_2C_6H_3$	**2c** (0.2)	250	0.50	5190	24.4	1.9	
16	1-adamantyl	$2,6\text{-}{}^iPr_2C_6H_3$	**3c** (0.2)	500	0.50	2850	16.5	2.6	14.9
24	C_6H_5	$2,6\text{-}{}^iPr_2C_6H_3$	**4c** (0.1)	500	0.50	7080	18.8	2.4	14.5
40	1-adamantyl	$2,6\text{-}{}^iPr_2C_6H_3$	**5c** (0.2)	500	0.50	3450	15.9	2.0	10.0
10	$2,6\text{-}Me_2C_6H_3$	$2,6\text{-}{}^iPr_2C_6H_3$	**1c** (0.2)	500	0.90	2250	18.5	2.4	23.2
34	$2,6\text{-}Me_2C_6H_3$	$2,6\text{-}{}^iPr_2C_6H_3$	**2c** (0.2)	250	0.90	3060	17.5	2.4	24.0
19	1-adamantyl	$2,6\text{-}{}^iPr_2C_6H_3$	**3c** (0.2)	500	0.90	1710	10.7	2.1	19.4
27	C_6H_5	$2,6\text{-}{}^iPr_2C_6H_3$	**4c** (0.2)	500	0.90	4710	12.8	2.1	21.9
42	1-adamantyl	$2,6\text{-}{}^iPr_2C_6H_3$	**5c** (0.2)	500	0.90	1920	9.6	2.5	17.7

[a] Conditions: toluene 30 mL, ethylene 8 atm, 10 min, 0 °C, Et_2AlCl cocatalyst. [b] Molar ratio of Al/V. [c] Norbornene (NBE) concentration charged (mol/L). [d] Activity in kg-polymer/mol-V·h. [e] GPC data in *o*-dichlorobenzene vs polystyrene standards. [f] Estimated by ^{13}C NMR spectra.

although the activities decreased under high NBE concentrations. Significant differences were not observed in terms of NBE incorporation by **2c** and **5c** under these conditions, although, as described above, the activities were affected by the nature of the imido ligand. It might also be interesting to note that the NBE content in the resulting copolymers was not affected by the Al cocatalyst employed (Et_2AlCl, Me_2AlCl), although the activities were indeed.

It is interesting to note that the NBE contents in the resulting copolymer increased upon conducting these copolymerizations at low ethylene pressure (ethylene 2 or 4 atm, runs 38, 46, 47), although the NBE contents did not exceeded values of ca. 25−27 mol % if these copolymerizations were conducted even under high NBE concentration (ethylene 8 atm). It is an interesting observation that the NBE content in the copolymer can be increased to rather high values by varying the ethylene pressure (and the reaction temperature for the **1c** Et_2AlCl catalyst system).

Table 7 summarizes the selected results for the copolymerization using the imidazolin-2-iminato and the imidazolidin-2-iminato analogues employed in this study for comparison. It is clear that the activities were affected by the imido ligand employed. The activity was also affected by the substituents present in the imidazolin-2-iminato ligands (see **1a**−**c**). No significant differences were observed between the imidazolin-2-iminato and imidazolidin-2-iminato precatalysts in terms of both activity and NBE incorporation. Moreover, no significant ligand effects were observed with respect to the NBE content in the copolymers, although it seems justified to state that the adamantylimido complexes (**3c**, **5c**) showed rather less efficient

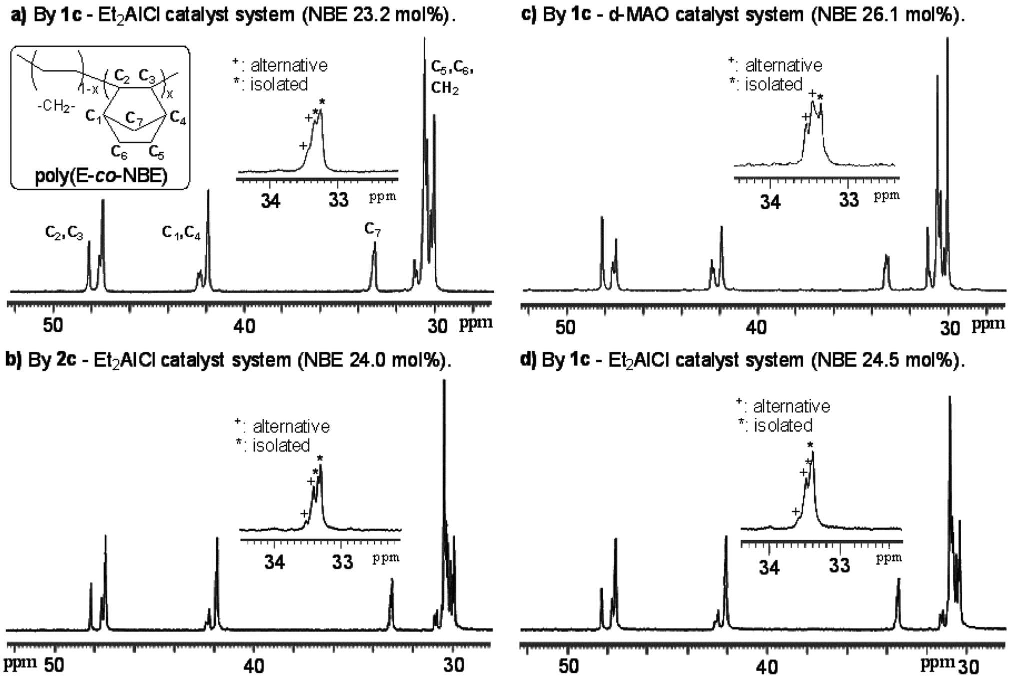


Figure 5. ^{13}C NMR spectra (in 1,2,4-trichlorobenzene/C_6D_6 at 120 °C) for poly(ethylene-*co*-norbornene)s prepared by (a) V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-(2,6-$^{i}Pr_2C_6H_3$)$_2$(CHN)$_2$C=N] (**1c**) Et_2AlCl catalyst system (NBE 0.90 M, run 10), (b) V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-(2,6-$^{i}Pr_2C_6H_3$)$_2$(CH_2N)$_2$C=N] (**2c**) Et_2AlCl catalyst system (NBE 0.90 M, run 34), (c) **1c** d-MAO catalyst system (NBE 0.90 M, run 12), d) **1c** Et_2AlCl catalyst system (NBE 2.50 M, run 13).

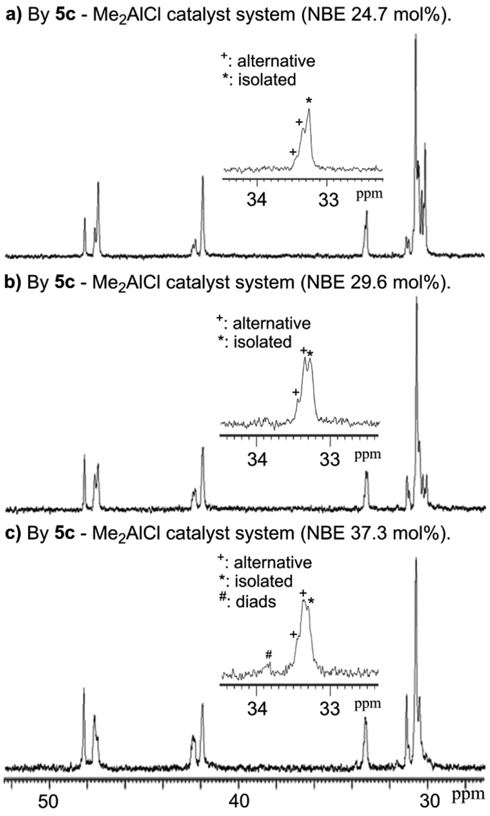


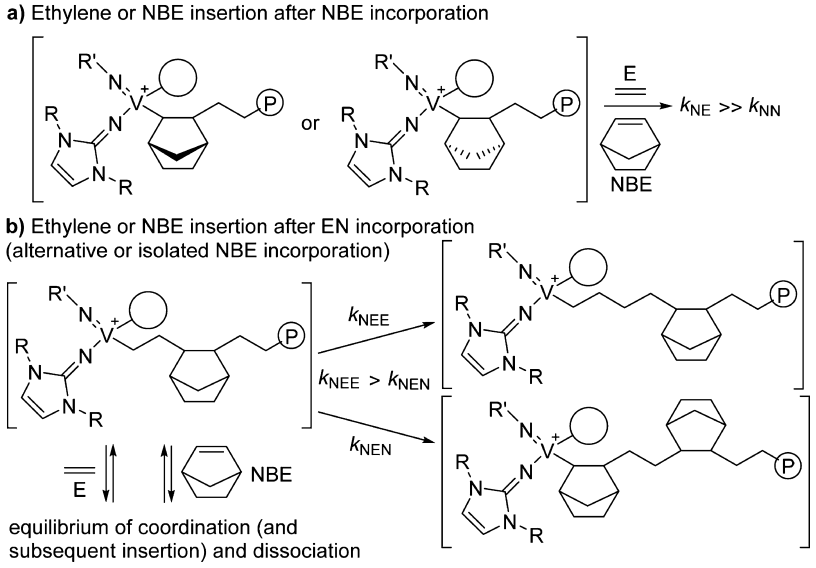
Figure 6. ^{13}C NMR spectra (in 1,2,4-trichlorobenzene/C_6D_6 at 120 °C) for poly(ethylene-*co*-norbornene)s prepared by V(NAd)-Cl_2[1,3-(2,6-$^{i}Pr_2C_6H_3$)$_2$(CH_2N)$_2$C=N] (**5c**) Me_2AlCl catalyst system (a) NBE content 24.7 mol % (NBE 2.50 M, ethylene 8 atm, run 45), (b) NBE content 29.6 mol % (NBE 2.50 M, ethylene 4 atm, run 46), (c) NBE content 37.3 mol % (NBE 2.50 M, ethylene 2 atm, run 47).

NBE incorporation under these conditions (especially under NBE 0.90 M conditions, runs 19, 42).

Figure 5 shows selected ^{13}C NMR spectra in the resultant poly(ethylene-*co*-NBE)s prepared by **1c**, **2c** Al cocatalyst systems.[22] Resonances ascribed to carbon atoms corresponding to isolated and alternating NBE insertions were observed in the spectra in all cases,[22] and integration ratio revealed that the ratio of the peaks corresponding to isolated and alternating NBE units were not changed even under high NBE concentration conditions (Figures 5a,d; NBE 0.90 vs 2.50 M), although the activity decreased remarkably upon increasing the NBE concentration charged (runs 10 vs 13). Moreover, no significant differences were observed in the spectra of the polymers obtained from imidazolin-2-iminato (**1c**) or imidazolidin-2-iminato (**2c**) derivatives. It might be interesting to note that the ratio of peaks corresponding to isolated and alternating NBE units in the copolymer prepared by the **1c** MAO catalyst system was somewhat different from that obtained from the **1c** Et_2AlCl catalyst system conducted under the same conditions, although the NBE content in the resulting copolymers was similar (Figures 5a,c; runs 10, 12). Because the resonances ascribed to NBE repeated insertions were not observed in these NMR spectra,[22] we assume that these spectra might explain why the synthesis of copolymer with high NBE contents is difficult by use of these catalysts.

Figure 6 shows selected ^{13}C NMR spectra of the resulting poly(ethylene-*co*-NBE)s prepared by the **5c** Me_2AlCl catalyst system conducted under high NBE concentrations (NBE 2.50 M), and under various ethylene pressures (ethylene 2−8 atm, runs 45−47).[22] As described above, resonances ascribed to carbon atoms corresponding to isolated and alternating NBE insertions were observed in the spectra,[22] and a small amount of the resonances ascribed to the NBE repeat units was also observed in the copolymer obtained under low ethylene

Scheme 4. Possible Insertion Modes after Norbornene (NBE) or Ethylene Insertion in the Ethylene/NBE Copolymerization[a]



[a] k_{NE} denotes a rate of ethylene insertion after NBE incorporation, and k_{NN} denotes a rate of NBE insertion after NBE incorporation (NBE repeated insertion). k_{NEE} denotes a rate of ethylene insertion (isolated NBE incorporation), and k_{NEN} denotes a rate of NBE insertion (alternative NBE incorporation).

pressure conditions (Figure 6c, ethylene 2 atm, run 47). Although the activity dropped upon decreasing the ethylene pressure (runs 45–47), these results clearly indicate that the NBE contents in the copolymer can be modified even under high NBE concentration conditions by varying the ethylene pressure. This fact is interesting with regard to the observation that the NBE content did not increase even under high NBE concentration conditions, as described above.

On the basis of the above facts that (i) the NBE content as well as the microstructures of the copolymer can be modified by ethylene pressure under high NBE concentration conditions and that (ii) significant changes in the NBE content and the microstructure of the copolymers were not observed when the copolymerizations were conducted under rather high NBE concentration (NBE 0.90–2.50 M) under the same ethylene pressure, we may consider an assumption shown in Scheme 4. There might be equilibrium of coordination and dissociation of two olefins to the metal center, and it seems clear (from the ^{13}C NMR spectra) that repeated NBE incorporation would be difficult (probably) due to a steric bulk. This suggests that the rate of NBE incorporation after NBE insertion (denoted as k_{NN}) should be much smaller than that of ethylene incorporation after NBE insertion (denoted as k_{NE}, Scheme 4a). A decrease in the activity by increasing the NBE concentration (without increase in the NBE content) may be due to a favored NBE coordination without incorporation (formation of certain dormant species that suppress ethylene coordination).[6d,23] Moreover, it may be assumed that the rate of NBE alternating incorporation (NBE incorporation after insertion of NBE followed by ethylene, denoted as k_{NEN}) would be smaller than that of ethylene incorporation after NBE insertion (ethylene incorporation after insertion of NBE followed by ethylene, denoted as k_{NEE}). This fact may also explain that use of the **1c** d-MAO catalyst system (probably forming isolated cationic alkyl species because of the bulky, delocalized MAO anion) showed better NBE incorporation than the **1c** Et_2AlCl catalyst system (formation of associated cationic alkyl species through interaction with halogenated Al alkyls).[5e,6c,d,8b] Based on these facts, it seems likely that the NBE contents as well as the microstructures in the copolymers are controlled by the ethylene concentration charge and, therefore, by the degree of ethylene insertion but not by the [NBE]/[E] molar ratio in the solution under these conditions. Although it seems difficult to obtain copolymers with high NBE contents, the present catalysts are suited for the synthesis of ultrahigh molecular weight copolymers with high catalytic activities; they might also be suited for synthesis of the end-functionalized copolymers in the presence of certain chain transfer reagents.

4. Copolymerization of Ethylene with 5-Ethylidene-2-norbornene (ENB) Using (Imido)vanadium(V) Dichloride Complexes Containing Imidazolin-2-iminato and Imidazolidin-2-iminato Ligands in the Presence of Al Cocatalysts. Table 8 summarizes results in copolymerization of ethylene with 5-ethylidene-2-norbornene (ENB) using $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)(CH_2N)_2C{=}N]$ (**2c**) and $V(NPh)Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2\text{-}(CHN)_2C{=}N]$ (**4c**) cocatalyst systems.[24] Complexes **2c** and **4c** have been chosen because these complexes showed high catalytic activities in the ethylene copolymerization with norbornene (NBE), as shown above. The ENB contents were estimated on the basis of ^{1}H NMR spectra according to the previous reports.[24]

The catalytic activities in the copolymerization with ENB displayed by the **2c** Et_2AlCl catalyst system were higher than those in the copolymerization with NBE [e.g., NBE or ENB 0.50 M: activity 5190 kg-polymer/mol-V·h (NBE, run 31) vs 7620 (ENB, run 50)], although the activity of **4c** was similar in these copolymerizations [e.g., activity 7080 kg-polymer/mol-V·h (NBE, run 24) vs 7020 (ENB, run 60)]. The activity of **2c** decreased upon increasing the ENB concentration (runs 50, 52, 53).

The resulting copolymers possessed uniform molecular weight distributions but rather low molecular weights (M_n = 7000–128 000, M_w/M_n = 2.4–2.8). Interestingly, this is in contrast to the characteristics of the resulting poly(ethylene-*co*-NBE)s obtained under the similar conditions [M_n = 1.02–2.51 × 10^6 (with **2c**), 6.4–19.8 × 10^5 (with **4c**)]. It should be noted that the ENB contents in the resulting copolymers were higher

Table 8. Copolymerization Results of Ethylene with 5-Ethylidene-2-norbornene (ENB) by $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)(CH_2N)_2C{=}N]$ (2c), $V(NPh)Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)_2(CHN)_2C{=}N]$ (4c) Cocatalyst Systems[a]

run	complex (μmol)	Al cocatalyst	Al/V	ENB (mol/L)[b]	yield (mg)	activity[c]	$M_n \times 10^{-3}$[d]	M_w/M_n	ENB (mol %)[e]
48	**2c** (0.1)	Et_2AlCl	500	0.50	98	5880	7.0	2.8	38.7
49	**2c** (0.1)	Et_2AlCl	1000	0.50	110	6600	7.4	2.7	38.2
50	**2c** (0.1)	Et_2AlCl	1500	0.50	127	7620	8.5	2.8	39.7
51	**2c** (0.1)	Et_2AlCl	2000	0.50	123	7380	7.8	2.7	
52	**2c** (0.1)	Et_2AlCl	1500	1.50	93	5580	6.4	2.7	44.6
53	**2c** (0.1)	Et_2AlCl	1500	2.50	58	3480	6.2	2.8	53.5
54	**2c** (1.0)	d-MAO	1000	0.50	56	336	9.2	2.5	18.3
55	**2c** (1.0)	d-MAO	1500	0.50	68	408	10.1	2.6	19.5
56	**2c** (1.0)	d-MAO	2000	0.50	64	384	9.6	2.5	
57	**4c** (0.1)	Et_2AlCl	500	0.50	86	5160	9.4	2.5	36.5
58	**4c** (0.1)	Et_2AlCl	1000	0.50	95	5700	10.7	2.4	37.1
59	**4c** (0.1)	Et_2AlCl	1500	0.50	115	6900	12.8	2.5	35.9
60	**4c** (0.1)	Et_2AlCl	2000	0.50	117	7020	11.5	2.7	

[a] Conditions: toluene 30 mL, ethylene 8 atm, 10 min, 0 °C, Et_2AlCl or d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO) cocatalyst. [b] Initial monomer concentration charged (mol/L). [c] Activity in kg-polymer/mol-V·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] Estimated by ^1H NMR spectra.

than the NBE contents under similar comonomer (NBE or ENB) concentration [e.g., by **2c**, NBE 11.3 mol % (run 32) vs ENB 39.7 mol % (run 50); **4c**, NBE 14.5 mol % (run 24) vs ENB 35.9 mol % (run 59); ethylene 8 atm, NBE or ENB 0.50 M]. Moreover, synthesis of the copolymer with ENB content higher than 50 mol % has been attained upon increasing the ENB concentration. This can be regarded as unique contrast between these two types of copolymerizations, although the reasons for the observed difference are not clear at this moment. It might also be interesting to note that the ENB content in the resulting copolymers prepared with the **2c** MAO catalyst system were lower than those prepared with the **2c** Et_2AlCl catalyst system, despite the observation of significant differences in the copolymerization with NBE.

Although the molecular weights of the resulting copolymers were lower than those obtained in the copolymerization with NBE, the observation described above are interesting to the effect that the norbornene substituent does not only affect the catalytic activity but also the comonomer incorporation and the molecular weights of the resulting copolymers.

■ CONCLUSION

We have prepared a series of (imido)vanadium complexes containing imidazolin-2-iminato and imidazolidin-2-iminato ligands and reported their use as catalyst precursors for ethylene polymerization and copolymerization with cyclic olefins. The results of this study can be summarized as follows:

(1) A series of (imido)vanadium(V) dichloride complexes containing 1,3-imidazolin-2-iminato or 1,3-imidazolidin-2-iminato ligands of the type, $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}R_2(CHN)_2C{=}N]$ [R = ^{t}Bu (**1a**), 2,6-$Me_2C_6H_3$ (**1b**), 2,6-$^iPr_2C_6H_3$ (**1c**), 2,6-$(C_6H_5)_2CH$-4-MeC_6H_2 (**1e**)], $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}R_2(CH_2N)_2C{=}N]$ [R = ^{t}Bu (**2a**), 2,6-$Me_2C_6H_3$ (**2b**), 2,6-$^iPr_2C_6H_3$ (**2c**), C_6H_5 (**2d**)], $V(NR')Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)_2(CHN)_2C{=}N]$ [R′ = 1-adamantyl (Ad, **3c**), C_6H_5 (**4c**)], or $V(NAd)Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N]$ (**5c**)] have been prepared and identified. The crystal structures of **1a**, **2a**,**c**,**d**, **3c**, **4c**, and **5c** were determined by X-ray crystallography, revealing in all cases a distorted tetrahedral geometry around the vanadium atom. The *tert*-butyl analogues (**1a**, **2a**) possess rather unique (small) V—N—C bond angles, especially in the arylimido ligands, probably because of a steric reason.

(2) These complexes showed high catalytic activity for ethylene polymerization especially in the presence of Et_2AlCl cocatalyst. Both the 2,6-$Me_2C_6H_3$ (**1b**, **2b**) and the 2,6-$^iPr_2C_6H_3$ (**1c**, **2c**) derivatives showed higher catalytic activities than the ^{t}Bu analogues (**1a**, **2a**): a reason for the low activities displayed by **1a** and **2a** may be tentatively related to rather small V—N—C(imido) bond angles (as described above). Among the (arylimido)vanadium(V) dichloride complexes, the imidazolin-2-iminato analogues exhibited higher activities than their imidazolidin-2-iminato congeners. A relatively good relationship between the activity and the chemical shift [^{51}V NMR spectra in $CDCl_3$ (*δ* in ppm, at 25 °C)] was observed for the (arylimido)vanadium complexes (**1a**−**c**,**e**, **2a**−**d**, **4c**), indicating that a certain degree of electron donation through the anionic ligands play a role toward the high activity probably by a stabilization of the active site by more electron-donating substituents.

(3) The copolymerization of ethylene with norbornene (NBE) proceeded with high catalytic activities, affording ultrahigh molecular weight polymers with uniform molecular weight distributions. The activities of the 2,6-$^iPr_2C_6H_3$ analogues (**1c**) showed higher than those by the others (**1a**,**b**), and the activity of $V(NR')Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)_2(CHN)_2\ C{=}N]$ increased in the order: **3c** (R′ = Ad) < **1c** (R′ = 2,6-$Me_2C_6H_3$) < **4c** (R′ = Ph). No significant differences were observed between the imidazolin-2-iminato and imidazolidin-2-iminato complexes in terms of both activity and NBE incorporation. Although it seems difficult to obtain copolymers with high NBE contents, the present catalysts are promising candidates for the efficient synthesis of ultrahigh molecular weight copolymers with high catalytic activities.

(4) The complexes **2c** and **4c** showed high catalytic activities for the ethylene copolymerization with 5-ethylidene-2-norbornene (ENB) in the presence of Et_2AlCl cocatalyst. Notable improvement in the comonomer (ENB) incorporations can be achieved, although the resulting polymers possessed rather low molecular weights compared to those obtained from the copolymerization with NBE. This constitutes another interesting feature of this type of catalysis.

We are currently exploring the possibility of synthesizing polymers containing reactive functionalities by using comonomers (cyclic olefins) containing reactive functional groups on the basis of the above facts through this study. We highly believe that the results presented herein are highly promising for further design of the catalysts for this purpose, and we hope to be able to introduce more details in the near future.

■ EXPERIMENTAL SECTION

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade toluene, *n*-hexane, and 1,2-dichloromethane (Kanto Chemical Co., Inc.) were transferred into bottles containing molecular sieves (mixture of 3 Å 1/16 and 4 Å 1/8, and 13X 1/16) under a nitrogen stream in the drybox and passed through a short alumina column under N_2 prior to use. Imidazolin-2-iminato ligands, $1,3\text{-}R_2(CHN)_2C{=}N$(R = ^tBu,[9a] $2,6\text{-}^iPr_2C_6H_3$[9b]), and imidazolidin-2-iminato ligands, $1,3\text{-}R_2(CH_2N)_2\ C{=}N$(R = ^tBu,[13b] $2,6\text{-}Me_2C_6H_3$,[13a] $2,6\text{-}^iPr_2C_6H_3$,[16] C_6H_5[13a]), and $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3$,[14] $V(NAd)Cl_3$,[15] $V(NPh)Cl_3$,[8a] $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CHN)_2\ C{=}N]$ (**1c**)[12n] were prepared according to previous reports. 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 at >100 °C for 1 h for completion) in the drybox to give white solids. Et_2AlCl and Me_2AlCl in *n*-hexane (Kanto Chemical Co., Inc.) were used as received under N_2 stream in the drybox. Polymerization grade ethylene (purity >99.9%, Sumitomo Seika Co., Ltd.) was used as received.

Elemental analyses were performed by using EAI CE-440 CHN/O/S Elemental Analyzer (Exeter Analytical, Inc.). All ^1H, ^{13}C, and ^{51}V NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^1H, 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 ppm and are referenced to $SiMe_4$ (δ 0.00 ppm, ^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. Molecular weights and molecular weight distributions for the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mm i.d.), ranging from $<10^2$ to $<2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene amples.

Synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}^tBu_2(CHN)_2\ C{=}N]$ (1a). To a toluene solution containing $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3$ (420 mg, 1.50 mmol) was added $1,3\text{-}^tBu_2(CHN)_2C{=}NSiMe_3$ at −30 °C. The reaction mixture was warmed slowly to room temperature, and was then stirred for 6 h. The solution was filtered 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 volatiles. The resultant solids were dissolved in a minimum amount of toluene and placed in the freezer (cooled at −30 °C). The green crystals were grown from the chilled solution. Yield: 463 mg (1.06 mmol, 71%). ^1H NMR ($CDCl_3$): δ 6.83 (d, 2H, *J* = 7.60, C*H*=), 6.75−6.70 (m, 3H, Ar—*H*), 2.52 (s, 6H, ArC*H*$_3$), 1.62 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 135.3, 126.8, 125.1, 111.7, 59.5, 28.9, 18.8. ^{51}V NMR ($CDCl_3$): δ −85 ($\Delta\nu_{1/2}$ = 862 Hz) Anal. Calcd for $C_{19}H_{29}Cl_2N_4V$: C, 52.42; H, 6.71; N, 12.87. Found: C, 52.58; H, 6.51; N, 12.53.

Synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}(2,6\text{-}Me_2C_6H_3)_2(CHN)_2\ C{=}N]$ (1b). The ligand precursor, $1,3\text{-}(2,6\text{-}Me_2C_6H_3)_2(CHN)_2C{=}NSiMe_3$ was prepared according to the literature procedure.[9a,b] To a toluene solution containing 1,3-bis(2,6-dimethylphenyl)-imidazolin-2-ylidene $[1,3\text{-}(2,6\text{-}Me_2C_6H_2)_2(CHN)_2C]$ (1.0 g, 3.62 mmol), which was prepared from 1,3-bis-(2,6-dimethylphenyl)-1H-imidazol-3-ium chloride[25] by treatment of KO^{t}Bu in THF followed by extraction with hot toluene,[9a,b] was added N_3SiMe_3 (583 mg, 5.07 mmol) in a sealed tube. The mixture was refluxed for 72 h. After the solvent cooled, it was removed under vacuum and the resulting residue was extracted with *n*-hexane. After *n*-hexane was removed, the product was dissolved in a small amount of *n*-hexane (about 1.5 mL). The solution was kept at −30 °C. The brown solid (983 mg, 2.70 mmol) was obtained in 53% yield. ^1H NMR ($CDCl_3$): δ 7.02 (t, 2H, Ar—*H*), 6.96 (d, 4H, Ar—*H*), 5.70 (s, 4H, =C—*H*), 2.20 (s, 12H, C*H*$_3$), −0.11 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 137.6, 137.2, 128.5, 128.4, 112.2, 18.3, 3.3.

The synthetic procedure of **1b** is similar to that for **1a**, except that $1,3\text{-}(2,6\text{-}Me_2C_6H_3)_2(CHN)_2C{=}NSiMe_3$ (545 mg, 1.50 mmol) was used in place of $1,3\text{-}^tBu_2(CHN)_2C{=}NSiMe_3$. Green microcrystals were collected in a yield of 79% (630 mg, 1.19 mmol). ^1H NMR ($CDCl_3$): δ 7.23 (t, 2H, *J* = 7.40, Ar—*H*), 7.06 (d, 4H, *J* = 7.60, Ar—*H*), 6.76−6.71 (m, 5H, C*H* = and Ar—*H*), 2.09 (s, 12H, ArC*H*$_3$), 2.05 (s, 6H, ArC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 135.8, 134.8, 133.2, 130.1, 128.8, 126.9, 125.0, 116.7, 19.1, 17.9. ^{51}V NMR ($CDCl_3$): δ −148 ($\Delta\nu_{1/2}$ = 1038 Hz). Anal. Calcd for $C_{27}H_{29}Cl_2N_4V$: C, 61.03 (58.77 + VC, vanadium carbide); H, 5.50; N, 10.54. Found: C, 60.41; H, 5.68; N, 10.28. The observed C values were somewhat low because of the incomplete combustion (by production of vanadium carbide), whereas both H and N observed values were close to the calculated values.

Synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}(2,6\text{-}(Ph_2CH)_2\text{-}4\text{-}Me\text{-}C_6H_2)_2(CHN)_2\ C{=}N]$ (1e). The ligand $1,3\text{-}(2,6\text{-}(Ph_2CH)_2\text{-}4\text{-}Me\text{-}C_6H_2)_2(CHN)_2C{=}NSiMe_3$ was prepared according to the literature procedure.[9b] To a toluene solution (30 mL) containing 1,3-bis{2,6-bis(diphenylmethyl)-4-methylphenyl}-imidazolin-2-ylidene,[26] $[1,3\text{-}(2,6\text{-}(Ph_2CH)_2\text{-}4'\text{-}Me\text{-}C_6H_2)_2(CHN)_2C]$ (1.30 g, 1.42 mmol) in a sealed Schlenk tube was added N_3SiMe_3 (0.23 g, 2 mmol) dropwise at room temperature. The reaction mixture was stirred at 110 °C for 72 h. The solution was filtered through a Celite pad, and the filtercake was washed with toluene. The combined filtrate and the wash were placed in a rotary evaporator to remove all volatiles. A pale yellow precipitate was obtained (0.65 g, 0.65 mmol) in 46% yield. ^1H NMR ($CDCl_3$): δ 7.22−7.17 (br, 20H, Ar—*H*), 7.07−7.05 (m, 12H, Ar—*H*), 6.87−6.85 (m, 12H, Ar—*H*), 5.57 (s, 4H, Ph$_2$C*H*), 4.58 (s, 2H, C*H*=), 2.20 (s, 6H, C*H*$_3$), −0.43 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 144.0, 143.5, 142.9, 137.8, 133.6, 130.1, 129.4, 129.2, 128.9, 128.4, 128.1, 128.0, 127.8, 126.1, 126.0, 125.9, 125.1, 112.8, 51.7, 21.6, 3.7.

The synthetic procedure of **1e** is similar to that for **1a**, except that $1,3\text{-}(2,6\text{-}(Ph_2CH)_2\text{-}4\text{-}Me\text{-}C_6H_2)_2(CHN)_2C{=}NSiMe_3$ (250 mg, 0.25 mmol) was used in place of $1,3\text{-}^tBu_2(CHN)_2C{=}NSiMe_3$. Green microcrystals were collected in a yield of 82% (241 mg, 0.206 mmol). ^1H NMR ($CDCl_3$): δ 7.19 (br, 8H, Ar—*H*), 7.14−7.12 (m, 12H, Ar—*H*), 7.07−7.06 (m, 12H, Ar—*H*), 6.82 (s, 4H, Ar—*H*), 6.77 (br, 8H, Ar—), 6.68 (m, 3H, V=NAr—*H*), 5.41 (s, 4H, Ph$_2$C*H*), 4.62 (s, 2H, C*H*=), 2.21 (s, 6H, C*H*$_3$), 2.08 (s, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 143.3, 142.0, 141.8, 140.1, 135.5, 130.3, 130.1, 130.0, 129.1, 129.0, 128.9, 128.6, 128.2, 128.1, 128.0, 127.0, 126.9, 126.4, 125.1, 124.5, 115.9, 52.0, 31.4, 22.5, 21.9, 21.7, 18.8, 14.0. ^{51}V NMR ($CDCl_3$): δ −107 ($\Delta\nu_{1/2}$ = 2794 Hz). Anal. Calcd for $C_{77}H_{65}Cl_2N_4V$: C, 79.17 (78.14 + VC, vanadium carbide); H, 5.61; N, 4.80. Found: C, 78.13; H, 5.95; N, 4.52.

Synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}^tBu_2(CH_2N)_2\ C{=}N]$ (2a). To a THF solution (20 mL) containing $1,3\text{-}^tBu(CH_2N)_2C{=}NH$ (0.197 g,1.0 mmol) was added *n*-BuLi (0.65 mL, 1.0 mmol, *n*-hexane solution) at −30 °C. The reaction mixture was slowly warmed to room temperature, and was stirred for 3 h. The solvent was removed in vacuo, and the white solid was dissolved in 20 mL of toluene. The solution was cooled to −30 °C, and $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3$ (0.276 g, 1.0 mmol) was then added. The reaction mixture was warmed slowly to room temperature and then stirred for 12 h. The solvent was removed in vacuo, and the resulting green solid was extracted with hot toluene. The solution was then placed in a rotary evaporator to remove volatiles. The solid was then dissolved in a minimum amount of CH_2Cl_2 and layered with *n*-hexane. Dark green crystals (0.240 g, 0.55 mmol) were grown from the chilled solution (−30 °C). Yield of 55%. ^1H NMR ($CDCl_3$): δ 6.89 (d, 2H, *J* = 7.50, Ar—*H*), 6.80 (t, 1H, *J* = 7.50, Ar—*H*), 3.52 (s, 4H, C*H*$_2$), 2.71 (s, 6H, ArC*H*$_3$), 1.41 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 136.3, 127.1,

Table 9. Crystal Data and Collection Parameters for V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-$^tBu_2$(CHN)$_2$ C═N](1a), V(N-2,6-$Me_2C_6H_3$)Cl_2[1,3-R_2(CH_2N)$_2$ C═N][R = ^{t}Bu (2a), 2,6-$^iPr_2C_6H_3$ (2c), Ph (2d)], V(NAd)Cl_2[1,3-(2,6-$^iPr_2C_6H_3$)$_2$(CHN)$_2$ C═N](3c)] V(NPh)Cl_2[1,3-(2,6-$^iPr_2C_6H_3$)$_2$(CHN)$_2$ C═N](4c), V(NAd)Cl_2[1,3-R_2(CH_2N)$_2$C═N] [R = 2,6-$^iPr_2C_6H_3$ (5c)]^a

	1a	2a	2c	2d	3c^b	4c	5c
formula	$C_{19}H_{29}Cl_2N_4V$	$C_{19}H_{31}Cl_2N_4V$	$C_{35}H_{47}Cl_2N_4V$	$C_{23}H_{23}Cl_2N_4V$	$C_{37.25}H_{51}Cl_{2.50}N_4V$	$C_{33}H_{41}Cl_2N_4V$	$C_{37}H_{53}Cl_2N_4V$
formula weight	435.31	437.33	645.63	477.31	694.41	615.56	675.67
crystal color, habit	blue, prism	blue, block	green, block	black, block	blue, block	brown, block	orange, platelet
crystal size (mm)	0.280 × 0.270 × 0.150	0.210 × 0.180 × 0.100	0.190 × 0.160 × 0.090	0.55 × 0.50 × 0.30	0.150 × 0.140 × 0.120	0.170 × 0.160 × 0.120	0.250 × 0.100× 0.100
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	tetragonal	orthorhombic	monoclinic
space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$Pca2_1$ (#29)	$P2_1/c$ (#14)	$P4_2/n$ (#86)	$Pbca$ (#61)	$P2_1/c$ (#14)
a (Å)	13.419(3)	14.203(13)	21.6558(3)	16.5014(5)	27.7170(5)	17.6192(4)	18.748(3)
b (Å)	9.445(2)	9.587(9)	10.4457(1)	11.4398(3)		19.2225(4)	12.3893(17)
c (Å)	18.054(5)	18.14(2)	15.1149(2)	12.7034(5)	9.6802(2)	19.7733(4)	18.714(3)
α (deg)							
β (deg)	104.273(11)	109.598(10)		112.4495(10)			102.065(8)
γ (deg)							
V (Å^3)	2217.6(8)	2326(4)	3419.11(8)	2216.31(12)	7436.6(3)	6696.9(3)	4250.8(11)
Z value	4	4	4	4	8	8	4
D_{calcd} (g/cm^3)	1.304	1.249	1.254	1.430	1.240	1.221	1.056
F_{000}	912.00	920.00	1368.00	984.00	2944.00	2592.00	1440.00
temp (K)	273	93	123	123	123	123	93
μ (Mo Kα) (cm^{-1})	6.977	6.653	4.753	7.057	4.766	4.822	3.157
no. of reflections measured	22666	23995	32995	19384	125138	111167	43805
no. of observations	5086	5328	7823	4218	8519	7671	9726
no. of variables	351	320	389	294	432	369	406
R1($I > 2.00\sigma(I)$)	0.0338	0.0811	0.0284	0.0265	0.0504	0.0645	0.0707
wR2	0.0912	0.2291	0.0701	0.0969	0.1437	0.1725	0.1742
goodness of fit	1.073	1.071	1.176	1.009	1.152	1.060	1.077

[a] The structure reports including CIF files are shown in the Supporting Information. [b] The crystal contained CH_2Cl_2 in the formula (with certain ratio).

126.1, 56.1, 43.5, 28.7, 19.1. ^{51}V NMR ($CDCl_3$): δ −77 ($\Delta\nu_{1/2}$ = 597 Hz) Anal. Calcd for $C_{19}H_{31}Cl_2N_4V$: C, 52.18 (49.43 + VC, vanadium carbide); H, 7.14; N, 12.81. Found: C, 50.72; H, 6.90; N, 12.34.

Synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}(2,6\text{-}Me_2C_6H_3)_2(CH_2N)_2C{=}N]$ (2b). The synthetic procedure for **2b** is similar to that for **2a**, except that $1,3\text{-}(2,6\text{-}Me_2C_6H_3)_2(CH_2N)_2C{=}NH$ (2.0 g, 6.8 mmol) was used in place of $1,3\text{-}^t\text{Bu}(CH_2N)_2C{=}NH$. Green microcrystals were collected in a yield of 97% (3.50 g, 6.6 mmol). ^{1}H NMR ($CDCl_3$): δ 7.15 (t, 2H, *J* = 7.60, Ar—*H*), 7.02 (d, 4H, *J* = 7.20, Ar—*H*), 6.81−6.74 (m, 3H, Nar—*H*), 4.00 (s, 4H, CH_2), 2.28 (s, 12H, ArCH_3), 2.10 (s, 6H, ArCH_3). ^{13}C NMR ($CDCl_3$): δ 136.8, 134.8, 134.0, 129.0, 128.7, 126.7, 125.5, 46.8, 18.8, 17.8. ^{51}V NMR ($CDCl_3$): δ −158 ($\Delta\nu_{1/2}$ = 964 Hz). Anal. Calcd for $C_{27}H_{31}Cl_2N_4(0.4\ CH_2Cl_2)$: C, 58.00; H, 5.65; N, 9.87. Found: C, 57.90; H, 5.58; N, 9.88.

Synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N]$ (2c). The synthetic procedure for **2c** is similar to that for **2a**, except that $1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CH_2N)_2C{=}NH$ (1.24 g, 6.0 mmol) was used in place of $1,3\text{-}^t\text{Bu}(CH_2N)_2C{=}NH$. Green microcrystals were collected in a yield of 46% (0.894 g, 1.38 mmol). ^{1}H NMR ($CDCl_3$): δ 7.36 (t, 2H, *J* = 7.60, Ar—*H*), 7.18 (d, 4H, *J* = 8.00, Ar—*H*), 6.68−6.60 (m, 3H, Ar—*H*), 4.04 (s, 4H, CH_2), 3.21−3.14 (m, 4H, $CH(CH_3)_2$), 1.98 (s, 6H, ArCH_3), 1.30−1.27 (m, 24H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 147.4, 135.1, 132.2, 129.7, 126.5, 125.1, 124.4, 49.2, 29.2, 24.9, 23.9, 18.5. ^{51}V NMR ($CDCl_3$): δ −140 ($\Delta\nu_{1/2}$ = 816 Hz). Anal. Calcd for $C_{35}H_{47}Cl_2N_4V$: C, 65.11(63.25 + VC, vanadium carbide); H, 7.34; N, 8.68. Found: C, 64.08; H, 7.38; N, 8.52.

Synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}Ph_2(CH_2N)_2C{=}N]$ (2d). The synthetic procedure of **2d** is similar to that for **2a**, expect that $1,3\text{-}Ph_2(CH_2N)_2C{=}NH$ (0.948 g, 4 mmol) was used in place of $1,3\text{-}^tBu_2(CH_2N)_2C{=}NH$. Green microcrystals were collected in a yield of 93% (1.782 g, 3.74 mmol). ^{1}H NMR ($CDCl_3$): δ 7.31−7.26 (m, 8H, Ph—*H*), 7.17 (t, 2H, *J* = 6.60, Ph—*H*), 6.81−6.74 (m, 3H, NAr—*H*), 4.19 (s, 4H, CH_2), 2.23 (s, 6H, ArCH_3). ^{13}C NMR ($CDCl_3$): δ 137.1, 135.8, 128.9, 126.8, 125.9, 125.8, 122.7, 46.6, 18.1, 18.0. ^{51}V NMR ($CDCl_3$): δ −99 ($\Delta\nu_{1/2}$ = 723 Hz). Anal. Calcd for $C_{23}H_{23}Cl_2N_4V$: C, 57.88 (55.36 + VC, vanadium carbide); H, 4.86; N, 11.74. Found: C, 57.28; H, 5.04; N, 11.47.

Synthesis of $V(NAd)Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CHN)_2C{=}N]$ (3c). To a toluene solution containing $V(NAd)Cl_3$ (193 mg, 0.63 mmol) was added $1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CHN)_2C{=}NSiMe_3$ (300 mg, 0.63 mmol) at −30 °C. The reaction mixture was slowly warmed to room temperature and stirred for 6 h. The solution was then filtered 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 volatiles. Bluish green crystals were grown from a chilled solution (dissolution in a minimum amount of CH_2Cl_2/toluene and placed in drybox freezer) at −30 °C. Yield: 362 mg (85%). ^{1}H NMR (C_6D_6): δ 7.21 (t, 2H, *J* = 7.70, Ar—*H*), 7.19 (d, 4H, *J* = 7.70, Ar—*H*), 5.91 (s, 4H, CH_2), 2.98−2.95 (m, 4H, $CH(CH_3)_2$), 1.77 (s, 3H, Ad—*H*), 1.54 (d, 12H, $CH(CH_3)_2$), 1.34 (s, 6H, Ad—*H*), 1.21 (s, 6H, Ad—*H*) 1.11 (d, 12H, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 146.2, 131.7, 130.5, 124.1, 116.3, 42.9, 35.7, 29.5, 28.9, 24.1, 23.6. ^{51}V NMR (C_6D_6): δ −268 ($\Delta v_{1/2}$ = 1415 Hz). ^{51}V NMR ($CDCl_3$): δ −257 ($\Delta v_{1/2}$ = 1087 Hz). Anal. Calcd for $C_{37}H_{51}Cl_2N_4V$: C, 65.97 (64.18 + VC, vanadium carbide); H, 7.63; N, 8.32. Found (1): C, 64.82; H, 7.41; N, 8.12. Found (2): C, 64.64; H, 7.54; N, 8.05. Found (3): C, 64.52; H, 7.64; N, 8.07.

Synthesis of $V(NPh)Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CHN)_2C{=}N]$ (4c). The synthetic procedure for **4c** is similar to that for **3c**, except that $V(NPh)Cl_3$ (132 mg, 0.53 mmol) was used in place of $V(NAd)Cl_3$. Greenish brown microcrystals were grown from a chilled CH_2Cl_2/*n*-hexane solution (−30 °C) and collected in 79% yield (257 mg, 0.42 mmol). ^{1}H NMR ($CDCl_3$): δ 7.41 (t, 2H, *J* = 7.67, Ph—*H*), 7.24 (d, 4H, *J* = 7.86, Ar—*H*), 7.02 (t, 2H, *J* = 7.67, Ph—*H*), 6.89 (t, 1H, *J* = 7.32, Ph—*H*), 6.77 (s, 2H, *C*H=) 6.62 (d, 2H, *J* = 7.86, Ar—*H*), 2.83−2.75 (m, 4H, $CH(CH_3)_2$), 1.26−1.18 (m, 24H, $CH(CH_3)_2$. ^{13}C NMR ($CDCl_3$): δ 145.9, 130.8, 130.7, 127.5, 125.1, 124.4, 124.0, 117.4, 29.2, 24.4, 23.2. ^{51}V NMR ($CDCl_3$): δ −180 ($\Delta v_{1/2}$ = 951 Hz). Anal. Calcd for $C_{33}H_{41}Cl_2N_4V$: C, 64.39; H, 6.71; N, 9.10. Found: C, 64.27; H, 6.72; N, 9.01.

Synthesis of $V(NAd)Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N]$ (5c). To a THF solution (20 mL) containing $1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N$(0.649 g,1.60 mmol) was added *n*-BuLi (1.01 mL, 1.60 mmol, *n*-hexane solution) at −30 °C. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. All volatiles were removed in vacuo, and the resulting white solid was dissolved in 20 mL of toluene. The solution was cooled to −30 °C, and $V(NAd)Cl_3$ (0.49 g, 1.60 mmol) was added. The reaction mixture was allowed to slowly warm up to room temperature and stirred for 12 h. The solvent was then removed in vacuo, and the green solid was extracted with hot toluene. The solution was placed under vacuum to remove all volatiles. The remaining solid was dissolved in a minimum amount of CH_2Cl_2 and layered with *n*-hexane. Purple microcrystals were grown from the chilled solution (−30 °C) and collected in a yield of 79.6% (0.86 g, 1.27 mmol). ^{1}H NMR ($CDCl_3$): δ 7.33 (t, 2H, *J* = 7.70, Ar—*H*), 7.19 (d, 4H, *J* = 7.70, Ar—*H*), 4.03 (s, 4H, CH_2), 3.21−3.14 (m, 4H, $CH(CH_3)_2$), 1.95(s, 3H, Ad—*H*), 1.82(s, 6H, Ad—*H*), 1.50 (d, 12H, $CH(CH_3)_2$), 1.48 (s, 6H, Ad—*H*) 1.33 (d, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 147.4, 132.4, 129.4, 124.1, 49.2, 42.7, 35.7, 29.5, 29.1, 25.1, 24.6. ^{51}V NMR ($CDCl_3$): δ −251 ($\Delta v_{1/2}$ = 801 Hz). Anal. Calcd for $C_{37}H_{53}Cl_2N_4V$: C, 65.77; H, 7.91; N, 8.29. Found: C, 65.73; H, 7.89; N, 8.00.

Ethylene Polymerization. Ethylene polymerizations were conducted in toluene by using a 100 mL scale autoclave. The solvent and the prescribed amount of cocatalyst (total solvent volume = 30 mL) were charged into the autoclave in the drybox, and the apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of the vanadium precatalyst via a syringe, the reaction apparatus was immediately pressurized to 8, 4, or 2 atm and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resulting polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried in vacuo.

Copolymerization of Ethylene with Norbornene (NBE), 5-Ethylidene-2-norbornene (ENB). Experimental procedures for the copolymerization of ethylene with NBE and ENB were the same as those for the ethylene polymerization described above except that prescribed amounts of NBE or ENB were added into an autoclave and the total volume of toluene and ENB was set to 30 mL.

Crystallographic Details. The X-ray diffraction analyses of **2c**,**d**, **3c**, and **4c** were performed on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The analyses of **1a**, **2a**, and **5c** were carried out on a Rigaku XtaLAB mini diffractometer with graphite-monochromated Mo Kα radiation. The structures were solved by direct methods[27] and expanded using Fourier techniques. The non-hydrogen atoms for were refined anisotropically: some non-hydrogen atoms for **2a** were refined anisotropically, whereas the rest were refined isotropically. Hydrogen atoms were refined isotropically. The crystal collection parameters are listed below (Table 9). All calculations were performed using the CrystalStructure[28,29] crystallographic software package except for refinement, which was performed using SHELXL-97.[30] All calculations for **2d** were performed using the CrystalStructure[28,29] crystallographic software package. Detailed structure reports including CIF files are shown in the Supporting Information.[17]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected NMR spectra for poly(ethylene-*co*-norbonene)s, poly(ethylene-*co*-ethylidene-2-norbonene) and structural reports including CIF files for $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}^tBu_2(CHN)_2C{=}N]$ (**1a**), $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}R_2(CH_2N)_2C{=}N]$ [R = ^{t}Bu (**2a**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2c**), Ph (**2d**)], $V(NR')Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CHN)_2C{=}N]$ [R′ = Ad (**3c**), Ph (**4c**)], $V(NAd)Cl_2[1,3\text{-}(2,6\text{-}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N]$ (**5c**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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