Synthesis and Structural Analysis of (Arylimido)vanadium(V) Complexes Containing Phenoxyimine Ligands: New, Efficient Catalyst Precursors for Ethylene Polymerization

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A series of (arylimido)vanadium(V) complexes containing phenoxyimine ligands of the type $V(NAr)Cl_2[O\text{-}2\text{-}R\text{-}6\text{-}\{(2,6\text{-}^iPr_2C_6H_3)N{=}CH\}C_6H_3]$ [Ar = 2,6-$Me_2C_6H_3$; R = H (**1a**), Me (**1b**), ^{t}Bu (**1c**)] have been prepared in 64−78% yields from $V(NAr)Cl_3$ with $LiO\text{-}2\text{-}R\text{-}6\text{-}[(2,6\text{-}^iPr_2C_6H_3)N{=}CH]C_6H_3$. The structures for **1a**−**c** determined by X-ray crystallography indicate that these complexes have distorted square-pyramidal structures around vanadium, consisting of the arylimido ligands in the apical site of a distorted square-pyramid and the N,O-chelate ligand, which forms a plane including both the aryloxo ring and the imino nitrogen. The Cl−V−Cl bond angle for **1c** [90.49(2)°] is apparently smaller than those in **1a**,**b** [91.97(7)°, 91.25(2)°, respectively], and the V−N(imine) bond distance in **1c** [2.203(2) Å] is shorter than those in **1b**,**c** [2.216(4), 2.2165(17) Å, respectively]. These complexes (especially **1c**) exhibited notable catalytic activities for ethylene polymerization in the presence of MAO, and the *ortho* substituent in the aryloxo ligand strongly affected the catalytic activity; the activity of the ^{t}Bu analogue (**1c**) was higher than that of the reported $V(NAr)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ under the same conditions. The reaction of 1.1 equiv of $2\text{-}Me\text{-}6\text{-}\{(2,6\text{-}^iPr_2C_6H_3)N{=}CH\}C_6H_3OH$ with $V(NAr)Me(N{=}C^tBu_2)_2$ afforded another methyl complex without reaction with the methyl group occurring; unique reactivity of the methyl complex with phenol could thus be observed.

Introduction

The design and synthesis of efficient transition metal complex catalysts for olefin coordination polymerization has attracted considerable attention in the fields of catalysis, organometallic chemistry, and polymer chemistry.[1–4] Classical Ziegler-type vanadium catalyst systems [consisting of vanadium compounds {$V(acac)_3$, $VOCl_3$, etc.} and organometallic reagents (Et_2AlCl, $Et_2AlCl\cdot EtAlCl_2$, ^{n}BuLi, etc.)] are known to display unique characteristics[4,5] due to their high reactivity toward olefins in olefin coordination polymerization. Therefore, the design and synthesis of new vanadium complex catalysts for the controlled polymerization is one of the most important subjects in this research area.[1f–h,4–8] Although there have been many reports especially with vanadium(III) and vanadium(IV) complexes for the above purpose,[4,6–8] we focused on high oxidation state

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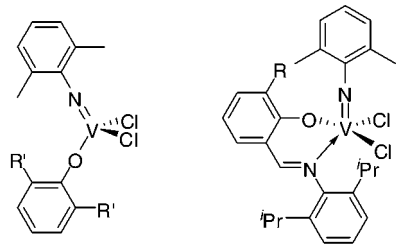
Chart 1

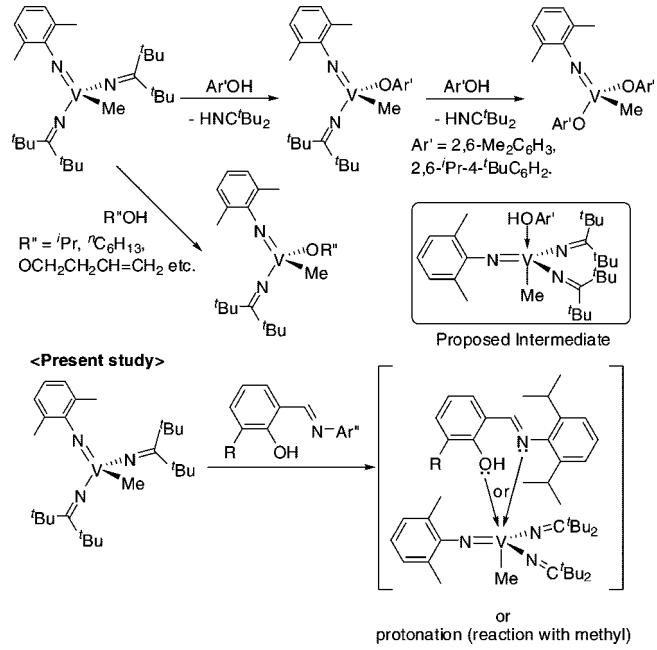


R' = Me, ^{i}Pr, Ph etc. R = H (**1a**), Me (**1b**), ^{t}Bu (**1c**)

(arylimido)vanadium(V) complexes containing an anionic ancillary donor ligand.[4c,7]

We reported recently that (arylimido)vanadium(V) complexes containing aryloxo ligands of type V(NAr)Cl_2(OAr′) (Ar = 2,6-$Me_2C_6H_3$; 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 for ethylene polymerization,[7] and the activities in the presence of halogenated Al alkyls were higher than those in the presence of MAO (methylaluminoxane).[7b,d,e] In this catalysis, the anionic donor ligand should play an essential role to stabilize the catalytically active species and/or control the electronic/steric environment in the catalytic reactions (which should strongly affect both the catalytic activities and the monomer reactivity). We thus have an interest in the use of the phenoxyimine ligand, because we assumed that a coordination of the imino nitrogen to the vanadium would lead to better stabilization than the above aryloxo ligands,[9] as established in certain zirconium complexes containing this series of ligands.[10,11] Moreover, the resultant complexes would have a five-coordinate square-pyramidal or trigonal-bipyramidal geometry around vanadium, which may form a more suited steric environment for the effective coordination/insertion than the complexes with tetrahedral geometry (Chart 1). Therefore, in this paper, we herein report the syntheses and structural analyses of a series of (arylimido)-vanadium(V) complexes containing phenoxyimine ligands of the type V(NAr)Cl_2[O-2-R-6-{(2,6-$^iPr_2C_6H_3$)N=CH}C_6H_3] [R = H (**1a**), Me (**1b**), ^{t}Bu (**1c**), Chart 1] and their use as catalyst precursors for ethylene polymerization in the presence of MAO.

Scheme 1



We previously observed that reaction of V-(NAr)Me(N=C^{t}Bu$_2$)$_2$ with 1 equiv of various alcohols cleanly afforded other methyl complexes, V(NAr)Me(N=C^{t}Bu$_2$)(OR) [OR = O-2,6-$Me_2C_6H_3$, O-4-^{t}Bu-2,6-$^iPr_2C_6H_2$, OPh, O^{i}Pr, etc.], and a reaction with the methyl group did not occur in all cases (Scheme 1).[12] We thus proposed that these reactions proceed via pentacoordinated trigonal-bipyramidal intermediates formed by coordination of the oxygen atom in the phenol *trans* to the methyl group. In order to explore whether the observed unique reactivity is also preserved in the reaction with phenol containing an imino group (Scheme 1, bottom), we thus examined the reaction with 2-Me-6-{(2,6-$^iPr_2C_6H_3$)N=CH}C_6H_3OH.

Results and Discussion

1. Synthesis and Structural Analysis for (Arylimido)-vanadium(V) Complexes Containing Phenoxyimine Ligands, V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-R-6-{(2,6-$^iPr_2C_6H_3$)N=CH}C_6H_3]-(R = H, Me, ^{t}Bu). A series of substituted salicylaldimines (iminophenols), 2-R-6-[(2,6-$^iPr_2$-C_6H_3)N=CH]C_6H_3OH (R = H, Me, ^{t}Bu), were prepared according to the reported procedures, by reaction of alkyl-substituted salicylaldehyde with 2,6-diisopropylaniline, respectively.[10a] V(NAr)Cl_3 (Ar = 2,6-

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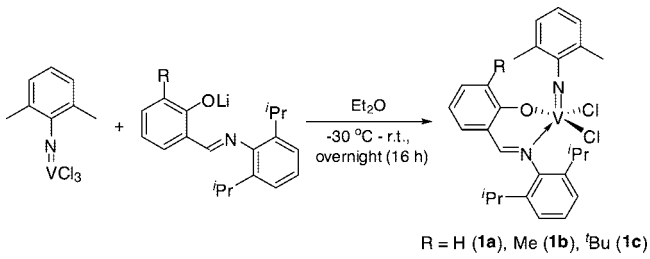
Scheme 2



$Me_2C_6H_3$) was prepared from $VOCl_3$ by treating with ArNCO in octane, according to the reported procedure.[13] Reactions of $V(NAr)Cl_3$ with LiO-2-R-6-[(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH]C$_6$H$_3$ (prepared by treating the corresponding iminophenol with ^{n}BuLi in *n*-hexane at −30 °C) in Et_2O afforded $V(NAr)Cl_2$[O-2-R-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] [R = H (**1a**), Me (**1b**), ^{t}Bu (**1c**)] in good yields (64−78%, Scheme 2). Analytically pure samples were collected as black microcrystals from a concentrated dichloromethane solution layered with toluene at −30 °C. The resultant complexes (**1a**−**c**) were identified by ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy and elemental analyses, and their structures were also determined by X-ray crystallography (Figure 1). Resonances characteristic of **1** were observed in their ^{1}H and ^{13}C NMR spectra. For example, resonances ascribed to terminal protons of the isopropyl groups were observed as nonequivalent double−doublets in the ^{1}H NMR spectra, whereas the resonance in the free ligand was observed as an equivalent doublet; two resonances ascribed to the terminal carbons of isopropyl groups in the imine were observed in the ^{13}C NMR spectra. These should be explained as the fact that free rotation of the isopropyl groups is prevented due to the steric bulk by complexation.

Selected bond distances and angles for **1a**−**c** determined by X-ray crystallography are summarized in Table 1. The crystal structures for **1a**−**c** showed that these complexes have a distorted square-pyramidal geometry around the vanadium center in all cases, and the imino nitrogen was coordinated to vanadium. The vanadium atom is pentacoordinated with the arylimido ligands in the apical site of a distorted square pyramid, and the N,O-chelate ligand forms a plane including both the aryloxo and the imino nitrogen.

The V−N(imido)−C bond angles for **1a**−**c** are 176.7(3)°, 173.19(17)°, and 175.63(19)°, respectively, and the distances [1.6376(18)−1.654(4) Å] are somewhat close to those in $V(NAr)Cl_2(N{=}C^tBu_2)$ [1.660 Å][14] and $V(NAr)X(N{=}C^tBu_2)_2$ [1.645(2), 1.661(2) Å for X = Cl, Me, respectively].[12a] These results clearly suggest that not only the σ donation but also a better strong π donation from the nitrogen to vanadium can be seen.[1h] The V−O distances for **1a**−**c** [1.797(3)−1.8222(15) Å] are close to those in the tris(aryloxoamine) analogue, VO[(O-2,4-R′$_2$C$_6$H$_2$-6-CH$_2$)$_3$N] (R′ = Me, ^{t}Bu) (1.798−1.812 Å),[15] and the role of the strong π donation of oxygen to vanadium (acts as 3*e* donor ligand) can be thus seen. The distances between vanadium and the imino nitrogen [2.216(4)−2.203(2) Å] are apparently longer than those in the V−N(arylimido) [1.6376(18)−1.654(4) Å], as well as that in $V(NAr)Cl_2(N{=}C^tBu_2)$ [1.839(4) Å].[14] These results suggest that these imino nitrogens do not form σ-bonds and coordinate to vanadium as a π-donor.

The V−Cl(1) (*trans* to O atom) distances [2.2452(18)−2.2614(6) Å] for **1a**−**c** are shorter than those in V−Cl(2) [*trans* to the imino nitrogen, 2.269(2)−2.2828(7) Å]; the observed differences are explained as the result of the *trans* influence. The V−Cl distances in **1c** [2.2614(6), 2.2828(7) Å] are longer than those in **1a**,**b**, and the Cl−V−Cl bond angle for **1c** [90.49(2)°] is apparently smaller than those in **1a**,**b** [91.97(7)°, 91.25(2)°, respectively]; the observed facts are due to the steric bulk of the ^{t}Bu group in **1c**. In contrast, the V−N(imine) bond distance in **1c** [2.203(2) Å] is shorter than those in **1b**,**c** [2.216(4), 2.2165(17) Å, respectively], suggesting that the imino nitrogen in **1c** strongly coordinates to vanadium.

2. Ethylene Polymerization by V(N-2,6-Me$_2$C$_6$H$_3$)Cl$_2$-[O-2-R-6-{(2,6-^{i}Pr$_2$-C$_6$H$_3$)N=CH}C$_6$H$_3$]−MAO Catalyst Systems. Ethylene polymerizations by $V(NAr)Cl_2$[O-2-R-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] [R = H (**1a**), Me (**1b**), ^{t}Bu (**1c**)] were conducted in toluene in the presence of MAO (white solid prepared by removing toluene and $AlMe_3$ from commercial MAO).[16] The polymerization using the aryloxo analogue, $V(NAr)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**A**), was also conducted for comparison under the same conditions. The results are summarized in Table 2.

The catalytic activity by **1a**−**c**−MAO catalyst systems at 25 °C (ethylene, 8 atm) increased in the order 2150 kg PE/mol·V·h (**1c**, R = ^{t}Bu, run 5) > 680 (**1b**, R = Me, run 3) > 380 (**1a**, R = H, run 1). The results thus suggest that the activity was strongly affected by the *ortho* substituent in the phenoxy ligand. It is simply speculated that the *ortho* substituent stabilizes the catalytically active species. This would be assumed from the structural analysis, in which the Cl−V−Cl bond angle in **1c** (90.49°) is smaller than those in **1a**,**b** (91.97°, 91.25°), that the *ortho* substituent decreases the bond angle between the alkyl and the coordinated olefin in the assumed catalytically active species [speculated as cationic alkyl], leading to the better insertion. The resultant polymers prepared at 25 °C possessed high molecular weights with unimodal molecular weight distributions ((1.18−1.66) × 10^6, M_w/M_n = 2.8−3.1), as seen previously.[7]

Note that the observed activity of **1c** at 25 °C (2150 kg PE/mol·V·h) was higher than that of the aryloxo analogue (**A**, 880 kg PE/mol·V·h) under the same conditions. We thus assumed that the observed improvement in the activity is due to the coordination of the imino nitrogen to the vanadium, which should stabilize the catalytically active species by more electron donation. However, both the activity and the molecular weight in the resultant polyethylene decreased when these polymerizations were conducted at 50 °C (as also seen in the polymerization by the **A**−MAO catalyst system).[7c] The molecular weight distribution in the polymer prepared by **1a** became broad, and this is probably due to a partial decomposition of the active species.

3. Reaction of V(NAr)Me(N=C^{t}Bu$_2$)$_2$ with 2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$OH: Unique Reactivity of the Methyl Group toward Phenol. As described in the Introduction, we previously observed that reaction of $V(NAr)Me(N{=}C^tBu_2)_2$ with 1 equiv of various alcohols cleanly afforded the other methyl complexes, V(NAr)Me-(N=C^{t}Bu$_2$)(OR) (OR = aryloxo, alkoxo), and a reaction with the methyl group did not occur in any cases (Scheme 1).[12] We thus were interested in exploring whether the observed unique

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(16) We previously reported[7b,d,e] that halogenated Al alkyls such as Et_2AlCl and $EtAlCl_2$ are better cocatalysts than white solid MAO. Due to the highly exothermic reaction, MAO has thus been chosen to compare the activity with high reproducibility.

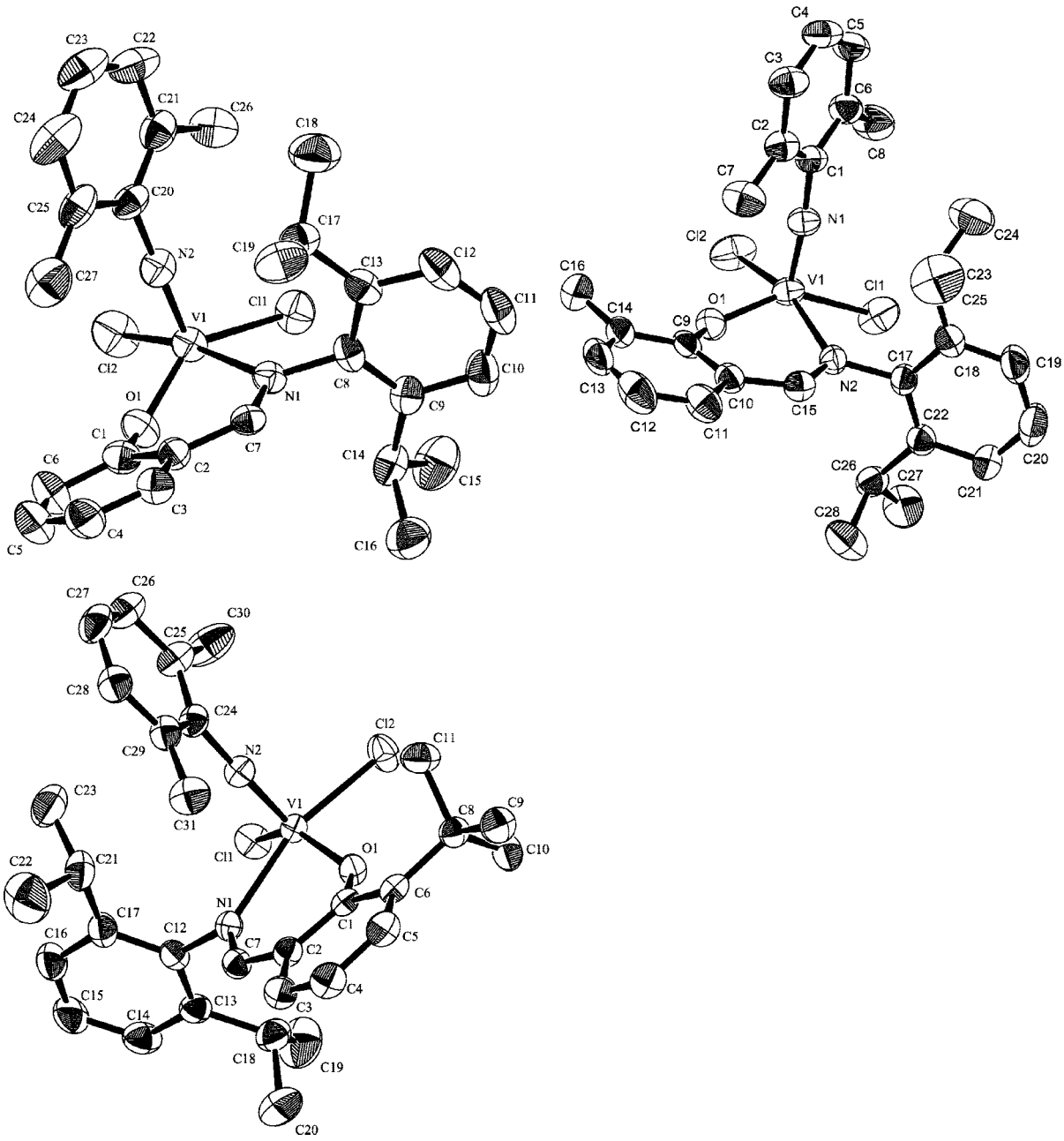

Figure 1. ORTEP drawings of V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-R-6-{(2,6-^{i}Pr$_2$$C_6H_3$)N=CH}$C_6H_3$] [R = H (**1a**, top left), Me (**1b**, top right), ^{t}Bu (**1c**, bottom left)]. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

reactivity is preserved in the reaction with phenol containing an imino group that would also coordinate to vanadium.

2-Me-6-{(2,6-^{i}Pr$_2$$C_6H_3$)N=CH}$C_6H_3$OH (1.1 equiv to V) was added into a C_6D_6 solution containing V(NAr)Me(N=C^{t}Bu$_2$)$_2$, and the mixture was warmed slowly to room temperature and stirred for 3 days. Although the reaction with 2,6-^{i}Pr$_2$$C_6H_3$OH and 2,6-$Me_2C_6H_3$OH was completed cleanly within 3 h, the reaction with the iminophenol did not complete within a couple of hours. Monitoring the mixture revealed that the reaction reached completion after 3 days. The reaction product was V(NAr)Me(N=C^{t}Bu$_2$)[O-2-Me-6-{(2,6-^{i}Pr$_2$$C_6H_3$)N=CH}$C_6H_3$] (**2**) (yield 92%, Scheme 3), and complex **2** was identified by ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy and elemental analysis. Moreover, the structure of **2** was determined by X-ray crystallography (Figure 2). It is thus clear that the reaction with methyl (protonation of methyl) did not occur under these conditions, indicating that a unique reactivity toward alcohol in the vanadium−methyl complex was preserved even in the reaction with the iminophenol.

The structure of **2** is shown in Figure 2, and selected bond distances and angles are summarized in Table 3. Complex **2** has a rather distorted trigonal-bipyramidal geometry around V, consisting of an O−V−N(imido) axis [172.34(13)°] and a C(methyl)−N(ketimide)−N(imine) plane [bond angles for C−V−N(ketimide), C−V−N(imine), and N−V−N are 128.02(5)°, 109.96(16)°, and 118.43°, respectively, total 356.41°]. The V−C(Me) bond distance [2.100(4) Å] in **2** is somewhat longer than that in V(NAr)Me(N=C^{t}Bu$_2$)$_2$ [2.064(2) Å],[12a] but the V−N(ketimide) bond distance in **2** [1.803(3) Å] is shorter than that in the above complex [1.825−1.827 Å].[12a] The V−N(imine) bond distance [2.113(2) Å] is shorter than that in **1b** [2.2165(17) Å], and the V−N(imido) distance in **2** [1.685(2) Å] is also shorter than that in **1b** [1.6376(18) Å]. In contrast, the V−O bond distance in **2** [2.012(2) Å] is longer than that in **1b**

Table 1. Selected Bond Distances and Angles for V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-R-6-{(2,6-$^i Pr_2C_6H_3$)N=CH}C_6H_3] [R = H (1a), Me (1b), ^{t}Bu (1c)]

	1a	1b	1c
		Bond Distances (Å)	
V(1)−Cl(1)	2.2452(18)	2.2454(6)	2.2614(6)
V(1)−Cl(2)	2.269(2)	2.2705(8)	2.2828(7)
V(1)−O(1)	1.797(3)	1.8222(15)	1.8124(16)
V(1)−N(2)imido	1.654(4)	1.6376(18), V(1)−N(1)	1.6488(15)
V(1)−N(1)imine	2.216(4)	2.2165(17), V(1)−N(2)	2.203(2)
		Bond Angles (deg)	
Cl(1)−V(1)−Cl(2)	91.97(7)	91.25(2)	90.49(2)
Cl(1)−V(1)−N(1)imine	85.23(12)	85.05(4), Cl(1)−V(1)−N(2)	84.27(4)
Cl(2)−V(1)−O(1)	92.43(14)	91.34(5)	92.20(5)
O(1)−V(1)−N(1)	82.18(16)	81.59(6), O(1)−V(1)−N(2)	81.81(7)
V(1)−O(1)−C(1)	134.2(3)	139.12(15), V(1)−O(1)−C(9)	137.01(12)
V−N(imido)-C(Ar)	176.7(3)	173.19(17)	175.63(19)
	V(1)−N(2)−C(20)	V(1)−N(1)−C(1)	V(1)−N(2)−C(24)
Cl(2)−V(1)−N(1)	167.87(11)	161.49(5), Cl(2)−V(1)−N(2)	162.08(4)
Cl(1)−V(1)−O(1)	139.35(11)	144.99(5)	142.43(4)
N(2)−V(1)−O(1)	111.01(18)	106.19(7), N(1)−V(1)−O(1)	107.90(7)
N(2)−V(1)−Cl(1)	108.36(17)	107.51(6), N(1)−V(1)−Cl(1)	108.20(6)

Table 2. Ethylene Polymerization by V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-R-6-{(2,6-$^i Pr_2C_6H_3$)N=CH}C_6H_3] [R = H (1a), Me (1b), ^{t}Bu (1c)]−MAO Catalyst Systems[a]

run	catalyst R	temp/°C	polymer yield/mg	activity[b]	M_w[c] × 10^{-5}	M_w/M_n[c]
1	H (**1a**)	25	64	380	16.6	2.8
2	H (**1a**)	50	29	170	9.45	5.6
3	Me (**1b**)	25	114	680	11.8	3.0
4	Me (**1b**)	50	47	280	3.34	3.4
5	^{t}Bu (**1c**)	25	358	2150	12.2	3.1
6	^{t}Bu (**1c**)	50	66	400	4.69	4.3
7	**A**[d]	25	147	880	12.7	3.4

[a] Reaction conditions: **1a**−**c** 1.0 μmol, toluene 30 mL, ethylene 8 atm, 10 min, 100 mL scale autoclave, *d*-MAO (prepared by removing $AlMe_3$ and toluene from commercially available MAO) 3.0 mmol. [b] Activity = kg PE/mol·V·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] V(NAr)Cl_2(O-2,6-$Me_2C_6H_3$) (**A**) 1.0 μmol was used in place of **1a**−**c**.

[1.8222(15) Å]. This could be due to the presence of electron-donating ketimide ligands as well as a change in the geometry around the vanadium center [square pyramidal to trigonal bipyramidal]. It is thus assumed based on the experimental facts that these reactions proceed via pentacoordinated trigonal-bipyramidal intermediates formed by coordination of the oxygen atom in the phenol *trans* to the methyl group.[12]

In summary, we have prepared a series of (arylimido)vanadium(V) complexes containing phenoxyimine ligands of the type V(NAr)Cl_2[O-2-R-6-{(2,6-$^i Pr_2C_6H_3$)N=CH}C_6H_3] [Ar = 2,6-$Me_2C_6H_3$; R = H (**1a**), Me (**1b**), ^{t}Bu (**1c**)], and their structures have been determined by X-ray crystallography. These complexes, especially **1c**, exhibited higher catalytic activities than the aryloxo analogue, V(NAr)Cl_2(O-2,6-$Me_2C_6H_3$), for ethylene polymerization in the presence of MAO; the resultant polymers were linear polyethylene possessing high molecular weights with unimodal molecular weight distributions. The reaction of V(NAr)Me(N=C$^t Bu_2$)$_2$ with 1.1 equiv of 2-Me-6-{(2,6-$^i Pr_2C_6H_3$)N=CH}C_6H_3OH afforded another methyl complex without reaction with the methyl occurring. Since attempted isolations of the reaction products with alkyl lithium ($LiCH_2SiMe_3$, etc.) were unsuccessful, we are thus exploring another possibility. These will be introduced in the near future.

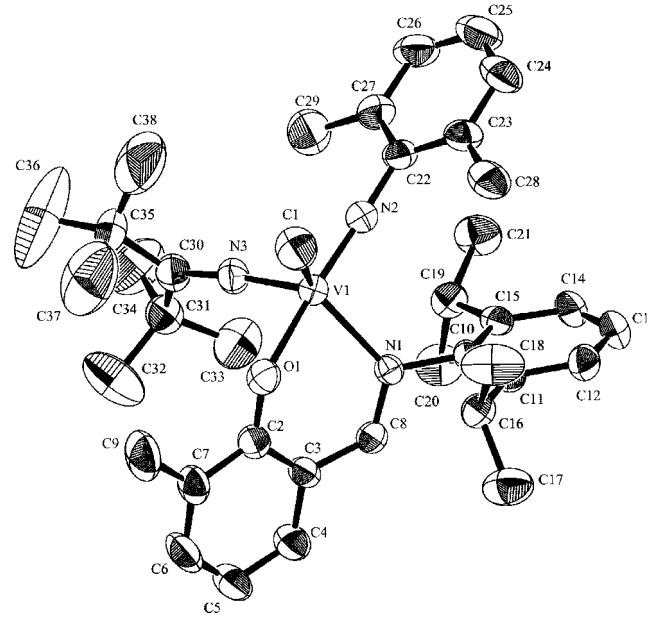

Figure 2. ORTEP drawings of V(N-2,6-$Me_2C_6H_3$)Me(N=C$^t Bu_2$)[O-2-Me-6-{(2,6-$^i Pr_2C_6H_3$)N=CH}C_6H_3] (**2**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using

Scheme 3

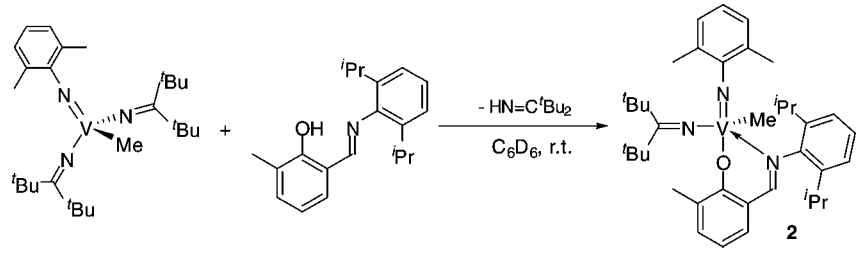

Table 3. Selected Bond Distances and Angles for V(N-2,6-$Me_2C_6H_3$)Me[N=C^{t}Bu$_2$][O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] (2)

Bond Distances (Å)			
V(1)−C(1)	2.100(4)	V(1)−O(1)	2.012(2)
V(1)−N(1)	2.113(2)	V(1)−N(2)	1.685(2)
V(1)−N(3)	1.803(3)	O(1)−C(2)	1.307(4)
N(1)−C(8)	1.314(4)	N(1)−C(10)	1.454(3)
N(2)−C(22)	1.389(4)	N(3)−C(30)	1.263(5)
Bond Angles (deg)			
N(1)−V(1)−C(1)	128.02(15)	N(3)−V(1)−C(1)	109.96(16)
N(1)−V(1)−N(3)	118.43(13)	O(1)−V(1)−N(2)	172.34(13)
V(1)−O(1)−C(2)	129.2(2)	V(1)−N(2)−C(22)	177.2(2)
V(1)−N(1)−C(8)	123.9(2)	V(1)−N(1)−C(10)	122.0(2)

standard Schlenk techniques. All chemicals used were of reagent grade and were purified by standard purification procedures. Anhydrous grade diethyl ether, *n*-hexane, and toluene (Kanto Kagaku Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 and were passed through a short alumina column under N_2 stream before use. V(N-2,6-$Me_2C_6H_3$)Cl_3[13] and V(N-2,6-$Me_2C_6H_3$)Me(N=C^{t}Bu$_2$)$_2$[12] were prepared according to the published method. Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.), and some analytical runs were performed twice to confirm the reproducibility in the independent analysis/synthesis runs. Certain C values were somewhat lower than those calculated, whereas their N, H values were close; this is due to incomplete combustion (to form vanadium carbide).

All ^{1}H, ^{13}C, and ^{51}V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^{1}H, 100.40 MHz for ^{13}C, 105.31 MHz for ^{51}V). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^{1}H, ^{13}C) and $VOCl_3$ (δ 0.00, ^{51}V). Coupling constants and half-width values, $\Delta\nu_{1/2}$, are given in Hz.

Synthesis of V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_4$] (1a). Into a Et_2O solution (50 mL) containing V(N-2,6-$Me_2C_6H_3$)Cl_3 (1.382 g, 5 mmol) was added LiO-2-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_4$ (1.437 g, 5 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred overnight. The solution was then removed *in vacuo*, and the resultant residue was extracted with hot toluene (ca. 200 mL). The toluene extract was then removed *in vacuo* to give a black solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of toluene. The chilled solution placed in the freezer gave a black solid. Yield: 2.044 g (78%). ^{1}H NMR ($CDCl_3$): δ 0.98 (dd, 12H, (CH_3)$_2$CH−), 2.40 (s, 6H, CH_3), 2.83 (m, 2H, (CH_3)$_2$CH−), 6.82 (s, 3H), 7.18 (m, 3H), 7.26 (t, 1H), 7.34 (d, 1H), 7.56 (d, 1H), 7.76 (t, 1H), 8.56 (s, 1H, −CH=N−). ^{13}C NMR ($CDCl_3$): δ 18.6, 22.3, 24.9, 28.7, 117.6, 119.2, 122.6, 123.4, 127.2, 127.6, 130.8, 133.0, 137.1, 140.1, 140.3, 153.1, 166.1, 167.1, 170.1. ^{51}V NMR ($CDCl_3$): δ 178 ($\Delta\nu_{1/2}$ = 489 Hz). Anal. Calcd for $C_{27}H_{31}Cl_2N_2OV$: C, 62.20; H, 5.99; N, 5.37. Found: C, 62.33; H, 6.05; N, 5.32.

Synthesis of V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] (1b). Synthesis of **1b** was carried out by the same procedure as that for **1a** except that V(N-2,6-$Me_2C_6H_3$)Cl_3 (1.382 g, 5 mmol) and LiO-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$ (1.507 g, 5 mmol) were used. Yield: 1.762 g (66%). ^{1}H NMR ($CDCl_3$): δ 0.98 (dd, 12H, (CH_3)$_2$CH−), 2.36 (s, 6H, CH_3), 2.47 (s, 3H, CH_3), 2.85 (m, 2H, (CH_3)$_2$CH−), 6.82 (s, 3H), 7.12 (m, 3H), 7.26 (t, 1H), 7.39 (d, 1H), 7.62 (d, 1H), 8.53 (s, 1H, −CH=N−). ^{13}C NMR ($CDCl_3$): δ 16.0, 18.5, 22.3, 25.0, 28.7, 118.6, 122.6, 123.5, 127.2, 127.6, 130.3, 130.7, 137.8, 140.2, 140.5, 152.9, 165.1, 167.3, 169.9. ^{51}V NMR ($CDCl_3$): δ 165 ($\Delta\nu_{1/2}$ = 556 Hz). Anal. Calcd for $C_{28}H_{33}Cl_2N_2OV$: C, 62.81; H, 6.21; N, 5.23. Found: C, 61.40; H, 6.15; N, 4.89.

Synthesis of V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-^{t}Bu-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] (1c). Synthesis of **1c** was carried out by the same procedure as that for **1a** except that V(N-2,6-$Me_2C_6H_3$)Cl_3 (1.382 g, 5 mmol) and LiO-2-^{t}Bu-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$ (1.717 g, 5 mmol) were used. Yield: 1.860 g (64%). ^{1}H NMR ($CDCl_3$): δ 0.97 (dd, 12H, (CH_3)$_2$CH-), 1.52 (s, 9H, (CH_3)$_3$C−), 2.40 (s, 6H, CH_3), 2.82 (m, 2H, (CH_3)$_2$CH−), 6.82 (s, 3H), 7.16 (m, 3H), 7.26 (t, 1H), 7.43 (d, 1H), 7.79 (d, 1H), 8.57 (s, 1H, −CH=N−). ^{13}C NMR ($CDCl_3$): δ 18.5, 22.3, 24.9, 28.7, 29.5, 35.1, 119.4, 122.5, 123.5, 127.2, 127.6, 130.6, 131.4, 134.5, 138.9, 139.8, 140.5, 153.2, 165.4, 167.9, 169.8. ^{51}V NMR ($CDCl_3$): δ 136 ($\Delta\nu_{1/2}$ = 590 Hz). Anal. Calcd for $C_{31}H_{39}Cl_2N_2OV$: C, 64.47; H, 6.81; N, 4.85. Found: C, 64.07; H, 7.05; N, 4.74.

Synthesis of V(N-2,6-$Me_2C_6H_3$)Me(N=C^{t}Bu$_2$)[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] (2). Into a C_6D_6 solution (50 mL, placed in a freezer at −30 °C) containing V(N-2,6-$Me_2C_6H_3$)-Me(N=C^{t}Bu$_2$)$_2$ (0.233 g, 0.5 mmol) was added 2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$OH (0.162 g, 0.55 mmol). The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for 3 days. The solution was then removed *in vacuo* to give a red solid. The solid was then dissolved in a minimum amount

Table 4. Crystal Data and Selected Bond Distances (Å) and Angles (deg) for V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-R-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] [R = H (1a), Me (1b), ^{t}Bu (1c)] and V(N-2,6-$Me_2C_6H_3$)Me[N=C^{t}Bu$_2$][O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] (2)[a]

	1a	1b	1c	2
formula	$C_{27}H_{31}Cl_2N_2OV$	$C_{28}H_{33}Cl_2N_2OV$	$C_{31}H_{39}Cl_2N_2OV$	$C_{38}H_{54}ON_3V$
fw	521.40	535.43	577.51	619.81
cryst color, habit	black, block	black, block	black, block	red, block
cryst size (mm)	0.20 × 0.15 × 0.07	0.60 × 0.20 × 0.14	0.34 × 0.30 × 0.15	0.30 × 0.30 × 0.25
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	Cc (#9)	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)	$C2/c$ (#15)
a (Å)	19.4008(14)	11.2178(4)	18.7923(3)	37.8086(15)
b (Å)	9.8601(6)	14.2133(4)	19.5289(4)	9.6536(4)
c (Å)	16.1374(8)	16.9951(6)	19.3387(4)	20.2844(7)
V (Å^3)	2644.8(3)	2709.72(16)	6203.5(2)	7381.8(5)
Z value	4	4	8	8
D_{calcd} (g/cm^3)	1.309	1.312	1.237	1.115
F_{000}	1088.00	1120.00	2432.00	2672.00
no. of reflns measd	12 707	26 395	93 174	34 784
no. of observations	1736	4535	9952	4150
no. of variables	329	341	745	442
R1	0.0323	0.0293	0.0332	0.0542
wR2	0.0560	0.0594	0.0951	0.1536
goodness of fit	1.016	1.008	1.001	1.000

[a] Diffractometer: Rigaku RAXIS-RAPID imaging plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\sum w(F_o - F_c)^2$ (w = least-squares weights). Standard deviation of an observation of unit weight: $[\sum w(F_o - F_c)^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables).

of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled solution placed in the freezer gave a red solid. Yield: 0.284 g (92%). ^{1}H NMR (C_6D_6): δ 0.86 (d, 6H, $(CH_3)_2CH-$), 1.01 (d, 6H, $(CH_3)_2CH-$), 1.15 (s, 18H, $(CH_3)_3C-$), 1.88 (s, 3H, VCH_3), 2.38 (s, 6H, CH_3), 2.60 (s, 3H, CH_3), 3.19 (br, 2H, $(CH_3)_2CH-$), 6.60 (q, 2H), 6.76 (d, 2H), 6.97 (t, 3H), 7.07 (t, 1H), 7.29 (d, 1H), 8.06 (s, 1H, $-CH=N-$). ^{13}C NMR (C_6D_6): δ 17.2, 19.5, 24.0, 28.6, 30.6, 43.5, 49.8, 116.4, 119.2, 124.0, 127.0, 127.3, 130.4, 132.0, 136.2, 139.1, 141.1, 153.2, 158.4, 168.5, 169.2, 185.6. ^{51}V NMR (C_6D_6): δ −62 ($\Delta\nu_{1/2}$ = 1643 Hz). Anal. Calcd for $C_{38}H_{54}N_3OV$: C, 73.64; H, 8.78; N, 6.78. Found: C, 73.67; H, 8.96; N, 6.37.

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. The selected crystal collection parameters are summarized in Table 4, and the detailed results are described in the Supporting Information. All structures were solved by direct methods and expanded using Fourier techniques,[17] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **1a**, **1b**, **1c**, and **2** were performed using the Crystal Structure[18] crystallographic software package.

Polymerization of Ethylene. Ethylene polymerizations were conducted in toluene by using a 100 mL scale autoclave. Solvent (29.0 mL) and white solid MAO (174 mg, 3.0 mmol), prepared by removing toluene and $AlMe_3$ from commercially available MAO (PMAO-S, Tosoh Finechem Co.), were charged into the autoclave in the drybox. The autoclave was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of **1a**, **1b**, and **1c** via a syringe, the reaction apparatus was pressurized to 7 atm (total 8 atm), and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into EtOH (200 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with EtOH and then dried *in vacuo*. Table 2 summarizes the polymerization results under optimized Al/V molar ratios.

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Supporting Information Available: CIF files and structure analysis reports for V(N-2,6-$Me_2C_6H_3$)Cl_2[O-2-R-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] [R = H (**1a**), Me (**1b**), ^{t}Bu (**1c**)] and V(N-2,6-Me$_2$C$_6$H$_3$)Me[N=C^{t}Bu$_2$][O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] (**2**). These materials are available free of charge via the Internet at http://pubs.acs.org.

OM800177G

(17) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Delder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF94 Program System*; Technical report of crystallography laboratory; University of Nijmegen: The Netherlands, 1994.

(18) (a) *CrystalStructure 3.6.0*, Crystal Structure Analysis Package; Rigaku and Rigaku/MSC: The Woodlands, TX, 2000−2004. (b) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, UK, 1996.