

Synthesis of (Arylimido)vanadium(V) Complexes Containing (2-Anilidomethyl)pyridine Ligands and Their Use as the Catalyst Precursors for Olefin Polymerization

Shu Zhang,[†] Shohei Katao,[†] Wen-Hua Sun,[‡] and Kotohiro Nomura^{*†}

[†]Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan, and [‡]Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

Received July 19, 2009

A series of (arylimido)vanadium(V) dichloride complexes containing (2-anilidomethyl)pyridine ligands of the type V(NAr)Cl₂[2-Ar'NCH₂(C₅H₄N)] [Ar = 2,6-Me₂C₆H₃; Ar' = 2,6-Me₂C₆H₃ (**1a**), 2,6-ⁱPr₂C₆H₃ (**1b**), 2,6-F₂C₆H₃ (**1c**)] have been prepared from V(NAr)Cl₃ by treating with Li-[2-Ar'NCH₂(C₅H₄N)], and the structures of **1b,c** have been determined by X-ray crystallography. These complexes are effective catalyst precursors for ethylene polymerization in the presence of Al cocatalysts: **1b** showed the highest catalytic activities in the presence of Et₂AlCl (6000 kg PE/mol V · h), and the observed activities of **1a,b** in the presence of Et₂AlCl were much higher than those in the presence of MAO. V(NAr)(CH₂SiMe₃)₂[2-Ar'NCH₂(C₅H₄N)] (**2a,b**) have been prepared by treating **1a,b** with 2.0 equiv of LiCH₂SiMe₃, and their structures have been determined by X-ray crystallography. The dialkyl complex **2b** cleanly reacted with 2.0 equiv of (CF₃)₂CHOH in C₆D₆ at 25 °C to afford V(NAr)(CH₂SiMe₃)[OCH(CF₃)₂][2-Ar'NCH₂(C₅H₄N)] (**3**), and the reaction with 3.0 equiv of (CF₃)₂CHOH eventually afforded V(NAr)[OCH(CF₃)₂]₂[2-Ar'NCH₂(C₅H₄N)] (**4**) from **3** after 3 days. The dialkyl complexes **2a,b** showed catalytic activities for ring-opening metathesis polymerization (ROMP) of norbornene in benzene at 80 °C in the presence of PMe₃. The ROMP did not occur in the absence of PMe₃ under the same conditions, suggesting that an additional coordination of PMe₃ may be required to induce the α-hydrogen elimination.

Introduction

Designing efficient transition metal complex catalysts for olefin coordination polymerization attracts considerable attention in the field of catalysis, organometallic chemistry,

and polymer chemistry.^{1–6} Classical Ziegler-type vanadium catalyst systems [consisting of vanadium compounds {V(acac)₃, VOCl₃, etc.} and organometallic reagents (Et₂-AlCl, Et₂AlCl-EtAlCl₂, ⁿBuLi, etc.)] are known to display unique characteristics^{6,7} due to the high reactivity toward olefins in olefin coordination polymerization, and the synthesis of new efficient vanadium complex catalysts for controlled olefin polymerization has thus been one of the most attractive targets.^{2f,2h,2i,6,8–10}

Although there have been many reports especially with vanadium(III) and vanadium(IV) complexes for the above purpose,^{6c,7,8c–8q} we focused on high oxidation state (imido)vanadium(V) complexes containing an anionic ancillary donor ligand.^{6c,8b,8c,9} We recently reported that (arylimido)vanadium(V) complexes containing anionic donor ligands of the type V(NAr)Cl₂(L) (Ar = 2,6-Me₂C₆H₃, L = aryloxo, ketimide, phenoxyimine, Chart 1) exhibited moderate/remarkable catalytic activities in ethylene polymerization

*Corresponding author. Tel: +81-743-72-6041. Fax: +81-743-72-6049. E-mail: nomurak@ms.naist.jp.

(1) Mason, A. F.; Coates, G. W. In *Macromolecular Engineering*; Matyjaszewski, K.; Gnanou, Y.; Leibler, L., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Vol. 1, p 217.

(2) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3903. (c) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143. (d) Suhm, J.; Heinemann, J.; Wörner, C.; Müller, P.; Stricker, F.; Kressler, J.; Okuda, J.; Mülhaupt, R. *Macromol. Symp.* **1998**, *129*, 1. (e) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (f) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429. (g) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236. (h) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (i) Bolton, P. D.; Mountford, P. *Adv. Synth. Catal.* **2005**, *347*, 355.

(3) *Frontiers in Metal-Catalyzed Polymerization* (special issue). Gladysz, J. A., Ed. *Chem. Rev.* **2000**, *100* (4). For example: (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (b) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (c) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(4) *Metalocene complexes as catalysts for olefin polymerization* (special issue). Alt, H. G., Ed. *Coord. Chem. Rev.* **2006**, *250* (1–2), 1.

(5) For more recent reviews, see: (a) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30. (b) Nomura, K.; Liu, J.; Padmanabhan, S.; Kitiyanan, B. *J. Mol. Catal. A* **2007**, *267*, 1. (c) Cano, J.; Kunz, K. *J. Organomet. Chem.* **2007**, *692*, 4411.

(6) For recent reviews (vanadium catalysts), see: (a) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357. (b) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229. (c) Nomura, K. In *New Developments in Catalysis Research*; Bevy, L. P., Ed.; NOVA Science Publishers: New York, 2005; p 199.

(7) Examples: (a) Carrick, W. L. *J. Am. Chem. Soc.* **1958**, *80*, 6455. (b) Carrick, W. L.; Kluiber, R. W.; Bonner, E. F.; Wartman, L. H.; Rugg, F. M.; Smith, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 3883. (c) Carrick, W. L.; Reichle, W. T.; Pennella, F.; Smith, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 3887. (d) Lehr, M. H. *Macromolecules* **1968**, *1*, 178.

in the presence of methylaluminumoxane (MAO), affording (ultra) high molecular weight polyethylene with uniform molecular weight distributions.^{9a-9c,9f,9h} It also turned out that the catalytic activities by the aryloxo analogue V(NAr)Cl₂(O-2,6-R¹₂C₆H₃) (R¹ = Me, ⁱPr, Ph, etc.) in the presence of halogenated aluminum alkyls (such as Et₂AlCl, EtAlCl₂, EtAlCl₂·Et₂AlCl, etc.) were higher than those in the presence of MAO,^{9b,9d,9e,9g} whereas the remarkable enhancement in the activities by the ketimide analogue V(NAr)Cl₂[N=C(R²)'Bu] (R² = ⁱBu, CH₂SiMe₃) was not seen in the presence of Et₂AlCl.^{9f}

We reported more recently that (arylimido)vanadium(V) complexes containing phenoxy-imine ligands of the type

(8) For selected initial examples for olefin polymerization with vanadium complex catalysts,⁹ see: (a) Feher, F. J.; Blanski, R. L. *Organometallics* **1993**, *12*, 958. (b) Coles, M. P.; Gibson, V. C. *Polym. Bull.* **1994**, *33*, 529. (c) Scheuner, S.; Fischer, J.; Kress, J. *Organometallics* **1995**, *14*, 2627. (d) Sobota, P.; Ejfler, J.; Szafert, S.; Glowiak, T.; Fritzy, I. O.; Szczegot, K. *J. Chem. Soc., Dalton Trans.* **1995**, 1727. (e) Desmangles, N.; Gambarotta, S.; Bensimon, C.; Davis, S.; Zahalka, H. J. *Organomet. Chem.* **1998**, *562*, 53. (f) Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Eur. J. Inorg. Chem.* **1998**, 1867. (g) Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 4090. (h) Witte, P. T.; Meetsma, A.; Hessen, B. *Organometallics* **1999**, *18*, 2944. (i) Janas, Z.; Jerzykiewicz, L. B.; Richards, R. L.; Sobota, P. *Chem. Commun.* **1999**, 1105. (j) Ricardon, D.; Conan, F.; Gambarotta, S.; Yap, G.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318. (k) Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2000**, 497. (l) Hagen, H.; Boersma, J.; Lutz, M.; Spek, A. L.; van Koten, G. *Eur. J. Inorg. Chem.* **2001**, 117. (m) Kotov, V. V.; Avtomonov, E. V.; Sundermeyer, J.; Aitola, E.; Repo, T.; Lemenovskii, D. A. *J. Organomet. Chem.* **2001**, *640*, 21. (n) Milione, S.; Cavallo, G.; Tedesco, C.; Grassi, A. *J. Chem. Soc., Dalton Trans.* **2002**, 1839. (o) Feghali, K.; Harding, D. J.; Reardon, D.; Gambarotta, S.; Yap, G.; Wang, Q. *Organometallics* **2002**, *21*, 968. (p) Ruther, T.; Cavell, K. J.; Braussaud, N. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 4684. (q) Reardon, D.; Guan, J.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R. *Organometallics* **2002**, *21*, 4390.

(9) (a) Nomura, K.; Sagara, A.; Imanishi, Y. *Chem. Lett.* **2001**, 36. (b) Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, *35*, 1583. (c) Wang, W.; Yamada, J.; Fujiki, M.; Nomura, K. *Catal. Commun.* **2003**, *4*, 159. (d) Nomura, K.; Wang, W. *Macromolecules* **2005**, *38*, 5905. (e) Wang, W.; Nomura, K. *Adv. Synth. Catal.* **2006**, *348*, 743. (f) Nomura, K.; Wang, W.; Yamada, J. *Stud. Surf. Sci. Catal.* **2006**, *161*, 123. (g) Nomura, K.; Wang, W. *Stud. Surf. Sci. Catal.* **2007**, *172*, 305. (h) Onishi, Y.; Katao, S.; Fujiki, M.; Nomura, K. *Organometallics* **2008**, *27*, 2590. (i) Zhang, W.; Nomura, K. *Inorg. Chem.* **2008**, *47*, 6482.

(10) For more recent examples for olefin polymerization with vanadium complex catalysts, see: (a) Redshaw, C.; Warford, L.; Dale, S. H.; Elsegood, M. R. J. *Chem. Commun.* **2004**, 1954. (b) Gibson, V. C.; Tomov, A. K.; Zaher, D.; Elsegood, M. R. J.; Dale, S. H. *Chem. Commun.* **2004**, 1956. (c) Liu, G.; Beetstra, D. J.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 3914. (d) Redshaw, C.; Rowan, M. A.; Homden, D. M.; Dale, S. H.; Elsegood, M. R. J.; Matsui, S.; Matsuura, S. *Chem. Commun.* **2006**, 3329. (e) Mountford, P.; Bigmore, H. R.; Zuideveld, M. A.; Kowalczyk, R. M.; Cowley, A. R.; Kranenburg, M.; McInnes, E. J. L. *Inorg. Chem.* **2006**, *45*, 6411. (f) Cuomo, C.; Milione, S.; Grassi, A. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3279. (g) Homden, D. M.; Redshaw, C.; Hughes, D. L. *Inorg. Chem.* **2007**, *46*, 10827. (h) Redshaw, C.; Rowan, M. A.; Warford, L.; Homden, D. M.; Arbaoui, A.; Elsegood, M. R. J.; Dale, S. H.; Yamato, T.; Casas, C. P.; Matsui, S.; Matsuura, M. *Chem.—Eur. J.* **2007**, *13*, 1090. (i) Jabri, A.; Korobkov, I.; Gambarotta, S.; Duchateau, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6119. (j) Homden, D.; Redshaw, C.; Wright, J. A.; Hughes, D. L.; Elsegood, M. *Inorg. Chem.* **2008**, *47*, 5799. (k) Tang, L.-M.; Wu, Y.-Q.; Duan, Y.-Q.; Pan, L.; Li, Y.-G.; Li, Y.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2038. (l) Bialek, M.; Czaja, K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6940. (m) Wu, J.-Q.; Pan, L.; Hu, N.-H.; Li, Y.-S. *Organometallics* **2008**, *27*, 3840. (n) Wu, J.-Q.; Pan, L.; Li, Y.-G.; Liu, S.-R.; Li, Y.-S. *Organometallics* **2009**, *28*, 1817. (o) Wu, J.-Q.; Pan, L.; Liu, S.-R.; He, L.-P.; Li, Y.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3573. (p) Meppelder, G. M.; Halbach, T. S.; Spaniol, T. P.; Mülhaupt, R.; Okuda, J. *J. Organomet. Chem.* **2009**, *694*, 1235. (q) Homden, D.; Redshaw, C.; Warford, L.; Hughes, D. L.; Wright, J. A.; Dale, S. H.; Elsegood, M. R. J. *Dalton Trans.* **2009**, in press (DOI: 10.1039/b901810g). (r) Arbaoui, A.; Redshaw, C.; Homden, D. M.; Wright, J. A. Elsegood, M. R. J. *Dalton Trans.* **2009**, in press (DOI: 10.1039/b902402f). Synthesis of (imido)vanadium-alkoxide complexes containing bis(phenolate) ligands and their use as the catalyst precursors for ethylene polymerization.

V(NAr)Cl₂[O-2-R³-6-((2,6-ⁱPr₂C₆H₃)N=CH)C₆H₃] (R³ = H, Me, ⁱBu) exhibited notable catalytic activities for ethylene polymerization in the presence of MAO,^{9h} and we assumed that a coordination of the imino nitrogen to the vanadium (with a distorted square-pyramidal or trigonal-bipyramidal geometry) should lead to better stabilization than the above aryloxo ligands. In this paper, we thus focused on using a (2-anilidomethyl)pyridine ligand, [2-Ar'NCH₂(C₅H₄N)]⁻, that can be simply derived from 2-iminopyridine (used as efficient ligands for ethylene polymerization by late transition metal catalysis)¹¹ and that can be used as promising ligands for olefin polymerization by group 4 transition metal catalysis.¹² We herein present the synthesis, structural analysis for (arylimido)vanadium(V) dichloride complexes containing (anilidomethyl)pyridine ligands, V(NAr)Cl₂[2-Ar'CH₂(C₅H₄N)] [Ar' = 2,6-R₂C₆H₃, R = Me (**1a**), ⁱPr (**1b**), F (**1c**), Chart 1], and their use as catalyst precursors for ethylene polymerization in the presence of Al cocatalysts (MAO, Et₂AlCl). Moreover, we have recently reported syntheses of various vanadium(V)-alkyl complexes and the reaction with alcohol^{13,14b} as well as the successful isolations of “olefin metathesis active” vanadium(V)-alkylidenes by subsequent α-hydrogen elimination,¹⁴⁻¹⁶ therefore, we herein present the synthesis of vanadium(V)-dialkyl complexes and ring-opening metathesis polymerization (ROMP) of norbornene with the dialkyl complexes including attempted isolation of the vanadium(V)-alkylidene.

Results and Discussions

1. Synthesis and Structural Analysis of (Arylimido)vanadium(V) Dichloride Complexes Containing (2-Anilidomethyl)pyridine Ligands of Type V(NAr)Cl₂[2-Ar'NCH₂(C₅H₄N)] [Ar' = 2,6-Me₂C₆H₃ (**1a**), 2,6-ⁱPr₂C₆H₃ (**1b**), 2,6-F₂C₆H₃ (**1c**)]. The ligands, 2-Ar'N(H)CH₂(C₅H₃N) [Ar' =

(11) (a) Sun, W.-H.; Tang, X.; Gao, T.; Wu, B.; Zhang, W.; Ma, H. *Organometallics* **2004**, *23*, 5037. (b) Jie, S.; Zhang, D.; Zhang, T.; Sun, W.-H.; Chen, J.; Ren, Q.; Liu, D.; Zheng, G.; Chen, W. *J. Organomet. Chem.* **2005**, *690*, 1739. (c) Tang, X.; Sun, W.-H.; Gao, T.; Hou, J.; Chen, J.; Chen, W. *J. Organomet. Chem.* **2005**, *690*, 1570. (d) Zhang, W.; Sun, W.-H.; Wu, B.; Zhang, S.; Ma, H.; Li, Y.; Chen, J.; Hao, P. *J. Organomet. Chem.* **2006**, *691*, 4759. (e) Zhang, W.; Sun, W.-H.; Zhang, S.; Tang, X.; Gao, T.; Chen, J. *J. Mol. Catal. A: Chem.* **2007**, *265*, 159.

(12) (a) Boussie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M. K.; Murphy, V.; Shoemaker, J. A. W.; Turner, H.; Rosen, R. K.; Stevens, J. C.; Alfano, F.; Busico, V.; Cipullo, R.; Talarico, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3278. (b) Nienkemper, K.; Keher, G.; Keher, S.; Fröhlich, R.; Erker, G. *J. Organomet. Chem.* **2008**, *693*, 1572. (c) Annunziata, L.; Pappalardo, D.; Tedesco, C.; Pellicchia, C. *Organometallics* **2009**, *28*, 688. (d) Lyubov, D. M.; Fukin, G. K.; Cherkasov, A. V.; Shavyrin, A. S.; Trifonov, A. A.; Luconi, L.; Bianchini, C.; Meli, A.; Giambastiani, G. *Organometallics* **2009**, *28*, 1227.

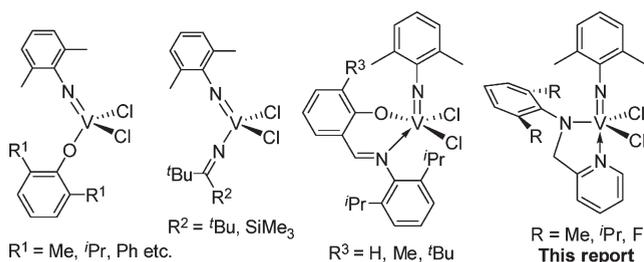
(13) (a) Yamada, J.; Nomura, K. *Organometallics* **2005**, *24*, 3621. (b) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2007**, *26*, 2579. (c) Zhang, W.; Katao, S.; Sun, W.-H.; Nomura, K. *Organometallics* **2009**, *28*, 1558.

(14) (a) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2005**, *24*, 2248. (b) Nomura, K.; Onishi, Y.; Fujiki, M.; Yamada, J. *Organometallics* **2008**, *27*, 3818. (c) Zhang, W.; Yamada, J.; Nomura, K. *Organometallics* **2008**, *27*, 5353. (d) Zhang, W.; Nomura, K. *Organometallics* **2008**, *27*, 6400.

(15) For a review article on the synthesis of vanadium-alkylidenes, see: (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Mendiola, D. *Acc. Chem. Res.* **2006**, *39*, 813. (c) Mendiola, D.; Bailey, B.; Basuli, F. *Eur. J. Inorg. Chem.* **2006**, *16*, 3135.

(16) Recent examples of the syntheses of vanadium-alkylidenes: (a) Basuli, F.; Kilgore, U. J.; Hu, X.; Meyer, K.; Pink, M.; Huffman, J. C.; Mendiola, D. *J. Angew. Chem., Int. Ed.* **2004**, *43*, 3156. (b) Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mendiola, D. *J. Am. Chem. Soc.* **2004**, *126*, 10506. (c) Kilgore, U. J.; Sengelaub, C. A.; Pink, M.; Fout, A. R.; Mendiola, D. *J. Angew. Chem., Int. Ed.* **2008**, *47*, 3769. (d) Kilgore, U. J.; Sengelaub, C. A.; Fan, H.; Tomaszewski, J.; Karty, J. A.; Baik, M.-H.; Mendiola, D. *J. Organometallics* **2009**, *28*, 843.

Chart 1



2,6-R₂C₆H₃; R = Me, ⁱPr, F] were prepared by condensation reactions between pyridinecarboxaldehyde and the corresponding anilines, followed by the reduction of imine by NaBH₄.^{12b} Reactions of V(NAr)Cl₃, prepared from VOCl₃ by treatment with ArNCO in *n*-octane,¹⁷ with LiN(2,6-R₂C₆H₃)CH₂(C₅H₃N) (R = Me, ⁱPr, F) [prepared by treating 2-Ar'ⁱN(H)CH₂(C₅H₃N) with 1 equiv of ⁿBuLi in *n*-hexane at -30 °C] in Et₂O afforded V(NAr)Cl₂[2-(2,6-R₂C₆H₃)NCH₂(C₅H₃N)] [R = Me (**1a**), ⁱPr (**1b**), F (**1c**)] in yields of 29–58% (Scheme 1). Analytically pure complexes **1b** and **1c** were collected as deep red microcrystals from a concentrated toluene solution layered with *n*-hexane at -30 °C, whereas pure **1a** was collected as red precipitates according to the same procedure. These complexes were identified on the basis of ¹H, ⁵¹V, and ¹³C NMR spectra and elemental analyses. The structures of **1b** and **1c** were determined by X-ray crystallography (Figure 1), and selected bond lengths and the angles are summarized in Table 1.¹⁸

The structures of **1b** and **1c** indicate that these complexes have a distorted trigonal-bipyramidal geometry around vanadium consisting of two nitrogen atoms in the pyridine and the imido ligands axis and an equatorial plane consisting of two chlorine atoms and the nitrogen in the anilide ligand [total bond angles of Cl(1)–V(1)–Cl(2), N(1)–V(1)–Cl(1), N(1)–V(1)–Cl(2) are 353.4° (**1b**), 354.94° (**1c**), respectively; N(2)–V(1)–N(3): 175.93(10)° for **1b**, 170.71(10)° for **1c**]. Two chlorine atoms are positioned in a *cis* form.

The V–Cl bond distances [2.2449(9)–2.2868(9) Å] are similar to those in V(NAr)Cl₂(N=C^tBu₂) [2.2338(5), 2.2710(5) Å]^{14a} and V(NAr)Cl₂[O-2-R³-6-(2,6-ⁱPr₂C₆H₃)N=CH}C₆H₃] (R³ = H, Me, ^tBu) [2.2452(18)–2.2828(7) Å],^{9h} but shorter than those in V(NAr)Cl₂(N=C^tBu₂)(PMe₃) [2.298(2), 2.314(2) Å] and V(NAr)Cl₂(N=C^tBu₂)(dmpe) [2.3652(7), 2.3751(9) Å, dmpe = 1,2-(dimethylphosphino)-methane].^{14a} The V–N bond distances in the arylimido ligand in **1b,c** [V(1)–N(3) = 1.679(3), 1.676(2) Å, respectively] are somewhat longer than those in V(NAr)Cl₂(N=C^tBu₂) [1.669(2) Å],^{14a} V(NAr)Cl₂(N=C^tBu₂)(PMe₃) [1.652(3) Å],^{14a} and V(NAr)Cl₂[O-2-R³-6-(2,6-ⁱPr₂C₆H₃)N=CH}C₆H₃] [1.6376(18)–1.654(4) Å],^{9h} but similar to that in V(NAr)Cl₂(N=C^tBu₂)(dmpe) [1.677(2) Å].^{14a} This would be thus explained as due to a *trans* influence of the pyridine ligand.

The bond angle of N(imido)–V–N(pyridine) [N(2)–V(1)–N(3)] in **1b** is larger than that in **1c** [175.93(10)° vs 170.71(10)°], the Cl(1)–V–Cl(2) in **1b** is also larger than that in **1c** [121.87(3)° vs 114.03(3)°], and the vanadium atom deviates from the equatorial plane by 0.317 Å for **1b** and

0.275 Å for **1c**. This would be explained as due to the steric bulk of the ⁱPr substituent in **1b** compared to the fluorine substituent in **1c**.

The V–N(pyridine) bond distances [2.211(2), 2.208(2) Å] are close to those in V(NAr)Cl₂[O-2-R³-6-(2,6-ⁱPr₂C₆H₃)N=CH}C₆H₃] [2.216(4)–2.203(2) Å].^{9h} The V–N(anilido) [V(1)–N(1)] bond distances [1.850(2), 1.877(2) Å] are longer than that in V(NAr)Cl₂(N=C^tBu₂) [1.787–(1) Å],^{14a} but apparently shorter than the V–N(pyridine) bond distances. The distances are, however, shorter than the covalent radii (1.964 Å) for a vanadium–nitrogen single bond according to Pauling's covalent radii.¹⁹ It is thus clear that the vanadium and nitrogen form a σ bond in addition to π donation from the nitrogen, although the π donation from nitrogen to vanadium may be weak compared to the ketimido complexes.^{14a}

2. Ethylene Polymerization by V(NAr)Cl₂[2-Ar'ⁱNCH₂(C₅H₃N)]–Cocatalyst Systems. Ethylene polymerizations by V(NAr)Cl₂[2-Ar'ⁱNCH₂(C₅H₃N)] [Ar' = 2,6-R₂C₆H₃; R = Me (**1a**), ⁱPr (**1b**), F (**1c**)] were conducted in toluene in the presence of d-MAO [white solid prepared by removing toluene and AlMe₃ from commercial PMAO-S (Tosoh Finechem Co.), as described in the Experimental Section] or Et₂AlCl (1 M in *n*-hexane). The results are summarized in Tables 2 and 3.

The catalytic activities at 25 °C in the presence of MAO were affected by the Al/V molar ratio, and the ratio of 3000 seems favored for **1a,b** (and the ratio of 1000 for **1c**) under these conditions. The activity increased in the order (Al/V = 3000 at 25 °C) 78 kg PE/mol V·h (**1a**, R = Me) < 189 (**1b**, R = ⁱPr) < 594 (**1c**, R = F). Both the activity and the *M*_w value in the resultant polymer increased if the polymerization by **1c** was conducted at 0 °C, but the activity decreased at 50 °C probably due to a partial decomposition of the catalytically active species as seen in the aryloxo analogue.^{9c} The resultant polymers possessed high molecular weights (*M*_w = (1.06–2.98) × 10⁶) with unimodal molecular weight distributions, suggesting that these polymerizations proceeded with uniform catalytically active species under these conditions. The *M*_w values in the resultant polymers prepared by **1c** were not strongly affected by the Al/V molar ratios (runs 5–8, Table 2), but the *M*_w values seemed to be affected by the substituent in the anilide moiety [*M*_w = (1.06–1.67) × 10⁶ (R = F, **1c**) vs (1.84–2.98) × 10⁶ (R = Me, ⁱPr, **1a,b**)].

In contrast, as shown in Table 3, the catalytic activity of **1c** in the presence of Et₂AlCl in place of MAO at 0 °C was much lower than those of **1a,b** [activity under the same conditions, complex 1.0 μmol, Al/V = 100 (molar ratio): 156 kg PE/mol V·h (run 23, **1c**) vs 840 (runs 12, **1a**), 3780 (run 17, **1b**)]. The ⁱPr analogue (**1b**) showed remarkable catalytic activities, and the activity of 6000 kg PE/mol V·h was attained under the optimized conditions (run 21). The observed catalytic activities of **1a,b** in the presence of Et₂AlCl were much higher than those in the presence of MAO, and the facts are somewhat analogous to those observed in the ethylene polymerization using (arylimido)vanadium(V) complexes containing aryloxo ligands.^{9b,9d} The activity decreased at 25 °C, as seen previously for ethylene polymerization using the aryloxo analogues.^{9d} The resultant polymers prepared by **1a–c** possessed high molecular weights (*M*_w = (1.72–3.52) × 10⁶, prepared at 0 °C) with unimodal distributions, as

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

(18) Structural analysis reports (including crystal data and collection parameters) and CIF files are shown in the Supporting Information.

(19) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542.

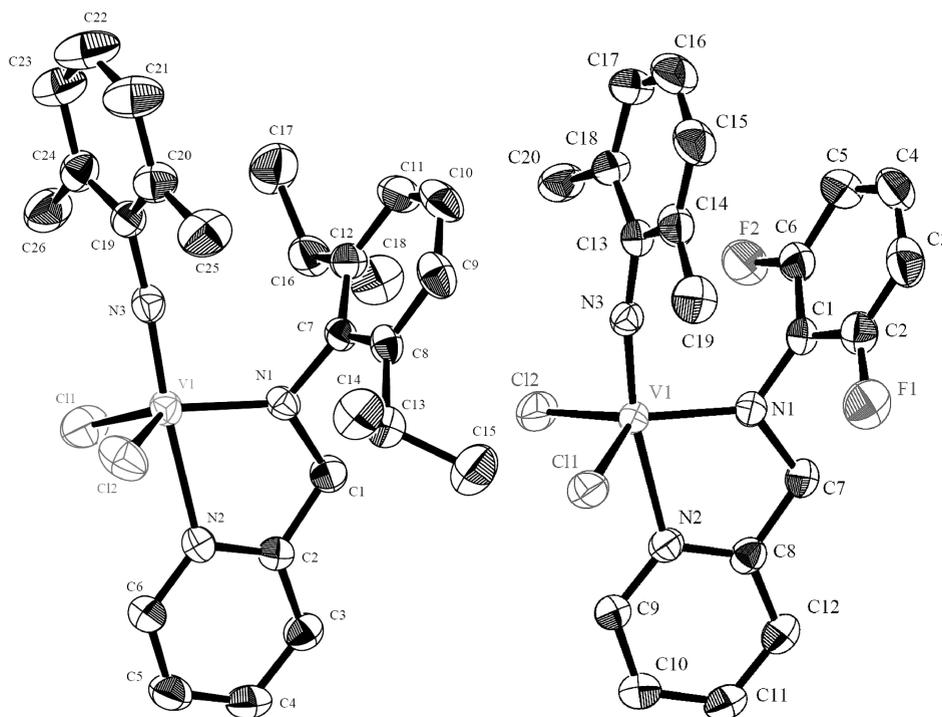


Figure 1. ORTEP drawings of $V(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2[(2,6\text{-R}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_5\text{N})]$ [$\text{R} = i\text{Pr}$ (**1b**, left), F (**1c**, right)]. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.¹⁸

Table 1. Selected Bond Lengths and Angles for $V(N\text{-}2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{Cl}_2[(2,6\text{-R}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_5\text{N})]$ [$\text{R} = i\text{Pr}$ (**1b**), F (**1c**)]^a

complex (R)	1b ($i\text{Pr}$)	1c (F)
	Bond Distances (Å)	
V(1)–N(1)	1.850(2)	1.877(2)
V(1)–N(2)	2.211(2)	2.208(2)
V(1)–N(3)	1.679(2)	1.676(2)
V(1)–Cl(1)	2.2645(10)	2.2661(9)
V(1)–Cl(2)	2.2868(9)	2.2449(9)
	Bond Angles (deg)	
N(1)–V(1)–N(2)	77.66(9)	76.93(9)
N(1)–V(1)–N(3)	98.52(11)	94.10(10)
N(1)–V(1)–Cl(1)	114.55(7)	120.40(8)
N(1)–V(1)–Cl(2)	116.98(8)	120.51(8)
N(2)–V(1)–N(3)	175.93(10)	170.71(10)
N(2)–V(1)–Cl(1)	82.45(7)	85.09(6)
N(2)–V(1)–Cl(2)	83.87(6)	85.86(7)
N(3)–V(1)–Cl(1)	100.56(9)	97.67(8)
N(3)–V(1)–Cl(2)	96.74(8)	100.97(8)
Cl(1)–V(1)–Cl(2)	121.87(3)	114.03(3)
V(1)–N(imido)–C(Ar)	176.2(2),	169.3(2),
	V(1)–N(3)–C(19)	V(1)–N(3)–C(13)

^aDetailed analysis results are shown in the Supporting Information.¹⁸

exemplified in Figure 3. The results also suggest that these polymerizations proceeded with uniform catalytically active species under these conditions. As also shown in Figure 3, the M_w values were dependent upon the polymerization temperature as well as the substituent in the anilide moiety.

3. Synthesis and Structural Analysis of the (Arylimido)vanadium(V) Dialkyl Complexes $V(\text{NAr})(\text{CH}_2\text{SiMe}_3)_2\text{-}[2\text{-Ar}'\text{NCH}_2(\text{C}_5\text{H}_5\text{N})]$ [$\text{Ar}' = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (2a**), $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ (**2b**)].** The vanadium(V)-dialkyl complexes of the type $V(\text{NAr})(\text{CH}_2\text{SiMe}_3)_2\text{-}[2\text{-Ar}'\text{NCH}_2(\text{C}_5\text{H}_5\text{N})]$ [$\text{Ar}' = 2,6\text{-R}_2\text{C}_6\text{H}_3$, $\text{R} = \text{Me}$ (**2a**), $i\text{Pr}$ (**2b**)] were prepared by treating the dichloride analogues (**1a,b**) with 2.0 equiv of $\text{LiCH}_2\text{SiMe}_3$ in toluene (Scheme 1). Alternatively, **2b** can also be prepared directly from

Table 2. Ethylene Polymerization by $V(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2\text{-}[(2,6\text{-R}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_5\text{N})]$ [$\text{R} = \text{Me}$ (**1a**), $i\text{Pr}$ (**1b**), F (**1c**)]–MAO Catalyst Systems^a

run	complex (R)	Al/V ^b	temp/°C	yield/mg	activity ^c	$M_w^d \times 10^{-6}$	M_w/M_n^d
1	1a (Me)	1000	25	24	72	1.84	2.6
2	1a (Me)	3000	25	26	78	2.98	2.0
3	1b ($i\text{Pr}$)	1000	25	22	66	2.55	1.9
4	1b ($i\text{Pr}$)	3000	25	63	189	2.93	2.6
5	1c (F)	100	25	66	198		
6	1c (F)	500	25	185	555	1.38	2.8
7	1c (F)	1000	25	206	618	1.06	2.3
8	1c (F)	3000	25	198	594	1.67	2.9
9	1c (F)	1000	0	274	822	2.42	2.6
10	1c (F)	1000	50	109	327	1.10	2.6

^a Conditions: complex 2.0 μmol , toluene 30 mL, ethylene 8 atm, 10 min, MAO (prepared by removing toluene and AlMe_3 from the commercially available MAO). ^b Molar ratio of Al/V. ^c Activity in kg polymer/mol V · h. ^d GPC data in *o*-dichlorobenzene versus polystyrene standards.

$V(\text{NAr})\text{Cl}_3$ without isolation of **1b**. A similar attempt for the synthesis of **2a** failed because of the difficulty in isolating **2a** from the reaction mixture. Attempts to isolate $V(\text{NAr})(\text{CH}_2\text{SiMe}_3)_2\text{-}[2\text{-}(2,6\text{-F}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_5\text{N})]$ by adopting the above two approaches were not successful. Analytically pure **2a,b** were collected as red microcrystals from a concentrated *n*-hexane solution at -30°C , and these complexes were identified by ^1H , ^{13}C , and ^{51}V NMR spectra and elemental analyses. The structures of **2a,b** were also determined by X-ray crystallography (Figure 2), and selected bond lengths and angles are summarized in Table 4.¹⁸

The structures of **2a** and **2b** indicate that the coordination geometry around vanadium is a distorted trigonal bipyramidal consisting of an axis with two nitrogen atoms (in the pyridine and the imido ligands) and an equatorial plane (with two carbon atoms in the CH_2SiMe_3 ligand and the nitrogen in the anilide ligand) [total bond angles of $\text{C}(23)\text{-V}(1)\text{-C}(27)$,

Scheme 1

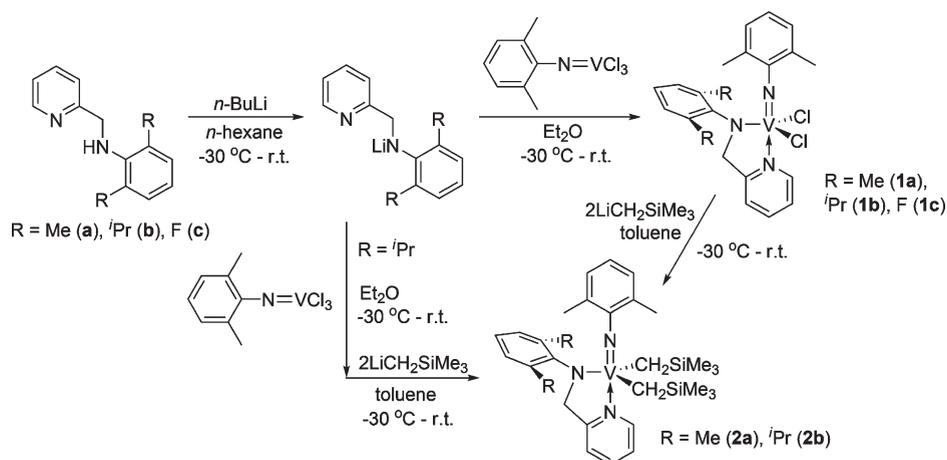


Table 3. Ethylene Polymerization by V(N-2,6-Me₂C₆H₃)Cl₂-(2,6-R₂C₆H₃)NCH₂(C₅H₃N) [R = Me (1a), ⁱPr (1b), F (1c)]-Et₂AlCl Catalyst Systems^a

run	complex (μmol)	Al/V ^b	temp/°C	yield/mg	activity ^c	$M_w^d \times 10^{-6}$	M_w^d/M_n^d
11	1a (1.0)	50	0	104	624		
12	1a (1.0)	100	0	140	840	3.12	4.1
13	1a (1.0)	200	0	102	612		
14	1a (1.0)	100	25	86	516	6.04	4.1
15	1b (1.0)	25	0	194	1164		
16	1b (1.0)	50	0	440	2640		
17	1b (1.0)	100	0	630	3780	2.57	3.1
18	1b (1.0)	200	0	418	2508	1.72	3.0
19	1b (1.0)	100	25	97	582	0.97	3.2
20	1b (0.2)	100	0	124	3720	3.42	3.4
21	1b (0.2)	200	0	200	6000	2.18	2.7
22	1b (0.2)	300	0	141	4230	3.36	3.4
23	1c (1.0)	100	0	26	156	3.52	3.7

^a Conditions: toluene 30 mL, ethylene 8 atm, 10 min, Et₂AlCl (1 M in *n*-hexane). ^b Molar ratio of Al/V. ^c Activity in kg polymer/mol V · h. ^d GPC data in *o*-dichlorobenzene versus polystyrene standards.

N(1)-V(1)-C(23), N(1)-V(1)-C(27) are 353.4° (**2a**), 352.97° (**2b**), respectively; N(2)-V(1)-N(3): 173.78(5)° for **2a**, 175.60(17)° for **2b**. Two carbon atoms in the CH₂-SiMe₃ ligands are positioned in a *cis* form, and the bond angles for N(1)-V(1)-N(3) are small [76.37(5)° for **2a**, 75.88(17)° for **2b**] due to the two nitrogen atoms coordinating to vanadium as a chelate bidentate ligand. Both the N(imido)-V-N(pyridine) and the N(imido)-V-N(anilide) bond angles in **2b** are larger than those in **2a**, probably due to an increased steric bulk of the ⁱPr substituent in **2b** compared to the Me substituent in **2a** [N(2)-V(1)-N(3) = 173.78(5)° (**2a**), 175.60(17)° (**2b**); N(1)-V(1)-N(3) = 97.60(6)° (**2a**), 99.74(19)° (**2b**)].

4. Some Reactions with the Vanadium(V)-Dialkyl Complexes (2a,b). The reaction of the ⁱPr analogue (**2b**) with 2.0 equiv of (CF₃)₂CHOH in C₆D₆ at 25 °C cleanly afforded

(20) ¹H and ⁵¹V NMR spectra for monitoring the reaction of V(N-2,6-Me₂C₆H₃)(CH₂SiMe₃)₂[2-(2,6-ⁱPr₂C₆H₃)NCH₂(C₅H₃N)] (**2b**) with 3.0 equiv of (CF₃)₂CHOH in C₆D₆ at 25 °C are shown in the Supporting Information. Although resonances ascribed to an intermediate were seen (in the ¹H, ¹⁹F, ⁵¹V NMR spectra) in the reaction of the (adamantyl)vanadium(V)-dialkyl complex containing a chelate alkoxo(imino)pyridine ligand, V(1-adamantyl)(CH₂SiMe₃)₂(L') [L' = 6-OC-(Me)₂-2-[(2,6-ⁱPr₂C₆H₃)N=CMe]C₅H₃N], with (CF₃)₂CHOH,^{13c} other resonances (in addition to **3** and **4**) were not seen in the ⁵¹V NMR spectra during the course of the reaction.

the monoalkoxo complex V(NAr)(CH₂SiMe₃)[OCH-(CF₃)₂][2-(2,6-ⁱPr₂C₆H₃)NCH₂(C₅H₃N)] (**3**), and the ⁵¹V NMR spectrum in the mixture showed a resonance of **3** in addition to a resonance ascribed to **2b** as a tiny trace (Scheme 2). A resonance ascribed to the bis(alkoxo) complex V(NAr)[OCH(CF₃)₂]₂[2-(2,6-ⁱPr₂C₆H₃)NCH₂(C₅H₃N)] (**4**) was seen in addition to the monoalkoxide (**3**) when **2b** was treated with 3.0 equiv of (CF₃)₂CHOH in C₆D₆ at 25 °C.²⁰ The percentage of **4** increased at prolonged reaction times, and a resonance ascribed to **4** became the major product in the ⁵¹V NMR spectrum after 3 days; **4** could thus be isolated in 63% yield as red microcrystals from the chilled *n*-hexane solution (-30 °C).²⁰ The complexes **3** and **4** were identified by NMR spectra and elemental analyses. The reaction proceeded slowly even upon addition of an excess amount of (CF₃)₂CHOH, probably because, as we recently proposed, the reactions proceeded via intermediates formed by coordination of ROH.^{13c,20}

Ring-Opening Metathesis Polymerization of Norbornene by 2a,b in the Presence of PMe₃: Attempt for Isolation of Vanadium(V)-Alkylidene. We previously reported that V-(NAr)(CH₂SiMe₃)₂(N=CⁱBu₂) and V(NAr)(CH₂SiMe₃)₂-(O-2,6-R¹C₆H₃) (R¹ = Me, ⁱPr) initiated ring-opening metathesis polymerization (ROMP) of norbornene at 50–80 °C in the presence of PMe₃.^{14a,14b} These results clearly indicated formation of the vanadium(V)-alkylidene species via α -hydrogen elimination.^{14,15} We thus explored possibilities of **2a,b** as the catalyst precursors for the ROMP of norbornene, and the results are summarized in Table 5. Ring-opened poly(norbornene)s, confirmed by ¹H NMR spectra,²¹ were collected when the reactions of **2a,b** were conducted in the presence of PMe₃, and the polymer yields were dependent upon the molar ratios of PMe₃/V (Scheme 3). The ROMP did not take place or afforded negligible amounts of polymers if the reactions were conducted in the absence of PMe₃. It is thus assumed that a certain amount of vanadium(V)-alkylidene was formed especially in the presence of PMe₃, as seen in the previous reports.^{14a,14b} Although the resultant polymers possessed ring-opened structures (which possessed a mixture of *cis*- and *trans*-olefinic double bonds) confirmed

(21) ¹H NMR spectra for the resultant ring-opened poly(norbornene)s are shown in the Supporting Information. As described in the text, however, attempts to measure the molecular weights and their distributions by GPC (in THF at 50 °C as well as in *o*-dichlorobenzene at 140 °C) failed due to their poor solubility.

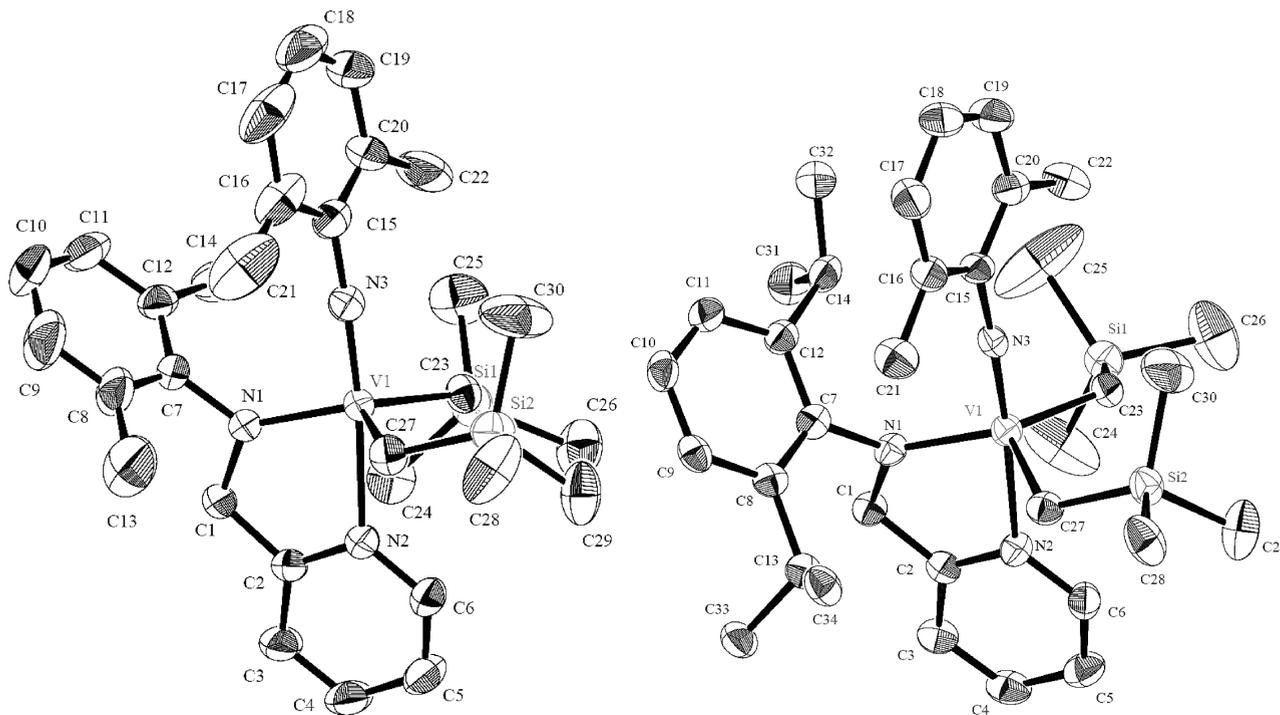


Figure 2. ORTEP drawings of $V(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)_2[(2,6\text{-R}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ [$\text{R} = \text{Me}$ (**2a**, left), $i\text{Pr}$ (**2b**, right)]. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.¹⁸

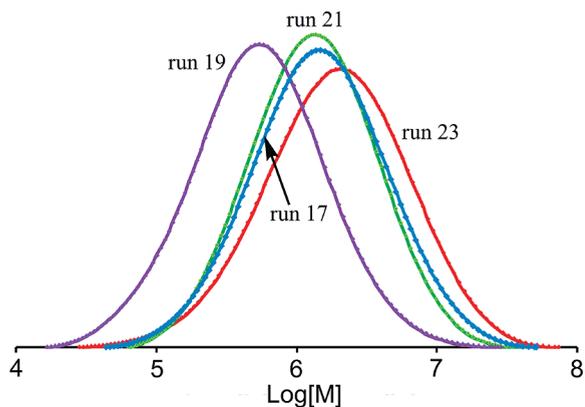


Figure 3. GPC traces for resultant polyethylene prepared by $V(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2[(2,6\text{-R}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ [$\text{R} = i\text{Pr}$ (**1b**), F (**1c**)]- Et_2AlCl catalyst systems (Table 3).

by ^1H NMR spectra, attempts for measurements of their molecular weights and their distributions by GPC measurement (in THF at 50 °C as well as in *o*-dichlorobenzene at 140 °C) failed due to their poor solubility probably owing to ultra high molecular weights.²¹

A C_6D_6 solution containing **2b** in the presence of PMe_3 (excess, 7 equiv) was heated at 80 °C on the basis of the above polymerization results.²² Resonances probably ascribed to alkylidene protons were observed at 16.7 and 17.1 ppm in the ^1H NMR spectrum after 6 h, and at least three resonances including **2b** were seen in the ^{51}V NMR spectrum.²² However, the observed resonances (assumed to be ascribed to the alkylidenes) disappeared after 24 h, probably due to decomposition.

(22) ^1H and ^{51}V NMR spectra for monitoring the reaction of $V(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)_2[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (**2b**) in C_6D_6 in the presence or absence of PMe_3 at 80 °C are shown in the Supporting Information.

Table 4. Selected Bond Lengths and Angles for $V(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)_2[(2,6\text{-R}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ [$\text{R} = \text{Me}$ (**2a**), $i\text{Pr}$ (**2b**)]^a

complex (R)	2a (Me)	2b ($i\text{Pr}$)
Bond Distances (Å)		
V(1)–N(1)	1.9006(13)	1.900(3)
V(1)–N(2)	2.2752(13)	2.259(4)
V(1)–N(3)	1.6807(14)	1.659(4)
V(1)–C(23)	2.0758(19)	2.101(5)
V(1)–C(27)	2.0864(18)	2.093(5)
Bond Angles (deg)		
N(1)–V(1)–N(2)	76.37(5)	75.88(17)
N(1)–V(1)–N(3)	97.60(6)	99.74(19)
N(1)–V(1)–C(23)	125.11(6)	125.0(2)
N(1)–V(1)–C(27)	114.21(6)	113.17(19)
N(2)–V(1)–N(3)	173.78(5)	175.60(17)
N(2)–V(1)–C(23)	82.32(6)	82.61(18)
N(2)–V(1)–C(27)	86.23(6)	85.45(18)
N(3)–V(1)–C(23)	100.24(7)	100.4(2)
N(3)–V(1)–C(27)	97.78(7)	96.1(2)
C(23)–V(1)–C(27)	114.08(6)	114.8(2)
V(1)–N(3)–C(15)	176.96(11)	179.0(3)

^a Detailed analysis results are shown in the Supporting Information.¹⁸

Scheme 2

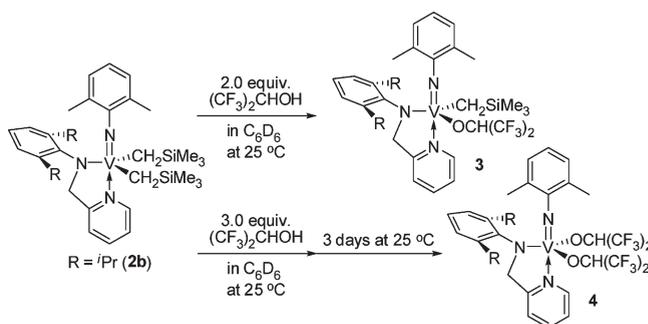
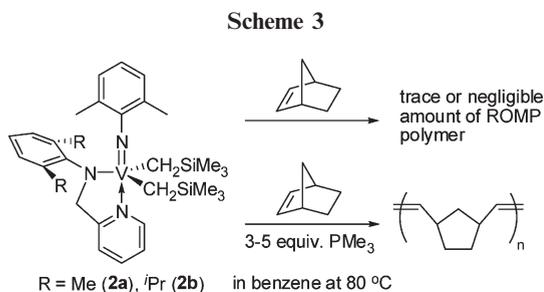


Table 5. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene by V(N-2,6-Me₂C₆H₃)(CH₂SiMe₃)₂-[(2,6-R₂C₆H₃)NCH₂(C₅H₃N)] [R = Me (2a), ^tPr (2b)]^a

complex	PMe ₃ /V ^b	time/min	yield/mg	TON ^c
2a	0	30	trace	
2a	3.0	30	10.2	55
2a	5.0	30	20.8	112
2b	0	30	trace	
2b	3.0	30	6.0	32
2b	5.0	30	29.1	158
2b	10.0	30	3.0	16

^a Reaction conditions: complex 2.0 μmol, benzene 2.5 mL, norbornene 2.12 mmol (0.85 mmol/mL), 80 °C. ^b Molar ratio. ^c TON = norbornene consumed (mmol)/V (mmol).



Although we initially expected that the pyridine moiety in the ligand [2-Ar'NCH₂(C₅H₃N)]⁻ might be used as the neutral donor ligand like PMe₃ to induce α-hydrogen elimination, a C₆D₆ solution containing **2b** caused only decomposition of **2b** after 18 h.²² The result thus clearly explains the fact that we could not collect the ROMP polymer if the polymerization by **2b** was conducted in the absence of PMe₃. The low polymer yields by **2a**, **b** would also be explained by the fact that the percentage of the vanadium(V)-alkylidene formed *in situ* was low under these conditions. We have thus not yet isolated the targeted vanadium(V)-alkylidene presumably due to the difficulty in isolating it from the mixture.

Concluding Remarks

We have prepared a series of (arylimido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligands of the type V(N-2,6-Me₂C₆H₃)Cl₂[2-Ar'NCH₂(C₅H₃N)] [Ar' = 2,6-Me₂C₆H₃ (**1a**), 2,6-^tPr₂C₆H₃ (**1b**), 2,6-F₂C₆H₃ (**1c**)], and the structures of **1b,c** have been determined as having a distorted trigonal-bipyramidal geometry around vanadium by X-ray crystallography. These complexes are effective catalyst precursors for ethylene polymerization in the presence of Al cocatalysts, and **1c** showed the highest catalytic activities among **1a–c** in the presence of MAO cocatalyst, whereas **1b** showed much higher catalytic activities in the presence of Et₂AlCl cocatalyst (6000 kg PE/mol V·h). The resultant polymers are linear polyethylene and possessed high molecular weights with unimodal molecular weight distributions in most cases, suggesting that the polymerizations proceeded with uniform catalytically active species. The activity by **1b** was much higher than that by V(NAr)Cl₂-(N=C'Bu₂)^{9f} but lower than that by V(NAr)Cl₂(O-2,6-Me₂C₆H₃)^{9d} under similar conditions (Et₂AlCl cocatalyst, ethylene 8 atm, 0 °C). The dialkyl complexes (**2a,b**) have been prepared by treating **1a,b** with 2.0 equiv of LiCH₂SiMe₃, and the structures have been determined by X-ray crystallography. Complex **2b** cleanly reacted with 2.0 equiv of (CF₃)₂CHOH in C₆D₆ at 25 °C to afford the mono(alkoxide)

V(NAr)(CH₂SiMe₃)[OCH(CF₃)₂][2-Ar'NCH₂(C₅H₃N)] (**3**) in high isolated yield. The reaction with 3.0 equiv of (CF₃)₂CHOH at 25 °C initially gave **3** (major) in addition to V(NAr)[OCH(CF₃)₂][2-Ar'NCH₂(C₅H₃N)] (**4**), and **4** became the major product after 3 days: a unique reactivity of these vanadium(V)-alkyls with alcohol was thus observed.^{13,14b}

The dialkyl complexes **2a,b** showed catalytic activities for ring-opening metathesis polymerization (ROMP) of norbornene in benzene in the presence of PMe₃, but the polymer yields were low and the reaction did not occur in the absence of PMe₃. The facts are in good agreement with those in the NMR experiments, in which resonances assumed to be ascribed to the vanadium(V)-alkylidene(s) were initially observed if a C₆D₆ solution of **2b** was heated at 80 °C in the presence of PMe₃, but these resonances were not seen in the absence of PMe₃. The facts also clearly indicate that the presence of a pyridine moiety in the chelate ligand in **2a,b** could not initiate the α-hydrogen elimination, and it is thus assumed that an octahedral geometry formed by coordination of an additional donor ligand may be required to induce α-hydrogen elimination.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Anhydrous grade toluene, *n*-hexane, diethyl ether, and benzene (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 N₂ and were passed through an short alumina column under a N₂ stream before use. Polymerization grade ethylene (purity > 99.9%, Sumitomo Seika Co. Ltd.) was used as received. Toluene and AlMe₃ in commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C to remove toluene and AlMe₃, and then at > 100 °C for 1 h for completion) in the drybox to give white solids (d-MAO). Et₂AlCl (1 M in *n*-hexane) was used as received. V(N-2,6-Me₂C₆H₃)Cl₂ was prepared according to a published method.¹⁷

Molecular weights and molecular weight distributions for polyethylene (shown in Table 2) were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mm φ), ranging from < 10² to < 2.8 × 10⁸ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. The molecular weights and molecular weight distributions of the polyethylene in Table 3 were measured at 145 °C by gel permeation chromatography (Waters 150 CV) using *o*-dichlorobenzene as the solvent and calibration with standard polystyrene samples (measured at Sumitomo Chemical Co., Ltd.).

Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.). All ¹H, ¹³C, and ⁵¹V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ¹H, 100.40 MHz for ¹³C, and 105.31 MHz for ⁵¹V). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in ppm and are referenced to SiMe₄ (δ 0.00, ¹H, ¹³C) and VOCl₃ (δ 0.00, ⁵¹V). Coupling constants and half-width values, Δν_{1/2}, are given in Hz.

Synthesis of V(N-2,6-Me₂C₆H₃)Cl₂[2-(2,6-Me₂C₆H₃)NCH₂(C₅H₃N)] (1a**).** Into an Et₂O solution containing V(N-2,6-Me₂C₆H₃)Cl₃ (277 mg, 1.0 mmol) was added Li[2-(2,6-Me₂C₆H₃)NCH₂(C₅H₃N)] (218 mg, 1.0 mmol) at -30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred overnight. The solvent was then removed

in vacuo, and the resultant deep red-tan residue was extracted with hot toluene. The solution was concentrated *in vacuo* and was layered with *n*-hexane. A red powder was obtained upon standing at $-30\text{ }^{\circ}\text{C}$. Yield: 289 mg (58%). $^1\text{H NMR}$ (CDCl_3): δ 9.04 (d, 1H, $J = 5.20$, Py-*H*), 7.95 (t, 1H, $J = 7.70$, Py-*H*), 7.57 (t, 1H, $J = 6.40$, Py-*H*), 7.49 (d, 1H, $J = 7.60$, Py-*H*), 6.90 (d, 2H, $J = 7.20$, Ar-*H*), 6.83 (t, 1H, $J = 8.80$, Ar-*H*), 6.69 (s, 3H, V=N-Ar-*H*), 5.31 (s, 2H, NCH_2), 2.60 (s, 6H, ArCH_3), 2.17 (s, 6H, ArCH_3). $^{13}\text{C NMR}$ (CDCl_3): δ 160.7, 157.0, 149.8, 142.9, 138.1, 128.0, 127.9, 127.4, 126.8, 123.6, 119.9, 71.9, 19.3, 18.2. $^{51}\text{V NMR}$ (CDCl_3): δ 76.7 ($\Delta\nu_{1/2} = 1424$ Hz). Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{N}_3\text{V}$ (0.5 toluene): C, 58.42; H, 5.35; N, 9.29. Found: C, 58.31; H, 5.44; N, 8.94.

Synthesis of $\text{V}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2[2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (1b**).** Synthesis of **1b** was similar to that of **1a**, except that $\text{Li}[2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (330 mg, 1.2 mmol) was used in place of $\text{Li}[2-(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$. Red microcrystals of **1b** were collected in a yield of 30% (yield: 190 mg). $^1\text{H NMR}$ (CDCl_3): δ 8.96 (b, 1H, Py-*H*), 7.95 (t, 1H, $J = 7.00$, Py-*H*), 7.56 (d, 1H, $J = 5.60$, Py-*H*), 7.48 (d, 1H, $J = 6.40$, Py-*H*), 7.23 (m, 1H, Ar-*H*), 7.14 (m, 2H, Ar-*H*), 6.76 (s, 3H, V=N-Ar-*H*), 5.38 (s, 2H, NCH_2), 3.02 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 2.36 (s, 6H, ArCH_3), 1.11 (m, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C NMR}$ (CDCl_3): δ 158.9, 156.4, 142.8, 139.4, 138.2, 128.1, 128.1, 127.6, 127.4, 124.2, 123.7, 119.9, 74.4, 27.8, 25.9, 23.3, 19.8. $^{51}\text{V NMR}$ (CDCl_3): δ 142.0 ($\Delta\nu_{1/2} = 3587$ Hz). Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{Cl}_2\text{N}_3\text{V}$ (0.25 toluene): C, 62.72; H, 6.45; N, 7.91. Found: C, 62.62; H, 6.46; N, 7.87.

Synthesis of $\text{V}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2[2-(2,6\text{-F}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (1c**).** Synthesis of **1c** was similar to that in **1a** except that $\text{Li}[2-(2,6\text{-F}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (415 mg, 1.5 mmol) was used in place of $\text{Li}[2-(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$. Red microcrystals of **1c** were collected in a yield of 29% (yield: 222 mg). $^1\text{H NMR}$ (CDCl_3): δ 9.09 (d, 1H, $J = 5.60$, Py-*H*), 7.95 (t, 1H, $J = 7.70$, Py-*H*), 7.56 (t, 1H, $J = 6.40$, Py-*H*), 7.49 (d, 1H, $J = 8.00$, Py-*H*), 7.17 (toluene), 6.82 (m, 1H, Ar-*H*), 6.70 (s, 3H, Ar-*H*), 6.67 (m, 2H, Ar-*H*), 5.46 (s, 2H, NCH_2), 2.62 (s, 6H, ArCH_3), 2.34 (toluene). $^{13}\text{C NMR}$ (CDCl_3): δ 157.3, 154.8, 152.2, 150.0, 143.2, 138.3, 129.0, 128.2, 128.0, 127.1, 126.9, 123.4, 119.9, 111.2, 111.0, 72.6, 18.8. $^{51}\text{V NMR}$ (CDCl_3): δ 55.0 ($\Delta\nu_{1/2} = 1988$ Hz). Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{F}_2\text{N}_3\text{V}$ (0.5 toluene): C, 55.75; H, 4.38; N, 8.33. Found: C, 55.71; H, 4.30; N, 8.33.

Synthesis of $\text{V}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)_2[2-(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (2a**).** Into a toluene solution (20 mL) containing $\text{V}(\text{N-2,6-Me}_2\text{Ar})(\text{L})\text{Cl}_2$ (0.114 g, 0.25 mmol) was added $\text{LiCH}_2\text{SiMe}_3$ (0.047 g, 0.50 mmol) at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was warmed slowly to room temperature and was stirred for 6 h. The solvent was then removed *in vacuo*, and the resulting residue was extracted with *n*-hexane. The *n*-hexane extracts were placed *in vacuo*, and the resultant red solid was dissolved in a small amount of *n*-hexane (ca. 1 mL). The solution was placed in a freezer ($-30\text{ }^{\circ}\text{C}$), and red microcrystals were grown from the chilled solution (0.083 g, 0.15 mmol) in a yield of 60%. $^1\text{H NMR}$ (C_6D_6): δ 9.06 (d, 1H, $J = 5.60$, Py-*H*), 7.03 (t, 1H, $J = 7.70$, Py-*H*), 6.84–6.65 (m, 8H, Py-*H* and Ar-*H*), 4.56 (s, 2H, NCH_2), 3.00 (d, 2H, $J = 10.00$, CH_2SiMe_3), 2.74 (s, 6H, ArCH_3), 2.10 (s, 6H, ArCH_3), 0.75 (d, 2H, $J = 10.40$, $\text{CH}_2\text{-SiMe}_3$), 0.07 (s, 18H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C NMR}$ (C_6D_6): δ 162.3, 159.1, 148.2, 139.0, 136.9, 130.7, 124.5, 124.3, 122.9, 120.6, 67.1, 20.5, 18.9, 2.8, 1.5. $^{51}\text{V NMR}$ (C_6D_6): δ 386.7 ($\Delta\nu_{1/2} = 622$ Hz). Anal. Calcd for $\text{C}_{30}\text{H}_{46}\text{N}_3\text{Si}_2\text{V}$: C, 64.83; H, 8.34; N, 7.56. Found: C, 64.81; H, 8.73; N, 7.53.

One-Pot Synthesis of $\text{V}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)_2[2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (2b**).** (i) **Method 1 from $\text{V}(\text{NAr})\text{Cl}_3$.** Into a Et_2O solution (40 mL) containing $\text{Li}[2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (0.482 g, 1.76 mmol) was added $\text{V}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)\text{Cl}_3$ (0.490 g, 1.76 mmol) at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was warmed slowly to room temperature and was stirred for 12 h. The solvent was then removed *in vacuo*, and

the red solid was washed by *n*-hexane (20 mL). The solid was dried *in vacuo* and then dissolved in toluene (40 mL). $\text{LiCH}_2\text{SiMe}_3$ (0.330 g, 3.52 mmol) was added into the solution at $-30\text{ }^{\circ}\text{C}$, and the reaction mixture was warmed slowly to room temperature and was stirred overnight. The solvent was then removed *in vacuo* to remove volatiles, and the resultant residue was extracted with *n*-hexane. The *n*-hexane was replaced *in vacuo*, and the resultant sticky brown oil was then dissolved with a small amount of *n*-hexane. The solution was placed in the freezer ($-30\text{ }^{\circ}\text{C}$), affording a red solid (0.603 g, 0.985 mmol) in 56% yield. (ii) **Method 2 from **1b**.** Complex **2b** can also be prepared from **1b**. Into a toluene solution (10 mL) containing $\text{V}(\text{N-2,6-Me}_2\text{Ar})\text{Cl}_2[2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (0.102 g, 0.20 mmol) was added $\text{LiCH}_2\text{SiMe}_3$ (0.038 g, 0.40 mmol) at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was warmed slowly to room temperature and was stirred for 6 h. The solvent was then removed *in vacuo*, and the resultant residue was extracted with *n*-hexane. The *n*-hexane extract was placed *in vacuo* to remove volatiles, and the resultant red solid was dissolved in a small amount of *n*-hexane (ca. 0.5 mL). The chilled solution placed in the freezer ($-30\text{ }^{\circ}\text{C}$) gave red microcrystals (0.089 g, 0.146 mmol) in a yield of 73%. $^1\text{H NMR}$ (C_6D_6): δ 9.05 (d, 1H, $J = 5.12$, Py-*H*), 7.08–7.01 (m, 4H, Py-*H* and Ar-*H*), 6.83 (t, $J = 5.12$, Py-*H*), 6.84–6.81 (m, 3H, Ar-*H*), 6.70–6.66 (m, 2H, Ar-*H*), 5.00 (s, 2H, NCH_2), 3.29–3.22 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.06 (d, 2H, $J = 10.24$, CH_2SiMe_3), 2.61 (s, 6H, ArCH_3), 1.08–1.00 (m, 14H, $\text{CH}(\text{CH}_3)_2$ and CH_2SiMe_3), 0.04 (s, 18H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C NMR}$ (C_6D_6): δ 161.8, 157.9, 148.6, 141.9, 140.0, 137.2, 125.7, 124.4, 124.2, 123.3, 120.2, 70.1, 27.6, 27.5, 23.0, 21.0, 2.8, 1.5. $^{51}\text{V NMR}$ (C_6D_6): δ 435.7 ($\Delta\nu_{1/2} = 1141$ Hz). Anal. Calcd for $\text{C}_{34}\text{H}_{54}\text{N}_3\text{Si}_2\text{V}$: C, 66.73; H, 8.89; N, 6.87. Found: C, 66.03; H, 8.97; N, 7.06.

Synthesis of $\text{V}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)[\text{OCH}(\text{CF}_3)_2][2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (3**).** A C_6D_6 solution of $(\text{CF}_3)_2\text{CHOH}$ (17 mg, 0.10 mmol) was added to a C_6D_6 solution containing **2b** (0.031 g, 0.05 mmol). The mixture was stirred for 1 h, and the solvent was then removed *in vacuo*. The resultant solid was dissolved with a small amount of *n*-hexane, and the chilled solution ($-30\text{ }^{\circ}\text{C}$) afforded red microcrystals (0.027 g, 0.039 mmol) in a yield of 78%. $^1\text{H NMR}$ (C_6D_6): δ 9.02 (d, 1H, $J = 5.20$, Py-*H*), 7.06–6.93 (m, 4H, Py-*H* and Ar-*H*), 6.69–6.52 (m, 5H, Ar-*H*), 5.20 (m, 1H, $\text{CH}(\text{CF}_3)_2$), 5.10 (d, 1H, $J = 20.80$, NCH_2), 4.83 (d, 1H, $J = 20.40$, NCH_2), 3.50 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.09 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 2.56 (d, 1H, $J = 10.80$, CH_2SiMe_3), 2.43 (s, 6H, ArCH_3), 2.35 (d, 1H, $J = 10.80$, $\text{CH}_2\text{-SiMe}_3$), 1.09–1.02 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 0.11 (s, 9H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C NMR}$ (CDCl_3): δ 160.3, 158.6, 148.1, 141.5, 141.4, 140.4, 137.9, 126.6, 125.9, 124.6, 124.3, 123.0, 120.0, 71.3, 28.0, 27.8, 27.3, 27.0, 23.2, 22.9, 19.8, 2.7. $^{51}\text{V NMR}$ (CDCl_3): δ 75.7 ($\Delta\nu_{1/2} = 716$ Hz). Anal. Calcd for $\text{C}_{33}\text{H}_{44}\text{F}_6\text{N}_3\text{OSiV}$: C, 57.30; H, 6.41; N, 6.07. Found: C, 56.32; H, 6.31; N, 5.96.

Synthesis of $\text{V}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)[\text{OCH}(\text{CF}_3)_2][2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_5\text{H}_3\text{N})]$ (4**).** A C_6D_6 solution of $(\text{CF}_3)_2\text{CHOH}$ (0.102 g, 0.60 mmol) was added to a C_6D_6 solution containing **2b** (0.124 g, 0.20 mmol). The mixture was stirred for 3 days, and the solvent was removed *in vacuo*. The resultant oil was dissolved with a small amount of *n*-hexane (ca. 0.5 mL), and the chilled solution ($-30\text{ }^{\circ}\text{C}$) afforded red microcrystals (0.097 g, 0.126 mmol) in a yield of 63%. $^1\text{H NMR}$ (C_6D_6): δ 8.79 (d, 1H, $J = 5.48$, Py-*H*), 7.09–7.02 (m, 3H, Py-*H*), 6.74 (t, 1H, $J = 7.60$, Ar-*H*), 6.52 (d, 2H, $J = 7.60$, Ar-*H*), 6.46–6.40 (m, 2H, Ar-*H*), 6.32 (d, 1H, $J = 7.60$, Ar-*H*), 4.99–4.95 (m, 4H, NCH_2 and $\text{CH}(\text{CF}_3)_2$), 3.38 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 2.36 (s, 6H, ArCH_3), 1.10–1.08 (m, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C NMR}$ (CDCl_3): δ 159.3, 159.0, 147.7, 142.3, 141.2, 138.7, 124.7, 123.4, 121.9, 119.9, 80.7 (m), 71.5, 28.0, 27.2, 23.0, 18.8. $^{51}\text{V NMR}$ (C_6D_6): δ 214.7 ($\Delta\nu_{1/2} = 1353$ Hz). Anal. Calcd for $\text{C}_{32}\text{H}_{34}\text{F}_6\text{N}_3\text{O}_2\text{V}$: C, 49.81; H, 4.44; N, 5.45. Found: C, 50.07; H, 4.61; N, 5.33. ^1H and ^{51}V NMR spectra for monitoring the reaction are shown in the Supporting Information.²⁰

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with

graphite-monochromated Mo K α radiation. Selected crystal collection parameters and the detailed results are described in the Supporting Information.¹⁸ All structures were solved by direct methods and expanded using Fourier techniques,²³ and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the CrystalStructure^{24,25} crystallographic software package, except for refinement for **1c** as well as **2b**, which was performed using SHELXL-97.²⁶

Polymerization of Ethylene. Ethylene polymerizations were conducted in a 100 mL scale stainless steel autoclave, and the typical reaction procedure is as follows. Toluene (29 mL) and MAO solid (prepared from ordinary MAO by removing toluene and AlMe₃) or Et₂AlCl (1 M in *n*-hexane) were added into the autoclave in the drybox. The reaction apparatus was then filled with ethylene (1 atm), and a toluene solution (1.0 mL) containing the dichloride complex **1** was then added into the autoclave, the reaction apparatus was then immediately pressurized to 7 atm (total 8 atm), and the mixture was magnetically stirred for 10 min. After the above procedure, remaining ethylene was purged upon cooling, and the mixture was then poured into MeOH containing HCl. The resultant polymer (white precipitate) was collected on a filter paper by filtration and was adequately washed with MeOH. The resultant polymer was then dried *in vacuo* at 60 °C for 2 h.

Ring-Opening Metathesis Polymerization of Norbornene. Into a sealed Schlenk tube containing a benzene solution (0.5 mL) containing norbornene (2.12 mmol, 200 mg) were added a

benzene solution containing **2b** (or **2a**, 2.0 μ mol) and a benzene solution (1.0 mL) containing a prescribed amount of PMe₃ in the drybox at room temperature. Then the mixture was magnetically stirred for a prescribed time at a prescribed temperature. The polymerization was then quenched by the addition of excess PhCHO, and the solution was stirred for an additional 1 h at room temperature for completion. The mixture was then poured into MeOH (ca. 100 mL). The resultant polymer was collected on filter paper and was adequately washed with MeOH. The polymer was then dried *in vacuo* for several hours. ¹H NMR (CDCl₃) of the PNBE: δ 5.31 (m), 5.19 (m), 2.76 (b), 2.40 (b), 1.85–1.74 (m), 1.33 (m), 1.07–0.99 (m).²¹

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 19028047, “Chemistry of Concerto Catalysis”) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This project is also partly supported by Bilateral Joint Projects between the Japan Society for the Promotion of Science (JSPS) and National Natural Science Foundation of China (NSFC). S.Z. expresses his sincere thanks to JSPS for a postdoctoral fellowship (P08361). K.N. and Z.S. express their thanks to Sumitomo Chemical Co., Ltd. (Petrochemicals Research Laboratory) for GPC analysis.

Supporting Information Available: ¹H and ⁵¹V NMR spectra for monitoring reactions of V(N-2,6-Me₂C₆H₃)(CH₂SiMe₃)₂-[2-(2,6-ⁱPr₂C₆H₃)NCH₂(C₅H₃N)] (**2b**) in C₆D₆ at 80 °C in the presence/absence of PMe₃, reaction of **2b** with 3.0 equiv of (CF₃)₂CHOH in C₆D₆ at 25 °C, affording V(N-2,6-Me₂C₆H₃)-[OCH(CF₃)₂]₂[2-(2,6-ⁱPr₂C₆H₃)NCH₂(C₅H₃N)] (**2b**), and ¹H NMR spectra of poly(norbornene)s prepared by **2b** in benzene in the presence of PMe₃. Text giving crystal structure reports (including crystal data and collection parameters) and CIF files for **1b**, **1c**, **2a**, and **2b**. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

(23) 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 the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 1994.

(24) *CrystalStructure 3.6.0*: Crystal Structure Analysis Package; Rigaku and Rigaku/MSK: The Woodlands, TX, 2000–2004.

(25) Watkin, D. J., Prout, C. K. Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, UK, 1996.

(26) Sheldrick, G. M. *SHELX97; Program for Crystal Structure Determination*; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1997.