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Syntheses of Various (Arylimido)vanadium(V)–Dialkyl Complexes Containing Aryloxo and Alkoxo Ligands, and Ring-Opening Metathesis Polymerization Using a Vanadium(V)–Alkylidene Complex

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Treatment of $V(NAr)(CH_2SiMe_3)_3$ (**1**, Ar = 2,6-$Me_2C_6H_3$) with 1.0 equiv of various alcohols in *n*-hexane at 25 °C cleanly afforded the corresponding dialkyl complexes of the type $V(NAr)(CH_2SMe_3)_2(OR)$ [R = 2,6-$Me_2C_6H_3$ (**2a**), 2,6-$^iPr_2C_6H_3$ (**2b**), C_6F_5 (**2c**), ^tBu (**2d**), $CMe(CF_3)_2$ (**2e**), yield 90−93%]. In contrast, the reactions with R′N(H)Me (R′ = Ph, cyclohexyl) or 2,6-$Me_2C_6H_3SH$ did not take place even if the reactions were attempted in $C_2D_2Cl_4$ at 50 °C. Complexes **2a** and **2b** showed high catalytic activities for the ring-opening metathesis polymerization (ROMP) of norbornene in the presence of PMe_3, and the activity increased at high temperature (80 °C). A vanadium(V)−alkylidene complex, $V(CHSiMe_3)(NAr)(O\text{-}2,6\text{-}^iPr_2C_6H_3)(PMe_3)_x$ (**3**, $x = 0.89$), has been isolated when the C_6D_6 solution containing **2b** was heated at 80 °C in the presence of PMe_3 (5.0 equiv). Complex **3** showed remarkable catalytic activity for the ROMP of norbornene, and the polymerization at 25 °C proceeded in a living manner.

Introduction

Transition metal−alkyl complexes are important reagents or intermediates in stoichiometric/catalytic organic reactions, as well as in olefin coordination/insertion polymerization.[1,2] The synthesis and reaction chemistry of transition metal−alkyl complexes have thus been considered to be important not only in designing the efficient catalysts but also for better understanding of the organic reactions, especially with regard to catalytic cycles or reaction pathways. Transition metal−alkylidene complexes are also important intermediates in olefin metathesis [such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), and cross metathesis (CM) reactions], which introduces promising possibilities for synthesis of both functional polymers and valuable organic compounds,[3] as demonstrated especially by molybdenum[4] and ruthenium.[5]

Classical Ziegler-type vanadium catalysts are known to exhibit unique characteristics, such as synthesis of ultrahigh molecular weight polymers with relatively narrow molecular weight distributions, due to their high reactivity toward olefins in olefin coordination/insertion polymerization.[2e,6,7] Therefore, the synthesis and reaction chemistry of vanadium complexes, especially the alkyl complexes, have attracted considerable attention.[8–11] Some reactions concerning the alkyl complexes that contain (one or two) cyclopentadienyl (Cp′) ligands were

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(1) For example (general text of metal−alkyl chemistry): (a) *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Crabtree, R. H., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2005; p 53. (b) *Synthesis of Organometallic Compounds: A Practical Guide*; Komiya, S., Ed.; John Wiley & Sons Ltd.: West Sussex, England, 1997.

(2) Related reviews for olefin polymerization catalysts (including vanadium complexes): (a) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229. (b) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357. (c) Bolton, P. D.; Mountford, P. *Adv. Synth. Catal.* **2005**, *347*, 355. (d) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (e) Nomura, K. In *New Developments in Catalysis Research*; BevyL. P., Ed.; Nova Science Publishers, Inc.: New York, 2005; p 199.

(3) For examples, see:(a) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (b) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003; Vol. 13. (c) Khosravi, E., Szymanska-Buzar, T., Eds. *Ring-Opening Metathesis Polymerisation and Related Chemistry*; Kluwer: Dordrecht, The Netherlands, 2002. (d) Imamoglu, Y., Dragutan, V., Eds. *Metathesis Chemistry*; Springer: Dordrecht, The Netherlands, 2007.

(4) For examples, see:(a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Schrock, R. R. In *Alkene Metathesis in Organic Synthesis*; FürstnerA., Ed.;Springer: Berlin, Germany, 1998; p 1. (c) SchrockR. R. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1, p 8.

(5) For examples, see:(a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29. (b) Nguyen, S. T.; Trnka, T. M. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 3, pp 61−85.

(6) Pioneering 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) Junghanns, V. E.; Gumboldt, A.; Bier, G. *Makromol. Chem.* **1962**, *58*, 18. (d) Carrick, W. L.; Reichle, W. T.; Pennella, F.; Smith., J. J. *J. Am. Chem. Soc.* **1960**, *82*, 3887. (e) Natta, G.; Mazzanti, G.; Valvassori, A.; Sartori, G.; Fiumani, D. *J. Polym. Sci.* **1961**, *51*, 411. (f) Gumboldt, V. A.; Helberg, J.; Schleitzer, G. *Makromol. Chem.* **1967**, *101*, 229. (g) Lehr, M. H. *Macromolecules* **1968**, *1*, 178. (h) Christman, D. L.; Keim, G. I. *Macromolecules* **1968**, *1*, 358. (i) Christman, D. L. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 471.

(7) Pioneering examples for synthesis of block copolymers by living polymerization using vanadium catalysts:(a) Doi, Y.; Ueki, S.; Soga, K. *Macromolecules* **1979**, *12*, 814. (b) Doi, Y.; Hizal, G.; Soga, K. *Makromol. Chem.* **1987**, *188*, 1273.

(8) Some structural characterizations, reaction chemistry of V(III),(IV) methyl complex:(a) Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 946. (b) Hessen, B.; Lemmen, T. H.; Luttikhedde, H. J. G.; Teuben, J. H.; Petersen, J. L.; Jagner, S.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1987**, *6*, 2354. (c) Hessen, B.; Meetama, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 5977. (d) Gerlach, C. P.; Arnold, J. *Organometallics* **1996**, *15*, 5260. (e) Aharonian, G.; Feghali, K.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2616. (f) Feghali, K.; Harding, D. J.; Reardon, D.; Gambarotta, S.; Yap, G.; Wang, Q. *Organometallics* **2002**, *21*, 968. (g) Choukroun, R.; Lorber, C.; Donnadieu, B. *Organometallics* **2002**, *21*, 1124. (h) Liu, G.; Beetstra, D. J.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 3914.

(9) Examples for structurally characterized V(V) alkyls:(a) de With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1990**, *9*, 2207. (b) Murphy, V. J.; Turner, H. *Organometallics* **1997**, *16*, 2495.

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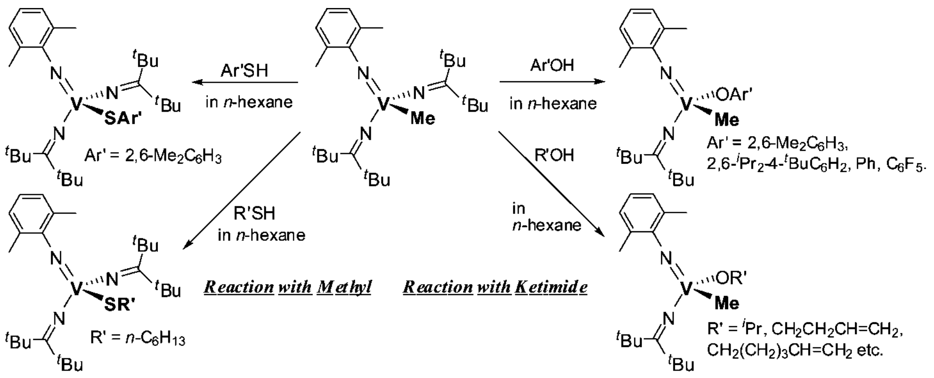
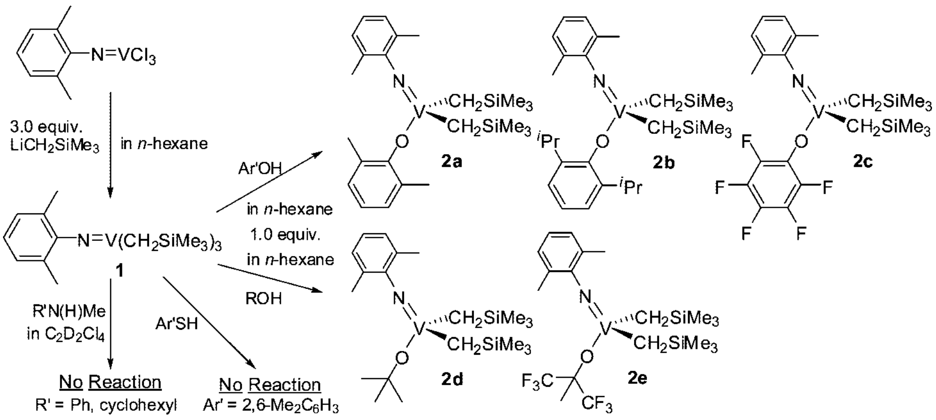
Scheme 1



Scheme 2



described,[8a–c] but there are still limited examples of the synthesis of vanadium–alkyls (especially that do not contain a Cp′ ligand). This may be due to the fact that these vanadium–alkyls tend to be reactive and/or thermally labile and reductions to lower oxidation states were often observed in reactions with organometallic reagents.[10] Although many examples of olefin polymerization using vanadium complex catalysts and Ziegler-type vanadium catalysts have been known, there have been only a few examples of olefin metathesis with vanadium.[12,13]

We recently reported that treatment of V(NAr)Me(N=C^{t}Bu$_2$)$_2$ with 1.0 equiv of various alcohols (phenols) cleanly afforded the other methyl complexes V(NAr)(Me)(N=C^{t}Bu$_2$)(OR) (OR = aryloxo, alkoxo), and reaction with the methyl group did not occur in any cases.[11] In contrast, the reactions of V(NAr)(Me)(N=C^{t}Bu$_2$)$_2$ with thiols afforded V(NAr)(N=C^{t}Bu$_2$)$_2$(SR′) (R′ = *n*-C$_6$H$_{13}$ or 2,6-Me$_2$C$_6$H$_3$) via reaction with the methyl group (Scheme 1). We also reported that a vanadium(V)–alkylidene complex, V(CHSiMe$_3$)(NAr)(N=C^{t}Bu$_2$)(PMe$_3$), was prepared by α-H elimination from the dialkyl analogue in the presence of PMe$_3$,[14] and the complex showed notable catalytic activity for the ROMP of norbornene even at 80 °C. Since syntheses of some low-coordinate vanadium(V)–dialkyl complexes by treatment of V(NAr′)(CH$_2$Ph)$_3$ (Ar′ = 2,6-^{i}Pr$_2$C$_6$H$_3$) with 2,6-^{i}Pr$_2$C$_6$H$_3$OH, (CF$_3$)$_3$COH, and PhN(H)Me were known,[9b] we are thus interested in exploring the possibility of establishing a systematic synthesis of various vanadium(V)–dialkyl complexes that contain anionic donor ligands from the trialkyl analogues.[15] Since we recently prepared another trialkyl complex, V(NAr)(CH$_2$SiMe$_3$)$_3$, in high yield (81%),[16] we herein explored reactions with alcohols, phenols, amines, and thiol to prepare various dialkyl derivatives. We also explored the possibility of isolation of "olefin metathesis active" vanadium(V)–alkylidenes via α-H abstraction from the dialkyl complexes in the presence of PMe$_3$.

Results and Discussions

1. Synthesis of V(NAr)(CH$_2$SiMe$_3$)$_3$ (1) and Reactions with Alcohols, Phenols, Amines, And Thiol. A vanadium(V)–trialkyl complex, V(NAr)(CH$_2$SiMe$_3$)$_3$ (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$), could be prepared by treatment of V(NAr)Cl$_3$ with 3.0 equiv of LiCH$_2$SiMe$_3$ in *n*-hexane (Scheme 2). The analytically pure complex (**1**) was isolated by simply extracting the mixture with *n*-hexane and was identified by ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy and elemental analysis. The resonance in the ^{51}V

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(10) Examples:(a) Preuss, F.; Ogger, L. *Z. Naturforsch.* **1982**, *37B*, 957. (b) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. *J. Am. Chem. Soc.* **1987**, *109*, 7408. (c) Preuss, F.; Becker, H.; Kraub, J.; Sheldrick, W. J. *Z. Naturforsch.* **1988**, *43B*, 1195. (d) Preuss, F.; Becker, H.; Wieland, T. *Z. Naturforsch.* **1990**, *45B*, 191. (e) Preuss, F.; Overhoff, G.; Becker, H.; Häusler, H. J.; Frank, W.; Reiss, G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1827. (f) Solan, G. A.; Cozzi, P. G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 2572. (g) Chan, M. C. W.; Cole, J. M.; Gibson, V. C.; Howard, J. A. K. *Chem. Commun.* **1997**, 2345.

(11) Our previous examples:(a) Yamada, J.; Nomura, K. *Organometallics* **2005**, *24*, 3621. (b) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2007**, *26*, 2579.

(12) Polymerization of 3-methylcyclobutene: Dall'Asta, G. *J. Polym. Sci., Part A1* **1968**, *6*, 2397. In the presence of VCl$_4$/^{n}BuLi as the catalyst, a ring-opened polymer was obtained.

(13) Polymerization of cyclopentene:(a) Natta, G.; Dall'Asta, G.; Mazzanti, G. *Angew. Chem.* **1965**, *76*, 765. (b) Natta, G.; Scaglione, P. *Rubber Chem. Technol.* **1969**, *42*, 1235. However, the resultant polymers were mixtures of polymers prepared by olefin metathesis and coordination insertion pathways.

(14) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2005**, *24*, 2248. References concerning the other vanadium–aklylidenes were also cited therein.

(15) In addition to V(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(CH$_2$Ph)$_3$,[9b] syntheses of V(N-4-MeC$_6$H$_4$)(CH$_2$SiMe$_3$)$_3$[10b] and V(N^{t}Bu)(CH$_2$SiMe$_3$)$_3$[10e] were known as examples.

NMR spectrum (δ 1070 ppm) is relatively close to that in V(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(CH$_2$Ph)$_3$ (1008 ppm),[9b] and the resonances in a series of (imido)vanadium−trialkyl complexes are found to be influenced by the imido substituent employed [ca. V(N-4-MeC$_6$H$_4$)(CH$_2$SiMe$_3$)$_3$[10b] (δ 1028), V(N^{t}Bu)(CH$_2$SiMe$_3$)$_3$ (δ 877)[10e]]. Although **1** is a low-coordinate unsaturated vanadium complex, the coordination of PMe$_3$ to **1** was not seen (by ^{51}V NMR spectra), even by addition of an excess amount (7.0 equiv) in C$_6$D$_6$ at 25 °C, and this observation is due to the steric hindrance of the three CH$_2$SiMe$_3$ ligands around the vanadium(V) metal center.

Reactions of **1** with alcohols, phenols, amines, and thiol were thus explored for comparison with the reactivity of V(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(CH$_2$Ph)$_3$,[9b] as well as of the reported V(NAr)(Me)(N═C^{t}Bu$_2$)$_2$.[11] Treatment of **1** with 2,6-Me$_2$C$_6$H$_3$OH, 2,6-^{i}Pr$_2$C$_6$H$_3$OH, and C$_6$F$_5$OH (in *n*-hexane at 25 °C) cleanly afforded the corresponding vanadium(V)−aryloxide complexes V(NAr)(CH$_2$SiMe$_3$)$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**2a**), V(NAr)(CH$_2$SiMe$_3$)$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2b**), and V(NAr)(CH$_2$SiMe$_3$)$_2$(OC$_6$F$_5$) (**2c**), respectively, in high yields (90−93%, Scheme 2). The resultant dialkyl−aryoloxo complexes were identified on the basis of ^{1}H, ^{13}C, and ^{51}V (and ^{19}F) NMR spectra and elemental analyses. In contrast, the reaction of **1** with 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$OH did not take place under the same conditions, and the reaction did not occur even if the C$_2$D$_2$Cl$_4$ solution containing **1** was heated at 50 °C in the presence of 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$OH with an excess amount (2.6 equiv).[17] This is probably due to the steric bulk of the two *tert*-butyl groups in the aryloxo ligand and three CH$_2$SiMe$_3$ ligands around V. The above fact is interesting, because V(NAr)Cl$_2$(O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$) was prepared from V(NAr)Cl$_3$ by treatment with 1.0 equiv of 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$OH (yield 94%).[18,19]

The similar reactions of **1** with 1.0 equiv of ^{t}BuOH and (CF$_3$)$_2$CMeOH in *n*-hexane also gave the corresponding alkoxides V(NAr)(CH$_2$SiMe$_3$)$_2$(O^{t}Bu) (**2d**) and V(NAr)(CH$_2$SiMe$_3$)$_2$[OCMe(CF$_3$)$_2$] (**2e**) in high yields (92−93%). The resultant vanadium(V) dialkyl−alkoxo complexes (**2d**,**e**) were also identified by ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy and elemental analysis. Substitution of the alkyl group in **1** with alcohol or phenol leads to upfield chemical shifts (δ 406−659 ppm) from the trialkyl complex (**1**, 1070 pm) in the ^{51}V NMR spectra, and the degree of the upfield shift in the dialkyl complexes (**2a**−**e**) increased in the order δ 406 (**2d**, O^{t}Bu) > 506−507 (**2a**,**b**, O-2,6-Me$_2$C$_6$H$_3$, O-2,6-^{i}Pr$_2$C$_6$H$_3$) > 595 [**2e**, OCMe(CF$_3$)$_2$] > 659 (**2c**, OC$_6$F$_5$). On the basis of the above results including the trend observed for a series of (imido)vanadium(V)−trialkyl complexes described above, these resonances seem to be influenced mostly by an electronic factor in the anionic donor ligand employed.

Note that the reactions of **1** with 1.0 equiv of amines such as PhN(H)Me and (cyclo-C$_6$H$_{13}$)N(H)Me did not take place under the same conditions (in *n*-hexane at 25 °C), whereas the reaction of V(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(CH$_2$Ph)$_3$ with PhN(H)Me in hexane afforded the corresponding anilide complex V(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(CH$_2$Ph)$_2$[N(Me)Ph], exclusively.[9b] The reactions of **1** with 2.8−2.9 equiv of amines in C$_2$D$_2$Cl$_4$ at 50 °C did not occur (even after >6 h), and resonances ascribed to **1** could be seen in both ^{1}H and ^{51}V NMR spectra of the reaction mixture.[17] Moreover, the reaction of **1** with 1.0 equiv of 2,6-Me$_2$C$_6$H$_3$SH did not take place in *n*-hexane, and the reactions of **1** with an excess amount of 2,6-Me$_2$C$_6$H$_3$SH (ca. 5.6 equiv to **1**) did not occur even in C$_2$D$_4$Cl$_2$ at 50 °C.[17] The fact should be interesting to note, because, as described in the Introduction, treatment of V(NAr)(Me)(N═C^{t}Bu$_2$)$_2$ with thiols cleanly afforded V(NAr)(N═C^{t}Bu$_2$)$_2$(SR′) (R′ = *n*-C$_6$H$_{13}$ or 2,6-Me$_2$C$_6$H$_3$) via reaction with the methyl group.[11] Although we do not have appropriate explanations why these reactions of **1** with amines and thiol did not occur, the present facts should be unique examples seen in the present trialkyl complex (**1**), probably due to the steric bulk of the three CH$_2$SiMe$_3$ ligands around the vanadium(V) metal center.[19]

2. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene with V(NAr)(CH$_2$SiMe$_3$)(O-2,6-R$^1_2$C$_6$H$_3$) [R^1 = Me (2a), ^{i}Pr (2b)] in the Presence of PMe$_3$. We recently reported that V(NAr)Cl$_2$(O-2,6-R$^1_2$C$_6$H$_3$) (R^1 = Me, ^{i}Pr) exhibited moderate or high catalytic activities for the ring-opening metathesis polymerization (ROMP) of norbornene (NBE) in the presence of MeMgBr and PMe$_3$.[20] We also reported that V(NAr)(CH$_2$Ph)$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) initiated the ROMP of NBE in toluene (37 turnovers after 11 h).[18] These facts suggested formation of the olefin metathesis active vanadium(V)−alkylidene species *in situ* probably via α-H elimination from the dialkyl analogues. We thus explored the ROMP of NBE using V(NAr)(CH$_2$SiMe$_3$)$_2$(O-2,6-R$^1_2$C$_6$H$_3$) [R^1 = Me (**2a**), ^{i}Pr (**2b**)] in the presence of PMe$_3$.

It turned out that the ROMP of NBE by **2a**,**b** proceeded at 50 °C in the presence of PMe$_3$ (PMe$_3$/V = 3, molar ratio, runs 1, 5), and the activities increased at 80 °C (runs 3, 7). The ROMP did not take place or showed extremely low activities in the absence of PMe$_3$ (runs 2, 6),[21] and the activity decreased upon excessive addition (PMe$_3$ 5 equiv, runs 4, 8). The facts suggest that certain vanadium(V)−alkylidene species are generated in the reaction mixture, and PMe$_3$ is necessary to facilitate formation of the active species *in situ*, as reported previously.[14,20,22] The observed decrease in the activity by the excessive addition of PMe$_3$ was similar to that in the ROMP by V(NAr)(CH$_2$SiMe$_3$)$_2$(N═C^{t}Bu$_2$):[14] this could be thus explained as due to coordination of PMe$_3$ into the vanadium center retarding the propagation (coordination of NBE for propagation), leading to the lower activities. The activity by **2a** was higher than that by **2b**, and the order in the activity was the same as that in the ROMP by

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(16) Some of these results were presented at the *XVIIth International Symposium on Olefin Metathesis (ISOMXVII)*, July 2007, Pasadena, CA.

(17) ^{1}H and ^{51}V NMR spectra for monitoring the reaction mixture of **1** with 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$OH, PhN(H)Me, (cyclo-C$_6$H$_{13}$)N(H)Me, and 2,6-Me$_2$C$_6$H$_3$SH are shown in the Supporting Information.

(18) Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, *35*, 1583.

(19) One speculation we may take into consideration for explaining the observed fact (especially the reaction with 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$OH) would be due to the steric bulk of both the substrate and the three CH$_2$SiMe$_3$ ligands for coordination of oxygen to the vanadium(V) metal center.[11b] This is because we proposed that the reaction of V(NAr)(Me)(N═C^{t}Bu$_2$)$_2$ with phenols proceeds via pentacoordinated trigonal-bypyramidal species by coordination of phenols to the vanadium metal center.[11b] However, we do not have clear, appropriate experimental facts to support this speculation in this case. We do not have appropriate explanations for why the reactions with 2,6-Me$_2$C$_6$H$_3$SH, PhN(H)Me, and (*cyclo*-C$_6$H$_{13}$)N(H)Me did not take place.

(20) Nomura, K.; Atsumi, T.; Fujiki, M.; Yamada, J. *J. Mol. Catal. A* **2007**, *275*, 1.

(21) We previously reported that V(NAr)(CH$_2$Ph$_2$)$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) catalyzed the ROMP of norbornene (NBE) at 25 °C to afford the ring-opened polymer with high molecular weight ($M_w = 4.69 \times 10^6$, $M_w/M_n = 1.93$), although the activity was low (37 turnovers after 11 h).[18] The ROMP was in fact conducted under rather high concentration conditions (NBE 2.50 mmol, 0.55 mmol/mL toluene). Therefore, we assumed that the catalytically active species, vanadium(V)−alkylidene, was formed partially (but a small amount) by coordination of NBE in place of PMe$_3$ under these conditions.

(22) Review article for synthesis of early transition metal−alkylidenes: (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Mindiola, D. *Acc. Chem. Res.* **2006**, *39*, 813. (c) Mindiola, D.; Bailey, B.; Basuli, F. *Eur. J. Inorg. Chem.* **2006**, *16*, 3135.

using a catalyst system consisting of V(NAr)Cl$_2$(O-2,6-R$^1_2$C$_6$H$_3$) (R^1 = Me, ^{i}Pr), MeMgBr, and PMe$_3$[18] as well as that in the ethylene polymerization in the presence of MAO.[18,23]

3. Isolation of a Vanadium(V)−Alkylidene, V(CHSiMe$_3$)(NAr)(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(PMe$_3$)$_x$ (3), and the Ring Opening Metathesis Polymerization (ROMP) of Norbornene. As described above, since the ROMP of NBE by the dialkyl analogues (**2a**,**b**) proceeded in the presence of PMe$_3$, we explored the possibility of isolation of the vanadium(V)−alkylidenes in C$_6$D$_6$ in the presence of PMe$_3$ at 80 °C.[14,22] The C$_6$D$_6$ solution containing **2b** and PMe$_3$ (5.0 equiv) was monitored by the ^{1}H NMR spectra, and consumption of the dialkyl species (**2b**) along with appearances in resonances corresponding to protons ascribed to the vanadium(V)−alkylidenes (described below)[24] were confirmed after 5 h: the brown microcrystals were thus grown from the chilled *n*-hexane solution (−30 °C) containing the reaction mixture upon addition of PMe$_3$. The corresponding vanadium(V)−alkylidene, V(CHSiMe$_3$)(NAr)(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(PMe$_3$)$_x$ (**3**, x = 0.89 by ^{1}H NMR spectrum and elemental analysis),[24] was thus identified on the basis of ^{1}H, ^{13}C, ^{31}P, and ^{51}V NMR spectra and elemental analysis. However, we have not yet isolated pure microcrystals from the reaction mixture containing **2a** instead of **2b** under the same conditions.[25] PMe$_3$ in **3** was partially dissociated from the metal center during the purification procedure (by placing the grown microcrystals *in vacuo* to remove solvent), probably due to the steric bulk of the two ^{i}Pr groups on the aryloxo ligand.

A resonance ascribed to the alkylidene carbon in **3** was observed at 322.8 ppm (broad), and the resonance is close to that in the reported V(CHSiMe$_3$)(NAr)(N=C^{t}Bu$_2$)(PMe$_3$) (**4**, 302.0 ppm).[14] Two sets of resonances ascribed to protons (corresponding to SiMe$_3$, isopropyl, and methyl groups, alkylidene, etc.) were seen in the ^{1}H NMR spectrum measured at 25 °C. No significant differences in the spectra were observed at 60 °C, except that protons ascribed to the alkylidene became somewhat broad.[2] In contrast, only one broad resonance in the protons ascribed to the alkylidene (in addition to one set of protons ascribed to SiMe$_3$, etc.) was seen in the ^{1}H NMR spectrum upon addition of 1.0 equiv of PMe$_3$.[24] Two resonances were observed in the ^{51}V NMR spectrum for **3** in C$_6$D$_6$, but only one resonance was seen if the spectrum was measured in the presence of PMe$_3$.[24] These facts clearly indicate the presence of both the PMe$_3$ coordinated and the PMe$_3$ free species (ratio = 8.15:1) in the spectra of **3**.[24] The partial dissociation of PMe$_3$ in **3** could also be explained by the elemental analysis. Resonances ascribed to the alkylidene protons in **3** (16.09 and 16.38 ppm, broad) are somewhat low-field from that in **4** (14.52 ppm),[14] probably due to the difference in the electronic nature between the ketimide ligand (N=C^{t}Bu$_2$ in **4**) and the aryloxo ligand (O-2,6-^{i}Pr$_2$C$_6$H$_3$ in **3**).

Table 1. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE) by V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2$ (O-2,6-R$^1_2$C$_6$H$_3$) [R^1 = Me (2a), ^{i}Pr (2b)]^a

run	complex	PMe$_3$/V^b	temp/°C	yield/ mg (%)	TON^c	M_n^{d} × 10^{-5}	M_w/M_n^{d}
1	**2a**	3	50	14 (7)	300	3.5	2.6
2	**2a**	0	80	trace			
3	**2a**	3	80	74 (37)	1570	2.9	2.6
4	**2a**	5	80	28 (14)	590	1.9	2.8
5	**2b**	3	50	4 (2)	80	2.0	2.4
6	**2b**	0	80	trace			
7	**2b**	3	80	41 (21)	870	2.5	2.4
8	**2b**	5	80	25 (13)	530	2.0	2.8

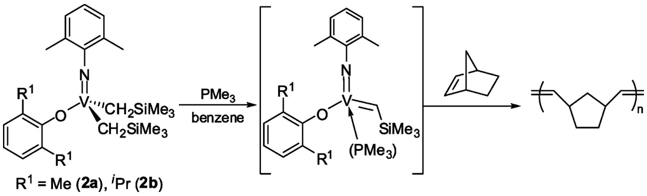
[a] Reaction conditions: catalyst 0.5 μmol, benzene 4.8 mL, NBE 2.12 mmol (0.44 mmol/mL), 1 h. [b] PMe$_3$/V molar ratio. [c] TON = NBE consumed (mmol)/V (mmol). [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

Table 2. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE) with V(CHSiMe$_3$)(NAr)(O-2,6-^{i}PrC$_6$H$_3$)(PMe$_3$)$_x$ (3, x = 0.89) and the Reported V(CHSiMe$_3$)(NAr)(N=C^{t}Bu$_2$)(PMe$_3$) (4)^a

run	complex	NBE/mmol	NBE conc^b	temp/°C	time/h	TON^d	M_w^{e} × 10^{-4}	M_w/M_n^{e}
9	**3**	2.12	0.22	25	3	300	3.6	1.1
10	**3**	2.12	0.22	25	6	480	6.7	1.1
11	**4**	2.12	0.22	25	6	270	46	2.3
12^e	**3**	4.24	0.89	25	1	150	3.1	1.1
					2	260	4.8	1.1
					3	390	6.7	1.1
					6	700	11	1.2
					10	1340	17	1.2
13	**3**	2.12	0.22	50	3	860	73	4.5^c

[a] Conditions: complex 1.0 μmol, NBE 2.12−4.24 mmol, benzene 9.6 mL. [b] Initial NBE concentration in mmol/mL. [c] TON = NBE consumed (mmol)/V (mmol). [d] GPC data vs polystyrene standards. [e] Polymerization was conducted in a flask (**3** 5.0 μmol, NBE 21.2 mmol, benzene 24 mL). A prescribed amount of the reaction mixture was removed via a syringe from the polymerization solution to monitor the time course.

Scheme 3



R^1 = Me (**2a**), ^{i}Pr (**2b**)

Synthesis of **3** was also explored from the dichloro analogue V(NAr)Cl$_2$(O-2,6-^{i}PrC$_6$H$_3$) for comparison. Reaction of the dichloro analogue with 2.0 equiv of LiCH$_2$SiMe$_3$ in *n*-hexane afforded a mixture of dialkyl complex (**2b**, >90%) and a tiny amount of unidentified byproduct (by ^{1}H NMR spectrum). Complex **2b** was highly soluble even in *n*-hexane and could not be purified by recrystallization from the mixture. Therefore, the reaction mixture was used for the subsequent reaction without further purification. The vanadium(V) aryloxo−alkylidene (**3**) could be isolated by heating the C$_6$D$_6$ solution containing the crude mixture at 80 °C in the presence of PMe$_3$ (5.0 equiv), and **3** was identified by NMR spectroscopy. Total isolated yield (59% from the dichloride) was slightly lower than those prepared from the trialkyl analogue (two steps, 92% and 68%, respectively). Although the total yields by these two approaches seem close, the route from the trialkyl analogue (**1**) should be more suited in terms of that synthesis and isolation of a series of vanadium(V) dialkyl derivatives would be possible from the trialkyl analogue.[25]

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(23) (a) Wang, W.; Yamada, J.; Fujiki, M.; Nomura, K. *Catal. Commun.* **2003**, *4*, 159. (b) Wang, W.; Nomura, K. *Macromolecules* **2005**, *38*, 5905.

(24) ^{1}H and ^{51}V NMR spectra for V(CHSiMe$_3$)(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(PMe$_3$)$_x$ (**3**) in C$_6$D$_6$ at 25 and 60 °C and in the presence of PMe$_3$ (at 25 °C) are shown in the Supporting Information.

(25) As described in the text, we have not yet isolated analytically pure microcrystals from the reaction mixture containing **2a** instead of **2b** under the same conditions, but a resonance which might be ascribed to a proton (vanadium) in the alkylidene was observed in the ^{1}H NMR (16.08 ppm) [and ^{51}V NMR (−111 and−20 ppm)] spectrum in the reaction mixture (Yamada, J., unpublished results). Since PMe$_3$ was dissociated partially in **3**, synthesis of V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2$(O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$) and the thermolysis reactions in C$_6$D$_6$ in the presence/absence of PMe$_3$ (5 equiv to V) were explored as related examples. Resonances that would be ascribed to the vanadium−alkylidene were seen in both ^{1}H and ^{51}V NMR spectra of the reaction mixture when the reaction was conducted in the presence of PMe$_3$. However, the reaction gave another product when the reaction was conducted in the absence of PMe$_3$. Synthesis of V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2$(O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$) and ^{1}H and ^{51}V NMR spectra for monitoring the reaction in C$_6$D$_6$ are shown in the Supporting Information.

The ROMPs of NBE using the aryloxo–alkylidene (**3**) were conducted in benzene, and the results are summarized in Table 2. The result by the ketimide–alkylidene (**4**)[14] is also cited for comparison. The aryloxo–alkylidene (**3**) showed higher catalytic activities at 25 °C than the ketimide–alkylidene (**4**, runs 10, 11), and the resultant polymers obtained at 25 °C possessed narrow molecular weight distributions and the M_n value increased over the time course (runs 9, 10). The polymerization was thus conducted in a flask, and a prescribed amount of the reaction mixture was removed via a syringe from the polymerization solution to monitor the time course (run 12). It turned out that the M_n value was increased upon increasing the TON value (polymer yield) with consistently narrow molecular weight distributions ($M_w/M_n = 1.1-1.2$) during polymerization. These results clearly indicate that the ROMP of NBE by **3** proceeded in a living manner at 25 °C. The resultant polymer possessed a mixture of *cis*- and *trans*-olefinic double bonds estimated by ^{1}H NMR spectra (*cis*/*trans* = ca. 2, for polymers prepared in run 12). The catalytic activity by **3** increased at 50 °C [480 turnovers at 25 °C (run 10) vs 860 turnovers at 50 °C (run 13)], but the molecular weight distribution in the resultant polymer became broad.

In summary, we have presented a unique reactivity of the (arylimido)vanadium(V)–trialkyl complex $V(NAr)(CH_2SiMe_3)_3$ (**1**, Ar = 2,6-$Me_2C_6H_3$), with alcohols, phenols, thiol, and amines and have thus demonstrated an efficient route for preparation of a series of (arylimido)vanadium(V)–dialkyl complexes containing alkoxo or aryloxo ligands from the trialkyl complex. In particular, treatment of **1** with 1.0 equiv of various alcohols and phenols cleanly afforded the corresponding dialkyl complexes $V(NAr)(CH_2SiMe_3)_2(OR)$ [R = 2,6-$Me_2C_6H_3$ (**2a**), 2,6-$^i Pr_2C_6H_3$ (**2b**), C_6F_6 (**2c**), ^{t}Bu (**2d**), $CMe(CF_3)_2$ (**2e**)], whereas no reaction took place upon addition of R′N(H)Me (R′ = Ph, cyclohexyl) or 2,6-$Me_2C_6H_3SH$ even if the $C_2D_2Cl_4$ solution was heated at 50 °C. The resultant dialkyl complexes (**2a**,**b**) showed high catalytic activities for ring-opening metathesis polymerization of norbornene in the presence of PMe_3, and the activity markedly increased even at 80 °C. The alkylidene complex $V(CHSiMe_3)(NAr)(O\text{-}2,6\text{-}^iPr_2C_6H_3)(PMe_3)_x$ (**3**, x = 0.89) was isolated from **2b** upon heating the C_6D_6 solution at 80 °C in the presence of PMe_3 (5.0 equiv). Complex **3** showed remarkable catalytic activity for ROMP of NBE, and the polymerization at 25 °C proceeded in a living manner. The present isolated vanadium(V)–alkylidene (**3**) is the second example of the "olefin metathesis active" vanadium(V)–alkylidene (followed by our exmaple[14]), and the living polymerization system has been achieved for the first time with vanadium. We are now exploring more details including the synthesis and isolation of other (arylimido)vanadium(V)–alkylidenes for better understanding and the reason that the trialkyl complex (**1**) reacted with alcohols but the reactions with thiol and amines did not take place.

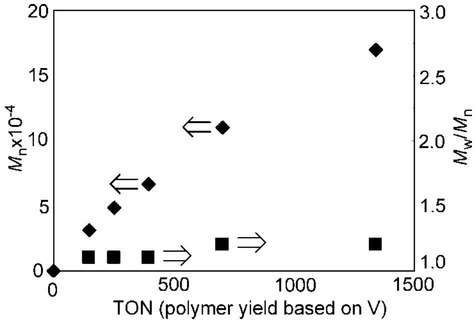
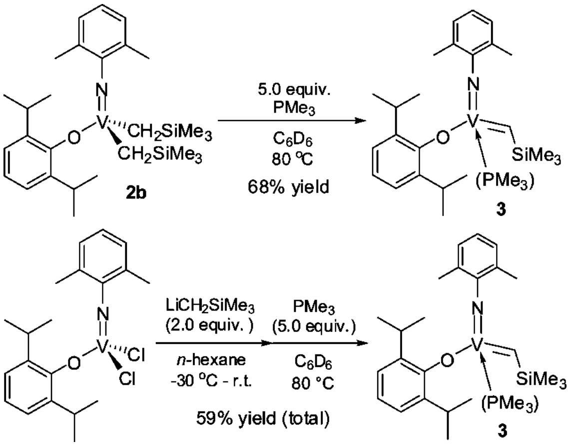


Figure 1. Plots of TON vs M_n and M_w/M_n in the ring-opening metathesis polymerization (ROMP) of norbornene by $V(NAr)(CHSiMe_3)(O\text{-}2,6\text{-}^iPr_2C_6H_3)(PMe_3)_x$ (**3**) in benzene (at 25 °C, x = 0.89, Table 2).

Scheme 4



Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were of reagent grade and were purified by standard purification procedures. Anhydrous grade *n*-hexane (Kanto Kagaku Co., Ltd.) was transferred to a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 flow and was passed through a short alumina column under a N_2 stream before use. V(N-2,6-$Me_2C_6H_3$)Cl_3 was prepared according to the published method.[26] 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, ^{19}F, ^{31}P, and ^{51}V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz for ^{1}H, 100.53 MHz for ^{13}C, 376.17 MHz for ^{19}F, 161.83 MHz for ^{31}P, and 105.15 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), $CF_3C_6H_5$ (δ −64.0, ^{19}F), H_3PO_4 (δ 0.00, ^{31}P), 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 ring-opened poly(norbornene)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH_{HR}-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 an eluent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Synthesis of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (1). Into an *n*-hexane solution (60 mL) containing V(N-2,6-$Me_2C_6H_3$)Cl_3 (2.765 g, 10.0 mmol) was added $LiCH_2SiMe_3$ (2.825 g, 30.0 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred overnight. A small amount of CH_2Cl_2

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

(ca. 5 mL) was added after the prescribed time, and the solution was then removed *in vacuo*. The resultant residue was extracted with hot *n*-hexane (ca. 200 mL). The *n*-hexane extract was then removed *in vacuo* to give an analytically pure, brown, sticky oil. Yield: 3.511 g (81%). ^{1}H NMR (C_6D_6): δ 0.15 (s, 27H, (CH_3)$_3$Si−), 1.82 (br, 6H, VCH_2−), 2.72 (s, 6H, CH_3), 6.81 (t, 1H), 6.97 (d, 2H). ^{13}C NMR (C_6D_6): δ 2.1, 20.2, 87.8, 125.2, 134.6. ^{51}V NMR (C_6D_6): δ 1070 ($\Delta\nu_{1/2}$ = 240 Hz). Anal. Calcd for $C_{20}H_{42}NSi_3V$: C, 55.64; H, 9.81; N, 3.24. Found: C, 55.50; H, 9.92; N, 3.42.

Synthesis of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-$Me_2C_6H_3$) (2a). Into an *n*-hexane solution (50 mL) containing V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (0.432 g, 1.00 mmol) was added 2,6-$Me_2C_6H_3OH$ (0.122 g, 1.00 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for 5 h. The solution was then removed *in vacuo* to give a brown oil. Yield: 0.435 g (93%). ^{1}H NMR (C_6D_6): δ 0.21 (s, 18H, (CH_3)$_3$Si−), 1.76 (br, 2H, VCH_2−), 2.17 (s, 6H, CH_3), 2.42 (s, 6H, CH_3), 2.63 (br, 2H, VCH_2−), 6.69 (t, 1H), 6.74 (t, 1H), 6.80 (d, 2H), 6.87 (d, 2H). ^{13}C NMR (C_6D_6): δ 1.8, 17.4, 19.1, 83.3, 122.4, 125.6, 126.9, 127.9, 128.7, 135.3, 163.7. ^{51}V NMR (C_6D_6): δ 506 ($\Delta\nu_{1/2}$ = 362 Hz). Anal. Calcd for $C_{24}H_{40}NOSi_2V$: C, 61.90; H, 8.66; N, 3.01. Found: C, 61.65; H, 8.95; N, 3.08.

Synthesis of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-^{i}$Pr_2C_6H_3$) (2b). Synthesis of **2b** was carried out by the same procedure as that in **2a** except that V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (0.432 g, 1.00 mmol) and 2,6-^{i}$Pr_2C_6H_3OH$ (0.178 g, 1.00 mmol) were used. Yield: 0.480 g (92%). ^{1}H NMR (C_6D_6): δ 0.26 (s, 18H, (CH_3)$_3$Si−), 1.16 (d, 12H, (CH_3)$_2$CH−), 1.84 (br, 2H, VCH_2−), 2.43 (s, 6H, CH_3), 2.55 (br, 2H, VCH_2−), 3.39 (m, 2H, (CH_3)$_2$C*H*−), 6.67 (t, 1H), 6.77 (d, 2H), 6.93 (t, 1H), 7.00 (d, 2H). ^{13}C NMR (C_6D_6): δ 1.9, 19.2, 23.5, 27.0, 83.0, 123.3, 123.5, 125.7, 135.3, 137.4, 139.3, 161.3. ^{51}V NMR (C_6D_6): δ 507 ($\Delta\nu_{1/2}$ = 337 Hz). Anal. Calcd for $C_{28}H_{48}NOSi_2V$: C, 64.45; H, 9.27; N, 2.68. Found: C, 64.36; H, 9.22; N, 2.76.

Synthesis of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(OC_6F_5) (2c). Synthesis of **2c** was carried out by the same procedure as that for **2a** except that V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (0.432 g, 1.00 mmol) and C_6F_5OH (0.184 g, 1.00 mmol) were used (stirred for 3 h). Yield: 0.477 g (90%). ^{1}H NMR (C_6D_6): δ 0.11 (s, 18H, (CH_3)$_3$Si−), 2.46 (s, 6H, CH_3), 2.50 (br, 2H, VCH_2−), 2.89 (br, 2H, VCH_2−), 6.72 (t, 1H), 6.81 (d, 2H). ^{13}C NMR (C_6D_6): δ 1.4, 19.1, 95.8, 126.5, 135.7, 137.0, 138.6, 139.4, 141.0, 164.8. ^{19}F NMR (C_6D_6): δ −159.8, −166.3, −169.1. ^{51}V NMR (C_6D_6): δ 659 ($\Delta\nu_{1/2}$ = 341 Hz).

Synthesis of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(O^{t}Bu) (2d). Synthesis of **2d** was carried out by the same procedure as that for **2a** except that V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (0.432 g, 1.00 mmol) and ^{t}BuOH (0.074 g, 1.00 mmol) were used (stirred for 3 h). Yield: 0.388 g (93%). ^{1}H NMR (C_6D_6): δ 0.24 (s, 18H, (CH_3)$_3$Si−), 1.22 (s, 9H, (CH_3)$_3$C−), 1.42 (br, 2H, VCH_2−), 2.55 (br, 2H, VCH_2−), 2.69 (s, 6H, CH_3), 6.77 (t, 1H), 6.92 (d, 2H). ^{13}C NMR (C_6D_6): δ 2.1, 20.2, 32.5, 77.5, 83.7, 124.8, 134.5. ^{51}V NMR (C_6D_6): δ 406 ($\Delta\nu_{1/2}$ = 316 Hz). Anal. Calcd for $C_{20}H_{40}NOSi_2V$: C, 57.52; H, 9.65; N, 3.35. Found: C, 57.03; H, 9.56; N, 3.58.

Synthesis of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$[OCMe(CF_3)$_2$] (2e). Synthesis of **2e** was carried out by the same procedure as that in **2a** except that V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (0.432 g, 1.00 mmol) and (CF_3)$_2$MeCOH (0.182 g, 1.00 mmol) were used (stirred for 12 h). Yield: 0.483 g (92%). ^{1}H NMR (C_6D_6): δ 0.16 (s, 18H, (CH_3)$_3$Si−), 1.26 (s, 3H, CH_3), 2.02 (br, 2H, VCH_2−), 2.64 (s, 6H, CH_3), 2.96 (br, 2H, VCH_2−), 6.74 (t, 1H), 6.85 (d, 2H). ^{13}C NMR (C_6D_6): δ 1.6, 19.7, 19.8, 83.1, 92.1, 119.4, 122.3, 125.2, 126.3, 128.1, 135.6. ^{19}F NMR (C_6D_6): δ −79.5. ^{51}V NMR (C_6D_6): δ 595 ($\Delta\nu_{1/2}$ = 333 Hz). Anal. Calcd for $C_{20}H_{34}F_6NOSi_2V$: C, 45.70; H, 6.52; N, 2.66. Found: C, 44.68; H, 6.48; N, 2.81.

Attempted Reaction of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (1) with PhN(H)Me, (cyclo-C_6H_{13})N(H)Me, and 2,6-$Me_2C_6H_3SH$. Attempted reaction of **1** with 1.0 equiv of 2,6-^{t}Bu_2-4-MeC_6H_2OH, PhN(H)Me, (cyclo-C_6H_{13})N(H)Me, or 2,6-$Me_2C_6H_3SH$ was conducted by the analogous procedure to that in the synthesis of **2a**. The typical NMR scale reaction [of **1** with (a rather excess amount of) 2,6-^{t}Bu_2-4-MeC_6H_2OH, PhN(H)Me, (cyclo-C_6H_{13})N(H)Me, and 2,6-$Me_2C_6H_3SH$] was carried out as follows. To a Teflon-sealed NMR tube containing $C_2D_2Cl_4$ (ca. 0.5 mL) and **1** (0.02 mmol) was added 2,6-^{t}Bu_2-4-MeC_6H_2OH (2.6 equiv to **1**) in one portion, and the resultant solution was monitored by both ^{1}H NMR and ^{51}V NMR (shown in the Supporting Information). The solution was then heated to 50 °C for a prescribed time. Detailed conditions are also shown in the Supporting Information.

Synthesis of V($CHSiMe_3$)(N-2,6-$Me_2C_6H_3$)(O-2,6-^{i}$Pr_2C_6H_3$)-(PMe_3)$_{0.89}$ (3). Method A [from V(N-2,6-$Me_2C_6H_3$)Cl_2(O-2,6-^{i}$Pr_2C_6H_3$)]. Into an *n*-hexane solution (100 mL) containing VCl_2(N-2,6-$Me_2C_6H_3$)(O-2,6-^{i}$Pr_2C_6H_3$) (560 mg, 1.18 mmol) was added $LiCH_2SiMe_3$ (234 g, 2.48 mmol) at −30 °C. The mixture was then warmed slowly to room temperature, and the mixture was then stirred for an additional 4 h. After the reaction, the mixture was filtered through a Celite pad, and the solvent was pumped off, leaving a sticky, dark red solid. Yield: 610 mg [1:0.08 mixture of dialkyl complex **2b** and an unidentified compound (estimated by the ^{51}V NMR spectrum)], and the solid was used for the next reaction without further purification. ^{1}H NMR (C_6H_6): δ 0.25 (s, 18H, (CH_3)$_3$Si−), 1.15 (d, 12H, (CH_3)$_2$CH−), 1.83 (br, 2H), 2.42 (s, 6H, CH_3), 2.54 (br, 2H), 3.38 (m, 2H, (CH_3)C*H*−), 6.66 (t, 1H), 6.76 (d, 2H), 6.91 (t, 1H), 6.99 (d, 2H). ^{51}V NMR (C_6H_6): δ 507 ($\Delta\nu_{1/2}$ = 337 Hz).

The solid was dissolved in 10 mL of C_6D_6, and PMe_3 (449 mg, 5.9 mmol) was added. The solution was heated for 5 h at 80 °C. All volatiles were removed *in vacuo*, and the resultant solid was dissolved in a minimum amount of *n*-hexane. Cooling the solution to −30 °C afforded the product. Yield: 348 mg (59% total yield).

Method B [from V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-^{i}$Pr_2C_6H_3$)]. Into a C_6D_6 solution (10 mL) containing V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-^{i}$Pr_2C_6H_3$) (0.522 g, 1.00 mmol) was added PMe_3 (0.380 g, 5.00 mmol). The reaction mixture was heated at 80 °C for 5 h. The solution was then removed *in vacuo*, and the resultant residue was extracted with hot *n*-hexane (ca. 100 mL). The extract was then removed *in vacuo* to give a brown solid. The solid was then dissolved in a minimum amount of *n*-hexane layered by a small amount of PMe_3. The chilled solution placed in the freezer gave a brown solid. Yield: 0.345 g (68%). ^{1}H NMR (C_6D_6 at 25 °C):[24] δ 0.28 and 0.41 (9H, (CH_3)$_3$Si−), 0.77 (br, P*Me*$_3$), 1.25 and 1.27 (12H, (CH_3)$_2$CH−), 2.75 and 2.84 (6H, CH_3), 3.36−3.98 (m, 2H, (CH_3)C*H*−), 6.80 (t, 1H), 6.98 (t, 1H), 7.07 (d, 2H), 7.25 (d, 2H), 16.09 and 16.38 (1H, V═C*H*−). ^{13}C NMR (C_6D_6): δ 3.1, 16.1, 20.5, 24.1, 26.8, 117.3, 122.7, 123.2, 134.6, 135.8, 163.7, 322.8. ^{31}P NMR (C_6D_6): δ −13.9. ^{51}V NMR (C_6D_6): δ −110 ($\Delta\nu_{1/2}$ = 1050 Hz), 54 ($\Delta\nu_{1/2}$ = 1106 Hz). Anal. Calcd for $C_{26.67}H_{44.01}NOP_{0.89}V$: C, 63.90 (61.50 + VC, vanadium carbide); H, 8.85; N, 2.79%. Found: C, 61.34; H, 8.69; N, 2.66.

ROMP of Norbornene. The typical reaction procedure (Table 1, run 2) is as follows. Into a sealed Schlenk tube (50 mL scale) containing norbornene (2.12 mmol) dissolved in benzene (2.8 mL) were added a benzene solution containing **2a** (0.5 μmol, 1.0 mL) and a benzene solution containing PMe_3 (1.5 μmol, 1.0 mL). The tube was then immediately placed in an oil bath preheated at 80 °C, and the mixture was stirred for a prescribed time. The polymerization was then quenched by the addition of excess PhCHO, and the solution was stirred for an additional 1 h at room temperature. The mixture was then poured into methanol (ca. 100 mL). The resultant solid was collected by filtration, washed with methanol, and then dried *in vacuo*. The ROMPs by **3** were performed similarly in the drybox without adding PMe_3 at 25 °C.

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Supporting Information Available: ^{1}H and ^{51}V NMR spectra for monitoring the reaction of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (**1**) with 2,6-^{t}Bu$_2$-4-MeC_6H_2OH, PhN(H)Me, (cyclo-C_6H_{13})N(H)Me, and 2,6-$Me_2C_6H_3SH$ in $C_2D_4Cl_2$ at 50 °C. ^{1}H and ^{51}V NMR spectra for V($CHSiMe_3$)(N-2,6-$Me_2C_6H_3$)(O-2,6-^{i}Pr$_2C_6H_3$)(PMe_3)$_x$ (**3**) in C_6D_6 at 25 and 60 °C and in the presence of PMe_3 (at 25 °C). Synthesis of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-^{t}Bu$_2$-4-MeC_6H_2) and ^{1}H and ^{51}V NMR spectra for monitoring the reactions in C_6D_6 (at 80 °C) in the presence/absence of PMe_3 (5 equiv to V). These materials are available free of charge via the Internet at http://pubs.acs.org.

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