Synthesis of Various (Arylimido)vanadium(V)−Methyl Complexes Containing Ketimide Ligands and Reactions with Alcohols, Thiols, and Borates: Implications for Unique Reactivity toward Alcohols

Junji Yamada, Michiya Fujiki, and Kotohiro Nomura*

Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

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The reactions of (ArN)VMe(N=C^{t}Bu$_2$)$_2$ (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$) with various alcohols, thiols, and borates (Brönsted and/or Lewis acids) were investigated. Treatment of complex **1** with 1.0 equiv of various alcohols cleanly afforded other methyl complexes of the type (ArN)VMe(N=C^{t}Bu$_2$)(OR) [OR = O-2,6-Me$_2$C$_6$H$_3$ (**2a**), O-4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$ (**2b**), OPh (**2c**), OC$_6$F$_6$ (**2d**), O^{i}Pr (**2e**), OCH$_2$CH$_2$-CH=CH$_2$ (**2f**), OCH$_2$(CH$_2$)$_3$CH=CH$_2$ (**2g**)], and a reaction with the methyl group did not occur in all cases. In contrast, protonolysis of the methyl group took place in the reaction of **1** with 2,6-Me$_2$C$_6$H$_3$SH or 1-hexanethiol. The reaction of **1** with [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] and [Ph$_3$C][B(C$_6$F$_5$)$_4$] in THF gave the cationic complex [(ArN)V(N=C^{t}Bu$_2$)$_2$(THF)$_2$][B(C$_6$F$_5$)$_4$] (**4a**), exclusively through abstraction or protonolysis of the methyl group. The reaction of **2a** (or **2b**) with 2,6-Me$_2$C$_6$H$_3$OH (or 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH) gave the bis(aryloxo) complex (ArN)VMe(OAr′)$_2$ [Ar′ = O-2,6-Me$_2$C$_6$H$_3$ (**5a**), O-4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$ (**5b**)], and the reaction with a methyl group did not occur even in the presence of an additional equivalent of phenol. The reaction of **2a** with 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH at 25 °C afforded the aryloxo scrambled mixture of **2a** and **2b** and then gave three bis(aryloxo) analogues upon heating to 60 °C for 12 h. The results clearly indicate that the reactions with phenols proceed via pentacoordinated trigonal bipyramidal intermediates formed by coordination of the oxygen atom in the phenol *trans* to the methyl group.

Introduction

Transition metal−alkyl complexes are some of the most important reagents or intermediates in stoichiometric/catalytic organic reactions, as well as in olefin polymerization.[1,2] The synthesis and reaction chemistry of transition metal−alkyl complexes have thus been important in the design of efficient catalysts as well as for obtaining a better understanding of the organic reactions, especially with regard to catalytic cycles or reaction pathways. Some classical Ziegler-type vanadium catalysts are known to exhibit unique characteristics, such as the synthesis of ultrahigh molecular weight polymer with a relatively narrow polydispersity through rapid propagation in olefin coordination/insertion polymerization and the synthesis of propylene−methyl methacrylate diblock copolymers by living polymerization.[2e,3,4] Therefore, the synthesis and reaction chemistry of vanadium complexes, especially (cationic) alkyl complexes, have attracted considerable attention.[5−8] Some reactions

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

(1) For example (general text of metal−alkyl chemistry): (a) In *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Crabtree, R. H., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2005; p 53. (b) In *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*; Bevy L. P., Ed.; Nova Science Publishers, Inc.: New York, 2005; p 199.

(3) 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.

(4) 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.

(5) Some structural characterizations and reaction chemistry of V(III),-(IV) methyl complexes: (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.

(6) 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.

(7) 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) Solan, G. A.; Cozzi, P. G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 2572. (f) Chan, M. C. W.; Cole, J. M.; Gibson, V. C.; Howard, J. A. K. *Chem. Commun.* **1997**, 2345.

(8) Our previous examples: (a) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2005**, *24*, 2248. (b) Yamada, J. and Nomura, K. *Organometallics* **2005**, *24*, 3621.

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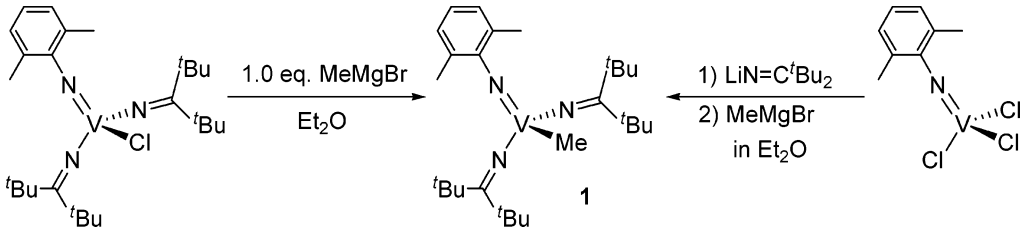
Scheme 1



concerning (cationic) vanadium−alkyl complexes that contain one or two cyclopentadienyl (Cp′) ligands have been described in the literature[5a−c] with regard to titanocene (zirconocene) or half-titanocene.[9] However, there are still few examples of the synthesis of vanadium−alkyls that do not include the 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.[7]

In general, metal−alkyl bonds, especially those with early transition metals, are more nucleophilic than those with late transition metals and are thus highly reactive toward Brönsted/Lewis acids.[1,9,10] For instance, cationic alkyl complexes, which have been proposed to be the catalytically active species for olefin coordination polymerization, are generated from their dialkyl analogues by reacting them with cocatalysts via facile protonolysis or alkyl abstraction.[9] Some organometallic complexes can thus be grafted onto a silica surface through the reaction of alkyl compounds with the silanol groups on the surface.[9c,11,12]

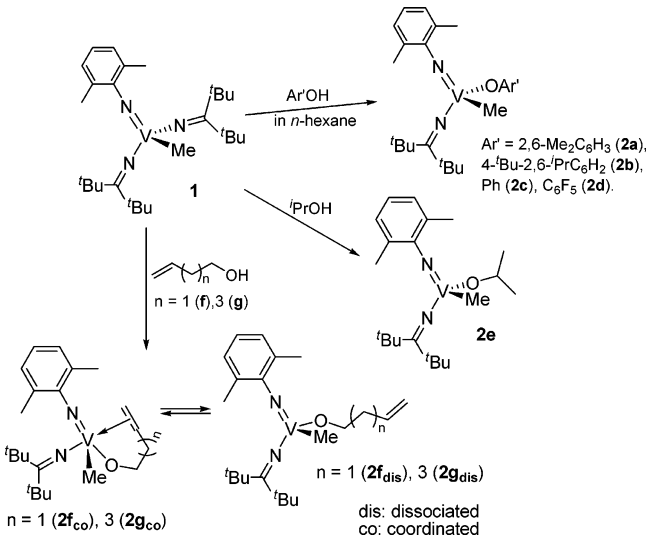
We recently communicated the synthesis and structural characterization of a vanadium−methyl complex of the type (ArN)V(Me)(N=C^{t}Bu$_2$)$_2$ (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$).[8b] Complex **1** showed unique reactivity toward alcohols (phenols) to exclusively give various methyl complexes by ligand exchange between the ketimide and alkoxy (aryloxo) groups without accompanying protonolysis of the methyl group with the alcohols (phenols). The results clearly indicated that the methyl group in **1** is not reactive toward alcohol under these conditions,[8b] although ordinary metal−alkyl bonds (especially in early transition metals) readily react with alcohol to give alkoxide (aryloxide).[10−12] Therefore, we conducted some reactions of **1** with various alcohols, thiols, and borates, including the isolation of cationic vanadium(V) complexes, to examine why **1** did not react with alcohol.

Results and Discussions

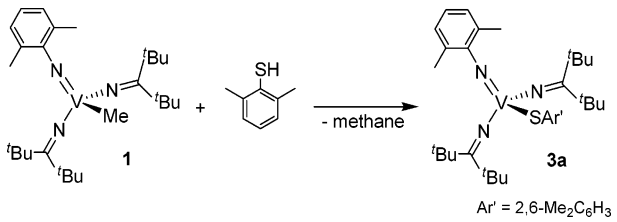
1. Synthesis of (ArN)VMe(N=C^{t}Bu$_2$)$_2$ (1) and Reactions of Alcohols and Thiols. The vanadium(V)−methyl complex, of the type (ArN)VMe(N=C^{t}Bu$_2$)$_2$ (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$), was prepared by treating (ArN)VCl(N=C^{t}Bu$_2$)$_2$ with 1.0 equiv of MeMgBr in Et$_2$O (yield 85%), as described previously (Scheme 1).[8b] Alternatively, **1** could also be prepared directly from (ArN)VCl$_3$ without isolation of (ArN)VCl(N=C^{t}Bu$_2$)$_2$ (yield 58%). The crystal structure[8b] showed that **1** has a distorted tetrahedral geometry around the vanadium, and the V−N(C^{t}Bu$_2$) distances (1.825−1.827 Å) are slightly longer than those in the chloride complex (1.803−1.805 Å).[8b] The V−Me distance (2.064 Å) is within the range of V(V)−C bond lengths in (arylimido)vanadium(V)−dibenzyl analogues (2.026−2.103 Å)[6b] and is close to that in Li[(^{t}Bu$_3$SiN)$_2$VMe$_2$] (2.043, 2.050 Å);[6a] the distance is shorter than those in some V(II−IV)−Me complexes (2.118,[6f] 2.206−2.222 Å[5a,b,g,h]).

Reactions of **1** with 1.0 equiv of phenols exclusively gave another vanadium(V)−methyl complex of the type (ArN)VMe(N=C^{t}Bu$_2$)(OAr′) [Ar′ = 2,6-Me$_2$C$_6$H$_3$ (**a**), 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$ (**b**), Ph (**c**), OC$_6$F$_5$ (**d**)], by replacement with the ketimide ligand (Scheme 2).[8b] The reaction with the methyl group did not proceed under these conditions, although **1** is a rather electron-deficient vanadium(V)−alkyl complex, and no significant differences were observed in the corresponding resonances (in ^{1}H and ^{13}C NMR spectra) as well as in the V−Me bond distance (2.064 Å) from those of reported vanadium−methyl complexes.[5] The selectivity in the reaction was not dependent upon the kind of phenol employed, and the exchange reaction of **1** took place

Scheme 2



Scheme 3



(9) For example (reviews): (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Chen, E. Y-. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(10) For example: In *Comprehensive Organometallic Chemistry II*; Abel, F. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 4.

(11) Related review article: (a) Copéret, C.; Chavanas, M.; Saint-Arroman, R. P.; Basset, J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 156. (b) Thomas, J. M.; Raja, R.; Lewis, D. W. *Angew. Chem., Int. Ed.* **2005**, *44*, 6456.

(12) Recent examples: (a) Rhers, B.; Salameh, A.; Baudouin, A.; Quadrelli, E. A.; Taoufik, M.; Copéret, C.; Lefebvre, F.; Basset, J. -M.; Solans-Monfort, X.; Eisenstein, O.; Lukens, W. W.; Lopez, L. P. H.; Sinha, A.; Schrock, R. R. *Organometallics* **2006**, *25*, 3554. (b) Nicholas, P.; Ahn, H. S.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 4325. (c) McKittrick, M. W.; Jones, C. W. *J. Am. Chem. Soc.* **2004**, *126*, 3052.

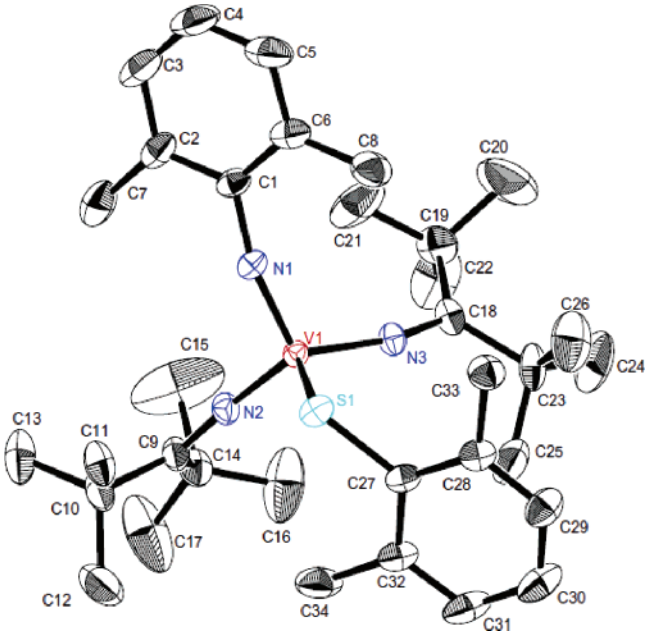


Figure 1. ORTEP drawing (30% probability ellipsoids) of **3a**. All hydrogen atoms are omitted for clarity.

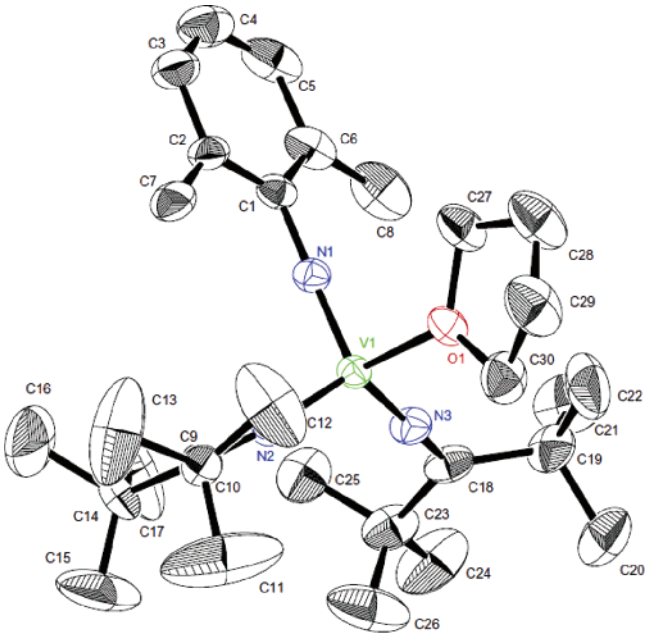


Figure 2. ORTEP drawing (30% probability ellipsoids) of **4a**. $B(C_6F_5)_4$ and all hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for V(N-2,6-Me$_2$C$_6$H$_3$)(NdC^{t}Bu$_2$)$_2$(S-2,6-Me$_2$C$_6$H$_3$) (3a)

Bond Distances			
V(1)−S(1)	2.300 (4)	S(1)−C(27)	1.775 (2)
V(1)−N (1)	1.661 (4)	V(1)−N(2)	1.808 (3)
V(1)−N (3)	1.819 (2)	N(1)−C(1)	1.389 (2)
N(2)−C (9)	1.267 (2)	N(3)−C(18)	1.267 (2)
Bond Angles			
N(1)−V(1)−S(1)	100.77 (7)	N(2)−V(1)−S(1)	116.22 (7)
N(3)−V(1)−S(1)	112.21 (6)	N(2)−V(1)−N(1)	107.95 (9)
N(3)−V(1)−N(1)	112.09 (8)	N(3)−V(1)−N(2)	107.49 (8)
V(1)−N(1)−C(1)	166.55 (2)	V(1)−N(2)−C(9)	172.8 (2)
V(1)−N(3)−C(18)	166.84 (2)	V(1)−S(1)−C(27)	108.14 (8)

exclusively even with C_6F_5OH (to give **2d**). Treatment of **1** with ^{i}PrOH afforded (ArN)VMe(N═C^{t}Bu$_2$)(O^{i}Pr) (**2e**), and the reaction with the methyl group did not take place.[8b] The reaction

Table 2. Selected Bond Distances (Å) and Angles (deg) for [V(N-2,6-Me$_2$C$_6$H$_3$)(N═C^{t}Bu$_2$)$_2$(THF)$_2$][B(C$_6$F$_5$)$_4$] (4a)

Bond Distances			
V(1)−O(1)	2.007 (2)		
V(1)−N(1)	1.655 (2)	V(1)−N(2)	1.808 (2)
V(1)−N(3)	1.808 (2)	N(1)−C(1)	1.385 (4)
N(2)−C(9)	1.264 (4)	N(3)−C(18)	1.260 (4)
Bond Angles			
O(1)−V(1)−N(1)	100.40 (12)	O(1)−V(1)−N(2)	107.27 (10)
O(1)−V(1)−N(3)	109.02 (12)		
N(1)−V(1)−N(3)	107.65 (13)	N(1)−V(1)−N(2)	108.11 (13)
N(2)−V(1)−N(3)	122.22 (13)	V(1)−N(1)−C(1)	174.6 (2)
V(1)−N(2)−C(9)	171.6 (2)	V(1)−N(3)−C(18)	178.9 (3)

Table 3. Crystal Data and Collection Parameters of Complexes 3a and 4a[a]

	3a	4a
formula	$C_{34}H_{54}N_3SV$	$C_{54}H_{53}BF_{20}N_3OV$
fw	587.82	1201.75
cryst color, habit	brown, prism	red, block
cryst size (mm)	0.80 × 0.60 × 0.20	0.80 × 0.80 × 0.44
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	12.086(3)	15.606(5)
b (Å)	16.246(4)	15.262(4)
c (Å)	17.986(7)	24.342(6)
β (deg)	84.449(14)	93.897(13)
V (Å^3)	3515.1(18)	5784.3(27)
Z value	4	4
D_{calcd} (g/cm^3)	1.111	1.380
F_{000}	1272.00	2456.0
temp (K)	243	243
μ(Mo Kα) (cm^{-1})	3.658	2.752
2θ range (deg)	6.05−54.97	6.01−54.97
no. of reflns measd	33 359	53 601
no. of observations ($I > 2.00\sigma(I)$)	11 424	7733
no. of variables	406	802
R1	0.0627	0.0565
wR2	0.1220	0.1632
goodness of fit	1.002	1.004

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

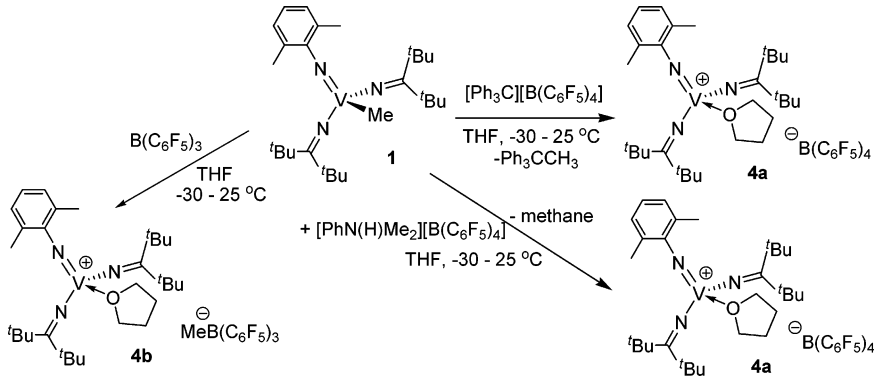
of the ketimide with alkoxide was also observed in the reaction of **1** with 3-buten-1-ol or 5-hexen-1-ol in *n*-hexane to give the corresponding (ArN)VMe(N═C^{t}Bu$_2$)[OCH$_2$(CH$_2$)$_n$CH═CH$_2$] [n = 1 (**2f**), 3 (**2g**)] exclusively (86% for **2f**, 66% for **2g**, respectively, Scheme 2).[13−15] Both **2f** and **2g** gave two resonances in the ^{51}V NMR spectra, and the ratios were highly dependent upon the temperature measured.[13] The species in the higher field was observed exclusively at 60 °C and was identified as olefin dissociated species (**2f$_{dis}$** and **2g$_{dis}$**) based on ^{1}H NMR spectra, not only because the resonances observed at 4.5−6.0 ppm were identical to those in our previous example with Ti,[15] but also because the reaction of **1** with *n*-hexanol

(13) For more details, see the Supporting Information.

(14) Selected related examples for synthesis of Ti(IV) or Zr(IV) alkoxide−alkene complexes: (a) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867. (b) Carpentier, J. F.; Wu, Z.; Lee, C. W.; Strömberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750. (c) Carpentier, J.-F.; Maryin, V. P.; Luci, J.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 898. (d) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 3222. (e) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2004**, *126*, 11170. (f) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 8162.

(15) Synthesis and structural determination of Cp*TiMe[OCH$_2$(CH$_2$)$_n$-CH═CH$_2$](O-2,6-^{i}Pr$_2$C$_6$H$_3$) (n = 1, 3) and Cp*Ti(CF$_3$SO$_3$)[OCH$_2$(CH$_2$)$_n$-CH═CH$_2$](O-2,6-^{i}Pr$_2$C$_6$H$_3$): Nomura, K.; Hatanaka, Y. *Inorg. Chem. Commun.* **2003**, *6*, 517.

Scheme 4



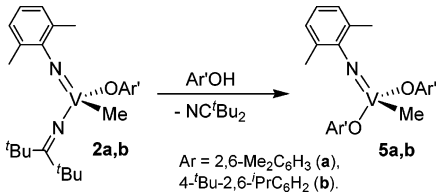
afforded a species observed at −238 ppm in the ^{51}V NMR spectrum that was accompanied by the formation of HN=C^{t}Bu$_2$, as reported previously.[8b] In contrast, the species observed in the lower field became dominant below −40 °C, and we assume that this would be the olefin-coordinated species (**2f$_{co}$** and **2g$_{co}$**).[16] The insertion did not take place under these conditions. ΔG values of 8.5 kcal/mol for **2f** and 8.6 kcal/mol for **2g** were thus assumed from the ^{51}V NMR spectra measured at various temperatures (−60 to 60 °C).[13] There was no significant difference in the effect of the methylene length in alkene-1-ol (3-buten-1-ol vs 5-hexen-1-ol) on the integration ratios (equilibrium) between the coordinated and dissociated species, and these findings were somewhat different from those in our previous report with titanium, Cp*Ti(CF$_3$SO$_3$)-[OCH$_2$(CH$_2$)$_n$CH=CH$_2$](O-2,6-^{i}Pr$_2$C$_6$H$_3$) (n = 1, 3), whereas olefin did not coordinate with titanium.[15]

To examine why the methyl group in **1** did not react with alcohol, we planned the reaction of **1** with thiols. The reaction of **1** with 1.0 equiv of 2,6-Me$_2$C$_6$H$_3$SH afforded (ArN)V(N=C^{t}Bu$_2$)$_2$(S-2,6-Me$_2$C$_6$H$_3$) (**3a**) via cleavage of the V−Me bond by facile protonolysis (75% yield, Scheme 3). The product was identified by ^{1}H, ^{13}C, and ^{51}V NMR spectra, and the structure was determined by X-ray crystallography, as shown in Figure 1. Selected bond distances and angles are also summarized in Table 1. The crystal structure showed that **3a** has a distorted tetrahedral geometry around the vanadium metal center, and the V−N(C^{t}Bu$_2$) distances (1.808−1.819 Å) were intermediate between those in the chloride analogue (ArN)VCl(N=C^{t}Bu$_2$)$_2$ (1.803−1.805 Å)[8b] and the methyl analogue (**1**, 1.825−1.827). The V−S distance (2.300 Å) is slightly longer than those in V(NC$_6$H$_4$Cl-4)[N(CH$_2$CH$_2$S)$_3$] (2.251 Å)[17b] and [V(CH$_3$CN)$_6$]-[VCl$_2${O(CH$_2$CH$_2$S)$_2$}]$_2$,[17c] is close to that in the penta-coordinated vanadium(III) thiolate complex V[P(C$_6$H$_4$-2-S)$_3$](1-methylimidazole) (average 2.302 Å)[18] and V(O-2,6-^{i}-Pr$_2$C$_6$H$_3$){O(CH$_2$CH$_2$S)$_2$}(pyridine) (average 2.298 Å),[17a] and is within the range expected for V−S single bonds and comparable to those in other vanadium(III) thiolate complexes.[19]

The reaction of **1** with n-C$_6$H$_{13}$SH in n-hexane afforded (ArN)V(N=C^{t}Bu$_2$)$_2$(S-n-C$_6$H$_{13}$) (**3b**) as the sole product, as confirmed by both ^{1}H and ^{13}C NMR spectra, via cleavage of the V−Me bond by facile protonolysis. These facts clearly indicate that the reaction mechanism should differ between alcohol and thiol, and the reaction with thiols favored protonolysis with V−Me bonds as seen in ordinary metal akyl complexes with early transition metals.[1,9,10]

2. Reactions of (ArN)VMe(N=C^{t}Bu$_2$)$_2$ (1) with Various Borates. As described above, cleavage of the V−Me bond in **1** was favored in the reaction with thiols, whereas exclusive ligand exchanges with the ketimide ligand were seen in the reaction with various alcohols. It is well known that cationic alkyl complexes, which have been proposed to be the catalytically active species for olefin coordination polymerization, are generated from its dialkyl analogues by reacting with borates.[9] To examine the detailed reactivity of the V−Me bond in **1**, reactions with borates (strong Brønsted acid) were conducted in this study.

Scheme 5



The reaction of **1** with 1.0 equiv of [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] in THF afforded cationic [(ArN)V(N=C^{t}Bu)$_2$(THF)$_2$]-[B(C$_6$F$_5$)$_4$] (**4a**) via protonolysis of the V−Me bond and free PhNMe$_2$. The exclusive formation of these compounds was confirmed by NMR spectroscopy (Scheme 4). The same compound (**4a**) could be isolated by the reaction of **1** with 1.0 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$], a strong alkyl abstracting reagent,

(16) A reviewer pointed out a possibility of formation of the [2+2] adduct with the arylimido complex as proposed by Odom et al. for synthesis of amines by titanium-mediated transfer of alkenyl groups from alcohol (Ramanathan, B.; Odom, A. L. *J. Am. Chem. Soc.* **2006**, *128*, 9344. Related report for hydroamination of alkynes by (arylimido) vanadium complexes: Lorber, C.; Choukroun, R.; Vendier, L. *Organometallics* **2004**, *23*, 1845). However, no significant differences in the resonances ascribed to aromatic and methyl protons in the arylimido ligand were observed between the dissociated and (proposed) coordinated species in the ^{1}H NMR spectra, and the observed equilibrium is reversible. In addition, no resonances ascribed to the carbene species were seen. On the basis of these results, it is concluded that the formed species are simple olefin-coordinated species, although we could not completely exclude a possibility of formation of the metallacycle. For example (tungsten, titanium): (a) Bennett, J.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696. (b) Lokare, K. S.; Ciszewski, J. T.; Odom, A. L. *Organometallics* **2004**, *23*, 5386. K.N. expresses his thanks to a reviewer for pointing out this issue.

(17) (a) Janas, Z.; Jerzykiewicz, L. B.; Richards, R. L.; Sobota, P. *Chem. Commun.* **1999**, 1105. (b) Davies, S. C.; Hughes, D. L.; Janas, Z.; Jerzykiewicz, L. B.; Richards, R. L.; Sanders, J. R.; Silverston, J. E.; Sobota, P. *Inorg. Chem.* **2000**, *39*, 3485. (c) Janas, Z.; Jerzykiewicz, L. B.; Przybylak, S.; Richards, R. L.; Sobota, P. *Organometallics* **2000**, *19*, 4252.

(18) Hsu, H. F.; Chu, W. C.; Hung, C. H.; Liao, J. H. *Inorg. Chem.* **2003**, *42*, 7369.

(19) For other examples: (a) Randall, C. R.; Armstrong, W. H. *J. Chem. Soc., Chem. Commun.* **1988**, 986. (b) Davies, S. C.; Hughes, D. L.; Janas, Z.; Jerzykiewicz, L. B.; R. L. Richards, R. L.; Sanders, J. R.; Sobota, P. *Chem. Commun.* **1997**, 1261. (c) Henkel, G.; Krebs, B.; Schmidt, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1366. (d) Wiggins, R. W.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1313. (e) Szeymies, D.; Krebs B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 885. (f) Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3179.

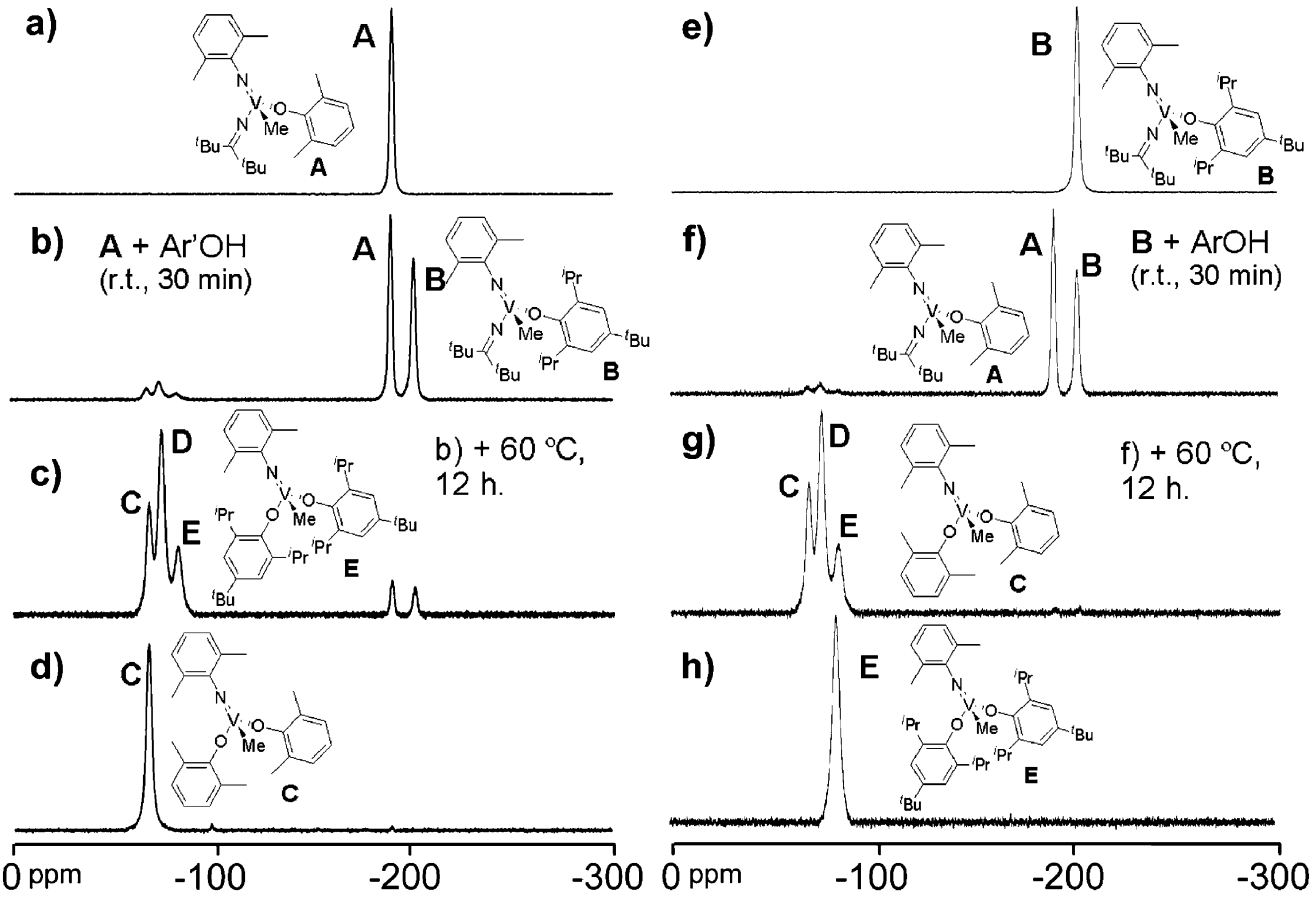
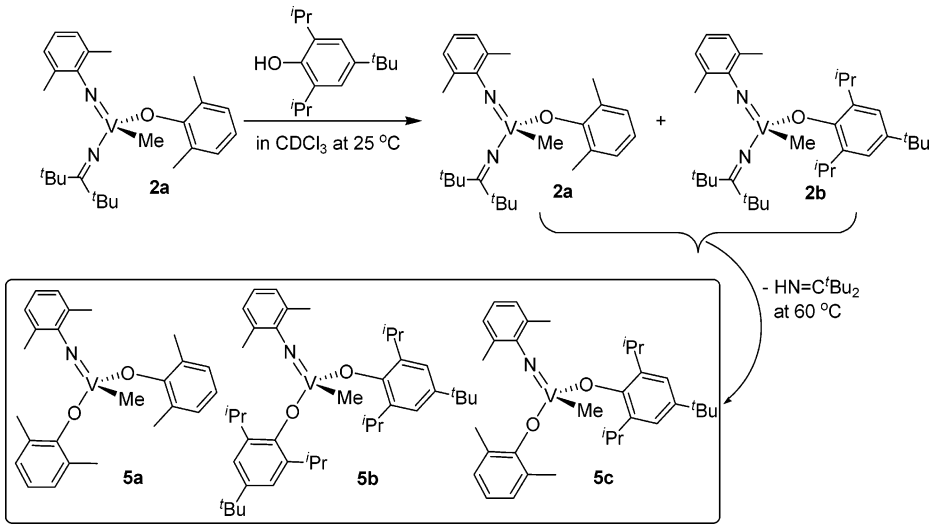


Figure 3. ^{51}V NMR spectra of the reaction of **2a** with 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (a−d) and **2b** with 2,6-Me$_2$C$_6$H$_3$OH (e−h) in CDCl$_3$. ^{51}V NMR spectra for (a) **2a**, (b) reaction mixture of **2a** with 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (after 30 min at 25 °C), (c) reaction mixture of **2a** with 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (at 60 °C for additional 12 h after b), and (d) **5a**. ^{51}V NMR spectra for (e) **2b**, (f) reaction mixture of **2b** with 2,6-Me$_2$C$_6$H$_2$OH (after 30 min at 25 °C), (g) reaction mixture of **2b** with 2,6-Me$_2$C$_6$H$_2$OH (at 60 °C for additional 12 h after f), and (h) **5b**.

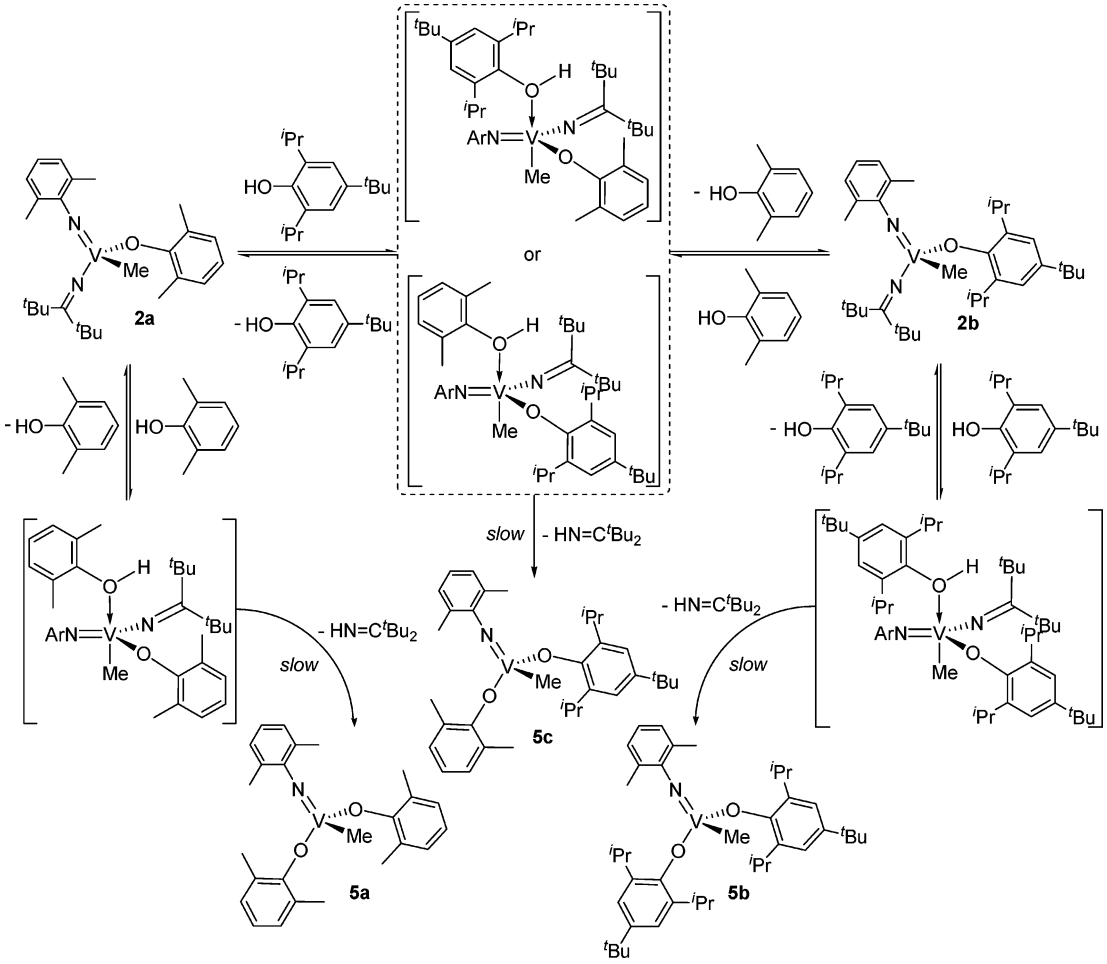
Scheme 6



and the quantitative formation of **4a** and Ph_3CCH_3 was confirmed by ^{1}H and ^{51}V NMR spectra. Compound **4a** could be cleanly isolated (90%) and was identified by ^{1}H, ^{13}C, ^{19}F, and ^{51}V NMR spectra and elemental analysis. On the basis of the results of both the ^{1}H NMR spectrum and elemental analysis, two THF molecules per vanadium remained in the resultant red microcrystals. The reaction of **1** with B(C$_6$F$_5$)$_3$ also gave similar clean ^{1}H and ^{51}V NMR spectra in addition to resonances ascribed to the formation of MeB(C$_6$F$_5$)$_3$ (0.48 ppm, B−Me), which strongly suggested the exclusive formation of [(ArN)V(N=C^{t}Bu)$_2$(THF)$_2$][MeB(C$_6$F$_5$)$_3$] (**4b**).

Moreover, the ^{1}H and ^{51}V NMR spectra for the reaction of **2a** with 1.0 equiv of [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] also suggested the exclusive formation of the corresponding cationic species

Scheme 7



4c via protonolysis of a V−Me group accompanied by the liberation of free $PhNMe_2$. These results clearly indicated that cleavage of the V−Me bond was favored in all cases.

Red block microcrystals of **4a** suitable for X-ray crystallographic study were obtained from a chilled (−30 °C) and concentrated THF solution containing **4a** layered by *n*-hexane (Figure 2). Selected bond distances and angles for **4a** are summarized in Table 2. The crystallographic analysis of **4a** indicates that **4a** has a pseudo-tetrahedral geometry around the vanadium center with the coordination of one THF molecule. The position of another THF molecule could not be defined/determined probably because the THF molecule might be located among crystal lattices. The V−N(C^{t}Bu$_2$) distances (1.802−1.808 Å) are comparable to those found in (ArN)VCl-(N=C^{t}Bu$_2$)$_2$ and somewhat shorter than those in **1**. The V−O distance (2.007 Å) is similar to that found in four-coordinated cationic vanadium(IV) alkylidene complex (2.000 Å) [(Nacnac)V=CH^{t}Bu(THF)](BPh$_4$) [Nacnac = {ArNC(Me)CHC(Me)NAr}$^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$][20] and somewhat shorter than that found in THF-coordinated vanadium(III) complexes containing amine tris(phenolate) and triamidoamine ligands (2.107−2.152 Å).[21]

3. Mechanistic Studies for Reaction of (2,6-Me$_2$C$_6$H$_3$N)-VMe(N=C^{t}Bu$_2$)$_2$ (1) with Alcohol. Exploration for Unique Reactivity of the Vanadium−Methyl Bonds toward Alcohol. As described above, the V−Me bond in **1** reacted with thiols and borates, whereas the V−Me bond in **1** did not react with alcohols. To explain this unique reactivity of **1**, especially toward alcohol, we explored the reaction chemistry in more detail.

When 1.0 equiv of 2,6-Me$_2$C$_6$H$_3$OH was added to a Teflon-sealed NMR tube containing a $CDCl_3$ solution of **2a**, the formation of HN=C^{t}Bu$_2$ (1.31 and 9.39 ppm) was observed in the ^{1}H NMR spectrum. In contrast, the generation of methane was not observed even after 24 h. A new resonance at −64 ppm was observed in the ^{51}V NMR spectrum in addition to **2a** (−185 ppm) in the above $CDCl_3$ solution, and the conversion of **2a** reached 60% after 24 h (at 25 °C). This result is in unique contrast to that in the reaction of **1** with 2,6-Me$_2$C$_6$H$_3$OH, since the reaction was complete within 30 min (starting at −30 to 25 °C). The quantitative conversion of **2a** could be achieved if 2.0 equiv of 2,6-Me$_2$C$_6$H$_3$OH was added to **2a** after 24 h (at 25 °C). Note that the formation of methane was not observed even if 2.0 equiv of 2,6-Me$_2$C$_6$H$_3$OH was added to **2a**. The ^{1}H NMR spectra for the resultant compound showed resonances that could be assigned to the ketimide/aryloxo exchange reaction product, (ArN)VMe(O-2,6-Me$_2$C$_6$H$_3$)$_2$ (**5a**), according to the integration ratio of the aryloxo group and the arylimido group in addition to a resonance at 2.11 ppm ascribed to the vanadium−methyl bond as well as to the disappearance of the

(20) Basuli, F.; Kilgore, U. J.; Hu, X.; Meyer, K.; Pink, M.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3156.

(21) (a) Nomura, K.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1996**, *35*, 3695. (b) Groysman, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2005**, *44*, 5073. (c) Smythe, N. C.; Schrock, R. R.; Mu1ller, P.; Weare, W. W. *Inorg. Chem.* **2006**, *45*, 9197.

ketimide ligand (Scheme 5). The formation of **5a** could also be confirmed by comparison of the resonances in ^{1}H and ^{51}V NMR spectra for the bis(aryloxo)-chloro analogue, (ArN)VCl(O-2,6-$Me_2C_6H_3)_2$ (**6**), and the tris(aryloxo) analogue, (ArN)V(O-2,6-$Me_2C_6H_3)_3$ (**7**), which could be prepared and identified independently by the reaction of (ArN)VCl_3 with 2.0 or 3.0 equiv of LiO-2,6-$Me_2C_6H_3$ in Et_2O according to an analogous method for the preparation of (ArN)VCl_2(O-2,6-$Me_2C_6H_3$).[22,23] It should be noted that the vanadium−methyl bond in the bis(aryloxo) analogue (**5a**) was stable even in the presence of an additional 1.0 equiv of 2,6-$Me_2C_6H_3OH$, and no reaction took place upon stirring for long hours (after 24 h at 25 °C). The formation of (ArN)VMe(O-4-^{t}Bu-2,6-^{i}Pr$_2C_6H_2)_2$ (**5b**) was also confirmed by the reaction of **2b** with 4-^{t}Bu-2,6-^{i}Pr$_2C_6H_2$OH under the similar conditions (12 h).

In order to explore the unique reactivity of the Me groups in both **2a** and **5a** toward phenol, we performed the reaction of **2a** with 4-^{t}Bu-2,6-^{i}Pr$_2C_6H_2$OH (and **2b** with 2,6-$Me_2C_6H_3OH$) according to Scheme 6, and the results are shown in Figure 3.

Rapid scrambling of **2a** and **2b** was seen when **2a** was treated with 1.0 equiv of 4-^{t}Bu-2,6-^{i}Pr$_2C_6H_2$OH in $CDCl_3$ at 25 °C (Figure 3b), and the resultant solution eventually gave a ca. 1:1 mixture of **2a** and **2b**, as confirmed by ^{1}H and ^{51}V NMR spectra (within 30 min at 25 °C). The solution gave three species, as confirmed by the ^{51}V NMR spectrum (−64, −70, and −78 ppm) in an approximately 1:2:1 ratio, respectively (Figure 3c), upon heating at 60 °C for 12 h. The resonances observed at −64 and −78 ppm could be assigned as **5a** and **5b**, respectively, and we estimated that the species at −70 ppm could be assigned as the mixed bis(aryloxo) complex (ArN)VMe(O-4-^{t}Bu-2,6-^{i}Pr$_2C_6H_2$)-(O-2,6-$Me_2C_6H_3$) (**5c**) on the basis of the ^{1}H NMR spectrum. Similar results were observed if **2b** was treated with 2,6-$Me_2C_6H_3OH$ in $CDCl_3$, as shown in Figure 3e−h. The reaction with the Me group did not occur in either **2a**,**b** or **5a**,**b** even after 12 h at 60 °C.

We believe that these results clearly explain the unique reactivity of both **1** and **2a**,**b** toward alcohol according to Scheme 7. Both phenol-scrambling and the phenol/ketimide exchange reaction should be preferred if the phenol approaches the electrophilic vanadium metal center *trans* to the Me group (NNN face in **1** or NNO face in **2a**,**b**, and not the NNC faces in **1** or **2a**,**b**), to give pentacoordinated trigonal bipyramidal intermediates (shown in brackets in Scheme 7). The reaction with the Me group would not occur if the reaction takes place via this proposed intermediate. A similar assumption was also proposed by Schrock et al.[24] in the alkoxide exchange reaction of Mo(NAr)(CH^{t}Bu)(CH$_2{}^t$Bu)(OAr) with ROH (OR = $OCMe_3$, OAd, OC_6F_5; Ad = adamantyl) and assumed a similar intermediate. Simple PM3 estimation also suggests that the proposed intermediate would be more stable than the other probable intermediate.[25] The same estimation suggests that the formation of a similar intermediate caused destabilization in the reaction with thiol, which suggests that simple protonation should be favored.[25] Thus, on the basis of Scheme 7, it is assumed that proton migration to the aryloxide ligand occurred quickly, whereas migration to the ketimide ligand was relatively slow under these conditions.[26]

Conclusion

We have explored the reactions of (ArN)VMe(N=C^{t}Bu)$_2$ (**1**) with various alcohols, thiols, and borates. The reaction of the V−Me bonds in **1** with thiols and borates took place exclusively to give corresponding thiolates and cationic complexes, respectively. In contrast, the V−Me in **1** did not react with alcohols to afford other methyl complexes via ligand substitution between the ketimide and the alkoxide/phenoxide. The reaction of (ArN)-VMe(N=C^{t}Bu)(OAr′) (**2**, Ar′ = 2,6-$Me_2C_6H_3$, 4-^{t}Bu-2,6-^{i}Pr$_2C_6H_2$) with phenols gave other methyl complexes, (ArN)VMe(OAr′)$_2$ (**5**), and the reaction with the Me group did not occur even in the presence of 2.0 equiv of phenol. On the basis of our experiments, we propose that the reaction with alcohols proceeded in the following steps: (1) the alcohols initially approached the electron-deficient metal center *trans* to the methyl group to give a pentacoordinated trigonal bipyramidal species, and (2) proton transfer to the aryloxide/ketimide occurred to give ketimine/phenol dissociation. In contrast to the reaction with alcohols, facile protonolysis took place in the reaction of **1** or **2** with thiols or borates to give thiolate complexes or cationic complexes, respectively. These results should be useful for the preparation of various vanadium−alkyl complexes as well as to achieve a better understanding of the basic reaction mechanism in vanadium-catalyzed organic synthesis.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous-grade benzene, diethyl ether, *n*-hexane, and THF (Kanto Kagaku Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 and were passed through an short alumina column under N_2 stream before use. All chemicals used were of reagent grade and were purified by the standard purification procedures. Reagent-grade $B(C_6F_5)_3$, $[Ph_3CB][(C_6F_5)_4]$, and $[PhN(H)Me_2][B(C_6F_5)_4]$ (Asahi Glass Co. Ltd.) were stored in the drybox and were used as received. Synthesis of LiN=C^{t}Bu$_2$ was also according to the reported procedure.[27] Elemental

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

(23) Although the exclusive formation of **5a** could be confirmed by both ^{1}H and ^{51}V NMR spectra, an attempt to isolate **5a** as microcrystals was unsuccessful probably due to the improved solubility in organic solvent and/or contamination of residual phenol in trace amounts. The identification of **5a** was thus made by comparison of both ^{1}H and ^{51}V NMR spectra with the chloro-bis(aryloxo) analogue, (ArN)VCl(O-2,6-$Me_2C_6H_3)_2$ (**6**), and the tris(aryloxo) analogue, (ArN)V(O-2,6-$Me_2C_6H_3)_3$ (**7**), which could be prepared and identified independently by the reaction of (ArN)VCl_3 with 2.0 or 3.0 equiv of LiO-2,6-$Me_2C_6H_3$ in Et_2O according to the analogous method for the preparation of (ArN)VCl_2(O-2,6-$Me_2C_6H_3$).[22]

(24) Sinha, A.; Lopez, L. P. H.; Schrock, R. R.; Hock, A. S.; Müller, P. *Organometallics* **2006**, *25*, 1412.

(25) The result for simple energy evaluations [coordination energies defined as $\Delta E_{coord} = E_{(complex\ 1)} + E_{(2,6-Me2C6H3OH)} - E_{(proposed\ intermediate)}$; $E_{(complex\ 1)}$, $E_{(2,6-Me2C6H3OH)}$, $E_{(proposed\ intermediate)}$ are heat of formation for complex **1**, 2,6-$Me_2C_6H_3OH$, and the proposed intermediates, respectively] for three proposed intermediates in the reaction [equilibrium geometry at ground state with semiempirical PM3, geometry optimization, RHF/PM3D Spartan '04 for Windows (Wavefunction Inc.)] suggested that coordination of phenol *trans* to the methyl group seemed more stable (ΔE_{coord} = 3.31 kcal/mol) than the others [ΔE_{coord} = −1.97 and −24.88 kcal/mol for the proposed intermediates when the phenol coordinates *trans* to arylimido and ketimide, respectively]. In contrast, the coordination of 2,6-$Me_2C_6H_3SH$ to the vanadium in **1** caused destabilization in all cases (ΔE_{coord} = −5.21, −12.35, and −20.88 kcal/mol; 2,6-$Me_2C_6H_3SH$ *trans* to arylimido, ketimide, and Me, respectively). These results may also suggest the formation of five-coordinated trigonal bipyramidal species by coordination of the phenol to **1**, although more precise geometry optimizations are necessary for a more precise evaluation.

(26) A reviewer commented that we do not mention the possibility of the arylimido ligand acting as a proton shuttle. As described in ref 25 and our experimental results, the reaction of **1** with thiols may occur by simple protonolysis not by coordination of thiols, although we do not have clear evidence for the mechanism.

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

analyses were performed by using a PE2400II Series (Perkin-Elmer Co.). Some analytical runs were performed twice to confirm the reproducibility in the independent analysis/synthesis runs.

All ^{1}H, ^{13}C, and ^{51}V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^{1}H, 100.40 MHz for ^{13}C, and 105.31 MHz for ^{51}V), and ^{19}F NMR spectra were recorded on a JEOL JNM-ECP600NK spectrometer (564.69 MHz for ^{19}F). 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.

One-Pot Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(N=C^{t}Bu$_2$)$_2$ (1). To an Et_2O solution (60 mL) containing VCl_3(N-2,6-$Me_2C_6H_3$) (1.38 g, 5.0 mmol) was added LiN=C^{t}Bu$_2$ (1.55 g, 10.5 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature (25 °C), and the mixture was stirred for an additional 6 h. MeMgBr (3.0 M in Et_2O, 1.83 mL) was then added dropwise to the reaction mixture that had been at −30 °C. The mixture was then warmed slowly to room temperature and was stirred for an additional 4 h. The solution was then placed in a rotary evaporator *in vacuo* to remove solvent (hexane, Et_2O), and the resultant residue was extracted with hot *n*-hexane (ca. 100 mL). The *n*-hexane extract was then placed *in vacuo*, and the resultant residue was layered by *n*-hexane (ca. 10 mL) at −30 °C. The chilled solution was placed in the freezer to give red microcrystals. Yield: 1.35 g (58%). ^{1}H NMR ($CDCl_3$): δ 0.88 (br, 3H, V−CH_3), 1.31 (s, 18H, (CH_3)$_3$C−), 2.44 (s, 6H, CH_3), 6.67 (t, 1H), 6.86 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 19.4, 30.8, 36.7, 45.6, 122.2, 126.8, 134.1, 162.7, 199.4. ^{51}V NMR ($CDCl_3$): δ −138.8 ($\Delta\nu_{1/2}$ = 324 Hz). Anal. Calcd for $C_{27}H_{48}N_3V$: C, 69.64; H, 10.39; N, 9.03. Found: C, 69.16; H, 10.14; N, 9.09.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(O-2,6-Me$_2$C$_6$H$_3$) (2a). To a *n*-hexane solution (10 mL) containing **1** (372 mg, 0.80 mmol) was added 2,6-$Me_2C_6H_2OH$ (98 mg, 0.80 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for an additional 3 h. The solution was concentrated *in vacuo*, and the chilled solution (−30 °C) yielded 335 mg (94%) of **2a** as red microcrystals. ^{1}H NMR ($CDCl_3$): δ 1.34 (3H, V−CH_3), 1.41 (s, 18H, (CH_3)$_3$C−), 2.33 (s, 6H, CH_3), 2.47 (s, 6H, CH_3), 6.81 (m, 2H), 6.96 (d, 2H), 7.03 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 17.6, 18.9, 30.5, 38.5 (br, V-*Me*), 45.4, 120.4, 123.9, 126.8, 127.1, 128.0, 162.8, 163.87, 201.3. ^{51}V NMR ($CDCl_3$): δ −185 ($\Delta\nu_{1/2}$ = 253 Hz). Anal. Calcd for $C_{26}H_{39}N_2OV$: C, 69.93; H, 8.80; N, 6.27. Found: C, 70.02; H, 8.98; N, 6.20.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(O-4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$) (2b). Synthesis of **2b** was carried out according to the same procedure as that in **2a** except that 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (47 mg, 0.20 mmol) was used in place of 2,6-$Me_2C_6H_2OH$. Yield: 104 mg (93%). ^{1}H NMR ($CDCl_3$): δ 1.18 (d, 12H, *Me*$_2$CH−), 1.34 (s, 9H, *para*-(CH_3)$_3$C), 1.37 (s, 18H, (CH_3)$_3$C), 2.52 (s, 6H, CH_3), 3.56 (hept, 2H, Me$_2$CH−), 6.79 (t, 1H), 6.94 (d, 2H), 7.08 (s, 2H). The V-*Me* signal was not found due to a peak overlapping with ^{t}Bu groups in both aryloxo and ketimide ligands. ^{13}C NMR ($CDCl_3$): δ 19.1, 23.2, 23.4, 26.8, 30.5, 31.7, 34.6, 38.3 (br, V-*Me*), 45.2, 119.5, 123.6, 127.0, 134.5, 136.5, 143.3, 158.1, 162.5, 200.7. ^{51}V NMR ($CDCl_3$): δ −197 ($\Delta\nu_{1/2}$ = 284 Hz). Anal. Calcd for $C_{34}H_{55}N_2OV$: C, 73.08; H, 9.92; N, 5.01. Found (1): C, 72.98; H, 10.14; N, 4.99. Found (2): C, 73.14; H, 9.72; N, 5.11.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(OPh) (2c). Synthesis of **2c** was carried out according to the same procedure as that in **2a** except that PhOH (39 mg, 0.41 mmol) was used in place of 2,6-$Me_2C_6H_2OH$. Yield: 154 mg (92%). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 18H, (CH_3)$_3$C−), 1.43 (3H, V−CH_3), 2.45 (s, 6H, CH_3), 6.77 (t, 1H), 6.89 (d, 3H), 7.04 (d, 2H), 7.19 (t, 2H). ^{13}C NMR ($CDCl_3$): δ 19.1, 30.4, 39.7 (br, V-*Me*), 45.0, 119.3, 121.0, 124.0, 127.0, 128.8, 135.8, 162.3, 165.3, 198.8. ^{51}V NMR ($CDCl_3$): δ −153 ($\Delta\nu_{1/2}$ = 1817 Hz). Anal. Calcd for $C_{24}H_{35}N_2OV$: C, 68.88; H, 8.43; N, 6.69. Found: C, 68.62; H, 8.36; N, 6.44.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(OC$_6$F$_5$) (2d). Synthesis of **2d** was carried out according to the same procedure as that in **2a** except that C_6F_5OH (92 mg, 0.50 mmol) was used in place of 2,6-$Me_2C_6H_2OH$. Yield: 202 mg (79%). ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 18H, (CH_3)$_3$C-), 1.49 (3H, V−CH_3), 2.42 (s, 6H, CH_3), 6.79 (t, 1H), 6.90 (d, 3H). ^{13}C NMR ($CDCl_3$): δ 18.7, 30.3, 43.1 (br, V-*Me*), 45.6, 125.1, 127.1, 133.4, 135.8, 136.6, 138.5, 139.1, 139.9, 140.9, 163.7, 203.9. ^{19}F NMR ($CDCl_3$): δ −171.64, −167.13, −160.94. ^{51}V NMR ($CDCl_3$): δ −98 ($\Delta\nu_{1/2}$ = 295 Hz).

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(O^{i}Pr) (2e). Synthesis of **2e** was carried out by the same procedure as that in **2a** except that ^{i}PrOH (48 mg, 0.80 mmol) was used in place of phenol. Yield: 286 mg (93%). ^{1}H NMR ($CDCl_3$): δ 1.03 (3H, V−CH_3), 1.28 (s, 18H, (CH_3)$_3$C−), 1.28 (d, 6H, (CH_3)$_2$CH−), 2.52 (s, 6H, CH_3), 4.87 (hept, 1H, (CH$_3$)$_2$CH−), 6.70 (t, 1H), 6.92 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 19.3, 26.9, 30.5, 35.0 (br V-*Me*), 44.8, 77.6, 123.0, 127.0, 134.2, 161.8, 198.8. ^{51}V NMR ($CDCl_3$): δ −244 ($\Delta\nu_{1/2}$ = 311 Hz).

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(OCH$_2$CH$_2$CH=CH$_2$) (2f). Synthesis of **2f** was carried out according to the same procedure as that in **2a** except that 3-butene-1-ol (30 mg, 0.42 mmol) was used in place of 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH. Yield: 137 mg (86%). ^{1}H NMR ($CDCl_3$): δ 1.15 (s, br, 3H, V-CH_3), 1.27 (s, 18H, (CH_3)$_3$C−), 2.62 (2H, OCH$_2$CH_2), 2.62 [s, 6H, (CH_3)$_2$], 4.55 (2H), 4.75−4.86 (2H), 5.56 (1H), 6.76 (t, 1H), 6.93 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 14.2, 19.4, 22.6, 30.6, 31.6, 39.3, 42.6, 45.0, 45.6, 75.2, 116.4, 123.5, 127.3, 134.7, 137.3, 158.1, 185.8. ^{51}V NMR ($CDCl_3$): δ −103 ($\Delta\nu_{1/2}$ = 1632 Hz), −231 ($\Delta\nu_{1/2}$ = 579 Hz). Anal. Calcd for $C_{22}H_{37}N_2OV$: C, 66.64; H, 9.41; N, 7.07. Found: C, 66.95; H, 9.70; N, 6.76.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(OCH$_2$CH$_2$CH$_2$CH$_2$CH=CH$_2$) (2g). Synthesis of **2g** was carried out by the same procedure as that in **2a** except that 5-hexene-1-ol (20 mg, 0.20 mmol) was used. Yield: 56 mg (66%). ^{1}H NMR ($CDCl_3$ at 20 °C): δ 1.07 (s, br, 3H, V-CH_3), 1.25 (s, 18H, (CH_3)$_3$C−), 1.41 (2H), 1.71 (2H), 1.97 (2H), 2.53 (s, 6H, CH_3), 4.52 (2H), 4.89−4.94 (2H), 5.71 (1H), 6.74 (t, 1H), 6.91 (d, 2H). ^{13}C NMR ($CDCl_3$ at 20 °C): δ 14.1, 19.4, 22.6, 25.0, 30.5, 31.6, 33.6, 34.2, 42.2, 44.9, 76.3, 114.2, 123.4, 127.2, 134.6−137.2, 138.9, 159.7, 185.4, 198.8. ^{51}V NMR ($CDCl_3$ at 20 °C): δ −105 ($\Delta\nu_{1/2}$ = 1685 Hz), −237 ($\Delta\nu_{1/2}$ = 527 Hz). Anal. Calcd for $C_{24}H_{41}N_2OV$: C, 67.90; H, 9.73; N, 6.60. Found: C, 67.97; H, 9.88; N, 6.62.

Reaction of 1 with *n*-Hexanol: Synthesis of V(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)[OCH$_2$(CH$_2$)$_4$CH$_3$]. The synthesis was carried out by the same procedure as that in **2a** except that *n*-hexanol (42 mg, 0.41 mmol) was used. ^{1}H NMR ($CDCl_3$): δ 0.82 (3H), 1.04 (s, br, 3H, V-CH_3), 1.23 (s, 18H, (CH_3)$_3$C−), 1.25−1.28 (m, 6H), 1.66 (2H), 2.51 (s, 6H, CH_3), 4.50 (2H), 6.73 (t, 1H), 6.90 (d, 2H). ^{51}V NMR ($CDCl_3$): δ −238 ($\Delta\nu_{1/2}$ = 419 Hz).

V(N-2,6-Me$_2$C$_6$H$_3$)(N=C^{t}Bu$_2$)(S-2,6-Me$_2$C$_6$H$_3$) (3a). To an *n*-hexane solution (10 mL) containing **1** (186 mg, 0.40 mmol) was added 2,6-$Me_2C_6H_3SH$ (57 mg, 0.41 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature (25 °C) and was stirred for an additional 3 h. The solution was concentrated *in vacuo*, and the chilled solution (−30 °C) yielded 176 mg (75%) of **3a** as brown crystals. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 36H, (CH_3)$_3$C−), 2.39 (s, 6H, CH_3), 2.51 (s, 6H, CH_3), 6.73 (t, 1H), 6.83 (t, 1H), 6.88 (d, 2H), 6.92 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 19.1, 23.9, 30.4, 45.2, 123.6, 124.4, 126.8, 126.9, 134.4, 139.5, 144.6, 163.3, 198.5. ^{51}V NMR ($CDCl_3$): δ −132 ($\Delta\nu_{1/2}$ = 341 Hz).

Reaction of 1 with *n*-C$_6$H$_{13}$SH (3b). To a NMR tube equipped with a Teflon (Young) valve containing a C_6D_6 solution (0.5 mL) of **1** (47 mg, 0.1 mmol) was added *n*-$C_6H_{13}SH$ (12 mg, 0.1 mmol) at room temperature (25 °C). Three sets of resonances

ascribed to the product (**3b**), methane (0.15 ppm), and the starting material (**1**) (conversion 72%) were observed in the ^{1}H NMR spectrum, and two resonances ascribed to **1** and **3b** were observed in the ^{51}V NMR spectrum. ^{1}H NMR (C_6D_6): δ 0.82, 0.94, 1.15−1.45, 1.28, 1.33, 1.88, 2.68 (s, 6H, CH_3), 2.93, 3.67, 6.72 (t, 1H), 6.91 (d, 2H). ^{51}V NMR (C_6D_6): δ −153.6 ($\Delta\nu_{1/2}$ = 316 Hz).

Synthesis of [V(N-2,6-Me$_2$C$_6$H$_3$)(N=C^{t}Bu$_2$)$_2$(THF)$_2$][B(C$_6$F$_5$)$_4$] (4a). To a THF solution (4 mL) containing **1** (186 mg, 0.40 mmol) was added [Ph$_3$C][B(C$_6$F$_5$)$_4$] (369 mg, 0.40 mmol) at −30 °C. The reaction mixture was allowed to warm to room temperature (25 °C) and was stirred for 1 h. Removal of solvent from the mixture *in vacuo* gave a mixture of **4a** and Ph$_3$CCH$_3$ quantitatively. Recrystallization from THF/*n*-hexane afforded red block microcrystals. Yield: 460 mg (90%). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 36H, (C*H*$_3$)$_3$C−), 1.85 (br, 8H, *thf*), 2.58 (s, 6H, C*H*$_3$), 3.73 (br, 8H, *thf*), 6.89 (t, 1H), 6.95 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 18.9, 25.5, 30.3, 45.8, 68.6, 123.8, 127.7, 135.0, 135.7, 136.9, 137.4, 139.3, 147.0, 149.4, 167.0, 207.2. ^{19}F NMR ($CDCl_3$): δ −134.4, −164.5, −168.3. ^{51}V NMR ($CDCl_3$): δ −92 ($\Delta\nu_{1/2}$ = 714 Hz). Anal. Calcd for $C_{58}H_{61}BF_{20}N_3O_2V$: C, 54.69; H, 4.79; N, 3.30. Found (1): C, 54.37; H, 4.79; N, 3.12. Found (2): C, 54.71; H, 4.82; N, 3.15.

Synthesis of [V(N-2,6-Me$_2$C$_6$H$_3$)(N=C^{t}Bu$_2$)$_2$(THF)$_2$][B(C$_6$F$_5$)$_4$] (4a) from 1 by Reaction with [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$]. One equivalent of [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] (160 mg, 0.20 mmol) was added to a solution of **1** (93 mg, 0.20 mmol) in THF at −30 °C, and the resulting mixture was warmed gradually under continuous stirring for 1 h at room temperature. Removal of solvent from the reaction mixture *in vacuo* gave a mixture of the product (**4a**) and PhNMe$_2$: the ^{1}H NMR spectrum of the mixture was identical to that of the isolated **4a** except for the signals of PhNMe$_2$. ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 36H, (C*H*$_3$)$_3$C−), 1.89 (br, 8H, *thf*), 2.58 (s, 6H, C*H*$_3$), 3.98 (br, 8H, *thf*), 6.89 (t, 1H), 6.95 (d, 2H). ^{51}V NMR ($CDCl_3$): δ −92 ($\Delta\nu_{1/2}$ = 704 Hz).

Synthesis of [V(N-2,6-Me$_2$C$_6$H$_3$)(N=C^{t}Bu$_2$)$_2$(THF)$_2$][MeB(C$_6$F$_5$)$_3$] (4b) from 1 by Reaction with [B(C$_6$F$_5$)$_3$]. To a THF solution (5.0 mL) containing **1** (186 mg, 0.40 mmol) was added B(C$_6$F$_5$)$_3$ (204 mg, 0.40 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature (25 °C) and was stirred for 1 h. Solvent in the mixture was then removed *in vacuo* to give analytically pure product (447 mg, quantitative) that was considered to be **4b**. ^{1}H NMR ($CDCl_3$): δ 0.48 (s, 3H, B*Me*), 1.34 (s, 36H, (C*H*$_3$)$_3$C−), 1.91 (br, 8H, *thf*), 2.57 (s, 6H, C*H*$_3$), 3.82 (br, 8H, *thf*), 6.88 (t, 1H), 6.97 (d, 2H). ^{51}V NMR ($CDCl_3$): δ −94 ($\Delta\nu_{1/2}$ = 816 Hz).

Synthesis of [V(N-2,6-Me$_2$C$_6$H$_3$)(N=C^{t}Bu$_2$)(O-2,6-Me$_2$C$_6$H$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (4c) from 2a by Reaction with [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$]. One equivalent of [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] (320 mg, 0.40 mmol) was added to a solution of **2a** (179 mg, 0.20 mmol) in THF at −30 °C. The resulting mixture was stirred for 1 h at room temperature (25 °C). The removal of THF from the solution gave a mixture of the product (**4c**) and free PhNMe$_2$. The exclusive formation of **4c** was confirmed by ^{1}H and ^{51}V NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 18H, (C*H*$_3$)$_3$C−), 1.97 (br, 8H, *thf*), 2.25 (s, 6H, C*H*$_3$ on aryloxo), 2.50 (s, 6H, C*H*$_3$ on arylimido), 4.00 (br, 8H, *thf*), 6.92 (t, 1H), 6.98 (s, 3H), 7.05 (d, 2H). ^{51}V NMR ($CDCl_3$): δ −77 ($\Delta\nu_{1/2}$ = 790 Hz).

Formation of VMe(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-Me$_2$C$_6$H$_3$)$_2$ (5a). To a $CDCl_3$ (ca. 0.5 mL) solution containing **2a** (45 mg, 0.10 mmol) was added 2,6-Me$_2$C$_6$H$_3$OH (24 mg, 0.20 mmol) at room temperature. NMR measurements were conducted after 0.5, 5.0, and 24 h. The quantitative conversion was achieved after 24 h. ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 6H, C*H*$_3$), 2.29 (s, 12H, C*H*$_3$), 6.75−6.84 (m, 5H), 6.97−7.01 (m, 4H). The V-*Me* signal was not found (observed as a shoulder at ca. 2.23 ppm) due to overlapping by the Me group in aryloxo. ^{13}C NMR ($CDCl_3$): δ 17.3, 18.0, 53.5 (br, V-*Me*), 122.0, 125.7, 126.1, 127.1, 128.1, 135.9, 164.1. ^{51}V NMR ($CDCl_3$): δ −64 ($\Delta\nu_{1/2}$ = 348 Hz).

Formation of VMe(N-2,6-Me$_2$C$_6$H$_3$)(O-4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$)$_2$ (5b). To a $CDCl_3$ (ca. 0.5 mL) solution containing **2b** (33 mg, 0.059 mmol) was added 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (14 mg, 0.059 mmol) at room temperature. NMR measurements were conducted after 1 and 12 h. The quantitative conversion was achieved after 12 h. ^{1}H NMR ($CDCl_3$): δ 1.15 (dd, 24H, ^{i}Pr-C*H*$_3$), 1.28 (s, 18H, ^{t}Bu), 2.15 (br, 3H, V-*Me*), 2.17 (s, 6H, C*H*$_3$ on arylimido), 3.47 (hept, 4H, ^{i}Pr-C*H*), 6.74 (1H), 6.81 (4H), 7.07, (s, 4H). ^{13}C NMR ($CDCl_3$): δ 18.3, 23.1, 23.5, 27.0, 31.6, 34.6, 52.8 (br, V-*Me*), 119.6, 125.2, 127.0, 135.1, 135.9, 144.9, 160.2, 163.5. ^{51}V NMR ($CDCl_3$): δ −78 ($\Delta\nu_{1/2}$ = 458 Hz).

Synthesis of VCl(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-Me$_2$C$_6$H$_3$)$_2$ (6). To an Et$_2$O solution (10 mL) containing VCl$_2$(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-Me$_2$C$_6$H$_3$) (724 mg, 2.0 mmol) was added LiO-2,6-Me$_2$C$_6$H$_3$ (256 mg, 2.0 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for an additional 3 h. The solution was then removed *in vacuo*, and the resultant residue was extracted with hexane (ca. 30 mL). The hexane extract was concentrated *in vacuo*, and the chilled solution (−30 °C) yielded 744 mg (83%) of the desired product. ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 6H, Me$_2$), 2.36 (s, 12H, aryloxo-Me$_2$), 6.74 (s, 3H), 6.88 (t, 2H), 7.02 (d, 2H). ^{13}C NMR ($CDCl_3$): δ17.4, 17.7, 123.9, 126.1, 127.2, 128.0, 128.3, 137.6, 167.0. ^{51}V NMR ($CDCl_3$): δ −207 ($\Delta\nu_{1/2}$ = 411 Hz). Anal. Calcd for $C_{24}H_{27}ClN_3O_2V$: C, 64.36; H, 6.08; N, 3.13. Found (1): C, 64.51; H, 6.12; N, 3.07. Found (2): C, 64.95; H, 6.07; N, 3.08.

Synthesis of V(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-Me$_2$C$_6$H$_3$)$_3$ (7). Treatment of V(N-2,6-Me$_2$C$_6$H$_3$)Cl$_3$ (138 mg, 0.5 mmol) with 3.0 equiv of LiO-2,6-Me$_2$C$_6$H$_3$ in Et$_2$O caused the precipitation of LiCl, and color of the solution changed from dark green to dark red. After 12 h, all volatiles were removed under reduced pressure and the product was extracted with hot *n*-hexane. Concentrating and cooling of the mixture to room temperature afforded 241 mg (90% yield) of **7** as dark red microcrystals. ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 6H, CH_3), 2.33 (s, 18H, CH_3), 6.72 (s, 3H, NAr), 6.82 (t, 3H, *p*-OAr), 7.00 (d, 6H, *m*-OAr). ^{13}C NMR ($CDCl_3$): δ 17.4, 17.5, 122.4, 126.6, 126.8, 127.1, 128.2, 136.2, 166.2. ^{51}V NMR ($CDCl_3$): δ −373 ($\Delta\nu_{1/2}$ = 395 Hz). Anal. Calcd for $C_{32}H_{36}NO_3V$: C, 72.03; H, 6.80; N, 2.63. Found: C, 72.13; H, 6.89; N, 2.58.

Typical Reaction of 2a with 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH in $CDCl_3$. To a Teflon-sealed NMR tube containing $CDCl_3$ (ca. 0.5 mL) and **2a** (45 mg, 0.10 mmol) was added 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (23 mg, 0.10 mmol) in one portion, and the resultant solution was monitored by both ^{1}H NMR and ^{51}V NMR (shown in Figure 3b). The solution was then heated to 60 °C and was stirred for an additional 12 h (the spectrum shown in Figure 3c).

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. The selected crystal collection parameters are listed below (Table 1), and the detailed results are described in the attached reports. All structures were solved by direct methods and expanded using Fourier techniques,[28] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **3a** and **4a** were performed using the CrystalStructure[29,30] crystallographic software package.

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Supporting Information Available: Figures giving fits used to determine ΔG values for reaction intermediates, ^{1}H and ^{51}V NMR spectra for **2f**,**g**; crystal structure determination reports for **3a** and **4a**. Crystallographic data are also given as CIF files. These materials are available free of charge via the Internet at http://pubs.acs.org.

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