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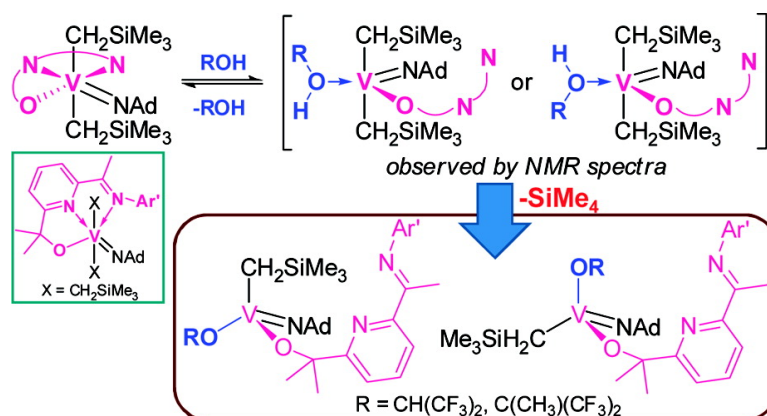
## Article

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# Synthesis of (1-Adamantylimido)vanadium(V)-alkyl Complexes Containing a Chelate Alkoxo(imino)pyridine Ligand, and Reactions with Alcohols (ROH) That Proceed via Intermediates Formed by Coordination of ROH

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An (1-adamantylimido)vanadium(V)-dialkyl complex containing a chelate alkoxo(imino)pyridine ligand, V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(L) (**2**, Ad = 1-adamantyl, L = 6-OC(Me)<sub>2</sub>-2-[(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CMe]-C<sub>5</sub>H<sub>3</sub>N], has been prepared, and some reactions with (CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)COH, (CF<sub>3</sub>)<sub>2</sub>CHOH, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH, and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH in C<sub>6</sub>D<sub>6</sub> have been explored. Two alkyl groups in **2** take a *trans* form, as determined by the dichloride analogue V(NAd)Cl<sub>2</sub>(L) (**1**), and no reaction took place or afforded a negligible amount of the product even if the C<sub>6</sub>D<sub>6</sub> solution containing **2** and PMe<sub>3</sub> (13 equiv) or NHC [2.1 equiv, NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] was heated at 80 °C for 72 h. The reaction of **2** with (CF<sub>3</sub>)<sub>2</sub>CHOH and (CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)COH at 25 °C afforded intermediates V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(L)[ROH] [R = CH(CF<sub>3</sub>)<sub>2</sub>, C(CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)], and the resultant species were converted to the original complex **2** if the mixed solutions were placed *in vacuo* (to remove volatiles). The reactions with ROH upon heating or by stirring for longer hours afforded the monoalkyl-alkoxo species V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)(L)(OR) [R = CH(CF<sub>3</sub>)<sub>2</sub> (**4**), C(CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>) (**5**)]; complex **4** determined by X-ray crystallography has a distorted tetrahedral geometry around vanadium. It has thus been proposed that reactions of the dialkyl complex **2** with ROH proceeded via pentacoordinated intermediates formed by coordination of ROH, accompanied by dissociation of two neutral nitrogen donors in the chelate ligand.

## Introduction

Transition metal-alkyl complexes are important reagents or intermediates in stoichiometric/catalytic organic reactions, as well as in olefin coordination/insertion polymerization.<sup>1,2</sup> Their synthesis and reaction chemistry have thus been considered to be important not only in designing efficient catalysts but also for a better understanding of organic reactions, especially with regard to catalytic cycles or reactions pathways.<sup>1</sup> In general, metal-alkyls, especially metal-alkyls with early transition metals, possessed a more nucleophilic nature than those with late transition metals and are thus highly reactive toward Brønsted/

Lewis acids.<sup>1–4</sup> For instance, cationic alkyl complexes, which have been proposed to be the catalytically active species in olefin coordination polymerization, are generated from their dialkyl analogues by reacting them with cocatalysts via facile protonolysis or alkyl abstraction;<sup>2</sup> some organometallic complexes can thus be grafted onto a silica surface by reaction of the alkyl compounds with silanol groups on the surface.<sup>5,6</sup>

Classical Ziegler-type vanadium catalysts are known to exhibit unique characteristics, such as synthesis of ultra high

(3) 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.

(4) A reviewer commented that we should introduce some exceptions. (a) Lubben, T. V.; Wolczanski, P. T.; van Duyne, G. D. *Organometallics* **1984**, *3*, 977. In this report, the reaction with Zr(CH<sub>2</sub>Ph)<sub>4</sub> with 1.14 equiv of <sup>t</sup>Bu<sub>3</sub>COH in benzene under reflux conditions for 7 h afforded Zr(CH<sub>2</sub>Ph)<sub>3</sub>(OC<sup>t</sup>Bu<sub>3</sub>), whereas synthesis of Zr(CH<sub>2</sub>Ph)<sub>3</sub>(OC<sup>t</sup>Bu<sub>3</sub>) by the reaction of Zr(CH<sub>2</sub>Ph)<sub>4</sub> with <sup>t</sup>Bu<sub>3</sub>COH in benzene required 30 h at 93–95 °C. (b) A reviewer pointed out that certain chromium(IV)-tetra(alkyl)s are stable even in alcohols under reflux conditions.

(5) 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. (c) Example of proposed mechanism for reaction of Cr(CH<sub>2</sub>Bu)<sub>4</sub> with silica surface: Ajou, J. A. N.; Scott, S. *Organometallics* **1997**, *16*, 86.

(6) Recent examples: (a) Nicholas, P.; Ahn, H. S.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 4325. (b) McKittrick, M. W.; Jones, C. W. *J. Am. Chem. Soc.* **2004**, *126*, 3052. (c) 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.

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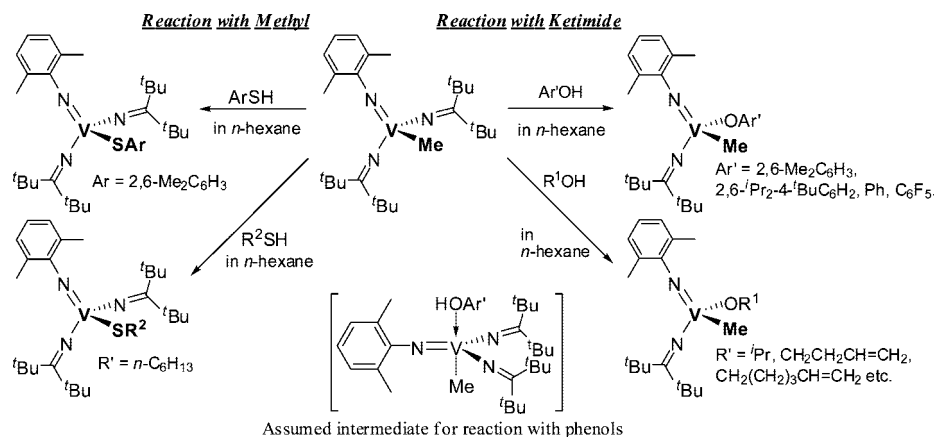
<sup>†</sup> NAIST.

<sup>‡</sup> Institute of Chemistry, Chinese Academy of Sciences.

(1) For example (general text of metal-alkyl chemistry): (a) *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Crabtree, R. H., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, 2005; p 53. (b) *Comprehensive Organometallic Chemistry III*; Crabtree, R. H.; Mingos, D. M. P., Eds.; Elsevier Science/Pergamon: New York, 2006. (c) *Synthesis of Organometallic Compounds: A Practical Guide*; Komiyama, S., Ed.; John Wiley & Sons Ltd.: West Sussex, England, 1997. (d) *Organometallics in Synthesis A Manual*, 2nd ed.; Schlosser, M., Ed.; John Wiley & Sons Ltd: West Sussex, England, 2002. (e) *Organometallic Chemistry and Catalysis*; Astruc, D., Ed.; Springer-Verlag: Berlin, Germany, 2007.

(2) 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.

Scheme 1



molecular weight polymers with relatively narrow molecular weight distributions, due to their high reactivity toward olefins in olefin coordination/insertion polymerization.<sup>3e,7</sup> Therefore, the synthesis and reaction chemistry of the vanadium-alkyl complexes attract considerable attention.<sup>8–12</sup> However, examples of their chemistry were limited until recently,<sup>8,10,12</sup> probably because these vanadium-alkyls tend to be reactive and/or thermally labile and reductions to lower oxidation states often occurred in the reactions with organometallic reagents.<sup>12</sup>

(7) 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.

(8) Some structural characterizations, 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.; Donnadiou, B. *Organometallics* **2002**, *21*, 1124. (h) Liu, G.; Beetsma, D. J.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 3914.

(9) Other recent selected examples for vanadium(III),(IV) alkyl complexes: (a) Basuli, F.; Kilgore, U. J.; Hu, X. L.; Meyer, K.; Pink, M.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3156. (b) Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 10506. (c) Kilgore, U. J.; Sengelaub, C. A.; Pink, M.; Fout, A. R.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 3769.

(10) Selected pioneering 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.

(11) (a) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2005**, *24*, 2248. (b) Yamada, J.; Nomura, K. *Organometallics* **2005**, *24*, 3621. (c) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2007**, *26*, 2579. (d) Onishi, Y.; Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2008**, *27*, 2590. (e) Nomura, K.; Onishi, Y.; Fujiki, M.; Yamada, J. *Organometallics* **2008**, *27*, 3818. (f) Zhang, W.; Yamada, J.; Nomura, K. *Organometallics* **2008**, *27*, 5353. (g) Zhang, W.; Nomura, K. *Organometallics* **2008**, *27*, 6400.

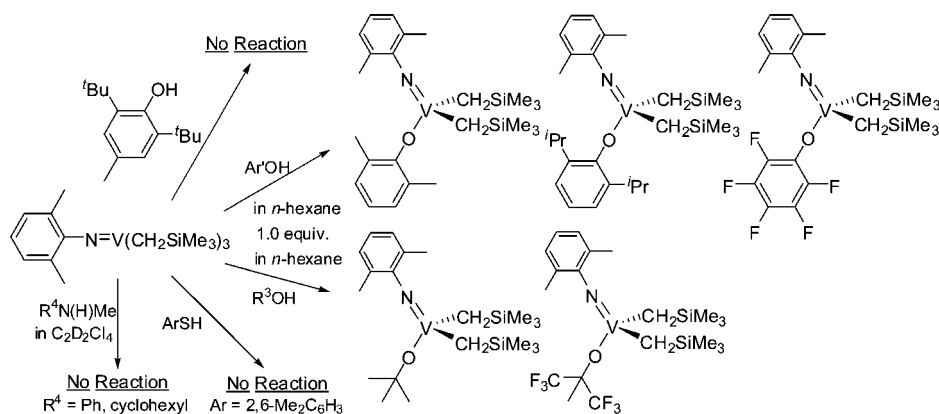
(12) Examples: (a) Preuss, F.; Ogger, L. *Z. Naturforsch.* **1982**, *37B*, 957. (b) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. *J. Am. Chem. Soc.* **1987**, *109*, 7408. (c) Preuss, F.; Becker, H.; Kraub, J.; Sheldrick, W. J. *Z. Naturforsch.* **1988**, *43B*, 1195. (d) Preuss, F.; 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.

We recently reported that reactions of V(NAr)Me(N=CtBu)<sub>2</sub> (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with 1.0 equiv of various alcohols (phenols) cleanly afforded other methyl complexes, V(NAr)-(Me)(N=CtBu)<sub>2</sub>(OR<sup>1</sup>) (OR<sup>1</sup> = aryloxo, alkoxo), without reaction with the methyl group in any case, whereas the reactions with thiols cleanly afforded V(NAr)(N=CtBu)<sub>2</sub>(SR<sup>2</sup>) (R<sup>2</sup> = *n*-C<sub>6</sub>H<sub>13</sub> or 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) via reaction with the methyl group (Scheme 1).<sup>11b,c</sup> On the basis of the reaction chemistry of V(NAr)Me(N=CtBu)<sub>2</sub> with various phenols (1–2 equiv), we proposed that these reactions proceed via pentacoordinated trigonal-bipyramidal intermediates formed by coordination of the oxygen atom in the phenol *trans* to the methyl group (Scheme 1),<sup>11c</sup> although we could not observe the proposed intermediates. More recently, we reported that reactions of V(NAr)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> with 1.0 equiv of alcohols (except 2,6-<sup>t</sup>Bu-4-MeC<sub>6</sub>H<sub>2</sub>OH) in *n*-hexane at 25 °C afforded the corresponding series of dialkyl complexes of the type V(NAr)-(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(OR<sup>3</sup>) [R<sup>3</sup> = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>, <sup>t</sup>Bu, CMe(CF<sub>3</sub>)<sub>2</sub>, yield 90–93%], whereas the reactions with Ph-N(H)Me, (*cyclo*-C<sub>6</sub>H<sub>11</sub>)N(H)Me, or 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH did not take place (Scheme 2).<sup>11e</sup> Moreover, we also reported that reaction of V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> (Ad = 1-adamantyl) with (CF<sub>3</sub>)<sub>2</sub>CHOH and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH at 25 °C did not take place or the trialkyl complex was recovered in high yields.<sup>11f</sup> The observed unique reactivities toward alcohols and thiols are noteworthy, because, as described above, metal-alkyls with early transition metals are generally highly nucleophilic and reactive toward Brønsted/Lewis acids.<sup>1–3</sup> We assumed that these reactions take place via coordination of alcohol/phenol to the vanadium(V) complexes not via addition of proton (H<sup>+</sup>), although we do not have any clear evidence including observation of the intermediate.

Although the reactions of early transition metal-alkyls with alcohols (phenols) should be important basic reactions in organometallic chemistry, as far as we know, a detailed mechanistic study including *direct* isolation and/or observation of the intermediates has never been explored so far. In this paper, we thus present results of our studies concerning the synthesis of a (1-adamantylimido)vanadium(V) dialkyl complex containing a chelate alkoxo(imino)pyridine ligand (L), V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(L) [L = 6-OC(Me)<sub>2</sub>-2-(Ar'N=CMe)-C<sub>5</sub>H<sub>3</sub>N, Ar' = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], and some reactions with (CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)COH, (CF<sub>3</sub>)<sub>2</sub>CHOH, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH, and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH in C<sub>6</sub>D<sub>6</sub>. In particular, we wish to propose herein that these reactions proceeded via intermediates by coordination of ROH, V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(L)(ROH).



Scheme 2

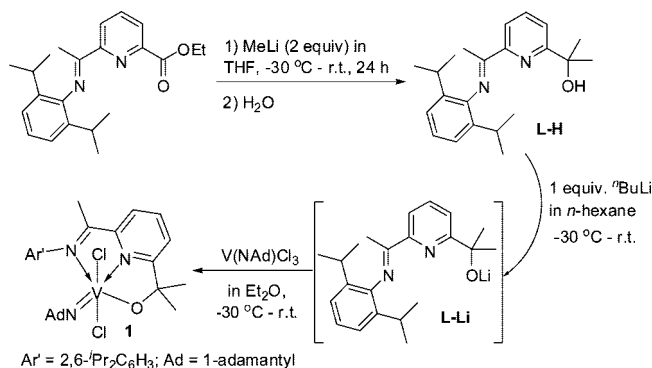


## Results and Discussion

**1. Synthesis of (1-Adamantylimido)vanadium(V)-dichloro, Dialkyl Complexes Containing a Chelate Alkoxo(imino)pyridine Ligand.** A monoanionic tridentate ligand has been chosen in this study, because these two neutral donor ligands should provide better stabilization (rather than a monodentate anionic donor ligand) of low-coordinate vanadium(V) dialkyl complexes of the type  $V(NA\text{d})(CH_2SiMe_3)_2(L)$  by better  $\pi$ -donation. We also expected that the presence of the two neutral donor ligands will facilitate formation of a vanadium(V)-alkylidene complex from the dialkyl complex (with *cis* geometry) by subsequent  $\alpha$ -hydrogen elimination, which is the common method to prepare high oxidation state metal alkylidenes from metal alkyl complexes lacking  $\beta$ -hydrogens, and addition of a neutral donor ligand should be required to promote the abstraction by steric crowding.<sup>11,13</sup> Therefore, we chose a chelate alkoxo(imino)pyridine ligand simply derived from 2-carboxylate-6-iminopyridine, 2-{C(Me)=NAr'}-6-(CO<sub>2</sub>Et)C<sub>5</sub>H<sub>3</sub>N (Ar' = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>14</sup> which had been developed by the group of Sun<sup>14</sup> and was proven to be effective as a ligand for iron/nickel-catalyzed ethylene polymerization/oligomerization.<sup>14</sup> 1-Adamantylimido ligand has also been chosen, because the imido ligand should be a better  $\sigma$ -donor than the arylimido analogues.<sup>15</sup>

The (imino)pyridyl alcohol 6-HOC(Me)<sub>2</sub>-2-(Ar'N=CMe)-C<sub>5</sub>H<sub>3</sub>N (**L-H**) was prepared from 2-{C(Me)=NAr'}-6-(CO<sub>2</sub>Et)-C<sub>5</sub>H<sub>3</sub>N by addition of MeLi in THF and subsequent hydrolysis (Scheme 3). The desired product could be obtained in pure form after separation by using column chromatography (yield 48.3%), and the compound was identified on the basis of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.<sup>16</sup> The (1-adamantylimido)vanadium(V) dichloride analogue,  $V(NA\text{d})Cl_2(L)$  (**1**), could be obtained in moderate yield (39.1%) by treating  $V(NA\text{d})Cl_3$  (prepared by the reported procedure)<sup>15</sup> with the corresponding lithium salt (**L-Li**) in Et<sub>2</sub>O, which was prepared by treating **L-H** with <sup>n</sup>BuLi in *n*-hexane (Scheme 3). The resultant complex (**1**) was identified on the basis of <sup>1</sup>H, <sup>13</sup>C, and <sup>51</sup>V NMR spectroscopy

Scheme 3



and elemental analysis, and the structure was determined by X-ray crystallography (Figure 1).<sup>17</sup>

The structure of **1** indicates that **1** has a distorted octahedral geometry around vanadium consisting of two chloride axes [bond angles: Cl(1)–V–Cl(2) 166.68(3)°, Cl(1)–V(1)–O(1) 93.83(10)°, Cl(1)–V(1)–N(1) 92.12(13)°, Cl(1)–V(1)–N(2) 85.70(10)°, Cl(1)–V(1)–N(3) 82.98(8)°] and a plane consisting of the chelate donor ligand and the adamantylimido ligand [bond angles: O(1)–V(1)–N(3) 150.78(10)°, N(1)–V(1)–N(3) 106.95(10)°, O(1)–V(1)–N(1) 102.18(11)°, total 359.91°]. The results thus indicate that two chlorine atoms are positioned in a *trans* form. The V–Cl bond distances [V(1)–Cl(1) 2.3427(13) Å, V(1)–Cl(2) 2.3550(13) Å] are longer than those in  $V(NA\text{d})Cl_2(O-2,6-Me_2C_6H_3)$  [2.1901(8), 2.1933(9) Å]<sup>15</sup> and  $V(NA\text{d})Cl_2(N=C^tBu_2)$  [V–Cl bond distances 2.2272(3), 2.2263(3) Å],<sup>15</sup> but shorter than those in  $V(NA\text{d})Cl_2(N=CPh_2)(PMe_3)_2$  [2.4954(12), 2.4382(12) Å].<sup>15</sup> The distances are in fact close to those in *trans*- $V(N-2,6-Me_2C_6H_3)Cl_2(dmpe)$  [*dmpe* = bis(dimethylphosphino)ethane, 2.3652(7), 2.3751(8) Å],<sup>11a</sup> suggesting that the distances are rather influenced by the ligand in the *trans* position. The V(1)–N(1)–C(1) is 171.6(2)°, suggesting that not only the  $\sigma$ -donation but also a stronger  $\pi$ -donation from the nitrogen to V can be seen.<sup>3c,15</sup>

Since an attempted isolation of the dialkyl analogue  $V(NA\text{d})(CH_2SiMe_3)_2(L)$  (**2**) by treating **1** with  $LiCH_2SiMe_3$  was not successful, we explored the possibility of isolating it from the trialkyl analogue  $V(NA\text{d})(CH_2SiMe_3)_3$ <sup>11g</sup> by treating it with the (imino)pyridyl alcohol (**L-H**). The dialkyl complex **2** was obtained in moderate yield (68.3%) as green microcrystals when  $V(NA\text{d})(CH_2SiMe_3)_3$  was treated with 1.0 equiv of **L-H** in C<sub>6</sub>D<sub>6</sub> at 50 °C for 3 days (Scheme 4). The reaction at 80 °C also

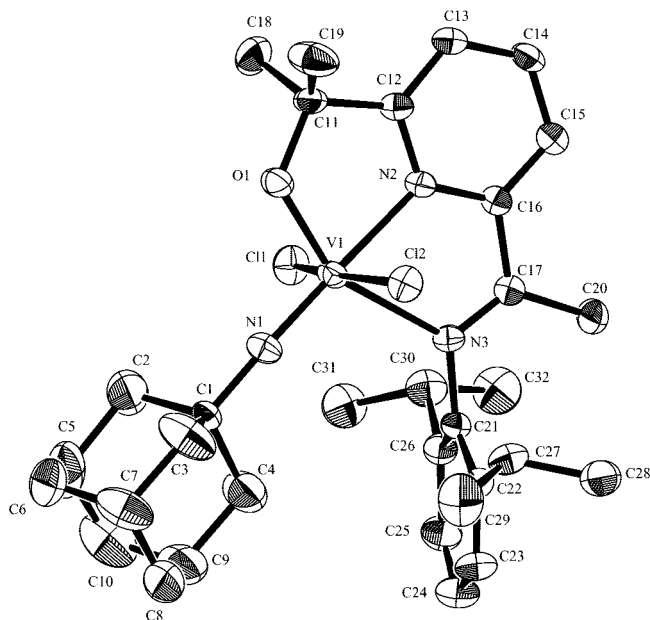
(13) For examples, see: (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (c) Mendiola, D. *Acc. Chem. Res.* **2006**, *39*, 813. (d) Mendiola, D.; Bailey, B.; Basuli, F. *Eur. J. Inorg. Chem.* **2006**, *16*, 3135.

(14) (a) Sun, W.-H.; Tang, X.; Gao, T.; Wu, B.; Zhang, W.; Ma, H. *Organometallics* **2004**, *23*, 5037. (b) Zhang, W.; Sun, W.-H.; Wu, B.; Zhang, S.; Ma, H.; Li, Y.; Chen, J.; Hao, P. *J. Organomet. Chem.* **2006**, *691*, 4759. (c) Zhang, W.; Sun, W.-H.; Zhang, S.; Tang, X.; Gao, T.; Chen, J. *J. Mol. Catal. A: Chem.* **2007**, *265*, 159.

(15) Zhang, W.; Nomura, K. *Inorg. Chem.* **2008**, *47*, 6482.

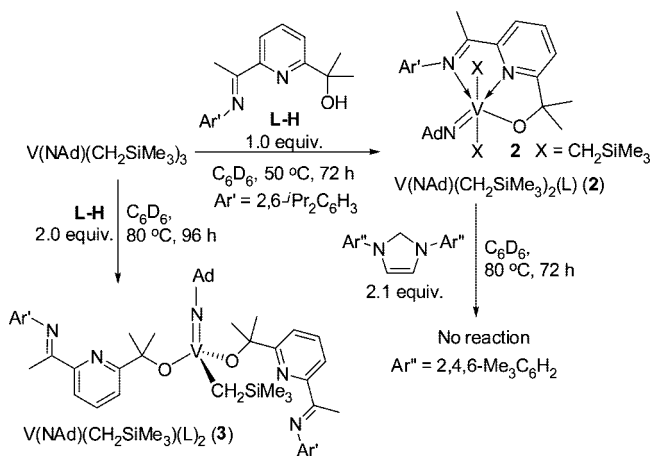
(16) Synthesis of 6-HOC(Me)<sub>2</sub>-2-{C(Me)=N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}-C<sub>5</sub>H<sub>3</sub>N (**L-H**) by another method: Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Organometallics* **2007**, *26*, 5119.

(17) Structural analysis reports and CIF files are shown in the Supporting Information.



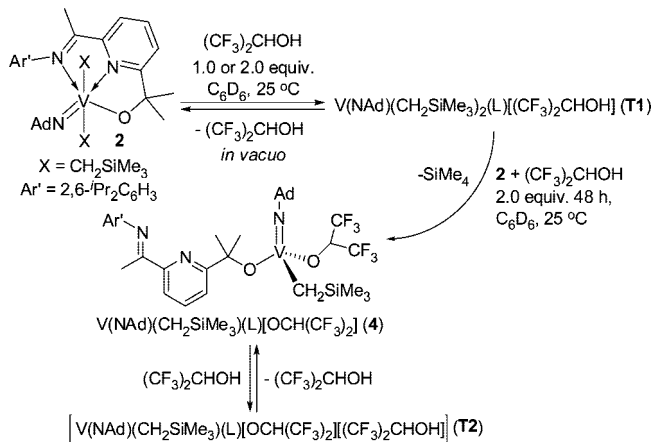
**Figure 1.** ORTEP drawing of  $V(Nad)Cl_2(L)$  [**1**,  $L = 6-OC(Me)_2-2-((2,6-Pr_2C_6H_3)N=CMe)-C_5H_3N$ ]. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.<sup>17</sup> Selected bond distances (Å):  $V(1)-Cl(1)$  2.3427(13),  $V(1)-Cl(2)$  2.3550(13),  $V(1)-O(1)$  1.8079(19),  $V(1)-N(1)$  1.658(3),  $V(1)-N(2)$  2.103(2),  $V(1)-N(3)$  2.345(2). Selected bond angles (deg):  $Cl(1)-V(1)-Cl(2)$  166.68(3),  $Cl(1)-V(1)-O(1)$  93.83(10),  $Cl(1)-V(1)-N(1)$  92.12(13),  $Cl(1)-V(1)-N(2)$  85.70(10),  $Cl(1)-V(1)-N(3)$  82.98(8),  $Cl(2)-V(1)-O(1)$  93.62(10),  $Cl(2)-V(1)-N(1)$  97.09(13),  $Cl(2)-V(1)-N(2)$  84.73(9),  $Cl(2)-V(1)-N(3)$  85.13(8),  $O(1)-V(1)-N(1)$  102.18(11),  $O(1)-V(1)-N(2)$  80.01(9),  $O(1)-V(1)-N(3)$  150.78(10),  $N(1)-V(1)-N(2)$  177.03(13),  $N(1)-V(1)-N(3)$  106.95(10),  $N(2)-V(1)-N(3)$  70.80(8),  $V(1)-N(1)-C(1)$  171.6(2).

Scheme 4



afforded **2**, whereas no reaction took place at 25 °C. Monitoring the mixture (at 80 °C) by  $^1H$  NMR spectroscopy did not show any further reactions, such as  $\alpha$ -hydrogen elimination [affording an alkylidene such as  $V(CHSiMe_3)(Nad)(L)$ ].<sup>18</sup> The dialkyl complex **2** was identified on the basis of  $^1H$ ,  $^{13}C$ , and  $^{51}V$  NMR spectroscopy and elemental analysis. Complex **2** is thermally stable in  $C_6D_6$  at 80 °C (after 72 h), and the attempted reaction in  $C_6D_6$  in the presence of NHC [2.1 equiv, NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] recovered **2**, as monitored by  $^1H$  and  $^{51}V$  NMR spectroscopy (80 °C, 72 h).<sup>17</sup> The reaction in the presence of  $PMe_3$  (13 equiv) afforded trace amounts of another product that may be ascribed to an

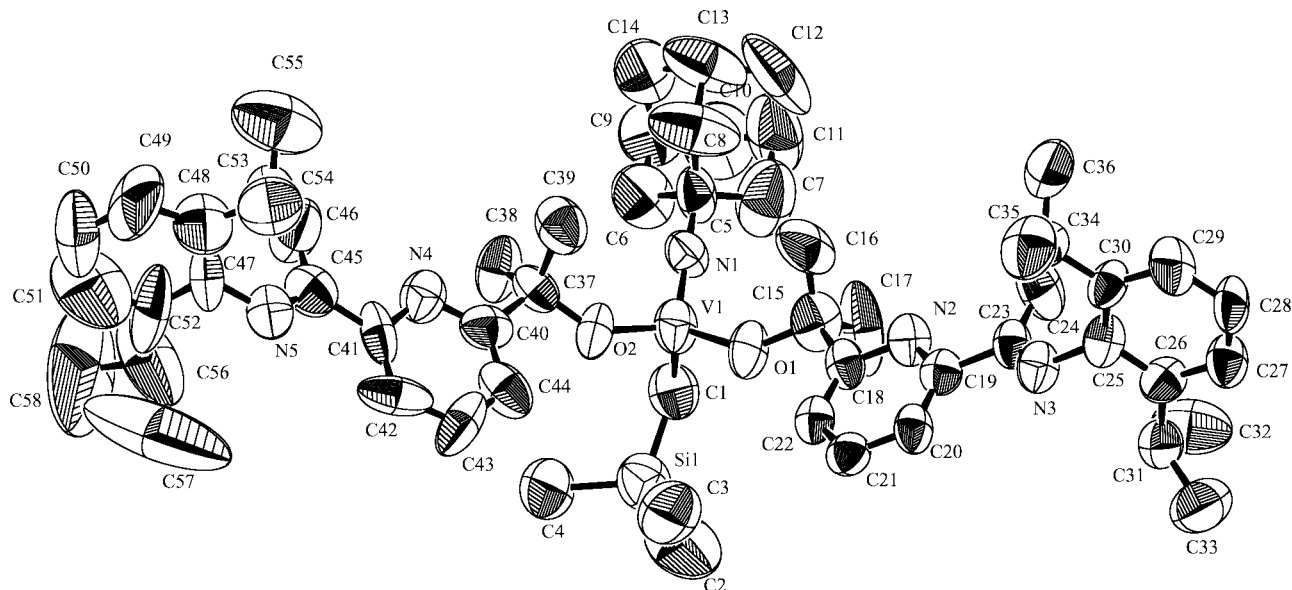
Scheme 5



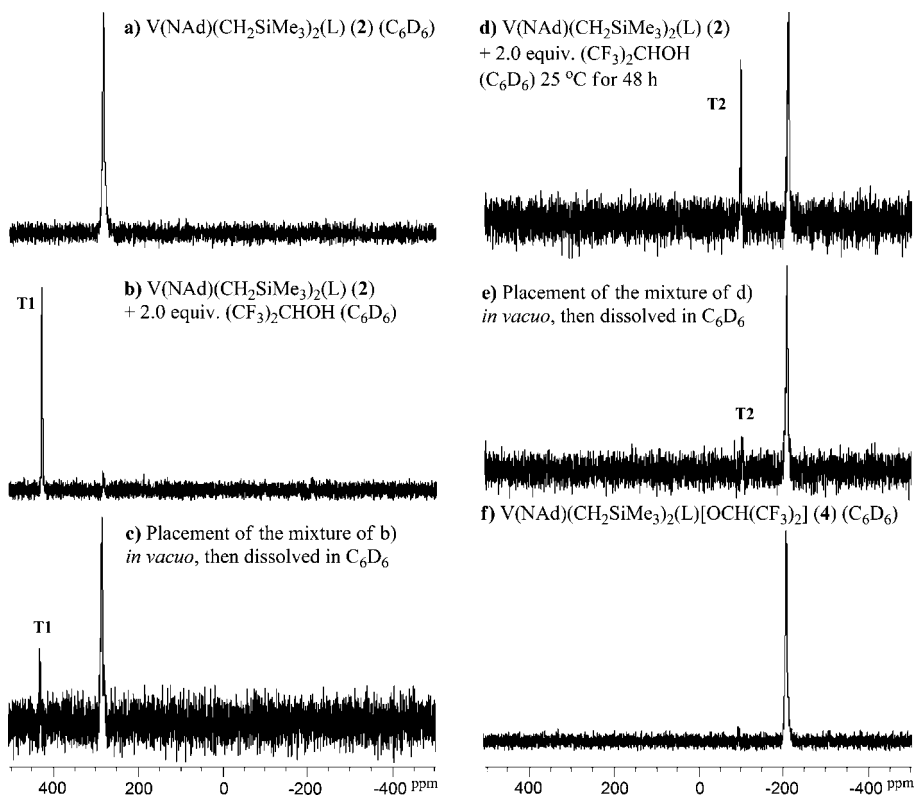
alkylidene by a  $^1H$  NMR spectrum (at ca. 12.9 ppm, 80 °C, 72 h).<sup>18</sup> Taking into account the above results in addition to the fact that only one resonance ascribed to the proton/carbon of the  $SiMe_3$  group was seen in the  $^1H/^{13}C$  NMR spectra, it is thus clear that two alkyl ligands in the resultant dialkyl complex **2** should have a *trans* (not *cis*) geometry,<sup>7</sup> as seen in the dichloride complex **1**, determined by X-ray crystallography, and dissociation of the neutral donor(s) in the chelate ligand ( $L$ ) did not take place.<sup>19</sup>

The reaction of **2** with 2.0 equiv of  $L-H$  in  $C_6D_6$  at 80 °C (after 4 days) afforded the corresponding monoalkyl complex  $V(Nad)(CH_2SiMe_3)(L)_2$  (**3**) in a moderate yield (41.5%). Complex **3** was identified on the basis of  $^1H$ ,  $^{13}C$ , and  $^{51}V$  NMR spectroscopy and elemental analysis, and the structure was determined by X-ray crystallography (Figure 2).<sup>16</sup> It should be noted that **3** has a distorted tetrahedral geometry around the vanadium(V) metal center, and two neutral nitrogen donor ligands are dissociated probably due to the steric bulk.<sup>17</sup> The  $V-O$  distances [ $V(1)-O(1)$  1.780(8) Å,  $V(1)-O(2)$  1.776(8) Å] are somewhat shorter than those in the dichloride analogue **1** [ $V(1)-O(1)$  1.8079(19) Å,  $V(1)-O(2)$  1.8222(15), 1.8124(16) Å, respectively],<sup>11d</sup> but are relatively close to that in  $V(Nad)Cl_2(O-2,6-Me_2C_6H_3)$  [1.7633(17) Å].<sup>15</sup> The  $V-N$  bond distance [ $V-N(1)$  1.632(11) Å] is slightly shorter than that in **1** [1.658(3) Å], but relatively close to that in  $V(Nad)Cl_2(O-2,6-Me_2C_6H_3)$  [1.623(2) Å].<sup>15</sup> The  $V-N-C$  bond angle [ $V(1)-N(1)-C(5)$  174.8(11)°] is larger than that in **1** [171.6(2)°], but smaller than that in  $V(Nad)Cl_2(O-2,6-Me_2C_6H_3)$  [179.10(18)°].<sup>15</sup> The  $V-C$  bond distance [2.020(12) Å] is close to that in  $V(Nad)(CH_2SiMe_3)_3$  [2.0267(18) Å], but shorter than that in  $V(CHSiMe_3)(Nad)(CH_2SiMe_3)(NHC)$  [2.069(3) Å].<sup>11g</sup>

**2. Reactions of (1-Adamantylimido)vanadium(V)-dialkyl Complex with Alcohols.** As described above, reactions of the (1-adamantylimido)vanadium(V) trialkyl analogue,  $V(Nad)(CH_2SiMe_3)_3$ , with 1 or 2 equiv of  $L-H$  (at 50 or 80 °C) afforded the corresponding dialkyl or monoalkyl analogues  $V(Nad)(CH_2SiMe_3)_2(L)$  (**2**) or  $V(Nad)(CH_2SiMe_3)(L)_2$  (**3**) in moderate yields. However, the reaction with 1 equiv of  $(CF_3)_2CHOH$  in *n*-hexane at 25 °C recovered the starting complex in high yield even if the mixture was stirred overnight (>12 h).<sup>11g</sup> As also described in the Introduction, we reported unique reactivities of (imido)vanadium(V)-alkyl complexes such as  $V(NAr)(Me)(N=C'Bu_2)$ ,  $V(NAr)(CH_2SiMe_3)_3$ , and  $V(Nad)(CH_2SiMe_3)_3$  toward alcohols (phenols). However, the detailed mechanisms, especially whether the reactions proceed via coordination of alcohol or addition of  $H^+$  to the metal center, have never been elucidated. In order to clarify the mechanism



**Figure 2.** ORTEP drawing of  $V(NAd)(CH_2SiMe_3)_2(L)$  [**3**,  $L = 6-OC(Me)_2-2-\{(2,6-iPr_2C_6H_3)N=CMe\}-C_5H_3N\}$ ]. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.<sup>17</sup> Selected bond distances (Å): V(1)–O(1) 1.780(8), V(1)–O(2) 1.776(8), V(1)–N(1) 1.632(11), V(1)–C(1) 2.020(12). Selected bond angles (deg): O(1)–V(1)–O(2) 113.4(3), O(1)–V(1)–N(1) 113.5(4), O(1)–V(1)–C(1) 107.8(4), O(2)–V(1)–N(1) 113.6(4), O(2)–V(1)–C(1) 109.6(4), N(1)–V(1)–C(1) 97.5(5), V(1)–O(1)–C(15) 137.3(8), V(1)–O(2)–C(37) 139.4(7), V(1)–N(1)–C(5) 174.8(11), V(1)–C(1)–Si(1) 116.6(6).

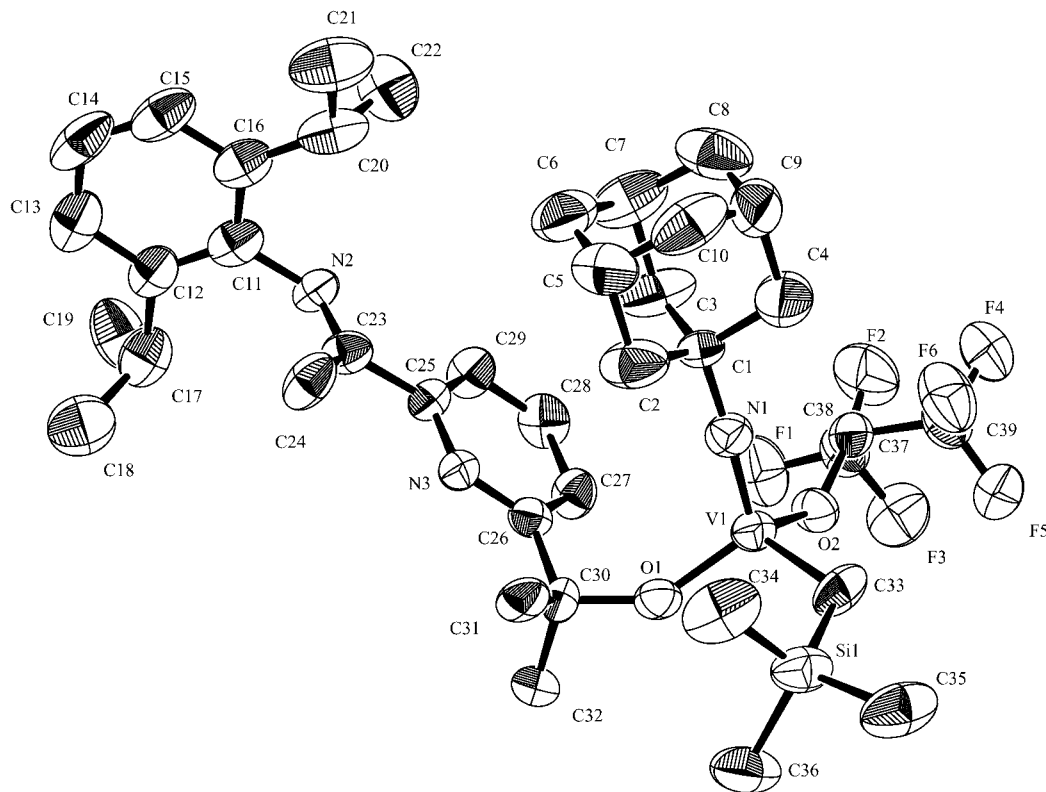


**Figure 3.**  $^{51}V$  NMR spectra (in  $C_6D_6$  at 25 °C) for monitoring the reaction of  $V(NAd)(CH_2SiMe_3)_2(L)$  (**2**) with 2.0 equiv of  $(CF_3)_2CHOH$  in  $C_6D_6$  at 25 °C: (a)  $V(NAd)(CH_2SiMe_3)_2(L)$  (**2**), (b) complex **2** with 2.0 equiv of  $(CF_3)_2CHOH$ , (c) placement of the mixture of b *in vacuo* (removal of  $C_6D_6$  and volatiles) after several hours, (d) complex **2** with 2.0 equiv of  $(CF_3)_2CHOH$  stirred for 48 h, (e) placement of the mixture of d *in vacuo* (removal of  $C_6D_6$  and volatiles), (f)  $V(NAd)(CH_2SiMe_3)(L)[OCH(CF_3)_2]$  (**4**) ( $C_6D_6$ ).

of this type of reaction, we explored some reactions of the dialkyl complex **2** with alcohols such as  $(CF_3)_2CHOH$ ,  $(CF_3)_2(Me)COH$ , 2,6- $Me_2C_6H_3OH$ , and 2,6- $Me_2C_6H_3SH$  in  $C_6D_6$ .

Reaction of the dialkyl complex **2** with 2 equiv of  $(CF_3)_2CHOH$  did not take place at 25 °C after several hours

and recovered **2** in high yield, as confirmed by  $^1H$  and  $^{51}V$  NMR spectroscopy (Figure 3c). The monoalkyl complex  $V(NAd)(CH_2SiMe_3)(L)[OCH(CF_3)_2]$  (**4**) became the major product on the basis of both  $^1H$  and  $^{51}V$  NMR spectroscopy if the above reaction solution was stirred for 48 h (Figure 3e, Scheme 5),

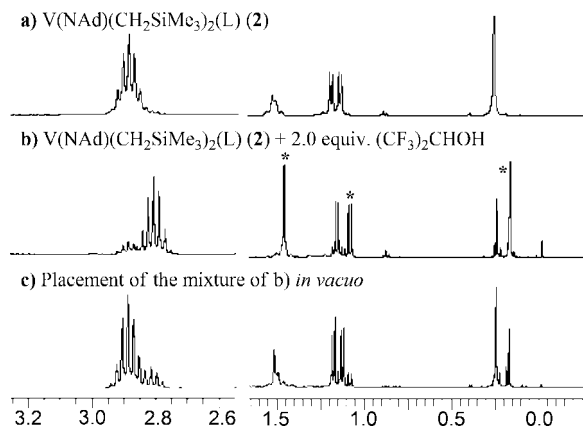


**Figure 4.** ORTEP drawing of  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})[\text{OCH}(\text{CF}_3)_2]$  (**4**,  $\text{L} = 6\text{-OC}(\text{Me})_2\text{-2-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}\text{-C}_5\text{H}_3\text{N}\}$ ). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.<sup>17</sup> Selected bond distances (Å): V(1)–O(1) 1.752(5), V(1)–O(2) 1.812(5), V(1)–N(1) 1.626(7), V(1)–C(33) 2.008(9), N(1)–C(1) 1.447(11). Selected bond angles (deg): O(2)–V(1)–N(1) 109.5(3), N(1)–V(1)–C(33) 104.2(3), V(1)–N(1)–C(1) 175.3(5), O(1)–V(1)–N(1) 112.3(2), V(1)–O(1)–C(30) 144.4(5), V(1)–O(2)–C(37) 136.2(4), V(1)–C(33)–Si(1) 122.5(4), O(1)–V(1)–C(33) 110.1(3), O(2)–V(1)–C(33) 107.4(2).

and **4** was thus isolated in moderate isolated yield (37.3%). Complex **4** was identified on the basis of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{51}\text{V}$  NMR spectroscopy and elemental analysis, and the structure was determined by X-ray crystallography (Figure 4).<sup>17</sup>

The structure indicates that **4** has a distorted tetrahedral geometry around the vanadium(V) metal center, and two neutral nitrogen donors in the chelate alkoxo(imino)pyridine ligand are dissociated, as seen in **3**, probably due to the steric bulk.<sup>17</sup> The V(1)–O(1) distance in the alkoxo(imino)pyridine ligand [1.752(5) Å] is shorter than the V(1)–O(2) distance in the  $(\text{CF}_3)_2\text{CHOH}$  ligand [1.812(5) Å] as well as those in **1** [1.8079(19) Å] and **3** [1.776(8), 1.780(8) Å]; the V(1)–N(1) distance [1.626(7) Å] is close to that in **3** [1.632(11) Å] but shorter than that in **1** [1.658(3) Å]. The structural analysis thus indicates that reaction of the dialkyl complex **2** with  $(\text{CF}_3)_2\text{CHOH}$  proceeds via dissociation of the alkoxo(imino)pyridine ligand.

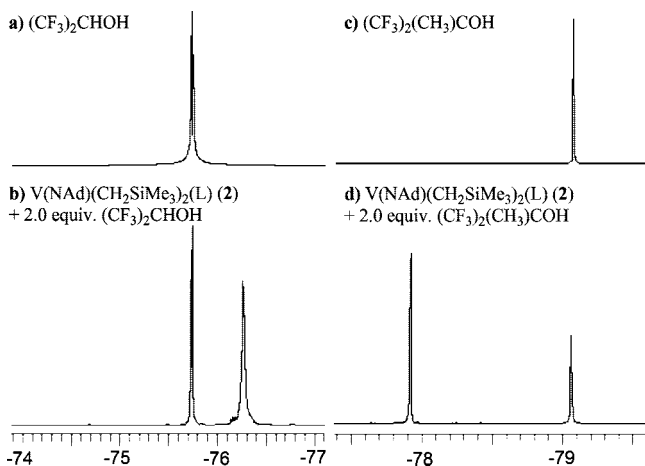
As shown in Figure 3b, a new resonance (shown as **T1**) at ca. 440 ppm was observed, when the dialkyl complex **2** was mixed with 2 equiv of  $(\text{CF}_3)_2\text{CHOH}$ .<sup>18,20</sup> Note that the species converted to the starting dialkyl **2** if the mixed solution was placed *in vacuo* to remove both the solvent and volatiles from the reaction mixture (Figure 3c); similar changes in the spectra were also observed in the  $^1\text{H}$  NMR spectra (Figure 5). A resonance ascribed to protons in the  $\text{SiMe}_4$  group was not observed in the  $^1\text{H}$  NMR spectra.<sup>18</sup> It should also be noted that a new broad resonance in addition to a resonance ascribed to  $(\text{CF}_3)_2\text{CHOH}$  was observed in the  $^{19}\text{F}$  NMR spectrum (Figure 6b) by mixing **2** with  $(\text{CF}_3)_2\text{CHOH}$  at 25 °C, and the resonance was apparently different from the monoalkyl complex **4**.<sup>18</sup> These results clearly indicate formation of the intermediate  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})[(\text{CF}_3)_2\text{CHOH}]$  (**T1**) by coordination of oxygen in  $(\text{CF}_3)_2\text{CHOH}$  to the vanadium in **2** (Scheme 5).



**Figure 5.**  $^1\text{H}$  NMR spectra (in  $\text{C}_6\text{D}_6$  at 25 °C) for monitoring the reaction of  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})$  (**2**) with 2.0 equiv of  $(\text{CF}_3)_2\text{CHOH}$  in  $\text{C}_6\text{D}_6$  at 25 °C: (a)  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})$  (**2**), (b) complex **2** with 2.0 equiv of  $(\text{CF}_3)_2\text{CHOH}$ , (c) placement of the mixture of b *in vacuo* (removal of  $\text{C}_6\text{D}_6$  and volatiles) after several hours.

One important question is the geometry of the intermediate (**T1**), especially the coordination mode of the monoanionic tridentate ligand (**L**, five-, six-, or seven-coordinate species). Resonances ascribed to the ligand in **T1** are apparently different from **2** and **4**, but somewhat similar to the original ligand (**L-H**), especially resonances ascribed to protons in the pyridine moiety.<sup>17</sup> The results thus strongly suggest that the two neutral nitrogen donors (imino groups) in **L** were dissociated by coordination of  $(\text{CF}_3)_2\text{CHOH}$ , as seen in the resultant monoalkyl complex **4**. This should be an interesting contrast to the

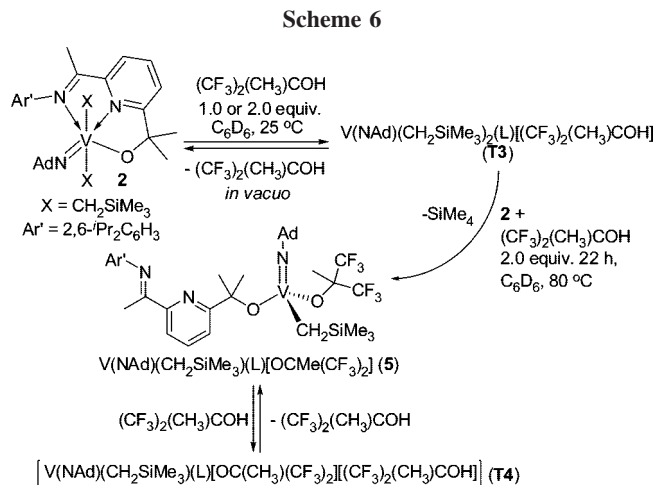




**Figure 6.**  $^{19}\text{F}$  NMR spectra (in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$ ) for monitoring the reaction of  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})$  (**2**) with  $(\text{CF}_3)_2\text{CHOH}$  or  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$ : (a)  $(\text{CF}_3)_2\text{CHOH}$ , (b) complex **2** with 2.0 equiv of  $(\text{CF}_3)_2\text{CHOH}$  (corresponds to Figures 3b and 5b), (c)  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$ , (d) complex **2** with 1.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  (corresponds to Figure 7b).

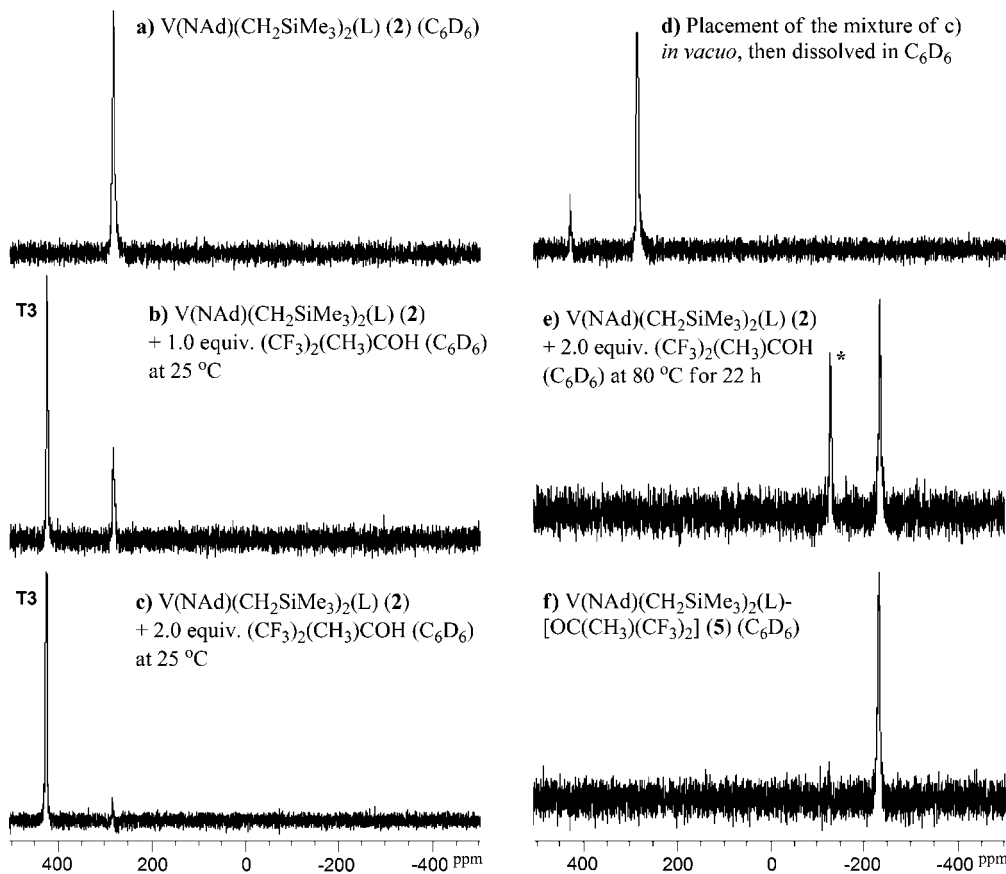
attempted reactions of the dialkyl complexes with NHC and  $\text{PMe}_3$ , in which no reaction took place even upon heating. Taking into account these facts, we propose that the reaction of **2** with  $(\text{CF}_3)_2\text{CHOH}$  proceeded via an intermediate (**T1**) formed by coordination of  $(\text{CF}_3)_2\text{CHOH}$  to vanadium in **2**.

Moreover, the reaction of **2** with 2 equiv of  $(\text{CF}_3)_2\text{CHOH}$  ( $25^\circ\text{C}$  after 48 h) afforded two resonances in the  $^{51}\text{V}$  NMR



spectrum (Figure 3d) including a resonance ascribed to the monoalkyl complex **4**; only one resonance due to **4** was observed if the reaction mixture was placed *in vacuo*.<sup>18</sup> These results may also suggest the formation of another intermediate, assumed as  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)(\text{L})[\text{OCH}(\text{CF}_3)_2][(\text{CF}_3)_2\text{CHOH}]$  (**T2**), generated by coordination of  $(\text{CF}_3)_2\text{CHOH}$  to **4**.<sup>20</sup>

The reaction of **2** with 1.0 or 2.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  in place of  $(\text{CF}_3)_2\text{CHOH}$  did not proceed at  $25^\circ\text{C}$ , but the reaction afforded the corresponding monoalkyl-alkoxo complex  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)(\text{L})[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]$  (**5**) if the mixture was heated at  $80^\circ\text{C}$  for 22 h. The resultant complex was isolated by recrystallization in *n*-hexane, and **5** was identified on the



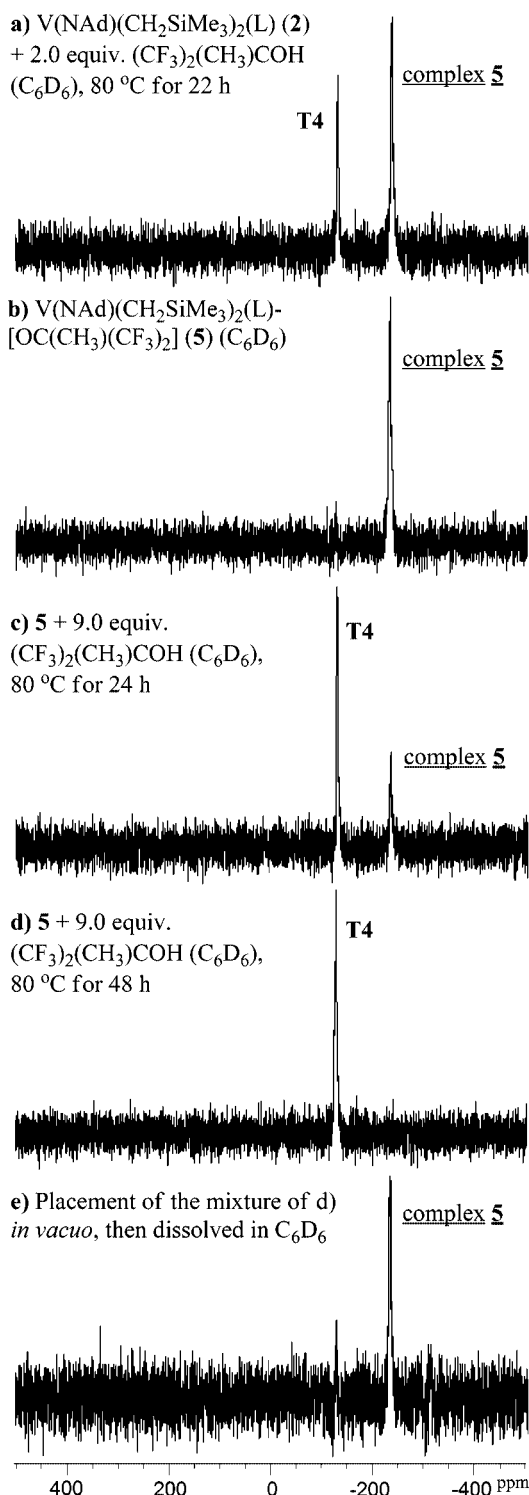
**Figure 7.**  $^{51}\text{V}$  NMR spectra (in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$ ) for monitoring the reaction of  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})$  (**2**) with  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  in  $\text{C}_6\text{D}_6$ : (a)  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})$  (**2**), (b) complex **2** with 1.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  at  $25^\circ\text{C}$ , (c) complex **2** with 2.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  at  $25^\circ\text{C}$ , (d) placement of the mixture of c *in vacuo* (removal of  $\text{C}_6\text{D}_6$  and volatiles) after several hours, (e) complex **2** with 2.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  stirred at  $80^\circ\text{C}$  for 22 h, (f)  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)(\text{L})[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]$  (**5**).

basis of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{51}\text{V}$  NMR spectroscopy and elemental analysis. The monoalkyl-alkoxo complex **5** was very stable at high temperature, and no significant differences in both  $^1\text{H}$  and  $^{51}\text{V}$  NMR spectra were observed even at high temperature.<sup>18</sup> The results also suggest that no apparent equilibrium between coordination and dissociation of one or two neutral nitrogen donors in **L** is present in the solution.

As shown in Figure 7b,c, a new resonance (shown as **T3**) at ca. 425 ppm was observed when the dialkyl complex **2** was mixed with 1 or 2 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$ , and the ratio of **T3/2** became high upon addition of 2.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$ .<sup>18,20</sup> Note that the species were converted to the starting dialkyl **2**, as seen in the reaction with  $(\text{CF}_3)_2\text{CHOH}$ , if the mixed solution was placed *in vacuo* (Figure 7d). Similar changes in the spectra to those seen in the reaction of **2** with  $(\text{CF}_3)_2\text{CHOH}$  were also observed in the  $^1\text{H}$  NMR spectra,<sup>18</sup> in addition to the fact that a peak ascribed to protons in the  $\text{SiMe}_4$  group was not observed; a new broad resonance (which was different from the monoalkyl complex **5**) in addition to a resonance ascribed to  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  was observed in the  $^{19}\text{F}$  NMR spectrum (Figure 6d) by mixing **2** with  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  at 25 °C.<sup>18</sup> These results also clearly indicate the formation of  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})[(\text{CF}_3)_2(\text{CH}_3)\text{COH}]$  (**T3**) by coordination of the alcohol to **2** (Scheme 6). As also seen in the reaction with  $(\text{CF}_3)_2\text{CHOH}$ , resonances ascribed to the ligand in **T3** in the  $^1\text{H}$  NMR spectrum were apparently different from **2** and **5**, but were similar to the original ligand (**L-H**), especially resonances ascribed to protons in the pyridine moiety.<sup>18</sup> Therefore, the result also suggests that two neutral nitrogen donors (imino groups) in the tridentate ligand (**L**) were dissociated by coordination of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$ . It is thus proposed that the reaction of **2** with  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  proceeded via an intermediate (**T3**) formed by coordination of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  to vanadium in **2**.

The resultant monoalkyl complex **5** did not react with  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  at 25 °C, but the reaction of **5** with 9 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  proceeded at 80 °C, affording two resonances in the  $^{51}\text{V}$  NMR spectrum (Figure 8c) including a resonance due to the monoalkyl complex **5** after 24 h. The resonance ascribed to **5** disappeared if the mixture was stirred at 80 °C for 48 h (Figure 8d). Note that only one resonance ascribed to **5** was observed in the  $^{51}\text{V}$  NMR spectrum when the reaction mixture was placed *in vacuo* (Figure 8e).<sup>18</sup> A similar spectrum was observed if the dialkyl complex **2** was reacted with 2.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  at 80 °C after 22 h (Figure 8a, corresponding to Figure 7e). These results also suggest the formation of an intermediate, presumably  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)(\text{L})[\text{OC}(\text{CH}_3)(\text{CF}_3)_2][(\text{CF}_3)_2(\text{CH}_3)\text{COH}]$  (**T4**), generated by coordination of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  to **5**, as depicted in Scheme 6.

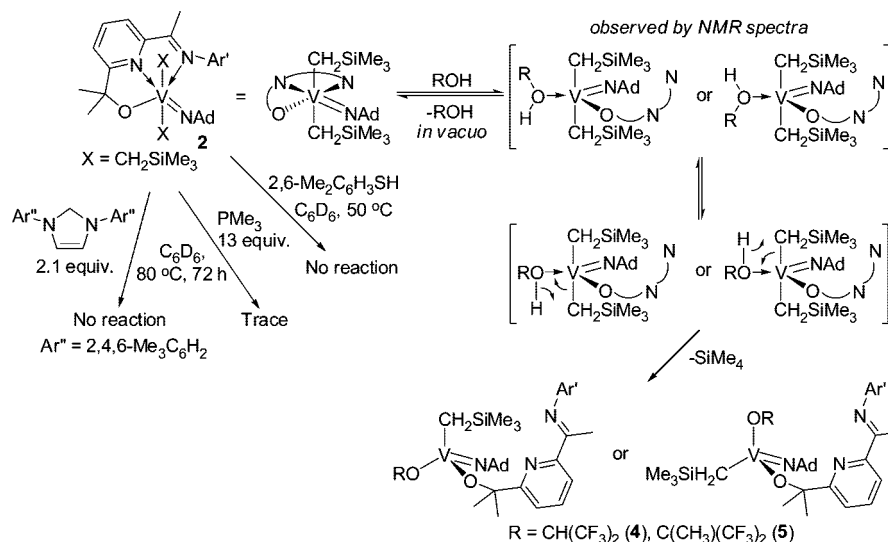
Reaction of **2** with 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$  was also explored in  $\text{C}_6\text{D}_6$ .<sup>18,21</sup> A new resonance (at ca. 370 ppm) in addition to a resonance ascribed to **2** was observed in the  $^{51}\text{V}$  NMR spectrum when **2** was simply mixed with 1.0 equiv of 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$  at 25 °C, and the resonance due to **2** almost disappeared when 2.0 equiv of 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$  was added.<sup>18</sup> Similar changes in the spectra to those seen in the reaction with  $(\text{CF}_3)_2\text{CHOH}$  or  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  were also observed in the  $^1\text{H}$  NMR spectra,<sup>18</sup> and a resonance ascribed to protons in the  $\text{SiMe}_4$  group was not observed.<sup>18</sup> The observed resonance in the  $^{51}\text{V}$  NMR spectrum was converted (to afford another species observed at ca. -155 ppm in the spectrum)<sup>18</sup> if the reaction with 2.5 equiv of 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$  was conducted at 25 °C for 6 days. However, an attempt to isolate the expected monoalkyl-phenoxide complex was not successful, because the reaction gave two products (seen in the  $^{51}\text{V}$  NMR spectra) that seemed difficult to separate for their isolations.<sup>18</sup> Since rapid removal



**Figure 8.**  $^{51}\text{V}$  NMR spectra (in  $\text{C}_6\text{D}_6$  at 25 °C) for monitoring the reaction of  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)(\text{L})[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]$  (**5**) with  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  in  $\text{C}_6\text{D}_6$ : (a)  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)_2(\text{L})$  (**2**) with 2.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  stirred at 80 °C for 22 h, (b)  $\text{V}(\text{NAd})(\text{CH}_2\text{SiMe}_3)(\text{L})[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]$  (**5**), (c) complex **5** with 9.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  at 80 °C after 24 h, (d) complex **5** with 9.0 equiv of  $(\text{CF}_3)_2(\text{CH}_3)\text{COH}$  at 80 °C after 48 h, (e) placement of the mixture of d *in vacuo* (removal of  $\text{C}_6\text{D}_6$  and volatiles).

of 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$  *in vacuo* was difficult, the mixed solution (2:2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$  = 1:1.4, molar ratio) was added with  $n\text{BuLi}$  at -30 °C, and the mixture was stirred for 3 h at 25 °C to generate lithium phenoxide for removal of the phenol moiety

Scheme 7



from the mixture by a simple filtration.<sup>18</sup> The new resonance that appeared by mixing **2** with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH was converted to the original complex **2**; this also suggests the formation of an intermediate generated by coordination of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH to the vanadium in **2**.

Reaction of **2** with 1.0 equiv of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH in place of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH was also attempted at 25 °C, but no changes in the <sup>51</sup>V NMR spectra were seen; the reaction, probably even coordination of the thiol to vanadium, did not take place even if the mixed solution was heated at 50 °C for 14 h. These facts should be a unique contrast between 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH, although further study is necessary to explore the details.

### Concluding Remarks

In this paper, we have prepared a (1-adamantylimido)vanadium(V) dialkyl complex containing a chelate alkoxo(imino)pyridine ligand,  $V(NAd)(CH_2SiMe_3)_2(L)$  [**2**,  $L = 6-OC(Me)_2-2-(Ar'N=CMe)-C_5H_3N$ ,  $Ar' = 2,6-Me_2C_6H_3$ ], and some reactions of **2** with  $(CF_3)_2CH_2OH$ ,  $(CF_3)_2CH_2COH$ , 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH, and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH have been explored. The dialkyl complex **2** has a distorted octahedral geometry around vanadium and two alkyl groups positioned in *trans* form, as determined by the dichloride analogue  $V(NAd)Cl_2(L)$  (**1**). The reaction of **2** in the presence of  $PMe_3$  (13 equiv) and NHC [2.1 equiv, NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] did not take place or afforded a negligible amount of the reaction product (only observed in the <sup>1</sup>H NMR spectrum in the reaction with  $PMe_3$ ) even if the mixed solution was heated at 80 °C for 72 h.

The reaction of **2** with  $(CF_3)_2CH_2OH$  and  $(CF_3)_2CH_2COH$  first generated intermediates, and these species were converted to the original complex **2** if the mixed solutions were placed *in vacuo*. The formed intermediates were identified as  $V(NAd)(CH_2SiMe_3)_2(L)[R'OH]$  [ $R' = CH(CF_3)_2$ ,  $C(CH_3)(CF_3)_2$ ] by <sup>1</sup>H, <sup>19</sup>F, and <sup>51</sup>V NMR spectroscopy, in which two neutral nitrogen donors (imino groups) in the chelate tridentate ligand (**L**) were dissociated by coordination of ROH. The reactions with these alcohols proceeded upon heating or by stirring for longer times to afford the corresponding monoalkyl species  $V(NAd)(CH_2SiMe_3)(L)(OR')$  [ $R' = CH(CF_3)_2$  (**4**),  $C(CH_3)(CF_3)_2$  (**5**)], identified on the basis of <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>51</sup>V NMR spectroscopy and elemental analyses. The monoalkyl complex **4**, determined by X-ray crystallography, has a distorted tetrahedral geometry

around vanadium with dissociation of the two neutral nitrogen donors in the chelate alkoxo(imino)pyridine ligand. Moreover, mixed solutions of the resultant monoalkyl-alkoxo complexes **4** and **5** and ROH formed other species assumed as  $V(NAd)(CH_2SiMe_3)(L)(OR')(R'OH)$ , which could be converted to the original complexes **4** and **5** if the mixed solutions were placed *in vacuo* (removal of C<sub>6</sub>D<sub>6</sub> and volatiles).

Taking into account these results, it is thus clear that reactions of the dialkyl complex **2** containing the alkoxo(imino)pyridine ligand with ROH [ $R = CH(CF_3)_2$ ,  $C(CH_3)(CF_3)_2$ , 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] proceeded via five-coordinate intermediates formed by coordination of the oxygen in ROH, not via addition of H<sup>+</sup>, accompanied by dissociation of two neutral nitrogen donors (imino groups) in the chelate tridentate ligand (Scheme 7). Confirmation of the intermediates,  $V(NAd)(CH_2SiMe_3)_2(L)[ROH]$ , is potentially important not only for a better understanding of the reactions of vanadium(V)-alkyls with alcohols but also for a better understanding of the observed unique reactivities of the vanadium(V)-alkyls in  $V(NAr)(Me)(N=C'Bu_2)_2$ ,  $V(NAr)(CH_2SiMe_3)_3$ , and  $V(NAd)(CH_2SiMe_3)_3$  with various alcohols we reported recently. We believe that this hypothesis should be applied to the reactions of early transition metal alkyls (especially in high oxidation states) with alcohols. Confirmation of dissociation of two neutral nitrogen donors in the chelate ligand during the reaction with alcohol should also be promising in terms of a better understanding of the catalytic reaction using transition metal complexes containing chelate tridentate ligands.<sup>14,22</sup> The observed dissociation of the two neutral nitrogen donor ligands should also be a unique contrast to the results not only in the presence of  $PMe_3$  and NHC but also in the reaction with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH, as summarized in Scheme 7. Therefore, the facts presented here should provide basic and important information concerning the reaction

(18) Experimental details by monitoring the NMR spectra in the reactions of  $V(NAd)(CH_2SiMe_3)_2(L)$  (**2**) with NHC,  $PMe_3$ , alcohols, and thiols are shown in the Supporting Information.

(19) Although two Cl ligands in the dichloride analogues (**1**) formed a *cis* geometry as determined by X-ray crystallography, we should consider the possibility that the alkoxo(imino)pyridine ligand in the resultant dialkyl complex **2** may be dissociated in solution and form a "cis-form" (tetrahedral or pentacoordinated species by dissociation of one or two imino groups). However, the reaction with  $PMe_3$  and NHC did not afford any reaction products, and only one resonance ascribed to protons/carbons in  $SiMe_3$  was observed. It is thus strongly suggested that the dialkyl complex **2** should be a *trans* form, as seen in the dichloride analogue **1**, with octahedral geometry around the vanadium.



chemistry of early transition metal alkyl complexes, and we are now exploring other reactions such as those of thiols and amines with these alkyl complexes.

## 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<sub>2</sub> and were passed through an short alumina column under N<sub>2</sub> stream prior to use. All chemicals used were of reagent grades and were purified by the standard purification procedures. Reagent grade MeLi (Kanto Kagaku Co., Ltd.) was stored in the drybox and was used as received. V(NAd)Cl<sub>3</sub><sup>15</sup> and V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub><sup>11g</sup> were prepared according to our previous reports, and ethyl 6-[1-((2,6-diisopropylphenyl)imino)ethyl]pyridine-2-carboxylate, 2-{C(Me)=NAr'}-6-(CO<sub>2</sub>Et)-C<sub>5</sub>H<sub>3</sub>N, was also prepared according to the reported procedure.<sup>14</sup> Elemental 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 <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>51</sup>V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for <sup>1</sup>H, 100.40 MHz for <sup>13</sup>C, 376.17 MHz for <sup>19</sup>F, and 105.31 MHz for <sup>51</sup>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<sub>4</sub> (δ 0.00, <sup>1</sup>H, <sup>13</sup>C), CF<sub>3</sub>COOH (δ -78.5, <sup>19</sup>F), and VOCl<sub>3</sub> (δ 0.00, <sup>51</sup>V). Coupling constants and half-width values, Δν<sub>1/2</sub>, are given in Hz.

**Synthesis of 6-HOC(Me)<sub>2</sub>-2-{C(Me)=N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}-C<sub>5</sub>H<sub>3</sub>N (L-H).** Into a THF (80 mL) solution containing ethyl 6-[1-((2,6-diisopropylphenyl)imino)ethyl]pyridine-2-carboxylate (1.385 g, 3.93 mmol) was added 2 equiv of MeLi (1.09 M in Et<sub>2</sub>O, 7.21 mL) at -30 °C. The reaction mixture was then warmed slowly to room temperature and was stirred for 24 h. The mixture was then added water, and the organic compound was extracted with CHCl<sub>3</sub> (50 mL × 3). The combined extracted solution was placed *in vacuo* to remove all the solvent and volatiles, and the resultant yellow oil was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 8:1). The compound, 6-HOC(Me)<sub>2</sub>-2-{C(Me)=N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}-C<sub>5</sub>H<sub>3</sub>N (L-H), was obtained as yellow crystals (0.643 g, 1.90 mmol, yield 48.3%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.34 (d, 1H, *J* = 7.32, Py-*H*), 7.90 (t, 1H, *J* = 8.08, Py-*H*), 7.53 (d, 1H, *J* = 8.0, Py-*H*), 7.23 (d, 2H, *J* = 6.60, Ph-*H*), 7.15 (t, 1H, *J* = 6.60, Ph-*H*), 5.27 (s, 1H, OH), 2.79 (m, 2H, -CH(CH<sub>3</sub>)<sub>2</sub>), 2.28 (s, 3H, CH<sub>3</sub>C=N), 1.66 (s, 6H, -(CH<sub>3</sub>)<sub>2</sub>COH), 1.21 (d, 12H, *J* = 7.32, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 166.3, 164.8, 154.0, 146.2, 137.6, 135.7, 123.6, 122.9, 122.7, 119.9, 119.3, 71.7, 30.7, 28.2, 23.1, 22.8, 17.2. <sup>1</sup>H NMR(C<sub>6</sub>D<sub>6</sub>): δ 8.35 (d, 1H, *J* = 6.80, Py-*H*), 7.20–7.11 (m, 4H, Py-*H* and Ph-*H*), 6.97 (d, *J* = 7.72, Ph-*H*),

4.63 (s, 1H, OH), 2.81 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.11 (s, 3H, CH<sub>3</sub>C=N), 1.50 (s, 6H, -(CH<sub>3</sub>)<sub>2</sub>COH), 1.15 (d, *J* = 6.76, CH(CH<sub>3</sub>)<sub>2</sub>), 1.07 (d, *J* = 6.76, CH(CH<sub>3</sub>)<sub>2</sub>).

**Synthesis of V(NAd)Cl<sub>2</sub>(L) [1, L = 6-OC(Me)<sub>2</sub>-2-{(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CMe}-C<sub>5</sub>H<sub>3</sub>N].** Into a *n*-hexane solution (20 mL) containing 6-HOC(Me)<sub>2</sub>-2-{C(Me)=N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}C<sub>5</sub>H<sub>3</sub>N (L-H) (261 mg, 0.771 mmol) was added 1 equiv of <sup>t</sup>BuLi (1.59 M in *n*-hexane, 0.48 mL) at -30 °C, and the reaction mixture was then warmed to room temperature. The solution was stirred for an additional 3 h, and white precipitates were collected by filtration and were dried *in vacuo* for 3 h. Yield: 172 mg (0.506 mmol). The resultant lithium alkoxide was added into a Et<sub>2</sub>O solution (20 mL) containing V(NAd)Cl<sub>3</sub> (155 mg, 0.506 mmol) at -30 °C, and the reaction mixture was warmed to room temperature and was stirred overnight (14 h). The reaction mixture was then placed *in vacuo* to remove solvents and volatiles, and the residue was extracted with hot toluene. The combined extract was concentrated *in vacuo* and was covered with *n*-hexane. The chilled solution (-30 °C) gave red microcrystals (120 mg, 0.197 mmol). Yield: 39.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.00 (t, 1H, *J* = 8.08, Py-*H*), 7.70 (d, 1H, *J* = 8.08, Py-*H*), 7.49 (d, 1H, *J* = 8.08, Py-*H*), 7.26 (s, 3H, Ph-*H*), 3.59 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.27 (s, 3H, CH<sub>3</sub>C=N), 1.84 (s, 3H, Ad-*H*), 1.73 (s, 12H, Ad-*H* and (CH<sub>3</sub>)<sub>2</sub>COH), 1.45 (d, 6H, *J* = 6.60, CH(CH<sub>3</sub>)<sub>2</sub>), 1.39 (s, 6H, Ad-*H*), 0.99 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>51</sup>V NMR (CDCl<sub>3</sub>): δ -235.0 (Δν<sub>1/2</sub> = 4080.7 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 171.6, 167.7, 147.5, 145.1, 140.4, 140.0, 129.0, 128.2, 127.1, 125.2, 125.0, 123.4, 122.9, 99.7, 41.2, 35.6, 28.7, 28.5, 27.5, 25.6, 25.2, 18.9. Anal. Calcd for C<sub>32</sub>H<sub>44</sub>Cl<sub>2</sub>N<sub>3</sub>OV · 1/3toluene: C, 64.51; H, 7.36; N, 6.57. Found: C, 64.46; H, 7.10; N, 6.30.

**Synthesis of V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(L) (2).** The solution of a mixture of L-H (805 mg, 2.38 mmol) and V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> (1.10 g, 2.38 mmol) in C<sub>6</sub>D<sub>6</sub> (15 mL) was heated at 50 °C for 3 days. Then the mixture was filtrated by Celite-Pad, all the solvent was removed, and the residue was recrystallized from *n*-hexane solution at -30 °C. The green microcrystals (1.16 g, 1.63 mmol) were obtained in 68.4% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.39 (d, 1H, *J* = 7.32, Py-*H*), 7.97 (d, 1H, *J* = 8.08, Py-*H*), 7.39 (t, 1H, *J* = 8.08, Py-*H*), 7.18–7.09 (m, 3H, Ph-*H*), 2.85 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.30 (s, 3H, (CH<sub>3</sub>)C=N), 2.15 (s, 6H, Ad-*H*), 2.06 (br, 2H, CH<sub>2</sub>Si), 1.91 (s, 3H, Ad-*H*), 1.80 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>CO), 1.70 (br, 2H, CH<sub>2</sub>Si), 1.46 (m, 6H, Ad-*H*), 1.14 (d, 6H, *J* = 6.6, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, 6H, *J* = 5.9, CH(CH<sub>3</sub>)<sub>2</sub>), 0.21 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>51</sup>V NMR (C<sub>6</sub>D<sub>6</sub>): δ 277.8 (Δν<sub>1/2</sub> = 526.5 Hz). <sup>13</sup>C NMR: δ 167.5, 166.5, 155.2, 147.2, 137.0, 135.9, 124.1, 123.4, 120.7, 119.4, 85.7, 79.8(br), 45.3, 36.2, 33.6, 30.1, 28.7, 23.4, 22.9, 17.0, 2.41. Anal. Calcd for C<sub>40</sub>H<sub>66</sub>N<sub>3</sub>OSi<sub>2</sub>V: C, 67.47; H, 9.34; N, 5.90. Found: C, 67.32; H, 9.64; N, 5.77.

**Synthesis of V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub> (3).** A mixed solution of L-H (439 mg, 1.29 mmol) and V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> (0.30 g, 0.65 mmol) in C<sub>6</sub>D<sub>6</sub> (8 mL) was heated at 80 °C for 4 days. Then the mixture was filtrated through a Celite-Pad, and the filtrate was placed *in vacuo* to remove the solvent and volatiles. The residue was dissolved in a minimum amount of *n*-hexane. The chilled solution (at -30 °C) gave green microcrystals (0.26 g, 0.27 mmol, yield 41.5%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.41 (d, 2H, *J* = 7.32, Py-*H*), 7.89 (d, 2H, *J* = 7.32, Py-*H*), 7.35 (t, 2H, *J* = 8.08, Py-*H*), 7.22–7.16 (m, 6H, Ph-*H*), 2.90 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.36 (s, 6H, (CH<sub>3</sub>)C=N), 2.06 (br, 2H, CH<sub>2</sub>SiMe<sub>3</sub>), 1.99 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>CO), 1.95 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>CO), 1.78 (s, 9H, Ad-*H*), 1.38 (br, 6H, Ad-*H*), 1.23–1.16 (m, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.39 (s, 9H, SiMe<sub>3</sub>). <sup>51</sup>V NMR (C<sub>6</sub>D<sub>6</sub>): δ -311.02 (Δν<sub>1/2</sub> = 663.45 Hz). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): 167.5, 167.2, 155.1, 147.2, 137.0, 135.9, 124.2, 123.4, 121.0, 119.3, 85.9, 79.0 (br), 72.0, 44.7, 36.1, 33.8, 32.9, 29.9, 28.7, 23.4, 22.8, 17.0, 2.1. Anal. Calcd for C<sub>58</sub>H<sub>84</sub>N<sub>3</sub>O<sub>2</sub>Si<sub>2</sub>V · *n*-hexane: C, 73.31; H, 9.42; N, 6.68. Found: C, 73.76; H, 9.49; N, 6.81.

**Synthesis of V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(L)[OCH(CF<sub>3</sub>)<sub>2</sub>] (4).** Complex 2 (111 mg, 0.156 mmol) and 2 equiv of (CF<sub>3</sub>)<sub>2</sub>CHOH (52 mg, 0.312 mmol) was mixed in C<sub>6</sub>D<sub>6</sub> (2 mL), and the solution was stirred at

(20) A reviewer commented that introducing an oxygen donor (formation of **T1** or **T3**) leads to an upfield shift from the original complex **2**, not a downfield shift as seen in Figures 3 and 7. This would be explained as the result of dissociation of two neutral nitrogen donor ligands in the chelate alokoxo(imino)pyridine ligand. In contrast, it is thus not clear that the resonance ascribed to an intermediate (**T2** or **T4**, described in brackets in Scheme 5 or 6) also showed the downfield shift from the monoalkoxide (**4** or **5**) upon the addition of alcohol, although the formation of another species by coordination of alcohol should be appropriate to explain the observed facts. Recent review of <sup>51</sup>V NMR spectra of organovanadium complexes: Rehder, D. *Coord. Chem. Rev.* **2008**, *252*, 2209.

(21) Several attempts to isolate the monoalkyl-phenoxide complex from the reaction mixture have not been successful.

(22) For example (recent review), see: (a) Bianchini, C.; Giambastiani, G.; Rios, G. I.; Mantovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391. (b) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745.



**Table 1.** Crystal Data and Collection Parameters of Complexes V(NAd)Cl<sub>2</sub>(L) (1), V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)(L)<sub>2</sub> (3), and V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)(L)[OC(CH<sub>3</sub>)<sub>2</sub>](4) [L = 6-OC(Me)<sub>2</sub>-2-(Ar'N=CMe)-C<sub>5</sub>H<sub>3</sub>N, Ar' = 2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sup>a,17</sup>

	1	3	4
formula	C <sub>32</sub> H <sub>44</sub> Cl <sub>2</sub> N <sub>3</sub> OV	C <sub>60</sub> H <sub>84</sub> N <sub>5</sub> SiVO <sub>2</sub>	C <sub>85</sub> H <sub>112</sub> F <sub>12</sub> N <sub>6</sub> O <sub>4</sub> Si <sub>2</sub> V <sub>2</sub>
fw	608.57	986.38	1667.89
cryst color, habit	red, block	yellow, block	green, block
cryst size (mm)	0.40 × 0.20 × 0.15	0.15 × 0.10 × 0.05	0.15 × 0.10 × 0.03
cryst syst	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>P</i> $\bar{1}$ (#2)
<i>a</i> (Å)	10.1796(4)	16.5172(16)	11.7792(10)
<i>b</i> (Å)	10.6325(5)	16.9839(15)	14.5592(12)
<i>c</i> (Å)	17.0560(6)	21.2017(18)	16.3464(14)
$\alpha$ (deg)	102.2975(17)		64.162(2)
$\beta$ (deg)	91.9098(13)	97.306(2)	77.042(2)
$\gamma$ (deg)	114.2485(15)		77.020(2)
<i>V</i> (Å <sup>3</sup> )	1629.37(10)	5899.4(9)	2433.0(4)
<i>Z</i> value	2	4	1
<i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	1.240	1.110	1.138
<i>F</i> <sub>000</sub>	644.00	2128.00	878.00
no. of reflns measd	total: 16 190; unique: 7409 (0.028)	total: 38 733, unique: 8407 (0.168)	total: 18 506, unique: 7952 (0.116)
no. of observations ( <i>I</i> > 2.00σ( <i>I</i> ))	5592	2250	2629
no. of variables	414	696	545
R1 ( <i>I</i> > 2.00σ( <i>I</i> ))	0.0625	0.0681	0.0676
wR2 ( <i>I</i> > 2.00σ( <i>I</i> ))	0.1118	0.1715	0.0772
goodness of fit	1.000	1.001	1.081

<sup>a</sup> Diffractometer: Rigaku RAXIS-RAPID imaging plate. Structure solution: Patterson methods. Detailed analysis conditions are shown in the Supporting Information.

room temperature for 48 h. The mixture was then filtrated through a Celite-Pad, and the filtrate was placed *in vacuo* to remove the solvent and volatiles. The residue was recrystallized in *n*-hexane at −30 °C, and green microcrystals were collected (46 mg, 0.058 mmol, yield 37.3%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.39 (d, 1H, *J* = 7.92, Py-*H*), 7.68 (d, 1H, *J* = 7.32, Py-*H*), 7.37 (t, 1H, *J* = 7.96, Py-*H*), 7.22–7.13 (m, 3H, Ph-*H*), 5.35 (m, 1H, CH(CF<sub>3</sub>)<sub>2</sub>), 2.88 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.53 and 2.45 (br, 2H, CH<sub>2</sub>Si-), 2.33 (s, 3H, (CH<sub>3</sub>)C=N), 1.90 (s, 3H, (CH<sub>3</sub>)<sub>2</sub>CO), 1.84 (s, 3H, (CH<sub>3</sub>)<sub>2</sub>CO), 1.77 (s, 9H, Ad-*H*), 1.36–1.32 (br, 6H, Ad-*H*), 1.20–1.21 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.28 (s, 9H, SiMe<sub>3</sub>). <sup>51</sup>V NMR (C<sub>6</sub>D<sub>6</sub>): δ −210.99 (Δ*ν*<sub>1/2</sub> = 473.89 Hz). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 167.1, 166.3, 155.1, 147.1, 137.4, 135.9, 135.8, 124.2, 123.5, 120.8, 119.6, 88.0, 86.1 (br), 82.2 (br), 44.4, 35.7, 33.3, 32.9, 32.3, 29.9, 29.7, 29.4, 28.7, 23.4, 22.9, 17.0, 1.47. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>): δ −77.5, −77.9. Anal. Calcd for C<sub>39</sub>H<sub>56</sub>F<sub>6</sub>N<sub>3</sub>O<sub>2</sub>SiV: C, 59.15; H, 7.13; N, 5.31. Found: C, 58.84; H, 7.09; N, 5.31.

**Synthesis of V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)(L)[OC(CH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)] (5).** Complex **2** (250 mg, 0.351 mmol) and 2 equiv of (CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)COH (166 mg, 0.702 mmol) were mixed in C<sub>6</sub>D<sub>6</sub> (5 mL), and the solution was heated at 80 °C for 24 h. The mixture was then filtrated through a Celite-Pad, and the filtrate was placed *in vacuo* to remove the solvent and volatiles. The residue was recrystallized in *n*-hexane at −30 °C, and green crystals were collected (95 mg, 0.118 mmol, yield 33.6%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.40 (d, 1H, *J* = 7.36, Py-*H*), 7.74 (d, 1H, *J* = 7.36, Py-*H*), 7.37 (t, 1H, *J* = 7.32, Py-*H*), 7.22–7.16 (m, 3H, Ph-*H*), 2.89 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.52 and 2.33 (br, 2H, CH<sub>2</sub>Si-), 1.90–1.80 (m, 15H, (CH<sub>3</sub>)<sub>2</sub>CO and Ad-*H*), 1.61 (s, 3H, OC(CH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)), 1.37 (s, 6H, Ad-*H*), 1.19–1.13 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.30 (s, 9H, SiMe<sub>3</sub>). <sup>51</sup>V NMR (C<sub>6</sub>D<sub>6</sub>): δ −233.63 (Δ*ν*<sub>1/2</sub> = 537.08 Hz). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 167.1, 166.4, 155.1, 147.1, 137.3, 135.9, 135.8, 124.2, 123.4, 120.8, 119.6, 87.9, 85.9, 81.9 (br), 44.2, 36.0, 35.9, 35.7, 33.4, 32.3, 29.8, 28.7, 23.4, 22.9, 20.6, 17.0, 1.47. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>): δ −80.3, −80.7. Anal. Calcd for C<sub>40</sub>H<sub>58</sub>F<sub>6</sub>N<sub>3</sub>O<sub>2</sub>SiV: C, 59.61; H, 7.25; N, 5.21. Found: C, 59.0; H, 7.36; N, 5.08.

**Crystallographic Analysis.** All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. All structures were solved by

direct methods and expanded using Fourier techniques,<sup>23</sup> and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **1**, **3**, and **4** were performed using the Crystal Structure crystallographic software package.<sup>24</sup> Selected crystal collection parameters are summarized in Table 1

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**Supporting Information Available:** Text giving (1) <sup>1</sup>H and <sup>51</sup>V NMR spectra for monitoring the reaction of V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(L) [2, L = 6-OC(Me)<sub>2</sub>-2-((2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CMe)-C<sub>5</sub>H<sub>3</sub>N] with PMe<sub>3</sub>, NHC, (2) (<sup>1</sup>H, <sup>19</sup>F, <sup>51</sup>V) NMR spectra for monitoring the reaction of **2** with (CF<sub>3</sub>)<sub>2</sub>CHOH, (CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)COH, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH, and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH in C<sub>6</sub>D<sub>6</sub>, (3) VT NMR spectra for V(NAd)(CH<sub>2</sub>SiMe<sub>3</sub>)(L)[OC(CH<sub>3</sub>)(CF<sub>3</sub>)<sub>2</sub>] (**5**), (4) crystal structure determinations. Reports of the 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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