

A Stable Vanadium(V)-Methyl Complex Containing Arylimido and Bis(ketimide) Ligands That Exhibits Unique Reactivity with Alcohol

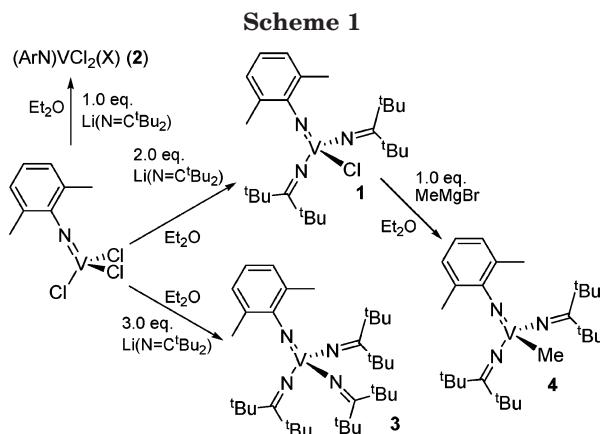
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Received May 30, 2005

Summary: An (arylimido)vanadium(V)-methyl complex containing a ketimide ligand, $(\text{ArN})\text{VMe}(\text{N}=\text{C}^t\text{Bu}_2)_2$ (**4**, $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$), could be isolated and identified by ^1H , ^{13}C , and ^{51}V NMR spectra, elemental analysis, and X-ray crystallography. The complex **4** was treated with alcohols (phenols), affording various methyl complexes by ligand exchange between the ketimide and alkoxy (aryloxo) groups exclusively, and reaction of the methyl group with the alcohols (phenols) did not take place.

Transition metal-alkyl complexes are one of the most important reagents or intermediates in stoichiometric/catalytic organic reactions as well as in olefin polymerization. Since classical Ziegler-type vanadium catalysts displayed unique characteristics (rapid propagation affording high molecular weight polymer) in olefin coordination/insertion polymerization,^{1,2} synthesis and reaction chemistry of the vanadium-alkyls attract considerable attention. However, these alkyl species tend to be reactive and/or thermally labile,^{3,4} and reductions to the lower oxidation states were often observed in some vanadium(V) alkyls.⁵ Here we introduce the unique first example that the reaction of a bis(ketimide)-



vanadium(V)-methyl complex, $(\text{ArN})\text{VMe}(\text{X})_2$ (**4**, $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $\text{X} = \text{N}=\text{C}^t\text{Bu}_2$), with alcoholic reagents affords the ligand exchange product between the ketimide and aryloxo (alkoxide) *without the reaction with the methyl group occurring*.

The bis(ketimide)vanadium chloride complex, $(\text{ArN})\text{VCl}(\text{X})_2$ (**1**), could be prepared in high yield (72.9%) by treating $(\text{ArN})\text{VCl}_3$ with 2.0 equiv of LiX in Et_2O (Scheme 1). The synthetic procedure is related to that for $(\text{ArN})\text{VCl}_2(\text{X})$ (**2**) reported recently,⁶ and the complex was identified by ^1H , ^{13}C , and ^{51}V NMR spectra, elemental analysis (EA), and X-ray crystallography.^{7,8} The reaction of $(\text{ArN})\text{VCl}_3$ with 3.0 equiv of LiX in Et_2O gave the corresponding tris(ketimide) complex, $(\text{ArN})\text{VX}_3$ (**3**), in a moderate isolated yield (37.9%), and the complex was identified by ^1H , ^{13}C , and ^{51}V NMR spectra and EA.⁸

The crystal structure showed that **1** has a distorted tetrahedral geometry around V, and the $\text{V}-\text{N}(\text{C}^t\text{Bu}_2)$ bond distances (1.805, 1.803 Å) were slightly longer than that in the monoketimide analogue (**2**, 1.787 Å), and the $\text{N}(\text{Ar})-\text{V}-\text{Cl}$ and $\text{N}(\text{Ar})-\text{V}-\text{N}(\text{C}^t\text{Bu}_2)$ bond angles (110.2°, 105.9°, or 106.1°, respectively) were somewhat larger than those in **2** (98.42°, 102.62°, or 103.95°, respectively). The resonances in the ^{51}V NMR spectra (in CDCl_3) were influenced by introduction of the ketimide ligand [$\delta = 72.4$ (mono, **2**), -195 (bis, **1**), and

(6) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* 2005, 24, 2248.

(7) Complex **1**: ^1H NMR (CDCl_3): δ 1.36 (s, 18H, $(\text{CH}_3)_3\text{C}-$), 2.52 (s, 6H, CH_3), 6.74 (t, 1H), 6.86 (d, 2H). ^{13}C NMR (CDCl_3): δ 19.0, 30.6, 46.0, 124.4, 126.9, 134.6, 164.9, 201.5. ^{51}V NMR (CDCl_3): δ -195 ($\Delta\nu_{1/2} = 432$ Hz). Anal. Calcd for $\text{C}_{26}\text{H}_{45}\text{N}_3\text{ClV}$: C, 64.25; H, 9.33; N, 8.65. Found: C, 64.19; H, 9.75; N, 8.54.

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

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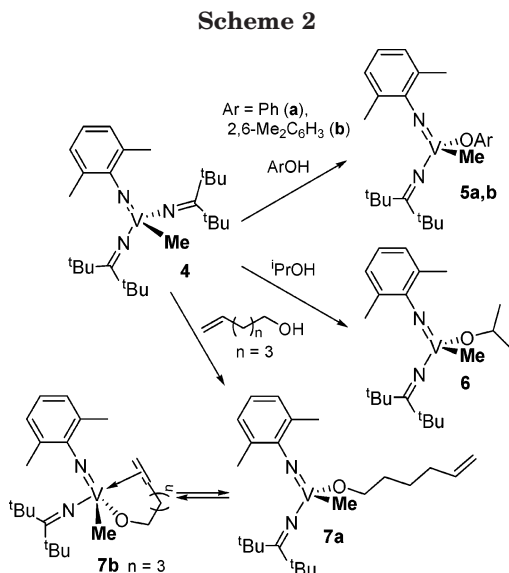
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(2) Pioneering examples: (a) Carrick, W. L. *J. Am. Chem. Soc.* 1958, 80, 6455. (b) Carrick, W. L.; Kluiber, R. W.; Bonner, E. F.; Wartman, L. H.; Rugg, F. M.; Smith, J. J. *J. Am. Chem. Soc.* 1960, 82, 3883. (c) Carrick, W. L.; Reichle, W. T.; Pennella,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

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

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(5) 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.



–387 (tris, **3**), strongly suggesting that an electron donation from the ketimide into the vanadium occurred.

The methyl analogue, (ArN)VMe(X)₂ (**4**), could be prepared in high yield (85.2%) by treating **1** with MeMgBr in Et₂O and was identified by ¹H, ¹³C, and ⁵¹V NMR spectra, EA, and X-ray crystallography.^{8,9} The crystal structure showed that **4** has a distorted tetrahedral geometry around V, and the V–N(C^tBu₂) distances (1.825–1.827 Å) were slightly longer than those in **1** (1.803–1.805 Å). The V–Me distance (2.064 Å) is in the range of V(V)–C bond lengths in (arylimido)-vanadium(V)-dibenzyl analogues (2.026–2.103 Å)^{4b} and is close to that in Li[(^tBu₃SiN)₂VMe₂] (2.043, 2.050 Å);^{4a} the distance is shorter than some V(II–IV)–Me complexes (2.118,^{3f} 2.206–2.222 Å^{3a,b,g,h}).

Note that the reaction of **4** with phenol and 2,6-dimethylphenol (1.0 equiv) in *n*-hexane exclusively afforded the other methyl complexes, (ArN)VMe(OAr)(X) (**5a**, **5b**), respectively (Scheme 2), and the reaction with the methyl group did not take place. The reaction of **4** with ⁱPrOH also afforded (ArN)VMe(OⁱPr)(X) (**6**). The results clearly indicate that the methyl group in **4** is not reactive toward alcohol under these conditions, although ordinary metal–alkyl bonds (especially in early transition metals) are readily reacted with alcohol to give alkoxide (phenoxide). Although some V(III)-methyl complexes catalyze ethylene polymerization/oligomerization without cocatalyst,¹⁰ **4** and **5b** did not react with ethylene (1 atm) in benzene-*d*₆.

The reaction of **4** with 5-hexen-1-ol in *n*-hexane afforded (ArN)VMe[OCH₂(CH₂)₃CH=CH₂](X) (**7**), and the complex was identified by ¹H, ¹³C, and ⁵¹V NMR spectra and EA.¹¹ Two species were observed in the ⁵¹V NMR spectrum (δ –102.7, –231.3 ppm at 20 °C), and the ratios depended upon the temperature (Figure 2).⁸ The species in the higher field was observed exclusively at 60 °C and was identified as **7a** by the ¹H NMR

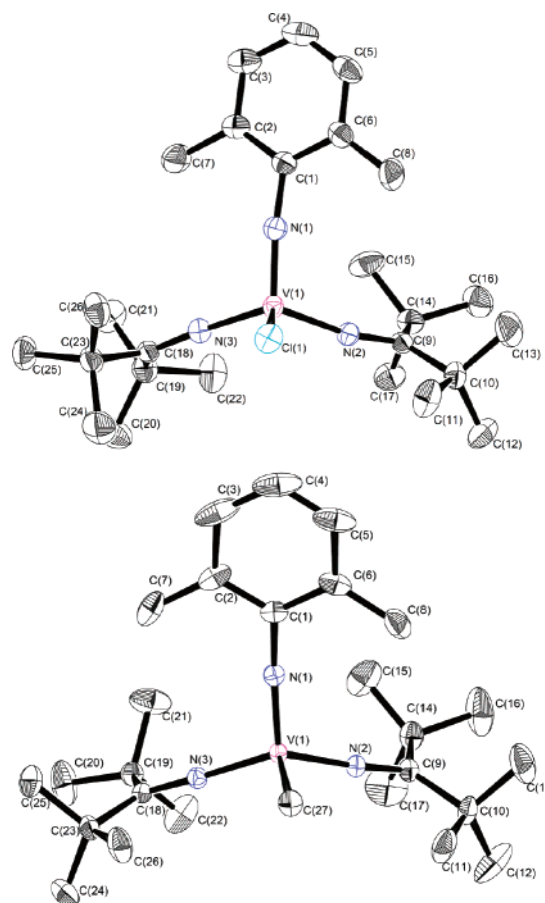


Figure 1. ORTEP drawings for **1** (top) and **4** (bottom). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

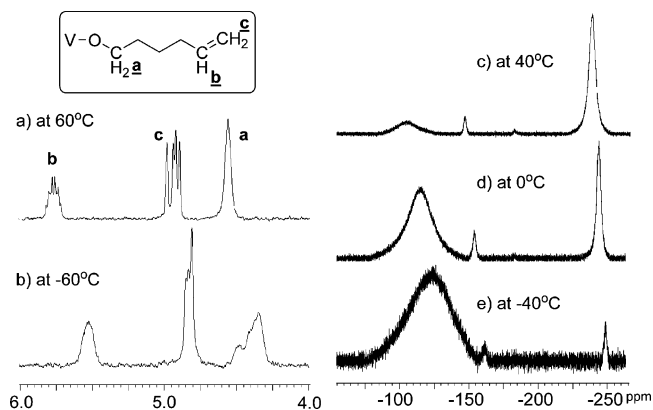


Figure 2. ¹H (extended at 4.0–6.0 ppm) and ⁵¹V NMR spectra (in CDCl₃) for **7** at various temperatures. ¹H NMR spectra at (a) 60 °C and (b) –60 °C. ⁵¹V NMR spectra at (c) 40 °C, (d) 0 °C, and (e) –40 °C.

spectrum (Figure 2a), because the resonances observed at 4.5–6.0 ppm were identical with those in our previous

(9) Complex **4**: ¹H NMR (CDCl₃): δ 0.88 (br, 3H, V-CH₃), 1.31 (s, 18H, (CH₃)₃C–), 2.44 (s, 6H, CH₃), 6.67 (t, 1H), 6.86 (d, 2H). ¹³C NMR (CDCl₃): δ 19.4, 30.8, 36.7, 45.6, 122.2, 126.8, 134.1, 162.7, 199.4. ⁵¹V NMR (CDCl₃): δ –138.8 ($\Delta\nu_{1/2}$ = 324 Hz). Anal. Calcd for C₂₇H₄₈N₃V: C, 69.64; H, 10.39; N, 9.03. Found: C, 69.16; H, 10.14; N, 9.09.

(10) Example: Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 4090. (b) Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2000**, 497.

(11) Complex **5a**, yield 92.1%. ¹H NMR (CDCl₃): δ 1.30 (s, 18H, (CH₃)₃C–), 1.43 (3H, V-CH₃), 2.45 (s, 6H, CH₃), 6.77 (t, 1H), 6.89 (d, 3H), 7.04 (d, 2H), 7.19 (t, 2H). ¹³C NMR (CDCl₃): δ 19.1, 30.4, 45.0, 119.3, 121.0, 124.0, 127.0, 128.8, 135.8, 162.3, 165.3, 198.8. ⁵¹V NMR (CDCl₃): δ –153 ($\Delta\nu_{1/2}$ = 1817 Hz). Anal. Calcd for C₂₄H₃₅N₂O₂V: C, 68.88; H, 8.43; N, 6.69. Found: C, 68.62; H, 8.36; N, 6.44. Complex **5b**, yield 93.8%. ¹H NMR (CDCl₃): δ 1.34 (3H, V-CH₃), 1.41 (s, 18H, (CH₃)₃C–), 2.33 (s, 6H, CH₃), 2.47 (s, 6H, CH₃), 6.81 (m, 2H), 6.96 (d, 2H), 7.03 (d, 2H). ¹³C NMR (CDCl₃): δ 17.6, 18.9, 30.5, 45.4, 120.4, 123.9, 126.8, 127.1, 128.0, 162.8, 163.87, 201.3. ⁵¹V NMR (CDCl₃): δ –185 ($\Delta\nu_{1/2}$ = 253 Hz). Anal. Calcd for C₂₆H₃₉N₂O₂V: C, 69.93; H, 8.80; N, 6.27. Found: C, 70.02; H, 8.98; N, 6.20.

example of Ti.⁹ This was also supported by the fact that the reaction of **4** with *n*-hexanol afforded a species observed at -238 ppm in the ⁵¹V NMR spectrum accompanying the formation of HN=C^tBu₂.⁸ In contrast, the species observed in the lower field became dominant below -40 °C, and we assume that this would be the olefin coordination species (**7b**), although the insertion did not take place under these conditions. A Δ*G* value of 8.6 kcal/mol was obtained from the ⁵¹V NMR spectra measured at various temperatures (-60 to 60 °C).⁸

Although **4** did not show any catalytic activities for initiating polymerization of ethylene, methyl methacrylate, and ε-caprolactone (CL), the ketimide-aryloxo analogue **5b** initiated polymerization of ε-CL, affording the ring-opened polymer.⁸ As far as we know, this is the first example that V initiates the ring-opening polymerization. Note that the *M_n* value for the polymers increased linearly upon increasing the polymer yields with narrow molecular weight distributions.¹³ Also note that the resultant polymer contained the aryloxo group as the polymer chain end, and the *M_n* value estimated by the ¹H NMR spectrum was close to that by GPC,^{8,13} clearly indicating that the polymerization took place in a living manner. Moreover, ethylene polymerization took place by **5b** in the presence of methyl aluminoxane

(12) Synthesis and identification of Cp*TiMe[OCH₂(CH₂)_{*n*}CH=CH₂](OAr) (*n* = 1, 3, Ar = 2,6-*i*-Pr₂C₆H₃) and Cp*Ti(CF₃SO₃)[OCH₂(CH₂)_{*n*}CH=CH₂](OAr): Nomura, K.; Hatanaka, Y. *Inorg. Chem. Commun.* **2003**, *6*, 517.

(13) Conditions: **5b** 20 μmol, ε-CL 5.0 mmol, CDCl₃ 2.5 mL, 100 °C.⁸ Yield 33 mg after 12 h, *M_n* = 0.9 × 10⁴, *M_w*/*M_n* = 1.2; 118 mg after 24 h, *M_n* = 1.8 × 10⁴ (1.72 × 10⁴ by ¹H NMR), *M_w*/*M_n* = 1.3; 314 mg after 48 h, *M_n* = 3.6 × 10⁴, *M_w*/*M_n* = 1.5. Detailed results are shown in the Supporting Information.

(MAO, activity = 160 kg PE/mol V h), affording linear polyethylene,¹⁴ although **5b** did not show catalytic activity without cocatalyst.

We have presented a unique example of stable vanadium(V)-methyl complexes and succeeded in preparing various methyl complexes by ligand exchange reactions. Although the exact reason the methyl group did not react with alcohol is not clear at this moment, this fact should introduce new insight into designing efficient organo-vanadium complex catalysts.

Acknowledgment. The authors express their thanks to Prof. Michiya Fujiki (NAIST) for helpful discussions and to Mr. Shohei Katao (NAIST) for help in crystallographic analysis. J.Y. expresses his thanks to the JSPS for a predoctoral fellowship (No. 5042). This research is partly supported by Tokuyama Science Foundation.

Supporting Information Available: Text and tables giving experimental details (including syntheses, identifications for **1**, **3**–**7**), results for polymerizations and some reactions, and ¹H and ⁵¹V NMR spectra for **7**. Crystal structure determinations and reports for **1**, **4**; 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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(14) Conditions: **5b** 5.0 μmol, toluene 5 mL, MAO 2.5 mmol, ethylene 8 atm, 10 min, 50 °C. Polymer yields 133 mg, *M_w* = 20.2 × 10⁴, *M_w*/*M_n* = 7.21. The broad PDI values maybe due to precipitation of polyethylene.