

Facile Synthesis of (Imido)vanadium(V)–Alkyl, Alkylidene Complexes Containing an N-Heterocyclic Carbene Ligand from Their Trialkyl Analogues

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Summary: (Imido)vanadium(V)–alkyl, alkylidene complexes containing an N-heterocyclic carbene (NHC) ligand, $V(\text{CHSiMe}_3)(\text{NR})(\text{CH}_2\text{SiMe}_3)(\text{NHC})$ [$\text{R} = 1\text{-adamantyl (Ad) or } 2,6\text{-Me}_2\text{C}_6\text{H}_3 \text{ (Ar)}$], $\text{NHC} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$], have been prepared from the trialkyl analogues, $V(\text{NR})(\text{CH}_2\text{SiMe}_3)_3$, by α -hydrogen elimination in C_6D_6 in the presence of NHC. The $\text{V}–\text{C}(\text{NHC})$ bond distance [$2.172(2) \text{ \AA}$] in $V(\text{CHSiMe}_3)(\text{NAd})(\text{CH}_2\text{SiMe}_3)(\text{NHC})$ is much longer than the $\text{V}–\text{C}(\text{alkylidene})$ [$1.829 \text{ \AA}$] and the $\text{V}–\text{C}(\text{alkyl})$ [$2.069 \text{ \AA}$] distances, indicating that NHC plays an important role in the stabilization of the high-oxidation-state vanadium(V)–alkylidene as a neutral carbene ligand.

High-oxidation-state early transition metal alkylidene complexes attract considerable attention¹ because they play essential roles as catalysts in olefin metathesis and Wittig-type group transfer reactions,^{1,2} as demonstrated by molybdenum.^{1a–d,2} Although classical Ziegler-type vanadium catalysts displayed unique characteristics in olefin coordination insertion polymerization (notable reactivity toward olefins),^{3,4} examples with vanadium(V)–alkylidenes still have been limited.^{1e,f,5–7} We recently introduced that (arylimido)vanadium(V)–alkylidene complexes containing ketimide^{6b,e} and aryloxo^{6d} ligands ex-

hibited high catalytic activities for ring-opening metathesis polymerization of norbornene. Although titanium(IV)–alkyl, alkylidene complexes display unique reactivities with various organic compounds via a “ $\text{Ti}=\text{C}^+\text{Bu}$ ” intermediate,⁸ synthesis and the reaction chemistry of the vanadium(V)–alkyl, alkylidene complexes have not been reported so far.⁹ We thus herein present that syntheses of (imido)vanadium(V)–alkyl, alkylidene complexes, $V(\text{CHSiMe}_3)(\text{NR})(\text{CH}_2\text{SiMe}_3)(\text{NHC})$ [$\text{R} = 1\text{-adamantyl (Ad)}$, $2,6\text{-Me}_2\text{C}_6\text{H}_3 \text{ (Ar)}$; $\text{NHC} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$], have been achieved from the trialkyl analogues by α -hydrogen abstraction in the presence of NHC.¹⁰

Reaction of $V(\text{NAd})\text{Cl}_3$ prepared by the reported method¹¹ with 3.0 equiv of $\text{LiCH}_2\text{SiMe}_3$ in *n*-hexane gave the trialkyl analogue $V(\text{NAd})(\text{CH}_2\text{SiMe}_3)_3$ (**1**) in moderate yield (64%), and the procedure is analogous to that for synthesis of the arylimido analogue $V(\text{NAr})(\text{CH}_2\text{SiMe}_3)_3$ (**2**).^{6d} Complex **1** was identified on the basis of NMR spectra and elemental analysis, and the structure was determined by X-ray crystallography (Figure 1).¹⁰ Complex **1** has a rather distorted tetrahedral geometry around V, and the $\text{V}–\text{N}–\text{C}$ bond angle is $180.00(17)^\circ$ and the $\text{V}–\text{N}$ distance is $1.6317(14) \text{ \AA}$; the results would be a unique contrast to those in $V(\text{N-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{Ph})_3$ [$\text{V}–\text{N}–\text{C}$ $169.0(5)^\circ$ and $1.641(6) \text{ \AA}$].¹² The three $\text{V}–\text{C}$ bond distances and angles are

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(1) For examples, see: (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Schrock, R. R. In *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Springer: Berlin, Germany, 1998; p 1. (c) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (d) Schrock, R. R. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1, p 8. (e) Mindiola, D. *Acc. Chem. Res.* **2006**, *39*, 813. (f) Mindiola, D.; Bailey, B.; Basuli, F. *Eur. J. Inorg. Chem.* **2006**, *16*, 3135.

(2) For examples, see: (a) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (b) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003; Vols. 1–3. (c) Khosravi, E.; Szymanska-Buzar, T., Eds. *Ring-Opening Metathesis Polymerisation and Related Chemistry*; Kluwer: Dordrecht, The Netherlands, 2002. (d) Imamoglu, Y.; Dragutan, V., Eds. *Metathesis Chemistry*; Springer: Dordrecht, The Netherlands, 2007.

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(5) Examples for isolation of terminal vanadium(III),(IV) alkylidenes:^{1e,f} (a) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 5977. (b) Hessen, B.; Meetsma, A.; Van Bolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925. (c) Basuli, F.; Kilgore, U. J.; Hu, X.; Meyer, K.; Pink, M.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3156. (d) 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.

(6) Examples for terminal vanadium(V)–alkylidenes: (a) Buijink, J.-K. F.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922. No reaction between $\text{CpV}(\text{CHPh})(\text{NAr})(\text{PMe}_3)$ and norbornene or acetone was observed. (b) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2005**, *24*, 2248. (c) Kilgore, U. J.; Sengelaub, C. A.; Pink, M.; Fout, A. R.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 3769. No descriptions concerning application as the catalysts. (d) Nomura, K.; Onishi, Y.; Fujiki, M.; Yamada, J. *Organometallics* **2008**, *27*, 3818. (e) Zhang, W.; Yamada, J.; Nomura, K. *Organometallics*, **2008**, *27*, 5353.

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(9) Synthesis of vanadium(IV)–alkyl, alkylidene yielding terminal vanadium(V)–neopentylidene upon addition of AgOTf ($\text{Tf} = \text{CF}_3\text{SO}_2$). 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.

(10) Experimental details including syntheses, identification, and structural analysis reports are shown in the Supporting Information.

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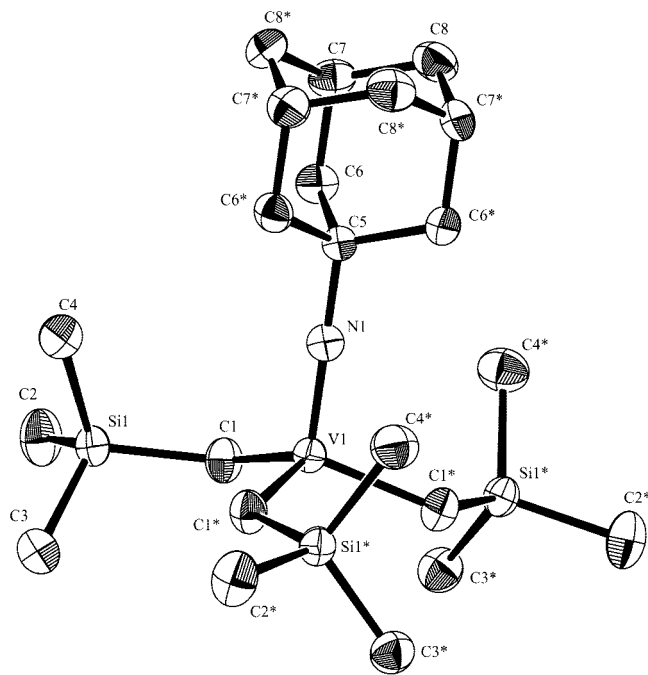


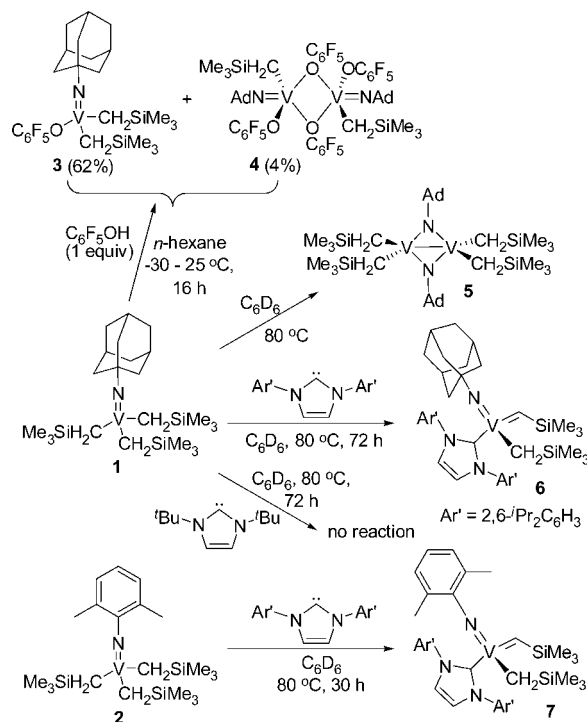
Figure 1. ORTEP drawing for **1**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.¹⁰ Selected bond angles (deg) and distances (Å): V–N–C(5) 180.00(17), C(1)–V–C(1)* 112.55(7); V–N 1.6317(14), V(1)–C(1) 2.0267(18).

the same [112.55(7)°, 2.0267(18) Å], and the facts are also a unique contrast to those in the arylimido-tribenzyl complex.¹²

Reaction of **1** with 1 equiv of C₆F₅OH in *n*-hexane afforded a mixture of V(NAd)(CH₂SiMe₃)₂(OC₆F₅) (**3**, 62% yield) and [V(NAd)(CH₂SiMe₃)(OC₆F₅)(μ₂-OC₆F₅)₂] (**4**, 4% yield), as shown in Scheme 1, and these two complexes were isolated by separation and were identified on the basis of NMR spectra and elemental analysis;¹⁰ the structure for **4** could be determined by X-ray crystallography as a dimeric structure bridged by oxygen.^{10,13} Although **1** is a low-coordinate unsaturated trialkyl complex, coordination of a donor ligand [such as PMe₃ (14 equiv) and CH₃CN (1 equiv)] was not observed in the ⁵¹V NMR spectra (in C₆D₆) at room temperature, as seen in the arylimido analogue (**2**),^{6d} probably due to the steric bulk of the three CH₂SiMe₃ ligands. One of the methods commonly employed generating metal–alkylidene is the α-hydrogen abstraction promoted by heat or upon irradiation,¹ but thermolysis of **1** in C₆D₆ at 80 °C afforded a dimeric species, [V(μ₂-NAd)-(CH₂SiMe₃)₂]₂ (**5**), identified by NMR spectra and elemental analysis. The structure of **5** was also confirmed by X-ray crystallography,¹⁴ which was analogous to [V(μ₂-4-MeC₆H₄)(2,4,6-Me₃C₆H₂)₂] reported previously.¹⁵

N-Heterocyclic carbenes (NHC) have been known to play an essential role as ligands in metal complex catalysts as well

Scheme 1



as organocatalysts,¹⁶ and NHC in VOCl₃(IMes) [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] previously proposed its utility to stabilize high-oxidation-state vanadium(V) complexes.¹⁷ We thus explored the reaction of **1** in the presence of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (NHC). Coordination of NHC was not seen if **1** was added with 1.0 equiv of NHC in C₆D₆ at 25 °C, but a new resonance ascribed to the alkylidene proton appeared in the ¹H NMR spectrum (13.4 ppm) when the solution was heated at 80 °C for 18 h.¹⁰ Only one resonance in addition to **1** was observed in the ⁵¹V NMR spectrum.¹⁰ However, isolation of the targeted complex failed due to the difficulty in separating the product from the NHC remaining in the mixture. Eventually, the targeted complex could be isolated (22% based on NHC, 15% based on V) when **1** was treated with 2/3 equiv of NHC at 80 °C in C₆D₆.¹⁰ The complex could be identified on the basis of NMR spectra and elemental analysis as V(CHSiMe₃)(NAd)(CH₂SiMe₃)(NHC) (**6**), having alkyl, alkylidene, and N-heterocyclic carbene ligands, and the structure could be determined by X-ray crystallography (Figure 2). Similarly, the reaction of the arylimido analogue (**2**) with NHC afforded V(CHSiMe₃)(NAr)(CH₂SiMe₃)(NHC) (**7**) in better yield (75% based on NHC, 60% based on V) than the adamantylimido analogue (**6**), and **7** was identified on the basis of NMR spectra and elemental analysis. The alkylidene protons (V=CHSiMe₃) in **6** and **7** were observed at 13.4 ppm as a broad resonance coupled with vanadium, and the resonance is somewhat close to that in V(CHSiMe₃)(NAr)(N=C'Bu₂)(PMe₃) (14.52 ppm)^{6b} but shifted to low field compared to V(CHSiMe₃)(NAr)(O-2,6-IPr₂C₆H₃)(PMe₃) (16.09 ppm).^{6d} However, the

(13) The reaction of **1** with 1 equiv of 2,6-Me₂C₆H₃SH in *n*-hexane did not take place, as seen in the attempted reaction of **2**.^{6d} The reaction of **1** with 1 equiv of (CF₃)₂CHOH in *n*-hexane at 25 °C recovered **1** in high yield even if the mixture was stirred overnight (> 12 h),¹⁰ and the results would be an interesting contrast to the fact that the reaction of **2** with (CF₃)₂C(Me)OH cleanly afforded the corresponding alkoxide.^{6d} Detailed results are shown in the Supporting Information.

(14) We attempted the crystallographic analysis several times, and the structure could be solved, but the *R* value may not be satisfactory; these results are shown in the Supporting Information.

(15) Synthesis and structural analysis for [V(μ₂-4-MeC₆H₄)(2,4,6-Me₃C₆H₂)₂]. Solan, G. A.; Cozzi, P. G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 2572.

(16) For example: (a) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (b) *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Springer: Berlin, Germany, 2007. (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5605.

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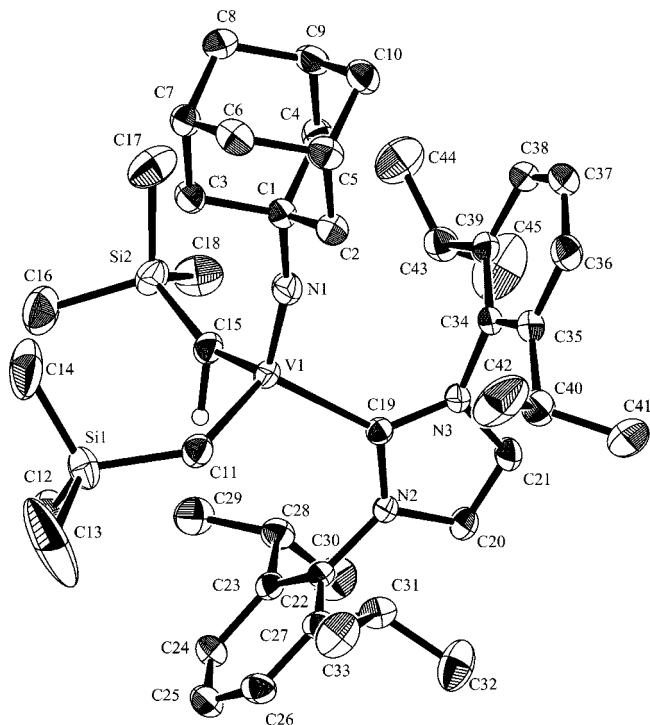


Figure 2. ORTEP drawing for **6**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.¹⁰ Selected bond angles (deg) and distances (Å): N–V–C(11) 107.00(12), C(11)–V–C(15) 111.10(12), C(11)–V–C(19) 115.26(11), C(15)–V–C(19) 101.96(11); V–N(1) 1.637(2), V–C(11) 2.069(3), V–C(15) 1.829(3), V–C(19) 2.172(2).

reaction of **1** with (more bulky and stable¹⁸) 1,3-di-*tert*-butylimidazole-2-ylidene did not show any changes in the ⁵¹V NMR spectra even at 80 °C for 3 days (Scheme 1).¹⁰ This thus suggests that this NHC stabilizes **1** probably by weak coordination but did not promote α -hydrogen elimination under these conditions.¹⁹

The (adamantylimido)vanadium(V)–alkyl, alkylidene complex containing NHC (**6**) has a rather distorted tetrahedral

geometry around vanadium (Figure 2), and the V–C bond distances for the alkyl, the alkylidene, and the NHC are 2.069(3), 1.829(3), and 2.172(2) Å, respectively; these values (alkyl, alkylidene) are similar to those in previous reports.^{6b,10,17} The V–C(NHC) distance is close to that in VOCl₃(IMes) (2.137 Å); the coordination seems like that of neutral carbene, and a similar explanation would be thus possible. Ring-opening metathesis polymerization of norbornene by **6** (and **7**) took place,²⁰ but the activities (at 80 °C in benzene) were lower than that by V(CHSiMe₃)(NAr)(N=C^tBu₂)(PMe₃)^{6b} and the activities at 25 °C were negligible.

We have presented the utility of NHC for stabilization of high-oxidation-state vanadium–alkylidenes (**6** and **7**), and an appropriate donor ligand is necessary to promote α -hydrogen elimination from two adjacent alkyl species. The present approaches should be widely applied for preparation of various early transition metal–alkylidene complexes. Moreover, the present alkyl–alkylidenes would also be promising intermediates for the syntheses of not only alkylidyne but also cationic alkylidenes or alkylidenes containing a series of anionic donor ligands. Further studies concerning their application as catalysts including the effect of adamantyl imido ligands are now under way.

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Supporting Information Available: Text giving experimental procedures, CIF files and structure reports for V(NAd)(CH₂SiMe₃)₃ (**1**), [V(NAd)(CH₂SiMe₃)(OC₆F₅)(μ_2 -OC₆F₅)]₂ (**4**), [V(μ_2 -NAd)-(CH₂SiMe₃)₂]₂ (**5**), and V(NAd)(CHSiMe₃)(CH₂SiMe₃)(NHC) [**6**, NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], and their reactions (described in the text and notes). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Two new resonances (may be ascribed to the alkylidene) were seen in the ⁵¹V (and ¹H) NMR spectrum when **1** was treated with 14 equiv of PMe₃ in C₆D₆ at 80 °C,¹⁰ but attempted isolation of any complexes from the mixture was unsuccessful.

(20) Conditions: **6** 1.0 μ mol, norbornene 200 mg, toluene 5.0 mL, 80 °C for 30 min. Activity 740 turnovers (TON), $M_w = 3.74 \times 10^5$, $M_w/M_n = 2.0$. TON after 1 h was 390 if the reaction with **7** was conducted under the same conditions.