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A Vanadium(V) Alkylidene Complex Exhibiting Remarkable Catalytic Activity for Ring-Opening Metathesis Polymerization (ROMP)

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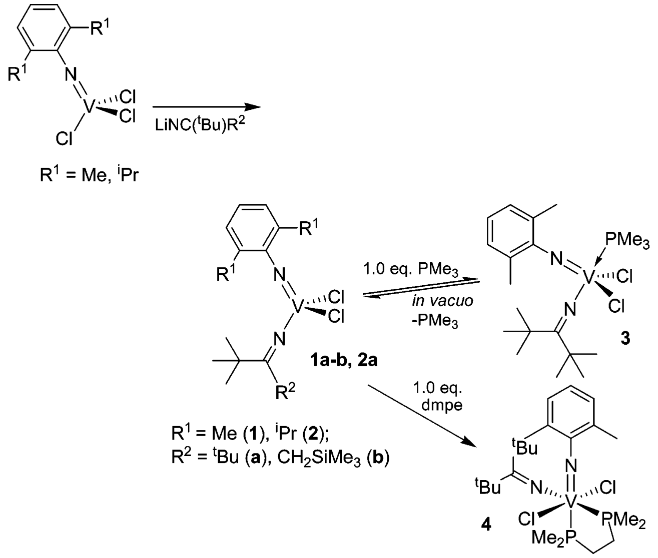
*Summary: The vanadium(V) alkylidene complex (ArN)V(=CHSiMe$_3$)(N=C^{t}Bu$_2$)(PMe$_3$) (**6**; Ar = 2,6-Me$_2$C$_6$H$_3$) has been isolated from (ArN)V(CH$_2$SiMe$_3$)$_2$(N=C^{t}Bu$_2$) (**5**) by α-hydrogen elimination in benzene-d$_6$ at 80 °C. The complex **6** initiated ring-opening metathesis polymerization (ROMP) of norbornene, yielding a high-molecular-weight polymer with unimodal molecular weight distribution (M_w = 1.15 × 10^6, M_w/M_n = 1.6) in high yield (98%), and the activity increased at higher temperatures (80 °C).*

High-oxidation-state transition-metal alkylidene complexes have attracted considerable attention[1] because of their promise as catalysts (initiators) for olefin metathesis such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), and cross-metathesis (CM), etc.,[1−3] and successful examples have been demonstrated by molybdenum[1b−d,2] and ruthenium.[2,3] However, examples of olefin metathesis with vanadium alkylidene complexes[4−7] have been limited,[7] although classical Ziegler type vanadium catalysts displayed unique characteristics such as synthesis of high-molecular-weight polymer with rapid propagation in olefin coordination insertion polymerization[8] and syntheses of some vanadium(III) and -(IV) alkylidenes[4,5] as well as vanadium(V) alkylidene complexes[6] are known. Since no examples for *catalytic* olefin metathesis by vanadium alkylidene complexes are known,[7] we explored the possibility of isolating an *olefin metathesis active* vanadium(V) alkylidene complex. In this paper, we wish to present the first example of isolation and structural determination of a *thermally stable* alkylidene complex that exhibits remarkable catalytic activity for the ROMP of norbornene (NBE) at high temperature.[9]

Scheme 1



We focused on (arylimido)vanadium(V) complexes containing anionic donor ligands, because (ArN)V-

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(1) For recent examples, see: (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145−179. (b) Schrock, R. R. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1, pp 8−32. (c) Schrock, R. R. In *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Springer: Berlin, 1998; pp 1−36.

(2) For recent examples (books and review), see: (a) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565−1604. (b) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1−3. (c) Khosravi, E., Szymanska-Buzar, T., Eds. *Ring-Opening Metathesis Polymerisation and Related Chemistry*; Kluwer: Dordrecht, The Netherlands, 2002. (d) Imamoglu, Y., Bencze, L., Eds. *Novel Metathesis Chemistry: Well-Defined Initiator Systems for Specialty Chemical Synthesis, Tailored Polymer and Advanced Material Applications*; Kluwer: Dordrecht, The Netherlands, 2003.

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

(4) Examples of isolated vanadium(III) and -(IV) alkylidene complexes: (a) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 5977−5978. (b) Hessen, B.; Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H.; Helgesson, G.; Hakansson, M.; Jagner, S. Spek, A. L. *Organometallics* **1993**, *12*, 2268−2276. (c) Basuli, F.; Kilgore, U. J.; Hu, X.; Meyer, K.; Pink, M.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3156−3159. (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*, 10506−10507.

(5) Related isolated examples for vanadium carbene complexes: (a) Erker, G.; Lecht, R.; Schlund, R.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 666−668. (b) Milczarek, R.; Rüsseler, W.; Binger, P.; Jonas, K.; Angermund, K.; Kruger, C.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 908−909. (c) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H. *Organometallics* **1990**, *9*, 1925−1936.

(6) (a) Buijink, J.-K. F.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922−2924. No reaction between CpV−(CHPh)(NAr)(PMe$_3$) and NBE or acetone was observed. (b) Moore, M.; Gambarotta, S.; Yap, G.; Liable-Sands, L. M.; Rheingold, A. L. *Chem. Commun.* **1997**, 643−644.

(7) Intramolecular metathesis[4d] and reaction of CpV(CHCMe$_3$)(dmpe) with NBE[4b] were reported previously. However, the latter case showed extremely low catalytic activity (TON 0.92 after 96 h at 20 °C) and no NMR or GPC results for the resultant polymers were given in the text.

(8) Examples: (a) Carrick, W. L. *J. Am. Chem. Soc.* **1958**, *80*, 6455−6456. (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*, 3883−3887. (c) Carrick, W. L.; Reichle, W. T.; Pennella, F.; Smith. J. J. *J. Am. Chem. Soc.* **1960**, *82*, 3887−3892. (d) Lehr, M. H. *Macromolecules* **1968**, *1*, 178−184.

(9) Part of these results were introduced at the XXIst International Conference on Organometallic Chemistry, P151, July 2004, Vancouver, Canada.

10.1021/om0501834 CCC: $30.25

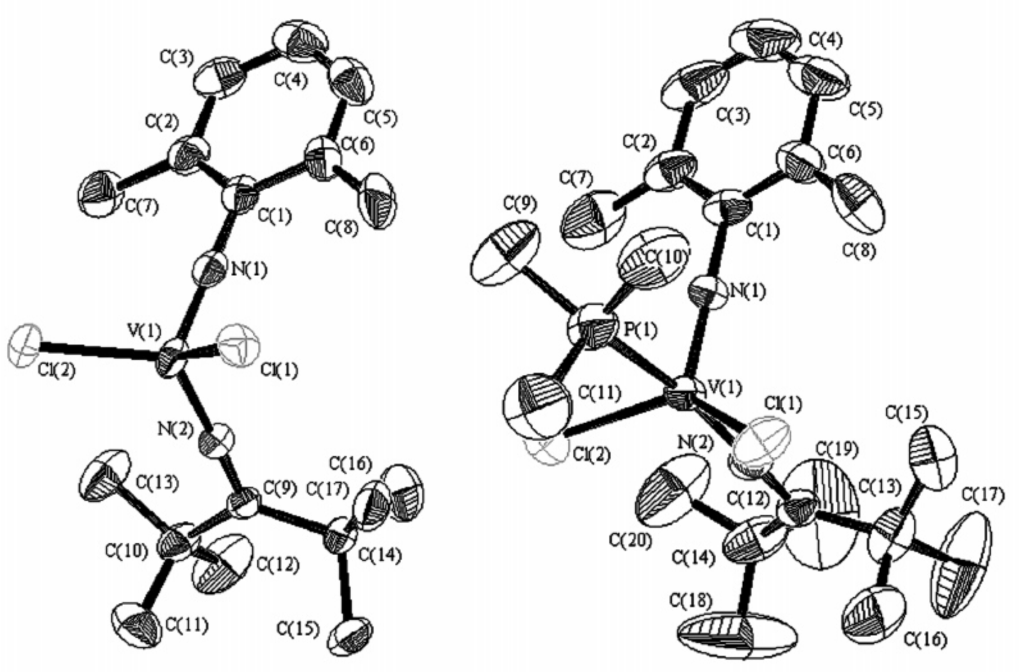
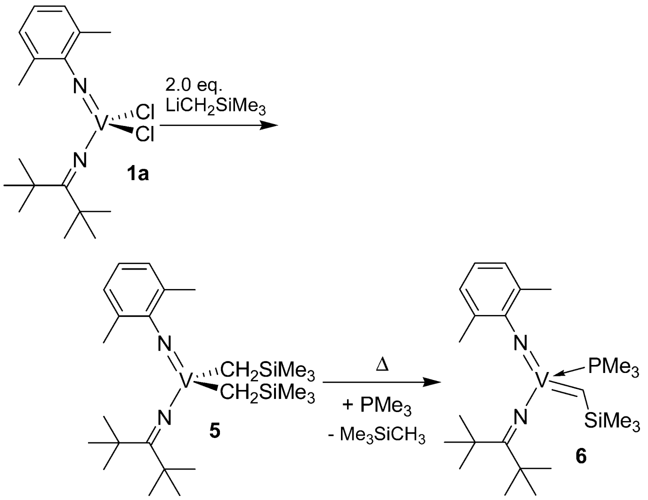


Figure 1. ORTEP drawings for **1a** (left) and **3** (right). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[11]

$(CH_2Ph)_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (Ar = $2,6\text{-}Me_2C_6H_3$) initiated the ROMP of NBE without cocatalyst, affording high-molecular-weight ring-opened poly(NBE).[10] The arylimido−ketimide complexes were thus chosen, because $(ArN)V(CH_2SiMe_3)_2(N{=}C^tBu_2)$ (**5**) showed better thermal stability than $(ArN)V(CH_2Ph)_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$.[11]

Various vanadium(V) dichloride complexes (**1** and **2**) could be prepared in high yields by treating $(ArN)VCl_3$ with $LiN{=}C^tBu_2$ in Et_2O (Scheme 1; 84−85%)[12] and were identified by ^1H, ^{13}C, and ^{51}V NMR spectra as well as by elemental analyses.[11,12] The crystal structure for **1a** (Figure 1, left) showed that **1a** has a distorted-tetrahedral geometry around V, and the bond distances for V−N(Ar) and $V{-}N(C^tBu_2)$ are 1.660 and 1.787 Å, respectively, suggesting that the complex **1a** is a 14-electron species. Complex **1a** reacted with 1 equiv of PMe_3 to afford $(ArN)VCl_2(L)(PMe_3)$ (**3**; L = $N{=}C^tBu_2$), which was exclusively confirmed by ^1H, ^{13}C, and ^{51}V NMR spectra.[13] The crystal structure for **3** (Figure 1, right) showed that **3** has a distorted-trigonal-bipyramidal structure around V; the P atom is positioned trans to the N atom in the ketimide ligand, and the V−N distance (1.839 Å) is thus influenced by electron donation from PMe_3. As suggested by both the rather long V−P distance (2.527 Å) and the fact that only broad resonances were seen in the ^{31}P NMR spectrum, the PMe_3 was dissociated exclusively, affording analytically pure **1a** quantitatively if **3** was placed in vacuo. The reaction of **1a** with bis(dimethylphosphino)ethane (dmpe) afforded $(ArN)VCl_2(L)(dmpe)$ (**4**),[11] and the crystal structure showed that **4** has a distorted-octahedral geometry around V; V−N(Ar) and $V{-}N(C^tBu_2)$ distances (1.677 and 1.843 Å) are longer than those in **1a**, due to the trans influence of dmpe.

Scheme 2



The reaction of **1a** with $LiCH_2SiMe_3$ in *n*-hexane afforded $(ArN)V(CH_2SiMe_3)_2(L)$ (**5**) in high yield (95%; Scheme 2), and the complex was identified by ^1H, ^{13}C, and ^{51}V NMR spectra and elemental analysis.[11] The coordination of PMe_3 to **5** was not observed, even by addition of an excess amount (7.0 equiv) at 25 °C, and this observation might be due to the steric hindrance of the rather bulky CH_2SiMe_3 group around the V metal center.

The complex **5** initiated the ROMP of NBE in toluene, and the activity increased especially by the addition of PMe_3 at higher temperature (Table 1; run 8 vs runs 1

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[10] Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, *35*, 1583−1590. Examples of ROMP by vanadium catalysts were cited therein.

[11] Detailed results (including the crystal structures) are given in the Supporting Information.

[12] Complex **1a**: yield 84%; ^1H NMR ($CDCl_3$) δ 1.35 (s, 18H, $(CH_3)_3C-$), 2.69 (s, 6H, CH_3), 6.94 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 18.9, 30.2, 47.1, 127.4, 128.2, 138.4, 169.3, 210.1; ^{51}V NMR ($CDCl_3$) δ 72.4 ($\Delta\nu_{1/2}$ = 237 Hz). Anal. Calcd for $C_{17}H_{27}N_2Cl_2V$: C, 53.55; H, 7.14; N, 7.35. Found: C, 53.71; H, 7.14; N, 7.26.

[13] Complex **3**: ^1H NMR ($CDCl_3$) δ 1.27 (d, 9H, $P(CH_3)_3$), 1.39 (s, 18H, $(CH_3)_3C-$), 2.51 (s, 6H, $(CH_3)_2$), 6.81 (t, 1H), 6.89 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.9, 30.9, 47.4, 126.6, 127.4, 138.6, 164.2, 190.0; ^{51}V NMR ($CDCl_3$) δ −76.7 ($\Delta\nu_{1/2}$ = 900 Hz).

Table 1. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE) with 5, 6, or Ru(CHPh)(Cl)$_2$(PCy$_3$)$_2$ (Ru, Cy = Cyclohexyl)[a]

run	complex (amt/ μmol)	solvent	NBE concn[b]	P/ V[c]	temp/ °C	time/ h	TON[d]	M_w[e] × 10^{-4}	M_w/ M_n[e]
1	**5** (10.0)	toluene	0.89	3	25	6	1.6		
2	**6** (1.0)	benzene	0.22		25	3	267	46	2.3
3	Ru (1.0)	toluene	0.22		25	1	1306	54	1.7
4	**6** (1.0)	benzene	0.22		50	3	1275	49	1.6
5	**6** (1.0)	toluene	0.22		50	3	166		
6	**5** (20.0)	toluene	0.89		80	6	6.8		
7	**5** (10.0)	toluene	0.22	3	80	3	101	97	3.0
8	**5** (10.0)	toluene	0.44	3	80	3	212	87	3.2
9	**5** (10.0)	toluene	0.44	5	80	3	40	47	3.0
10	**6** (1.0)	toluene	0.22		80	1	1244	32	2.8
11	**6** (1.0)	benzene	0.22		80	0.5	967	140	1.3
12	**6** (1.0)	benzene	0.22		80	1	1583	133	1.4
13	**6** (1.0)	benzene	0.22		80	2	2071[f]	115	1.6
14	Ru (1.0)	toluene	0.22		80	1	350		

[a] Conditions: NBE, 2.12 mmol (run 6, 4.24 mmol; run 7, 1.06 mmol); benzene or toluene, 9.6 mL (run 1, 2.4 mL; runs 6−9, 4.8 mL). [b] Initial NBE concentration in mmol/mL. [c] Molar ratio of PMe$_3$/V. [d] TON = NBE consumed (mmol)/V (mmol). [e] GPC data vs polystyrene standard. [f] Yield 98%.

and 6). The activity depended upon the NBE concentration (runs 7 and 8), and the activity decreased on further addition of PMe$_3$ (run 9).[11] The resultant polymer possessed a ring-opened structure containing a mixture of *cis*- and *trans*-olefinic double bonds.[11] Note that a significant increase in the activity on PMe$_3$ addition at higher temperature was observed, suggesting the formation of the vanadium alkylidene.[10]

Encouraged by the above findings, reaction of **5** with PMe$_3$ (7.0 equiv) was thus monitored by ^{1}H NMR in benzene-d_6 (at 80 °C),[14] because α-hydrogen elimination should be initiated by coordination of PMe$_3$ to the V. Although no reaction occurred at 25 °C, the reaction did take place at 80 °C;[14] the alkylidene complex (ArN)V(=CHSiMe$_3$)(L)(PMe$_3$) (**6**) could be thus isolated from the chilled *n*-hexane solution[15] and was identified by ^{1}H, ^{13}C, and ^{31}P NMR spectra and elemental analysis. The crystal structure (Figure 2) indicates that **6** has a distorted-tetrahedral geometry around the vanadium metal center, and the V−CHSiMe$_3$ bond distance (1.860 Å) is close to that in the bicyclic carbene−amide complex (1.876 Å)[6b] and is shorter than that in the benzylidene complex (1.922 Å);[6a] the distance is longer than those in neutral V^{III}−CH^{t}Bu (1.809 Å)[4a,b] and cationic V^{IV}−CH^{t}Bu complexes (1.787−1.795 Å).[4c,d] The V−C−Si bond angle is 121.4°, and the V−P bond distance (2.433 Å) is shorter than those in **3** and **4** (2.515−2.646 Å). The ^{1}H and ^{13}C NMR spectra showed resonances corresponding to V=CHSiMe$_3$ at 14.52 and 302.0 ppm, respectively. These results clearly indicate that **6** is a 16-electron vanadium(V) alkylidene complex.

It should be noted that **6** initiated the ROMP of NBE with remarkable catalytic activity, affording high-molecular-weight ring-opened polymer with unimodal molecular weight distributions (run 13, 98% yield, M_n = 1.15 × 10^6, M_w/M_n = 1.6).[16] Note that the activity markedly increased in benzene at higher temperature (80 °C), and the observed activity was higher than that by the known Ru(CHPh)(Cl)$_2$(PCy)$_2$ under the same conditions due to the improved thermal stability at 80 °C (runs 10 and 12 vs run 14). This is the first example that a vanadium alkylidene species catalytically initiates ROMP, and this is also a rare example of a "thermally stable" *olefin metathesis active* transition-metal alkylidene. Various applications such as ROMP, acyclic diene metathesis (ADMET) polymerization, CM, and RCM with **6** can be thus expected, and we are now exploring these possibilities in more detail.

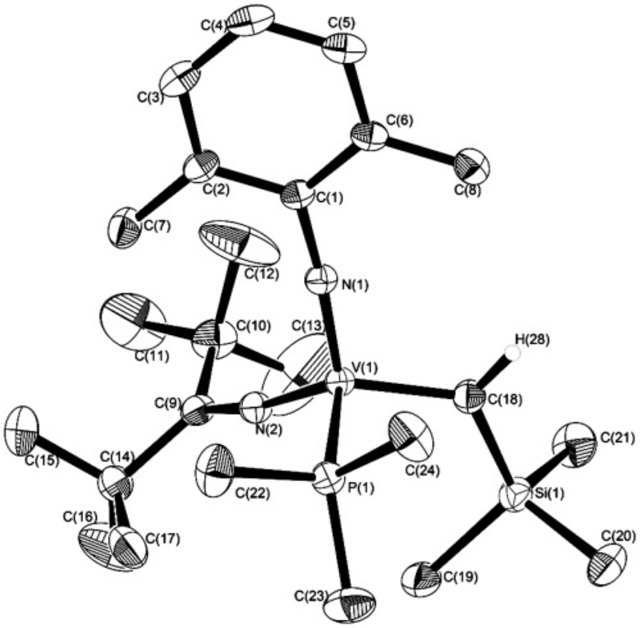

Figure 2. ORTEP drawing for **6**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[11]

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Supporting Information Available: Text and tables giving experimental details, additional polymerization results, and details of the crystal structure determinations for **1a**, **3**, **4**, and **6**; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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

(15) Compound **6**: yield 34%; ^{1}H NMR (C$_6$D$_6$) δ 0.38 (s, 9H, CHSi(CH_3)$_3$), 0.93 (d, 9H, PMe_3), 1.25 (s, 18H, (CH_3)$_3$C−), 2.78 (s, 6H, (CH_3)$_2$), 6.82 (t, 1H), 7.09 (d, 2H), 14.52 (br, 1H, CHSi(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$) δ 2.8, 17.4, 17.7, 20.2, 31.0, 42.4, 121.9, 127.6, 134.5, 161.7, 193.8, 302.0. Anal. Calcd for C$_{24}$H$_{46}$N$_2$PSiV: C, 60.99 (58.68 + VC); H, 9.81; N, 5.93. Found: C, 58.68; H, 9.72; N, 5.73.

(16) Since the molecular weights for resultant poly(NBE)s were higher than those estimated on the basis of NBE/V molar ratios, the catalyst (initiation) efficiency of **6** was not perfect. This is probably because the dissociation of PMe$_3$ is necessary for the formation of catalytically active species, because the observed catalytic activity decreased at higher PMe$_3$/V molar ratio in the ROMP by **5**. A study concerning the actual catalytically active species for the ROMP is now being carried out.