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Reactions of an (Arylimido)vanadium(V)−Alkylidene, $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(N{=}C^tBu_2)(PMe_3)$, with Nitriles, Diphenylacetylene, and Styrene

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Reactions of a vanadium(V)−alkylidene, $(ArN)V(CHSiMe_3)(N{=}C^tBu_2)(PMe_3)$ (**1**, Ar = 2,6-$Me_2C_6H_3$), with various nitriles, diphenylacetylene, and styrene have been explored. Treatment of **1** with RC≡N (R = Me, ^{t}Bu, Ph) afforded a ring-opened bis(imido) complex, $(ArN)V[NC(R){=}CHSiMe_3](N{=}C^tBu_2)(PMe_3)$ [R = Me (**2**), ^{t}Bu (**3**), Ph (**4**)], and the structure of **4** by X-ray crystallography indicates that **4** has a distorted tetrahedral geometry around vanadium. Insertion of the nitrile into **2**−**4** did not occur upon further addition. The reaction of **1** with 1.0 equiv of PhC≡CPh afforded the corresponding metallacyclobutene analogue, $(ArN)V[C(Ph){=}C(Ph)CHSiMe_3)](N{=}C^tBu_2)(PMe_3)$ (**5**). The reaction of **1** with styrene afforded the metallacyclopropane analogue, $(ArN)V(CH_2CHPh)(N{=}C^tBu_2)(PMe_3)$ (**6**), although the reaction with 1,1-diphenylethylene did not take place. The X-ray crystallographic analysis of **6** indicates that the vanadium atom in **6** is pentacoordinated with the arylimido ligands in the apical site of a distorted square pyramid.

Introduction

Transition metal−alkylidene complexes are important intermediates in olefin metathesis [such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), cross-metathesis (CM) reactions, etc.], which introduces promising possibilities for synthesis of both functional polymers and valuable organic compounds,[1] as demonstrated especially by molybdenum[2] and ruthenium.[3] High-oxidation-state early transition metal alkylidene complexes attract considerable attention,[2,4,5] because they play essential roles as catalysts in olefin metathesis and Wittig-type or group transfer reactions,[1,2,4] as demonstrated by molybdenum.[1,2] Although classical Ziegler-type vanadium catalysts displayed unique characteristics in olefin coordination insertion polymerization (notable reactivity toward olefins),[6,7] examples with vanadium−alkylidenes have been limited.[4,8−10] Since no examples had been known until recently concerning synthesis of “olefin metathesis active” vanadium−alkylidene, the synthesis and its reaction chemistry are thus promising subjects in terms of basic understanding in organometallic chemistry as well as application as the catalyst.

We recently focused on the high-oxidation state (arylimido)-vanadium(V) complexes containing anionic donor ligands

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(1) 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.

(2) 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. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1, p 8.

(3) For examples, 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*; GrubbsR. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 3, pp 61−85.

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

(5) For example (pioneering examples in titanium), see: (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (b) The role of the “Tebbe complex” in olefin metathesis: Grubbs, R. H. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1, p 4. (c) Pioneering work concerning the so-called Tebbe reagent (c−e): Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (d) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. (e) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

(6) 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.

(7) For reviews, see: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229. (c) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357. (d) Nomura, K. In *New Developments in Catalysis Research*; Bevy, L. P., Ed.; NOVA Science Publishers: New York, 2005; p 199.

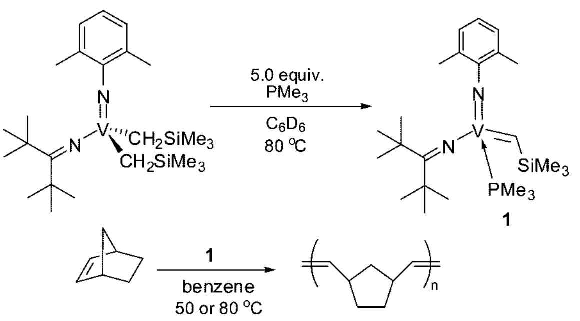
(8) Examples of isolation of terminal vanadium(III),(IV) alkylidenes: (a) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 5977. (b) Hessen, B.; Meetsma, A.; Van Bolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925. (c) Hessen, B.; Buijink, J.-K. F.; Meetsma, A; Teuben, J. H.; Helgesson, G.; Hakansson, M.; Jagner, S; Spek, A. L. *Organometallics* **1993**, *12*, 2268. (d) 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. (e) 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.

(9) Examples of isolation of terminal vanadium(V)−alkylidenes: (a) Buijink, J.-K. F.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922 No reaction between $CpV(CHPh)(NAr)(PMe_3)$ 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.

(10) Examples of related complexes containing vanadium(V)−carbon double bonds:(a) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H. *Organometallics* **1990**, *9*, 1925. (b) Moore, M.; Gambarotta, S.; Yap, G.; Liable-Sands, L. M.; Rheingold, A. L. *Chem. Commun.* **1997**, 643.

10.1021/om800479u CCC: $40.75

Scheme 1



including synthesis and some reactions of the alkyl[11,12] and the alkylidene[9b,12] complexes. We demonstrated that the dichloro complexes, $(ArN)VCl_2(X)$ (X = aryloxo, ketimide, phenoxyimine), exhibited promising characteristics as catalyst precursors for olefin coordination insertion polymerization in the presence of Al cocatalysts.[7d,11c,13] Moreover, we also demonstrated recently that an isolated (arylimido)vanadium(V)−alkylidene, $(ArN)V(CHSiMe_3)(N{=}C^tBu_2)(PMe_3)$ (**1**, Ar = 2,6-$Me_2C_6H_3$), exhibited notable catalytic activity for ring-opening metathesis polymerization (ROMP) of norbornene as the first example with vanadium, and the activity markedly increased at higher temperature (80 °C).[9b] Since, as described above, examples of the terminal vanadium(V)−alkylidenes are scarce,[9,12] in this paper, we thus explored some reactions of the isolated (arylimido)vanadium(V)−alkylidene (**1**) with various nitriles, diphenylacetylene, and certain olefins (styrene, 1,1-diphenylethylene).

Results and Discussion

An (arylimido)vanadium(V)−alkylidene complex, $(ArN)V(CHSiMe_3)(N{=}C^tBu_2)(PMe_3)$ (**1**, Ar = 2,6-$Me_2C_6H_3$), was prepared by α-H abstraction from $(ArN)V(CH_2SiMe_3)_2(N{=}C^tBu_2)$ upon heating in C_6D_6 in the presence of PMe_3 (Scheme 1).[9b] This is the common method to prepare high-oxidation-state metal alkylidenes by promoting α-hydrogen abstraction reactions from metal alkyl complexes lacking *β*-hydrogens, and addition of PMe_3 was required to promote the abstraction by steric crowding.[4] The analytically pure complex **1** was isolated by recrystallization from the chilled *n*-hexane solution (−30 °C). A resonance ascribed to the α-proton ($V{=}C\mathit{H}SiMe_3$) was appeared at 14.5 ppm (broad),[14] and the resonance ascribed to the α-carbon ($V{=}\mathit{C}HSiMe_3$) was observed at 302.0 ppm (broad).[9b,14] These results thus indicate that **1** is a nucleophilic carbene (alkylidene) of the general type.[4]

Two resonances were seen in the ^{51}V NMR spectra,[14] although only one resonance ascribed to the alkylidene proton/carbon was observed in the $^1H/^{13}C$ NMR spectrum. Two possibilities, (i) partial dissociation of PMe_3 (as observed in the alkylidene recently reported)[12] or (ii) a mixture of isomers (*syn*/*anti* isomers, as seen in the molybdenum−alkylidene complexes),[2,4b] are considered for the explanation.[15] Although PMe_3 coordinated to the vanadium metal center in the aryloxo-alkylidene $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}^iPr_2C_6H_3)$, dissociates partially in the solution,[12] the possibility of the presence of two (*syn*/*anti*) isomers is preferably considered in this case.[14,15] This is not only because the PMe_3-coordinated species (**1**, should be major) should have been observed in higher field than the dissociated one by electron donation with PMe_3[9b,12,15] but also because addition of (2 or 5 equiv of) PMe_3 into the C_6D_6 solution containing **1** afforded formation of several species observed in the ^{51}V NMR spectra (probably formation of two PMe_3-coordinated species).[15] This may also correspond to the observed fact in the reactions with CH_3CN and $PhC{\equiv}CPh$, as described below.

Complex **1** exhibited remarkable catalytic activity for ring-opening metathesis polymerization of norbornene without cocatalyst (Table 1).[9b] The catalytic activity (turnover number, TON) was low when the ROMP was conducted at 25 °C (runs 1, 2), whereas a standard Schrock-type initiator, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(O^tBu)_2$ (**Mo**), exhibited especially remarkable catalytic activity under similar conditions (run 4).[9b,16] The activity of **1** increased at 50 °C, whereas the activity of **Mo** was negligible due to the decomposition of the catalytically active species (runs 5−8). The activities of **1** in benzene were higher than those in toluene. Note that the activity markedly increased at the higher temperature of 80 °C, and the observed activity was higher than that by known $Ru(CHPh)(Cl)_2(PCy)_2$

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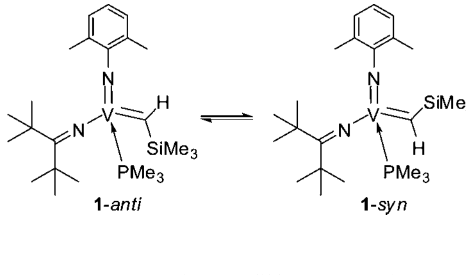
[11] (a) Yamada, J.; Nomura, K. *Organometallics* **2005**, *24*, 3621. (b) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2007**, *26*, 2579. (c) Onishi, Y.; Katao, S.; Fujiki, M.; Nomura, K. *Organometallics* **2008**, *27*, 2590.

[12] Nomura, K.; Onishi, Y.; Fujiki, M.; Yamada, J. *Organometallics* **2008**, *27*, 3818. These results were partly presented at *the XVIIth International symposium on olefin metathesis (ISOMXVII)*, July2007, Pasadena, CA.

[13] (a) Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, *35*, 1583. (b) Wang, W.; Yamada, J.; Fujiki, M.; Nomura, K. *Catal. Commun.* **2003**, *4*, 159. (c) Wang, W.; Nomura, K. *Macromolecules* **2005**, *38*, 5905. (d) Wang, W.; Nomura, K. *Adv. Synth. Catal.* **2006**, *348*, 743.

[14] The NMR spectra for **1** and the spectra monitoring the reaction of **1** with RCN (and with styrene) are shown in the Supporting Information.

[15] Two possibilities, (i) partial dissociation of PMe_3 (as observed in the alkylidene recently reported)[12] and (ii) a mixture of isomers (*syn*/*anti* isomers, as seen in the molybdenum−alkylidene complexes),[2,4b] have to be considered for explanation for the two resonances in the ^{51}V NMR spectra of **1**. PMe_3 in the aryloxo-alkylidene $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}^iPr_2C_6H_3)(PMe_3)$ dissociated partially, confirmed by both the elemental analysis and the NMR spectra,[12] and the ^1H NMR spectrum of **1** (in C_6D_6) showed only one broad resonance ascribed to the alkylidene proton and only one broad resonance ascribed to the alkylidene was observed in the ^{13}C NMR spectrum (and one broad resonance was seen in the ^{31}P NMR spectrum).[14] The latter possibility (the presence of isomers, shown below in eq a) should be, however, positively considered, not only because the PMe_3-dissociated species (should be minor) should have been observed in lower field than the coordinated one (**1**)[9b,12] but also because addition of PMe_3 into the C_6D_6 solution containing **1** gave the other species (probably formation of two PMe_3-coordinated species). The fact that the reactions of the alkylidene **1** with diphenylacetylene (or with CH_3CN) gave a mixture of two isomers would also support the latter possibility. Moreover, the fact that the resultant polymers in the ring-opening metathesis polymerization (ROMP) of norbornene possessed *cis*/*trans* olefinic double bonds[9b] may also suggest the latter possibility. K.N. would like to thank a reviewer for pointing out this issue. PMe_3 in **1** would be in fact partially dissociated in the solution, as seen in the aryloxo-alkylidene,[12] and this fact might suggest the former possibility, but the degree in **1** would probably be too low (according to the elemental analysis). These issues including full explanation of the observed facts should be solved in our future publications. NMR spectra of **1** for the full identification and the spectra upon addition of PMe_3 are shown in the Supporting Information.



(1)

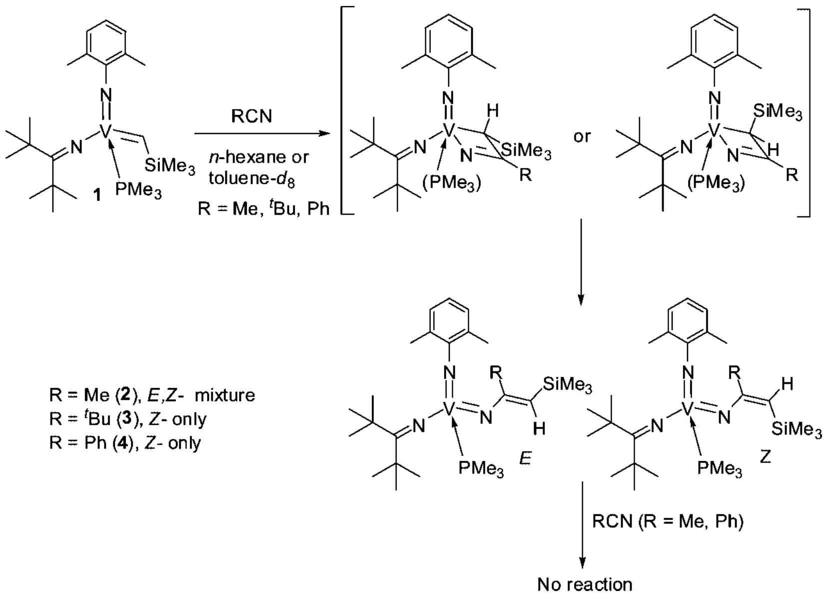
[16] Nomura, K.; Atsumi, T.; Fujiki, M.; Yamada, J. *J. Mol. Catal. A* **2007**, *275*, 1.

Table 1. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE) by $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(N{=}C^tBu_2)(PMe_3)$ (1), $Ru(CHPh)Cl_2(PCy_3)_2$ (Ru, Cy = cyclohexyl), and $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(O^tBu)_2$ (Mo)[a]

run	complex (μmol)	solvent	NBE/mmol	NBE conc[b]	temp/°C	time/min	TON[c]	M_w[d] × 10^{-4}	M_w/M_n[d]
1[e]	**1** (1.0)	benzene	2.12	0.22	25	360	267	46	2.3
2	**1** (1.0)	toluene	1.06	0.44	25	360	82		
3[e]	**Ru** (1.0)	toluene	2.12	0.22	25	60	1306	54	1.7
4[f]	**Mo** (0.20)	toluene	2.12	0.44	25	60	8550	160	1.2
5[e]	**1** (1.0)	benzene	2.12	0.22	50	180	1275	49	1.6
6[e]	**1** (1.0)	toluene	2.12	0.22	50	180	166		
7	**1** (1.0)	toluene	2.12	0.22	50	360	320		
8[f]	**Mo** (0.20)	toluene	2.12	0.44	50	40	trace		
9[e]	**1** (1.0)	benzene	2.12	0.22	80	30	967	140	1.3
10[e]	**1** (1.0)	benzene	2.12	0.22	80	60	1583	133	1.4
11[e]	**1** (1.0)	benzene	2.12	0.22	80	120	2071[g]	115	1.6
12	**1** (1.0)	toluene	2.12	0.22	80	60	1244	32	2.8
13	**1** (1.0)	toluene	2.12	0.22	80	120	1446	33	2.5
14[e]	**Ru** (1.0)	toluene	2.12	0.22	80	60	350		

[a] Conditions: catalyst 0.2 or 1.0 μmol, NBE 1.06 or 2.12 mmol, benzene or toluene 9.6 mL (run 2 2.4 mL, runs 4,8 4.8 mL). [b] Initial NBE conc. in mmol/mL, [c] TON = NBE consumed (mmol)/V (mmol). [d] GPC data vs polystyrene standards. [e] Cited from reference.[9b] [f] Cited from ref 16. [g] Yield 98%.

Scheme 2



under the same conditions due to the improved thermal stability (runs 9−14).[9b]

1. Reactions of $(ArN)V(CHSiMe_3)(N{=}C^tBu_2)(PMe_3)$ (1) with RCN. It is known that $CpV(CHCMe_3)(dmpe)$ [dmpe = 1,2-bis(dimethylphosphino)ethane] slowly reacts with ^{t}BuCN at 60 °C to afford the vinylimido analogue $CpV[NC(CMe_3){=}CHCMe_3](dmpe)$ (65% conversion after 16 h).[8c] It is also known that Ta(V)−alkylidenes, [Ta=CHR′] (R′ = CMe_3 or Ph), react with nitriles, RCN (R = CH_3, ^{t}Bu, or Ph), to afford the vinylimido complexes with a mixture of *E*- and *Z*-isomers formed by insertion of RCN into the Ta=CHCR′ bond.[2a,17] Moreover, the reactions of [Ti=CHR′] fragments (R′ = H, ^{t}Bu) with ^{t}BuCN[18a] or $(2,4,6\text{-}Me_3C_6H_2)CH_2CN$[18b] afforded the vinylimido complexes, and the subsequent reaction with an additional ^{t}BuCN (or reaction with 2 equiv of PhCN) gave the diazatitanacyclohexadiene complex.[18a,c] These reactions were assumed to proceed via formation of a putative azametallacyclobutene intermediate and the subsequent cross-metathesis. We thus explored the reactivity of our vanadium(V)−alkylidene $(ArN)V(CHSiMe_3)(N{=}C^tBu_2)(PMe_3)$ (**1**), including isolation of the reaction product with various nitriles.

Treatment of **1** with CH_3CN, ^{t}BuCN, and PhCN in *n*-hexane or in toluene-d_8 cleanly afforded the corresponding vinylimido complexes $(ArN)V[NC(R){=}CHSiMe_3](N{=}C^tBu_2)(PMe_3)$ [R = Me (**2**), ^{t}Bu (**3**), Ph (**4**)], and the isolated complexes were identified by ^{1}H, ^{13}C, and ^{51}V NMR spectra and elemental analysis (Scheme 2). The structure for **4** (including confirmation that **4** is not the azametallacyclobutene but the vinylimido analogue) was determined by X-ray crystallography (Figure 1). The reaction of **1** with ^{t}BuCN cleanly took place, and rapid, exclusive formation of **3** was observed (by ^{1}H NMR spectra in C_6D_6) even by simply mixing at 25 °C.[14] The analytically pure **3** was isolated from a chilled *n*-hexane solution (−30 °C).

The reaction of **1** with 1.0 equiv of PhCN also took place similarly, affording the vinylimido analogue **4** exclusively as monitored by ^{1}H NMR spectrum, and further addition of PhCN (2 equiv to V) did not give the diazavanadacyclohexadiene complex,[14] which was obtained in the reaction with the

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(17) Selected examples for reaction with nitriles (Ta): (a) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370. (b) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3220. (c) Mashima, K.; Yonekura, H.; Yamagata, T.; Tani, K. *Organometallics* **2003**, *22*, 3766–3772.

(18) Selected examples for reaction with nitriles (Ti): (a) Doxsee, K. M.; Farahi, J. B.; Hope, H. *J. Am. Chem. Soc.* **1991**, *113*, 8889. (b) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 1886. (c) van der Heiden, H.; Hessen, B. *Inorg. Chim. Acta* **2003**, *345*, 27.

(19) Detailed analysis parameters including CIF files are shown in the Supporting Information.

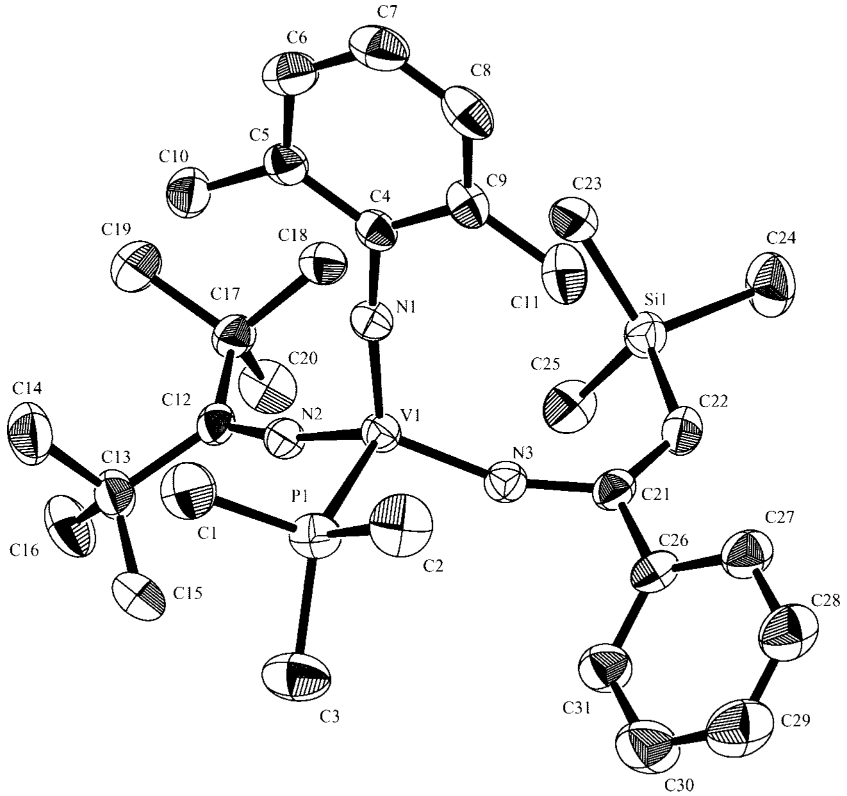


Figure 1. ORTEP drawings of $V(N\text{-}2,6\text{-}Me_2C_6H_3)[NC(Ph){=}CHSiMe_3](N{=}C^tBu_2)(PMe_3)$ (**4**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[19]

titanium−alkylidene.[18a,c] The vinylimido complex **4** was thus isolated from the reaction mixture. The reaction took place rapidly even if PMe_3 (1 equiv to V) was added in the reaction mixture before adding PhCN, and the reaction product **4** was observed exclusively by adding PhCN (1 or 2 equiv to V) into the NMR tube of a C_6D_6 solution containing **1** and PMe_3.[14] The results thus suggest that dissociation of PMe_3 may not be required for formation of the proposed azametallacyclobutene intermediate (shown in Scheme 2), which means that we are not sure whether the reaction proceeded via a dissociative (dissociation of PMe_3 and then coordination of PhCN) or an associative (coordination of both PMe_3 and PhCN) pathway. The reaction of **1** with 2.0 equiv of CH_3CN also afforded the vinylimido complex **2** as the sole isolated product. Only one resonance ascribed to the olefinic proton ($=CHSiMe_3$) was seen (at 4.86 ppm in **3** and 5.09 ppm in **4**) in the ^1H NMR spectra of **3** and **4**, whereas two peaks were seen in that of **2**, probably because complex **2** is a mixture of *E*- and *Z*-isomers because of the lesser steric bulk of CH_3CN compared to ^{t}BuCN and PhCN.

Table 2. Selected Bond Distances and Angles for $V(N\text{-}2,6\text{-}Me_2C_6H_3)[NC(Ph){=}CHSiMe_3](N{=}C^tBu_2)(PMe_3)$ (4)[a]

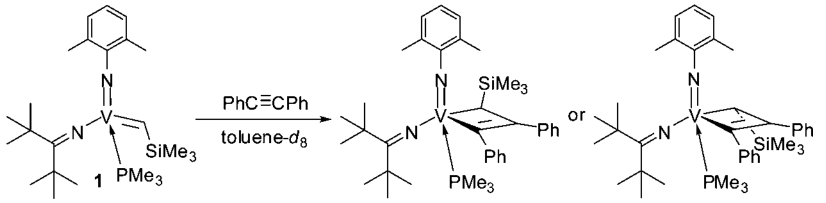
Bond Distances (Å)			
V(1)−P(1)	2.4204(11)	N(3)−C(21)	1.382(3)
V(1)−N(1)	1.693(2)	C(21)−C(22)	1.356(5)
V(1)−N(2)	1.844(2)	N(2)−C(12)	1.271(3)
V(1)−N(3)	1.721(2)	N(1)−C(4)	1.390(3)
Bond Angles (deg)			
P(1)−V(1)−N(1)	91.03(9)	N(2)−V(1)−N(3)	118.36(9)
P(1)−V(1)−N(2)	108.87(9)	V(1)−N(2)−C(12)	169.2(2)
P(1)−V(1)−N(3)	103.97(8)	V(1)−N(3)−C(21)	157.9(2)
N(1)−V(1)−N(2)	112.94(8)	N(3)−C(21)−C(26)	115.9(2)
N(1)−V(1)−N(3)	117.05(11)	N(3)−C(21)−C(22)	123.4(2)
V(1)−N(1)−C(4)	173.5(2)	Si(1)−C(22)−C(21)	126.1(2)

[a] Detailed analysis conditions, see the Supporting Information.[19]

Selected bond distances and angles for **4** are summarized in Table 2. The X-ray crystallographic analysis of **4** shows that **4** has a distorted tetrahedral geometry around vanadium,[19] and the structure also indicates the *Z* stereochemistry of the C=C bond. The V−N(vinylimido) bond distance [V(1)−N(3) 1.721(2) Å] is somewhat longer than that in the V−N(arylimido) [V(1)−N(1) 1.693(2) Å] but shorter than that in V−N(ketimide) [V(1)−N(2) 1.844(2) Å]. The difference in the bond distances between the vinylimido and the arylimido ligands is also influenced by their bond angles [V(1)−N(1)−C(4) 173.5(2)° vs V(1)−N(3)−C(21) 157.9(2)°]. The V−N(vinylimido) bond distance [1.721(2) Å] is longer than that in $CpV[NC(CMe_3){=}CHCMe_3](dmpe)$ [1.707(2) Å],[8c] and the value is apparently shorter than that in $Cp^*Ta[NC(^tBu){=}CHPh](\eta^4\text{-}supine\text{-}2,3\text{-}dimethyl\text{-}1,3\text{-}butadiene)$ [1.824(3) Å].[17c] The C(21)−C(22) distance [olefinic double bond, 1.356(3) Å] is close to that in $CpV[NC(CMe_3){=}CHCMe_3](dmpe)$ [1.353(4) Å].[8c] The V−P bond distance [V(1)−P(1) 2.4204(11) Å] is shorter than those in **1** [2.4331(7) Å] and in $V(NAr)Cl_2(N{=}C^tBu_2)(PMe_3)$ [2.527(2) Å],[9b] clearly suggesting that PMe_3 strongly coordinates to V. In contrast, the V−N(ketimide) distance [1.844(2) Å] is close to those in **1** [1.847(2) Å] and $(ArN)VCl_2(N{=}C^tBu_2)(PMe_3)$ [1.839(4) Å].[9b]

2. Reactions of $(ArN)V(CHSiMe_3)(N{=}C^tBu_2)(PMe_3)$ (1) with Diphenylacetylene. It is known that $CpTaCl_2(CHCMe_3)$ reacts with PhC≡CPh to afford another alkylidene, $CpTaCl_2[C(Ph)C(Ph){=}CHCMe_3]$,[4a,17b] and that $Ta(CHCMe_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3(THF)$ reacts with PhC≡CPh to afford THF-free metallacyclobutene, and the ring-opening reaction was induced upon addition of pyridine to afford the vinylalkylidene complex.[20] Living polymerization of 1-butyne was thus initiated by the vinylalkylidene complex in the presence of pyridine.[20] It is also known that $[Cp_2Ti{=}CH_2]$ reacts with substituted acetylenes to form titanacylobutenes.[21] We thus explored reaction of the

Scheme 3



5 (isolated yield 28.5 %)

vanadium–alkylidene **1** with PhC≡CPh including isolation of the reaction product.

Treatment of **1** with 1 equiv of PhC≡CPh in toluene-d_8 afforded the corresponding vanadacylobutene (ArN)V[C(Ph)=C(Ph)CHSiMe$_3$)](N=C^{t}Bu$_2$)(PMe$_3$) (**5**, Scheme 3), and the analytically pure **5** could be isolated by recrystallization from a chilled *n*-hexane solution (−30 °C). The resultant complex (**5**) was identified based on ^{1}H, ^{13}C, and ^{51}V NMR spectra and by elemental analysis. The ^{51}V NMR spectrum showed two resonances at −321.3 and −358.8 ppm, and the ^{1}H NMR spectrum also showed two resonances assigned to H$_\alpha$ (3.35, 3.34, =C*H*-SiMe$_3$), Ar-CH$_3$ (2.63, 2.50), PMe$_3$ (0.90, 0.64), and SiMe$_3$ (0.41, 0.21). A similar trend was observed in the ^{13}C NMR spectrum (188.8, 185.7, 144.6, 143.9, 89.5), and these results are similar to those in Ta[C(Ph)C(Ph)CH(CMe$_3$)](O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_3$.[20] The possibility of formation of the vinylalkylidene species [V=C(Ph)=C(Ph)CHSiMe$_3$] is rejected because no corresponding resonances ascribed to the alkylidene were seen.[17b] The results thus suggest that the resultant complex **5** is a mixture of two isomers (as shown in Scheme 3), probably formed via insertion of PhC≡CPh into *syn* or *anti* isomers (the arylimido and the alkylidene).

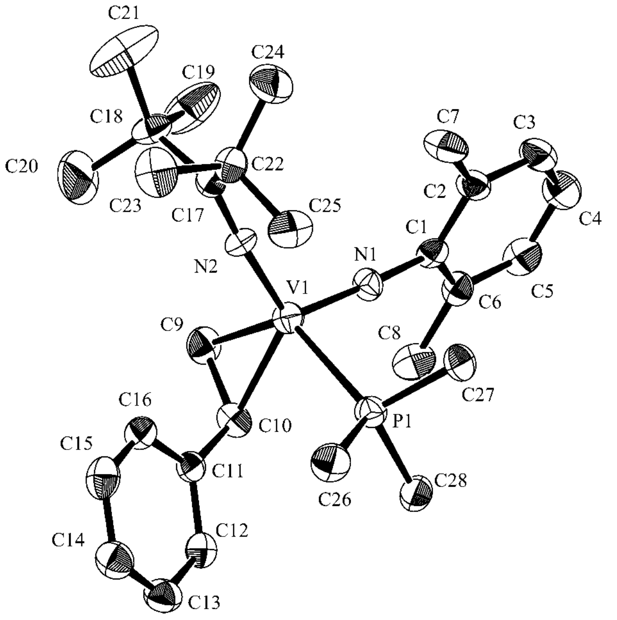


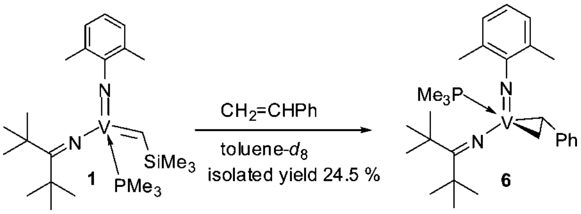
Figure 2. ORTEP drawings of V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$-CHPh)(N=C^{t}Bu$_2$)(PMe$_3$) (**6**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[19]

Table 3. Selected Bond Distances and Angles for V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$CHPh)(N=C^{t}Bu$_2$)(PMe$_3$) (6)^a

	Bond Distances (Å)		
V(1)−P(1)	2.4483(19)	C(9)−C(10)	1.422(8)
V(1)−N(1)	1.670(5)	C(10)−C(11)	1.465(10)
V(1)−N(2)	1.825(4)	C(11)−C(12)	1.403(9)
V(1)−C(9)	2.070(5)	C(11)−C(16)	1.390(10)
V(1)−C(10)	2.165(5)	N(2)−C(17)	1.262(7)
N(1)−C(1)	1.376(8)	C(2)−C(7)	1.500(9)
	Bond Angles (deg)		
N(1)−V(1)−P(1)	91.93(15)	N(1)−V(1)−C(9)	104.9(2)
N(1)−V(1)−N(2)	113.8(2)	N(1)−V(1)−C(10)	111.2(9)
N(2)−V(1)−P(1)	112.57(15)	N(2)−V(1)−C(9)	105.5(2)
N(2)−V(1)−C(10)	129.1(2)	P(1)−V(1)−C(9)	127.28(16)
P(1)−V(1)−C(10)	88.14(17)	V(1)−N(1)−C(1)	177.3(3)
V(1)−N(2)−C(17)	171.2(4)	C(9)−V(1)−C(10)	39.1(2)
V(1)−C(9)−C(10)	74.1(3)	V(1)−C(10)−C(9)	66.8(2)
V(1)−C(10)−C(11)	107.8(3)	C(9)−C(10)−C(11)	121.2(5)

[a] Detailed analysis conditions, see the Supporting Information.[19]

Scheme 4



3. Reactions with Styrene and 1,1-Diphenylethylene. The vanadium(V)−alkylidene **1** readily reacted with 1 equiv of styrene in d_8-toluene (at −30 to 25 C, 2 h), and the ^{51}V NMR spectrum showed two resonances.[14] The major product appeared at 180.3 ppm and was isolated in a pure form by recrystallization from a chilled *n*-hexane solution (−30 °C), and the complex was identified as a metallacyclopropane complex, (ArN)V-(CH$_2$CHPh)(N=C^{t}Bu$_2$) (**6**), based on ^{1}H, ^{13}C, and ^{51}V NMR spectra and elemental analysis. Three multiplet resonances at 4.14, 3.06, and 2.08 ppm were observed in the ^{1}H NMR spectrum, which can be ascribed to the three ring-protons of the metallacyclopropane. The metallacycle structure of **6** was eventually determined by X-ray crystallography (Figure 2), as described below. However, reactions of **1** with 1,1-diphenylethylene recovered the alkylidene **1** in high yields under the same conditions.[14] The reaction did not take place, even if the reaction continued overnight (24 h).[14]

Selected bond lengths and angles for **6** are summarized in Table 3.[19] The X-ray crystallographic analysis of **6** shows that the vanadium atom in **6** is pentacoordinated with the arylimido ligands in the apical site of a distorted square pyramid,[19] as exemplified by N(2)−V(1)−P(1) [112.57(15)°], N(2)−V(1)−C(9) [105.5(2)°], P(1)−V(1)−C(10) [88.14(17)°], and C(9)−V(1)−C(10) [39.1(2)] bond angles (total 345.31°). The V−N(imido)−C(phenyl) bond angle is 177.3(3)°, and the V−N(1) distance [1.670(5) Å] is somewhat shorter than those in the vinylimido complex [**4**, 1.693(2) Å] and the alkylidene [**1**, 1.679(2) Å], but is longer than those in (ArN)VCl$_2$(N=C^{t}Bu$_2$) [1.660(2) Å] and (ArN)VCl$_2$(N=C^{t}Bu$_2$)(PMe$_3$) [1.652(3) Å].[9b] The V(1)−C(10) bond distance [2.165(5) Å] is shorter than that in V(1)−C(9)

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(20) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.

(21) (a) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491. (b) Petasis, N. A.; Fu, D.-K. *Organometallics* **1993**, *12*, 3776.

[2.070(5) Å], and the V(1)−C(10)−C(9) bond angle [66.8(2)°] is smaller than that in V(1)−C(9)−C(10) [74.1(3)°]; this is probably due to an influence by the phenyl substituent in **6**. These bond distances are somewhat longer than that of V−Me in $V(NAr)(Me)(N{=}C^tBu)_2$ [2.064(2) Å].[11a] The V−P distance [2.4483(19) Å] is longer than those in the vinylimido complex [**4**, 2.4204(11) Å] and the alkylidene [**1**, 2.4331(7) Å] but shorter than that in $(ArN)VCl_2(N{=}C^tBu_2)(PMe_3)$ [2.527(2) Å].[9b]

It has been known that $Cp_2Ta(CH_2)(CH_3)$ decomposed via bimolecular bridged methylidene intermediate $[Cp_2Ta(CH_3)]_2(\mu_2\text{-}CH_2)_2$ in the presence of PMe_3 to afford a metallacyclopropane, $Cp_2Ta(CH_2CH_2)(CH_3)$, and $Cp_2Ta(CH_3)(PMe_3)$.[4a,22] Another metallacyclopropane complex, $W(NPh)(CH_2CH_2)[o\text{-}(Me_3SiN)_2\text{-}C_6H_4](PMe_3)_2$, was also formed from the (arylimido)tungsten dialkyl complex $W(NPh)(CH_2CH_3)_2[o\text{-}(Me_3SiN)_2C_6H_4]$ in the presence of PMe_3.[23] These reactions were postulated to proceed via dimeric intermediate such as $[Cp_2Ta(CH_3)]_2$, which was formed by loss of ethylene from the dimeric methylidene intermediate $[Cp_2Ta(CH_3)]_2(\mu_2\text{-}CH_2)_2$.[22,23] Moreover, it is also reported that (arylimido)tungsten dimer $[W(NAr)\{OCMe_2\text{-}(CF_3)\}]_2$ inserted ethylene to give a $[W(NAr)\{OCMe_2\text{-}(CF_3)\}]_2(CH_2CH_2)$ that contains a slightly bent ditungstenacyclobutane ring.[23] Although we have, however, no clear results concerning mechanistic details at this moment, we thus assume that the vanadacyclopropane **6** may be formed via a certain dimeric intermediate (as a scheme generating **6** from **1** with 1 equiv of styrene).[24] These decompositions (formation of the dimeric species) should be dependent upon the nature of the metal−alkylidene species including the electronic and steric nature of ligands employed,[25] and the results here are noteworthy in terms of designing efficient catalysts with vanadium.

Two vanadium carbon bond distances in the metallacyclopropane analogue **6** [V(1)−C(9), V(1)−C(10): 2.070(5), 2.165(5) Å, respectively] are shorter than those in $W(NPh)(CH_2CH_2)[o\text{-}(Me_3SiN)_2C_6H_4](PMe_3)_2$ [2.223(5), 2.234(5) Å][23] and are close to or somewhat shorter than those in $Mo(NAr')(Biphen)(ethylene)(Et_2O)$ [2.204(9), 2.128(9) Å] formed from $Mo(NAr')(CHCMe_2Ph)(Biphen)$ by treating with 2 equiv of ethylene via β-H elimination.[24] The C(9)−C(10) bond distance [1.422(8) Å] is shorter than that in $W(NPh)(CH_2CH_2)[o\text{-}(Me_3SiN)_2C_6H_4](PMe_3)_2$ [1.434(6) Å],[23] but longer than that in $Mo(NAr')(Biphen)(ethylene)(Et_2O)$ [1.400(13) Å]. These results thus suggest that styrene coordinates to vanadium in a η^2 fashion. Since the resultant complex is diamagnetic and the vanadium atom in **6** is pentacoordinated with the arylimido ligands in the apical site of a distorted square pyramid, confirmed by X-ray crystallography, the oxidation state of **6** is considered to be vanadium(V) (d^0, two vanadium−carbon σ-bonds with styrene) rather than vanadium(III) (d^2, π-bonding, η^2 fashion with styrene). Although $Mo(NAr')(Biphen)(ethylene)(Et_2O)$ initiated ROMP without a cocatalyst,[25a] **6** did not show catalytic activity under certain conditions.[26]

Concluding Remarks

Reactions of $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CHSiMe_3)(N{=}C^tBu_2)(PMe_3)$ (**1**) with nitriles (RC≡N, R = CH_3, ^{t}Bu, Ph), diphenylacetylene, and styrene have been explored. The vinylimido complexes $(ArN)V[NC(R){=}CHSiMe_3](N{=}C^tBu_2)(PMe_3)$ [R = Me (**2**), ^{t}Bu (**3**), Ph (**4**)] were formed exclusively by treating **1** with RC≡N, and these reactions proceeded via an azametalacyclobutene intermediate and subsequent cross-metathesis. However, insertions of nitriles into **2**−**4** did not occur upon further addition. The reaction of **1** with PhC≡CPh afforded vanadacylobutene **5** exclusively as a mixture of isomers. A metallacyclopropane analogue, $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2CHPh)(N{=}C^tBu_2)$ (**6**), was formed by reaction of **1** with styrene, and the structure was determined by X-ray crystallography. However, the reaction of **1** with 1,1-diphenylethylene did not take place, and **6** did not initiated ROMP of norbornene, as reported in $Mo(NAr')(Biphen)(ethylene)(Et_2O)$. The present vanadium(V)−alkylidene **1** initiates ROMP of norbornene without cocatalyst (as the first example with vanadium), and promising reactivities toward unsaturated compounds were observed. Therefore, we believe that the results presented here should be important information for better understanding of the vanadium(V)−alkylidene chemistry as well as for designing more efficient vanadium catalysts for both olefin metathesis and the other organic transformations through the vanadium−alkylidene.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were of reagent grade and were purified by standard purification procedures. Anhydrous grade benzene, toluene, diethyl ether, and *n*-hexane (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 a drybox under N_2 and were passed through a short alumina column under N_2 stream before use. The starting (arylimido)vanadium(V)−alkylidene, $V(CHSiMe_3)(N\text{-}2,6\text{-}C_6H_3)(N{=}C^tBu_2)(PMe_3)$ (**1**), was prepared according to a published procedure, as described below.[9b] Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.), and some analytical runs were performed twice to confirm the reproducibility in the independent analysis/synthesis runs. All ^1H, ^{13}C, and ^{51}V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^1H, 100.40 MHz for ^{13}C, 105.31 MHz for ^{51}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 $SiMe_4$ (δ 0.00, ^1H, ^{13}C) and $VOCl_3$ (δ 0.00, ^{51}V). Coupling constants and half-width values, $\Delta\nu_{1/2}$, are given in Hz.

Synthesis of $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)(PMe_3)$ (1).[9b] A C_6D_6 solution (60 mL) containing $(ArN)V(CH_2SiMe_3)_2\text{-}(N{=}C^tBu_2)$ (3.15 g, 6.50 mmol) and PMe_3 (3.46 g, 45.5 mmol) was allowed to warm at 80 °C. The mixture was stirred for 40 h, and the solution was filtered through a Celite pad. The filtrate was concentrated *in vacuo*, and the resultant tan residue was dissolved in a minimum amount of *n*-hexane. The concentrated solution was

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(22) Bimolecular decomposition of $Cp_2Ta(CH_2)(CH_3)$ in the presence of PMe_3 afforded $Cp_2Ta(V)(CH_2CH_2)(CH_3)$ and $Cp_2Ta(CH_3)(PMe_3)$: (a) Schrock, R. R *J. Am. Chem. Soc.* **1975**, *97*, 6577. (b) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(23) Wang, S. S.; Vander-Lende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1998**, *17*, 2628.

(24) Formation of Mo(NAr′)(Biphen)(ethylene) complex from $Mo(NAr')(CHCMe_2Ph)(Biphen)$ by reacting with 2 equiv of ethylene via β-H elimination: (a) Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. L.; Hultzsch, K. C.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2004**, *23*, 1997. In our case, we would be able to eliminate this possibility [a route via formation of vanadium(III) and subsequent addition of styrene], because the observed reaction product by ^{51}V NMR spectrum[14] from the reaction of **1** with 1 equiv of styrene was **6** exclusively. The related reaction in $CpTi(CHMe_3)[PMe_2\text{-}CH_2C(O)\text{-}CMe_2\text{-}o\text{-}C_6H_4CMe_2]$ (The titanium−alkylidene reacts with ethylene, initially forming a metallacycle, while subsequent reactions produce a stable ethylene complex). (b) van Doorn, J. A.; van der Heijden, H. *Organometallics* **1995**, *14*, 1278.

(25) (a) Schrock, R. R.; Lopez, L. P. H.; Hafer, J.; Singh, R.; Sinha, A.; Müller, P. *Organometallics* **2005**, *24*, 5211. (b) Lopez, L. P. H.; Schrock, R. R.; Müller, P. *Organometallics* **2006**, *25*, 1978.

(26) Negligible amount of polymer was collected when a toluene solution (5 mL) containing complex **6** (5 mg, 10 μmol) and norbornene 200 mg (2.1 mmol) was heated at 80 °C for 1 h.

placed in the freezer at −30 °C, yielding 1.05 g (2.22 mmol, 34%) of red prism-shape microcrystals that were suitable for crystal structure analysis. The reason for the low yield may be due to the difficulty in isolating as the microcrystals (because of high solubility in *n*-hexane), because the ^{1}H NMR spectrum for the reaction mixture showed formation of **1** exclusively. ^{1}H NMR (C_6D_6): δ 0.38 (s, 9H, $CHSi(CH_3)_3$), 0.93 (d, 9H, PMe_3), 1.25 (s, 18H, $(CH_3)_3C-$), 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 ($SiMe_3$), 17.4, 17.7, 20.2, 31.0, 42.4, 121.9, 127.6, 134.5, 161.7, 193.8, 302.0. ^{31}P NMR (C_6D_6): δ −10−20 (broad). ^{51}V NMR (C_6D_6): δ −27, 80. Anal. Calcd for $C_{24}H_{46}N_2PSiV$: C, 60.99 (58.68 + VC, vanadium carbide); H, 9.81; N, 5.93. Found: C, 58.68; H, 9.72; N, 5.73.

Preparation of V(N-2,6-Me$_2$C$_6$H$_3$)[NC(Me)=CHSiMe$_3$](N=C^{t}Bu$_2$)(PMe$_3$) (2). Into a toluene-d_8 (3 mL) solution containing **1** (318 mg, 0.67 mmol) was added at −30 °C 2 equiv of CH_3CN (55 mg, 1.34 mmol). The mixture was warmed slowly to room temperature and was stirred for 24 h. The solution was then filtrated through a Celite pad, and the filter cake was washed adequately with *n*-hexane. The combined filtrate and the wash were placed in a rotary evaporator to remove *n*-hexane and toluene *in vacuo*. The resultant solid was then dissolved in a minimum amount of *n*-hexane and was placed in the freezer (−30 °C). Analytically pure **2** (100 mg, 0.19 mmol) was collected from the chilled solution as dark brown microcrystals. Yield: 28.9% (mixture of isomers, *E*- and *Z*-). ^{1}H NMR (C_6D_6): δ 7.07 (d, 2H, $J = 7.32$, Ar-*H*), 6.79 (t, 1 H, $J = 6.60$, Ar-*H*), 4.77 and 4.46 (s, 1H, $VCHSiMe_3$), 2.74 and 2.70 (s, 6H, Ar-CH_3), 2.40 and 2.15 (s, 3H, $NCCH_3$), 1.30−1.24 (m, 18H, $J = 2.92$, $C(CH_3)_3$), 0.96 (d, 9H, $J = 8.8$, PMe_3-*H*), 0.41 + 0.31 (s, 9H, $Si(CH_3)_3$). ^{51}V NMR (C_6D_6): −484.9, −537.4. ^{13}C NMR (C_6D_6): 133.5, 125.1, 122.2, 122.0, 121.5, 103.2, 102.5, 42.1, 41.4, 31.2, 31.1, 30.9, 30.7, 24.3, 19.9, 19.6, 16.0, 15.8, 15.6, 1.4, 1.03, 0.96. The imido carbon, ketimide carbon, and =N-*C*(Me)= resonances were not observed probably due to their low intensities. Anal. Calcd for $C_{26}H_{49}N_3SiVP$: C, 60.79; H, 9.61; N, 8.18. Found: C, 60.93; H, 9.62; N, 7.86.

Preparation of V(N-2,6-Me$_2$C$_6$H$_3$)[NC(^{t}Bu)=CHSiMe$_3$](N=C^{t}Bu$_2$)(PMe$_3$) (3). Into a *n*-hexane solution (5 mL) containing **1** (236 mg, 0.50 mmol) was added at room temperature ^{t}BuCN (50 mg, 0.50 mmol). After the mixture was stirred for 6 h, the solution was placed in the freezer (−30 °C). The brown microcrystals were collected from the chilled solution. Yield: 224 mg (81%). ^{1}H NMR (C_6D_6): δ 7.07 (d, 2H, $J = 7.32$, Ar-*H*), 6.80 (t, 1H, $J = 7.32$, Ar-*H*), 4.78 (s, 1H, =*CH*Si), 2.66 (s, 6H, Ar-CH_3), 1.54 (s, 9H, $NC(C(CH_3)_3)$), 1.33 (s, 9H, $NC(C(CH_3)_3)$), 1.30 (s, 9H, $NC(C(CH_3)_3)$), 1.06 (d, $J = 8.8$, 9H, PMe_3), 0.39 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 189.5, 183.0, 160.0, 133.5, 127.7, 121.7, 101.1, 42.2, 41.8, 40.3, 31.2, 30.8, 20.6, 16.0, 1.6. ^{51}V NMR (C_6D_6): δ −466 ($\Delta\nu_{1/2}$ = 1356 Hz). Anal. Calcd for $C_{29}H_{55}N_3PSiV$: C, 62.67; H, 9.97; N, 7.56. Found: C, 62.40; H, 10.22; N, 7.57.

Preparation of V(N-2,6-Me$_2$C$_6$H$_3$)[NC(Ph)=CHSiMe$_3$](N=C^{t}Bu$_2$)(PMe$_3$) (4). Into a *n*-hexane (5 mL) solution containing **1** (208 mg, 0.44 mmol) was added at −30 °C 2.0 equiv of PhCN (90 mg, 0.88 mmol). The mixture was warmed slowly to room temperature and was stirred for 2 h. The solution was then concentrated *in vacuo* and was placed in the freezer (−30 °C). The brown microcrystals (120 mg, 0.21 mmol) were collected from the chilled solution. Yield: 47.3%. ^{1}H NMR (C_6D_6): δ 7.95 (d, $J = 6.84$, 2H, Ar-*H*), 7.04−7.09 (m, 5H, Ph-*H*), 6.79 (t, $J = 7.80$, 1H, Ar-*H*), 5.09 (s, 1H, V*CH*Si), 2.59 (s, 6H, Ar-CH_3), 1.36 (s, 9H, tBu-*H*), 1.22 (s, 9H, ^{t}Bu-H), 0.82 (d, $J = 8.8$, 9H, PMe_3-*H*), 0.47 (s, 9H, $Si(CH_3)_3$). ^{51}V NMR (C_6D_6): δ −485.3 ($\Delta\nu_{1/2}$ = 1638 Hz). ^{13}C NMR (C_6D_6): δ 190.9, 172.1, 145.9, 134.6, 127.5, 127.1, 122.2, 106.5, 42.3, 41.9, 31.2, 31.0, 23.0, 19.6, 15.5, 15.2, 1.3. The ketimide carbon signal was not observed about 160 ppm probably due to the low intensity. Anal. Calcd for $C_{31}H_{51}N_3PSiV$: C, 64.67; H, 8.93; N, 7.30. Found: C, 64.23; H, 9.19; N, 7.11.

Table 4. Crystal Data, Collection Parameters of V(N-2,6-Me$_2$C$_6$H$_3$)[NC(Ph)=CHSiMe$_3$](N=C^{t}Bu$_2$)(PMe$_3$) (4) and V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$CHPh)(N=C^{t}Bu$_2$)(PMe$_3$) (6)[a]

	4	6
formula	$C_{31}H_{51}N_3PSiV$	$C_{28}H_{44}N_2PV$
fw	575.76	490.58
cryst color, habit	red, block	brown, block
cryst size (mm)	0.22 × 0.18 × 0.12	0.30 × 0.20 × 0.06
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (#15)	*P*2$_1$/*n* (#14)
a (Å)	23.8758(10)	8.6734(6)
b (Å)	15.1189(5))	11.4636(9)
c (Å)	21.5604(8)	28.5749(19)
β (deg)	118.5805(10)	92.0450(17)
V (Å^3)	6834.4(4))	2839.4(4)
Z value	8	4
D_{calcd} (g/cm^3)	1.119	1.148
F_{000}	2480.00	1056.00
temp (K)	193	243
$\mu_{(Mo\ K\alpha)}$ (cm^{-1})	3.940	4.223
no. of reflns measd	total: 33 031, unique: 7791	total: 22 575, unique: 5169
no. of obsns ($I > 2.00\sigma(I)$)	4188	1832
no. of variables	385	333
R_1 ($I > 2.00\sigma(I)$)	0.0412	0.0478
wR_2 ($I > 2.00\sigma(I)$)	0.0886	0.0802
goodness of fit	1.013	1.011

[a] Detailed analysis conditions, see the Supporting Information.[19]

Preparation of V(N-2,6-Me$_2$C$_6$H$_3$)[C(Ph)=C(Ph)CHSiMe$_3$)]-(N=C^{t}Bu$_2$)(PMe$_3$) (5). Into a toluene-$d_8$solution containing **1** (300 mg, 0.63 mmol) was added 1 equiv of diphenylacetylene (113 mg, 0.63 mmol) at −30 °C. The mixture was warmed slowly to room temperature and was then stirred for 24 h. The solution was filtered through a Celite pad, and the filter cake was adequately washed with *n*-hexane. The combined filtrate and the wash were placed in a rotary evaporator to remove the solvent *in vacuo*. The resultant solid was then dissolved in a minimum amount of *n*-hexane. The chilled solution (−30 °C) gave brown microcrystals (118 mg, 0.18 mmol). Yield: 28.5%. ^{1}H NMR (C_6D_6): δ 7.94 (d, $J = 7.32$, 1H, Ar-*H*), 7.71 (m, 3H, *Ar-H and Ph-H*), 7.52 (m, 1H, Ar-*H*), 7.11−6.79 (m, 8H, Ph-*H*), 3.35 and 3.34 (d, 1H, $-CHSiMe_3$), 2.63 and 2.50 (s, 6H, Ar-CH_3), 1.34−1.05 (m, 18H, $C(CH_3)_3$), 0.74 and 0.63 (s, 9H, $P(CH_3)_3$), 0.41 and 0.21 (s, 9H, $Si(CH_3)_3$). ^{51}V NMR (C_6D_6): δ −326.4, −366.0. ^{13}C NMR (C_6D_6): δ 188.8, 185.7, 144.6, 143.9, 139.5, 138.6, 136.4, 134.9, 131.6, 130.8, 130.1, 129.6, 129.0, 127.0, 125.6, 125.3, 125.1, 123.6, 123.4, 123.2, 122.8, 92.8, 89.8, 62.0, 60.8, 60.0, 44.6, 42.6, 41.9, 41.4, 40.6, 31.2, 30.7, 30.3, 20.0, 19.4, 17.2, 17.0, 13.9, 13.7, 3.5, 2.9. Anal. Calcd for $C_{38}H_{56}N_2PSiV$: C, 70.12; H, 8.67; N, 4.30. Found: C, 70.58; H, 8.52; N, 4.42.

Preparation of V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$CHPh)(N=C^{t}Bu$_2$)-(PMe$_3$) (6). Into a toluene-d_8 solution containing **1** (500 mg, 1.06 mmol) was added styrene (110 mg, 1.06 mmol) at −30 °C. The mixture was warmed slowly to room temperature and was stirred for 2 h. The solvent was then removed *in vacuo*, and the residue was dissolved in a minimum amount of *n*-hexane. The chilled solution (−30 °C) afforded analytically pure **6** as brown microcrystals (128 mg, 0.26 mmol). Yield: 24.5%. ^{1}H NMR (C_6D_6): δ 7.09 (t, 1H, $J = 7.32$, Ar-*H*), 6.95 (d, 2 H, $J = 7.32$, Ar-*H*), 6.80−6.71 (m, 5H, Ph-*H*), 4.13 (m, 1H, cyclo-*H*), 3.05 (m, 1H, cyclo-*H*), 2.46 (s, 6H, CH_3), 2.08 (m, 1H, cyclo-*H*), 1.32 (s, 18 H, ^{t}Bu-*H*), 0.66 (d, 9H, $J = 7.32$, PMe_3). ^{51}V NMR (C_6D_6): δ 183.5 ($\Delta\nu_{1/2}$ = 1053.1 Hz). ^{13}C NMR (C_6D_6): δ 204.5, 183.2, 157.9, 147.3, 134.2, 134.1, 129.0, 128.6, 122.2, 121.8, 72.6, 43.6, 31.2, 23.2, 19.3, 14.9, 14.7. Anal. Calcd for $C_{28}H_{44}N_2PV$: C, 68.55; H, 9.04; N, 5.71. Found: C, 68.05; H, 9.28; N, 5.53.

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphitemonochromated Mo Kα radiation. The selected crystal collection parameters are summarized in Table 4, and the detailed results are described in the Supporting Information. All structures were solved by direct methods and expanded using Fourier techniques,[27] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **4** and **6** were performed using the Crystal Structure[28] crystallographic software package.

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Supporting Information Available: ^{1}H, ^{13}C, ^{31}P, and ^{51}V NMR spectra (in C_6D_6 at 25 °C) for V(N-2,6-Me$_2$C$_6$H$_3$)(CHSiMe$_3$)(N=C^{t}Bu$_2$)(PMe$_3$) (**1**) (and the spectra upon addition of PMe$_3$), selected NMR spectra for reactions of **1** with nitriles, styrene, and 1,1-diphenylethylene, and CIF files and structure reports for V(N-2,6-Me$_2$C$_6$H$_3$)[NC(Ph)=CHSiMe$_3$](N=C^{t}Bu$_2$)(PMe$_3$) (**4**) and V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$CHPh)(N=C^{t}Bu$_2$)(PMe$_3$) (**6**). These materials are available free of charge via the Internet at http://pubs.acs.org.

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