# ORGANOMETALLICS

Synthesis of (Adamantylimido)vanadium(V)-Alkyl, Alkylidene Complex Trapped with PMe₃: Reactions of the Alkylidene Complexes with Phenols

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Ⓢ *Supporting Information*

ABSTRACT: V(CHSiMe₃)(NAd)(CH₂SiMe₃)(PMe₃)₂ (**1**, Ad = 1-adamantyl) has been isolated from V(NAd)-(CH₂SiMe₃)₃ in the presence of PMe₃ (excess, 12 equiv) upon heating, and the reaction of **1** with 2,6-Me₂C₆H₃OH in *n*-hexane afforded V(CHSiMe₃)(NAd)(O-2,6-Me₂C₆H₃)-(PMe₃)₂ (**2a**); structures of **1** and **2a** have been determined by X-ray crystallography. Reaction of **1** with C₆F₅OH in C₆D₆ afforded a mixture of V(CHSiMe₃)(NAd)(OC₆F₅)(PMe₃)₂ (**2b**) and V(NAd)(CH₂SiMe₃)₂(OC₆F₅) (**3b**) and the PMe₃ adduct (**3b-PMe₃**), and the consumption rate of **1** decreased upon addition of PMe₃ or use of C₆F₅OD in place of C₆F₅OH, clearly suggesting that the reaction proceeds via coordination of C₆F₅OH and subsequent reaction with the alkylidene or the alkyl moiety. The catalytic activity in the ring-opening metathesis polymerization (ROMP) of norbornene by **1** increased upon addition of phenol; **1**-C₆F₅OH catalyst showed a remarkable activity (TOF 20 000 h⁻¹), affording high molecular weight polymer with a unimodal molecular weight distribution. Reactions with **2a,b** with phenol afforded the bis(phenoxy) complexes, and it has been suggested that these reactions proceed via coordination of phenol and subsequent reaction with the alkylidene accompanying phenoxy exchange on the vanadium.
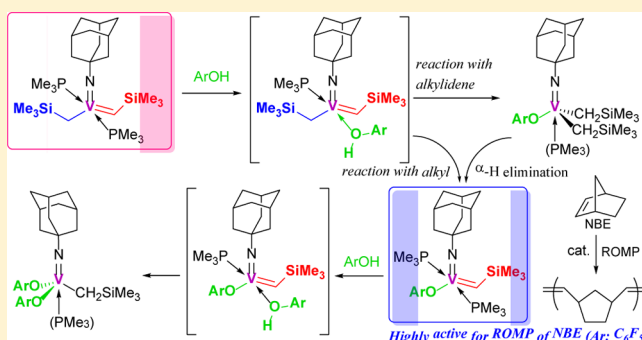
■ INTRODUCTION

Transition metal-alkyl and alkylidene (carbene) complexes are important reagents or intermediates in stoichiometric/catalytic organic reactions, as well as in olefin polymerization.[1−5] High oxidation state early transition metal alkylidene complexes attract considerable attention[3−5] because they play essential roles as catalysts in olefin metathesis and Wittig-type or group transfer reactions,[3−6] as demonstrated especially by molybdenum.[3,4a,b,e] Due to their promising characteristics (especially notable reactivity toward olefins) demonstrated by classical Ziegler-type vanadium catalyst systems,[2] the design of the vanadium complex catalysts has been considered an important subject.[2f,g,5] Synthesis of the alkylidene complexes and their reaction chemistry thus attract considerable attention in terms not only of better catalyst design but also of better understanding in organometallic chemistry.[5]

Synthesis and reaction chemistry of (imido)vanadium(V)-alkyl and alkylidene complexes[5,7,8] have thus been considered of fundamental importance (as described above) due to their promising applications in catalysis. We recently demonstrated that ketimide-[7a,e] and aryloxo[7d,j]-modified vanadium(V)-alkylidenes (Chart 1) exhibited catalytic activities in the ring-opening metathesis polymerization (ROMP) of norbornene (NBE). These alkylidenes were prepared by α-hydrogen elimination from the dialkyl analogues in C₆D₆ or *n*-hexane

Chart 1. Reported Olefin Metathesis Active Vanadium(V)-alkylidenes[7]
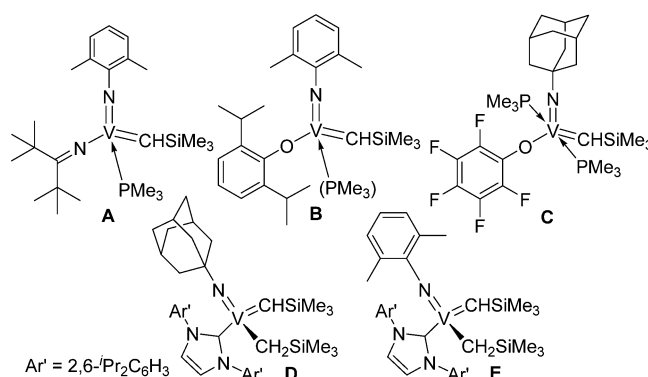
in the presence of PMe₃ or NHC [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene],[5,7a,d−f,h,j] known as a common approach for the preparation of high oxidation state early transition metal alkylidenes.[3−5]

In particular, the synthesis of (imido)vanadium-alkyl, alkylidene complexes should be of potent interest in terms of reaction chemistry (with alcohol, amine, etc., for the synthesis/modification of alkylidene species) and/or precursors for alkylidyne complexes. However, the NHC analogues (shown as **D** and **E** in Chart 1) showed low reactivities for ROMP of NBE, and the reactivity toward phenol was low (as described below),[7f] probably due to strong coordination as well as severe steric crowding of NHC toward the metal center. In this paper, we wish to present the synthesis and structural analysis of an (imido)vanadium(V)-alkyl, alkylidene complex containing PMe$_3$, V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ (**1**, Ad = 1-adamantyl),[9] reactions with phenols, including isolation, and reactions with aryloxo-modified alkylidenes, V(CHSiMe$_3$)-(NAd)(OAr)(PMe$_3$)$_2$ [Ar = 2,6-Me$_2$C$_6$H$_3$ (**2a**), C$_6$F$_5$ (**2b**)].

■ RESULTS AND DISCUSSION

1. Synthesis and Structural Analysis of V(CHSiMe$_3$)-(NAd)(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ (1). The PMe$_3$-coordinated alkyl-alkylidene complex V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ (**1**, Ad = 1-adamantyl) could be isolated when the trialkyl complex V(NAd)(CH$_2$SiMe$_3$)$_3$[7f] was heated in a sealed Schlenk tube containing *n*-hexane in the presence of PMe$_3$ (excess, 12 equiv) for 4 days at 70 °C (Scheme 1). The similar reaction in

Scheme 1
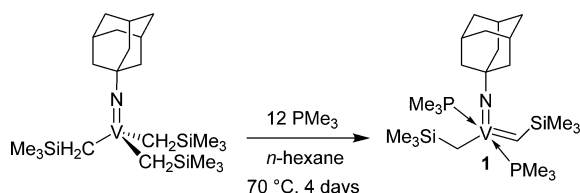
C$_6$D$_6$ (analogous procedure for isolation of the NHC analogue)[7f] in the presence/absence of PMe$_3$ afforded other products that were not observed in the ^{51}V NMR spectra; an attempt to isolate **1** in the reaction without solvent (in PMe$_3$) failed. Complex **1** was identified by NMR spectra and elemental analysis, and the structure was determined by X-ray crystallography (Figure 1).[10] Two resonances at −77.7 (major) and 43.3 (minor) ppm were observed in the ^{51}V NMR spectra, and the corresponding broad resonances ascribed to a proton in the vanadium-alkylidene were observed at 13.0 (major) and 15.3 (minor, ratio ca. 10:1) ppm.[11] Since the ratio did not change upon addition of PMe$_3$ (excess),[11] the results thus suggest that the resultant alkylidene is present as a *syn*/*anti* mixture in solution.[7d,j] Broad resonances were also observed in the ^{31}P NMR spectrum.[11]

The crystallographic result (Figure 1) indicates that **1** displays a distorted trigonal bipyramidal geometry around the vanadium atom consisting of two phosphorus axes [bond angles: P(1)−V−P(2) 173.09(4)°, P(1)−V−N(1) 93.31(14)°, P(1)−V−C(11) 86.81(13)°, P(1)−V−C(15) 89.10(16)°] and a plane consisting of the aryloxo, alkylidene, and the adamantylimido ligand [bond angles: N(1)−V−C(11) 131.32(17)°, N(1)−V−C(15) 111.79(16)°, C(11)−V−C(15) 116.89(16)°, total 360°]. The results thus indicate that two phosphorus atoms are positioned in a *trans* form. The V(1)−C(15) bond distance [1.857(5) Å] is apparently shorter than that in the V−C(11) [2.190(3) Å], strongly suggesting formation of the alkyl-alkylidene complex. Both the V(1)−
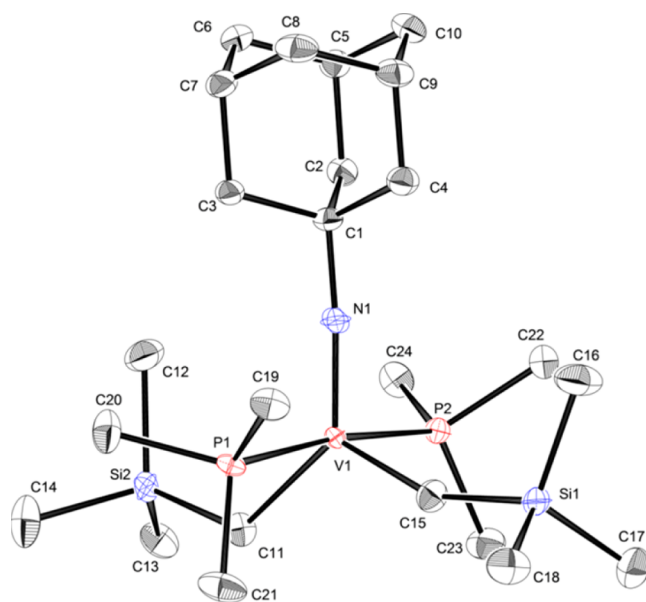
Figure 1. ORTEP drawing for **1**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[10] Selected bond distances (Å): V−P(1) 2.4452(15), V−P(2) 2.4634(15), V−N(1) 1.680(3), V−C(11) 2.190(3), V−C(15) 1.857(5). Selected bond angles (deg): P(1)−V−P(2) 173.09(4), P(1)−V−N(1) 93.31(14), P(1)−V−C(11) 86.81(13), P(1)−V−C(15) 89.10(16), P(2)−V−N(1) 93.52(14), P(2)−V−C(11) 87.95(13), P(2)−V−C(15) 89.26(16), N(1)−V−C(11) 131.32(17), N(1)−V−C(15) 111.79(16), C(11)−V−C(15) 116.89(16).

C(15) and the V−C(11) bond distances in **1** are longer than those in the NHC analogue, V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)-(NHC) [complex **D** in Chart 1, NHC = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; 1.829(3), 2.069(3) Å, respectively],[7f] which has a distorted tetrahedral geometry around V. The V(1)−C(15) bond distance [1.857(5) Å] is relatively close to that in V(CHSiMe$_3$)(NAd)(OC$_6$F$_5$)(PMe$_3$)$_2$ [complex **C** (corresponds to **2b** shown below), 1.845(4) Å][7j] but is shorter than those in V(CHSiMe$_3$)(N-2,6-Me$_2$C$_6$H$_3$)-(N=C^{t}Bu$_2$)(PMe$_3$) [complex **A**, 1.860(2) Å][7a] and V-(CHSiMe$_3$)(N-2,6-Me$_2$C$_6$H$_3$)[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N](PMe$_3$) [1.866(5) Å].[7h] The V−P bond distances [2.4452(15), 2.4634(15) Å] are slightly shorter than those in complex **C** [2.4869(10), 2.4665(11) Å],[7j] but are slightly longer than those in V(CHSiMe$_3$)(N-2,6-Me$_2$C$_6$H$_3$)[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N](PMe$_3$) [2.4202(14) Å][7i] and the ketimide complex **A** [2.4331(7) Å].[7a]

2. Reactions of V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ (1) with 2,6-Me$_2$C$_6$H$_3$OH and C$_6$F$_5$OH. The reaction of V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ (**1**) with 2,6-Me$_2$C$_6$H$_3$OH in *n*-hexane afforded the aryloxo-modified alkylidene V(CHSiMe$_3$)(NAd)(O-2,6-Me$_2$C$_6$H$_3$)(PMe$_3$)$_2$ (**2a**) (Scheme 2). The complex was identified by NMR spectra and elemental analysis, and the structure was determined by X-ray crystallography (Figure 2).[10] In contrast to the above alkyl-alkylidene complex (**1**), only one broad resonance at 16.4 ppm (in the ^{1}H NMR spectrum, proton of the vanadium alkylidene) or at −177.0 ppm (in the ^{51}V NMR spectrum) was observed.[11] The ^{31}P NMR spectrum of **2a** showed a broad resonance.[11] As described below, the reaction with C$_6$F$_5$OH in C$_6$D$_6$ afforded V(CHSiMe$_3$)(NAd)(OC$_6$F$_5$)(PMe$_3$)$_2$ (**2b**)[7j] and the dialkyl analogues (**3b**[12] and the PMe$_3$ adduct), and pure isolation of **2b** from the mixture was not successful.
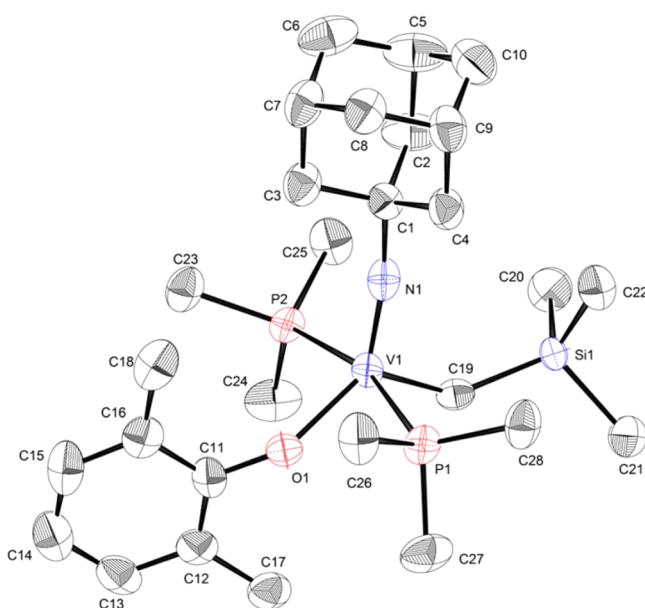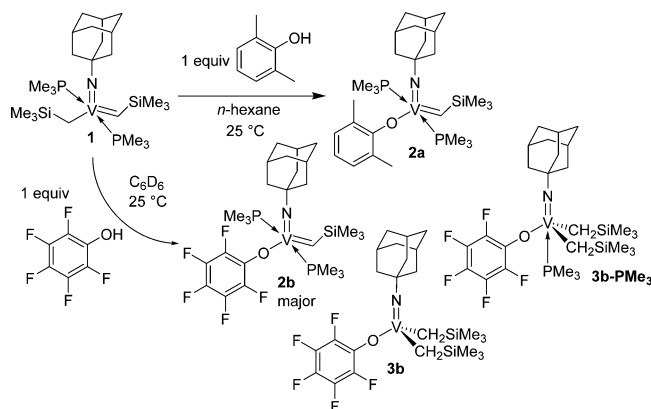
Scheme 2

Figure 2. ORTEP drawing for **2a**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[10] Selected bond distances (Å): V−P(1) 2.4810(15), V−P(2) 2.4764(14), V−O(1) 1.937(4), V−N(1) 1.637(5), V−C(19) 1.878(5). Selected bond angles (deg): P(1)−V−P(2) 164.89(6), P(1)−V−O(1) 77.74(10), P(1)−V−N(1) 96.11(13), P(1)−V−C(19) 94.26(14), P(2)−V−O(1) 87.41(10), P(2)−V−N(1) 96.06(13), P(2)−V−C(19) 90.78(14), O(1)−V−N(1) 132.92(16), O(1)−V−C(19) 120.3(2), N(1)−V−C(19) 106.7(2).

As shown in Figure 2, **2a** displays a distorted trigonal bipyramidal geometry around the vanadium atom consisting of two phosphorus axes [bond angles: P(1)−V−P(2) 164.89(6)°] and a plane consisting of the aryloxo, alkylidene, and the adamantylimido ligand [bond angles: O(1)−V−N(1) 132.92(16)°, O(1)−V−C(19) 120.3(2)°, N(1)−V−C(19) 106.7(2)°, total ca. 360°]. The results thus indicate that two phosphorus atoms are positioned in a *trans* form. The V(1)−C(19) bond distance [1.878(5) Å] is longer than that in the alkyl-alkylidene analogue [**1**, 1.857(5) Å] and the C₆F₅ analogue [**2b**, 1.845(4) Å]. On the basis of the crystallographic and the NMR data (one alkylidene resonance in the ¹H NMR spectrum and one resonance in the ⁵¹V NMR spectrum), the alkylidene complex **2a** adopts a *syn* structure due to a rather large steric bulk of the methyl group on the phenoxy ligand, whereas the C₆F₅ analogue (**2b**) is present as a *syn/anti* mixture

in solution.[7j] The bond angles of O(1)−V−N(1), 132.92(16)°, and O(1)−V−C(19), 120.3(2)°, are apparently different from those in the C₆F₅ analogue [**2b**, 140.47(13)°, 113.28(15)°, respectively], whereas N(1)−V−C(19) [106.7(2)°] in **2a** was close to that in **2b** [106.25(16)°]; these might be due to the steric bulk of the phenoxy ligand, although the exact reason is not clear at this moment.

In order to explore the reaction of **1** with C₆F₅OH in more detail, we conducted the reaction with C₆F₅OD, in place of C₆F₅OH, and the reaction in the presence of PMe₃ in C₆D₆. The reaction of **1** with C₆F₅OH was monitored by ⁵¹V NMR spectra (Figure 3a), and **1** was consumed completely after 9 h, affording a mixture of **2b** (identified independently),[7j] V(NAd)(CH₂SiMe₃)₂(OC₆F₅) (**3b**),[12] and the PMe₃ adduct of **3b** (assumed product by NMR spectra, **3b-PMe₃**). We thus assumed that the reaction of **1** with C₆F₅OH afforded a mixture of **2b** (by reaction with alkyl) and **3b** (by reaction with alkylidene). Moreover, the resonance ascribed to **3b** and **3b-PMe₃** decreased over the time course upon increasing the alkylidene species (**2b**), suggesting that **3b** converted to **2b** by α-hydrogen elimination. Note that the consumption of **1** was not complete even after 25 h (complete consumption observed after 31 h) if the same reaction was conducted with the addition of PMe₃ (5 equiv to **1**). Moreover, the reaction became slow if C₆F₅OD was used in place of C₆F₅OH; the completion of **1** was not observed even after 31 h (completion observed after 47 h, shown in the Supporting Information, Figure S1-7),[11] and the integration of a resonance ascribed to a proton of the alkylidene (ca. 16.1 ppm, V-CHSiMe₃) versus SiMe₃ decreased (shown in the Supporting Information, Figure S1-8).

Taking into account these results, we assume that the reaction of **1** with C₆F₅OH proceeds by (i) coordination of C₆F₅OH (after dissociation of PMe₃) and (ii) reaction with the alkyl (affording **2b**) or the alkylidene (affording the dialkyl complex, **3b**) followed by formation of **2b** by α-H elimination (Scheme 3).

3. Ring-Opening Metathesis Polymerization of Norbornene by V(CHSiMe₃)(NAd)(CH₂SiMe₃)(PMe₃)₂ (1)−ArOH Catalysts.
Since the reaction of V(CHSiMe₃)(NAd)(CH₂SiMe₃)(PMe₃)₂ (**1**) with phenols (ArOH) afforded the corresponding alkylidene complexes V(CHSiMe₃)(NAd)(OAr)(PMe₃)₂ (**2**), ROMP of NBE in benzene by **1** was conducted upon the addition of ArOH. ROMPs by the NHC-trapped alkyl-alkylidene V(CHSiMe₃)(NAd)(CH₂SiMe₃)(NHC) [**1-NHC**, NHC = 1,3-bis(2,6-diisopropylphenyl)-imidazole-2-ylidene, corresponds to complex **D** in Chart 1][7f] were conducted under the same conditions. The results are summarized in Table 1.

The alkyl-alkylidene complex **1** itself showed low activity (run 1), but the activity increased upon addition of ArOH (runs 2−7). The activity by **1** upon addition of 2,6-F₂C₆H₃OH (runs 4 and 5) or C₆F₅OH (runs 6 and 7) was higher than that upon addition of 2,6-Me₂C₆H₃OH (runs 2 and 3), and these experimental results are reproducible (runs 2−7). The activity by the **1**−C₆F₅OH catalyst showed the highest activity, affording high molecular weight polymers with unimodal molecular weight distributions, whereas the distributions prepared by **1**−2,6-Me₂C₆H₃OH or **1**−2,6-F₂C₆H₃OH were broad. The trend shown here is the same as that in the ROMP of NBE by the dialkyl analogue V(NAd)(CH₂SiMe₃)₂(OAr) upon addition of PMe₃.[12] Moreover, the activity **1**−C₆F₅OH is slightly lower than (or relatively similar to) that by the isolated alkylidene (**2b**)[7j] conducted under the same conditions.[13]
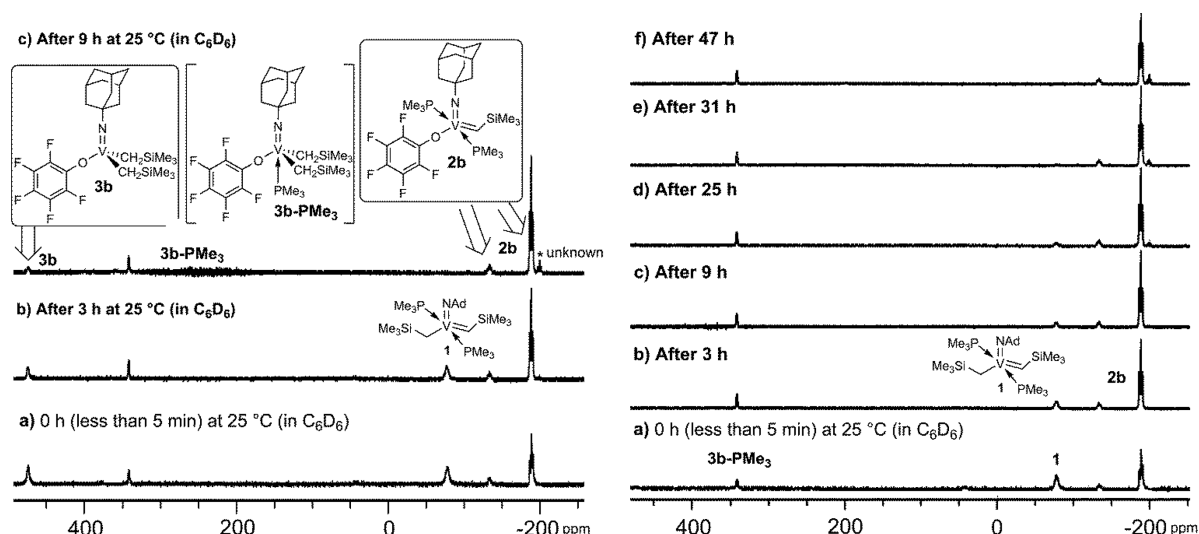
Figure 3. ^{51}V NMR spectra for monitoring the reaction of V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ (**1**) with C$_6$F$_5$OH (1equiv) in C$_6$D$_6$ at 25 °C. Right: The reaction in the presence of PMe$_3$ (5 equiv to **1**).

Scheme 3

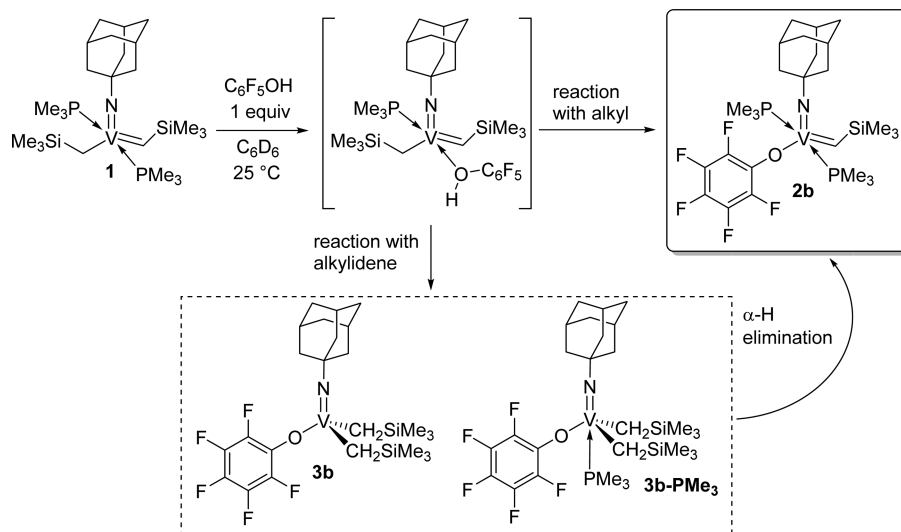**Table 1. Ring-Opening Metathesis Polymerization of Norbornene by V(CHSiMe$_3$)(NAd)(CH$_2$SiMe$_3$)(L)$_n$−ArOH Catalysts [L = PMe$_3$, n = 2 (1); L = NHC, n = 1 (1-NHC)]^a**

run	complex (μmol)	L	ArOH	temp/ °C	time/min	yield/mg	TON^b	TOF/h^{-1}	$M_n{}^c \times 10^{-4}$	$M_w/M_n{}^c$
1	**1** (5.0)	PMe$_3$		25	30	14	29	58	10	4.2
2	**1** (2.5)	PMe$_3$	2,6-Me$_2$C$_6$H$_3$OH	25	30	37	160	310	8.4	4.9
3	**1** (2.5)	PMe$_3$	2,6-Me$_2$C$_6$H$_3$OH	25	30	39	170	330	14	4.2
4	**1** (1.0)	PMe$_3$	2,6-F$_2$C$_6$H$_3$OH	25	5	119	1300	15 000	5.1	6.4
5	**1** (1.0)	PMe$_3$	2,6-F$_2$C$_6$H$_3$OH	25	5	119	1300	15 000	5.2	4.2
6	**1** (0.5)	PMe$_3$	C$_6$F$_5$OH	25	5	78	1700	20 000	44	1.4
7	**1** (0.5)	PMe$_3$	C$_6$F$_5$OH	25	5	70	1500	18 000	43	1.4
8	**1-NHC** (0.5)	NHC		25	5	trace				
9	**1-NHC** (0.5)	NHC		80	30	29	620	1230	54	1.4
10	**1-NHC** (0.5)	NHC	C$_6$F$_5$OH	25	5	trace				
11	**1-NHC** (5.0)	NHC	C$_6$F$_5$OH	80	30	40	85	170	43	1.7

^{a}Reaction conditions: NBE 2.12 mmol, benzene 9.6 mL (initial NBE conc 0.22 mmol/mL). ^{b}TON (turnovers) = NBE reacted (μmol)/V charged (μmol). ^{c}GPC data in THF vs polystyrene standards. NHC = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene.

In contrast, as communicated previously,[7f] the NHC analogue (**1-NHC**) showed negligible activity at 25 °C (run 8), and the activity (TON) was 620 at 80 °C after 30 min (run 9). Note that the activity decreased upon addition of C$_6$F$_5$OH even at 80 °C (runs 10 and 11), whereas a significant increase in the activity was observed by **1** (L = PMe$_3$) upon addition of

C_6F_5OH (runs 6 and 7). Since no new resonance(s) ascribed to a proton in the alkylidene was observed in the reaction of the NHC analogue (**1-NHC**) with C_6F_5OH (1.0 equiv) in C_6D_6 and the major resonance in the ^{51}V NMR spectra was **1-NHC** even after 1 h (shown in the Supporting Information., Figure S1-9), the results (decrease in the activity) would be due to a partial decomposition and/or formation of another species upon addition of C_6F_5OH probably due to the difficulty of the dissociation of the NHC (and/or steric crowding) for coordination of ArOH (for subsequent reaction with alkyl or alkylidene).[11]

4. Reactions of V(CHSiMe3)(NAd)(OAr)(PMe3)2 with ArOH (C_6F_5OH, 2,6-Me2C6H3OH). Reaction of V(CHSiMe3)-(NAd) (O-2,6-Me2C6H3)(PMe3)2 (**2a**) with 2,6-Me2C6H3OH (1.0 equiv) in C_6D_6 afforded V(NAd)(CH2SiMe3) (O-2,6-Me2C6H3)2 (**4a**), reported previously by another synthetic route,[12] as the exclusive product by ^{51}V NMR spectra (Scheme 4). An immediate consumption of **2a** was observed (Figure 4a,

Scheme 4
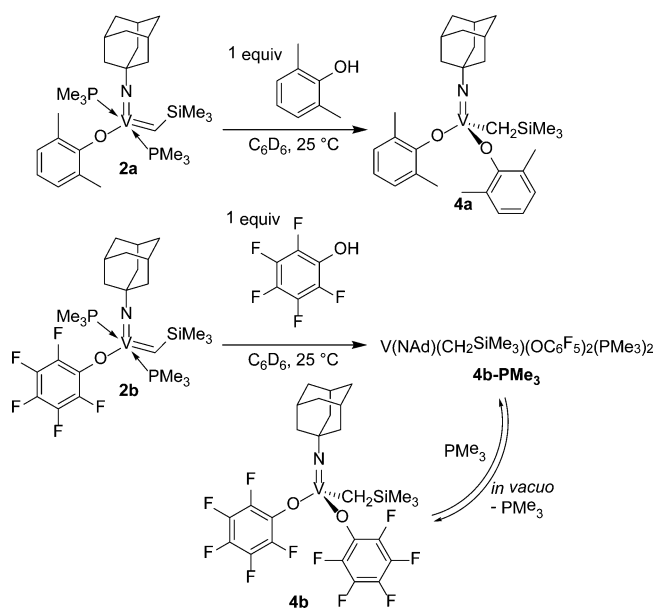
left), and the reaction reached completion after 1 h (Figure 4d, left), whereas the reaction did not reach completion even after 1 h upon addition of PMe3 (Figure 4d, right). The results would suggest, as suggested in Scheme 3 in the reaction of **1** with ArOH, that the reaction of **2a** with 2,6-Me2C6H3OH proceeds via dissociation of PMe3 for subsequent ArOH coordination. It seems likely (from ^{51}V NMR spectra) that PMe3 was not coordinated to vanadium in **4a**, probably due to steric bulk (of two methyl groups in the phenoxy ligand in an *ortho* position).

An immediate consumption of V(CHSiMe3)(NAd)(OC6F5)-(PMe3)2 (**2b**) was observed upon addition of C_6F_5OH in C_6D_6 at 25 °C to afford V(NAd)(CH2SiMe3)(OC6F5)2(PMe3)2 (**4b-PMe3**), which was identified by NMR spectra and isolated as reported V(NAd)(CH2SiMe3)(OC6F5)2 (**4b**),[12] after removal of volatiles of the reaction mixture *in vacuo*. Reversible coordination/dissociation of PMe3 was observed between **4b** and **4b-PMe3** (Scheme 4),[11] suggesting that coordination of PMe3 was relatively weak (NMR data are shown in the Supporting Information, Figure S1-10). This result also suggests that the reactions of **2a,b** with 2,6-Me2C6H3OH or

C_6F_5OH proceed via dissociation of PMe3 for subsequent ArOH coordination. The weak coordination was also observed by ^{31}P NMR spectra (addition of PMe3 to **4b**), because the observed resonances (at 25 °C) were free PMe3 (ca. −62 ppm), but different broad resonances (that probably indicate a coordination of PMe3 to the V, 8 and 13 ppm, analogous to **1** and **2a**) were observed when the spectra were measured at lower than −25 °C (Figure S1-11).[11]

In order to explore in more detail, we conducted reactions of **2a** with C_6F_5OH and of **2b** with 2,6-Me2C6H3OH in C_6D_6 under the same conditions (Scheme 5). The ^{51}V NMR spectra are shown in Figure 5. In the reaction of **2b** with 2,6-Me2C6H3OH, resonances at −149 (**4b-PMe3**), −88, and −166 (**4a**) ppm were observed with the ratio of 1:3:1, and similar spectra were observed in the reaction of **2a** with C_6F_5OH. Although we could not isolate the formed species at −88 pm, it seems likely that the product would be V(NAd)(CH2SiMe3)-(O-2,6-Me2C6H3)(OC6F5)(PMe3)$_n$ (denoted as **4c**) in high certainty. The other alkylidene (**2b**), formed by replacement of the phenoxy ligand, was also observed in low percentage in the reaction of **2a** with C_6F_5OH. These results clearly indicate that the reaction proceeds via coordination of ArOH, and proton transfer to both the alkylidene and the phenoxy ligand occurred under these conditions, as shown in Scheme 6.

In summary, we have prepared the PMe3-coordinated vanadium(V)-alkyl, alkylidene complex V(CHSiMe3)(NAd)-(CH2SiMe3)(PMe3)2 (**1**) and explored some reactions with phenols affording aryloxo-modified alkylidenes V(CHSiMe3)-(NAd)(OAr)(PMe3)2 [Ar = 2,6-Me2C6H3 (**2a**), C6F5 (**2b**)]. On the basis of the results in the reactions of **1** in the presence of PMe3 and with C_6F_5OD in place of C_6F_5OH, it can be demonstrated that these reactions proceed via coordination of phenol and subsequent proton transfer to the alkylidene (affording the dialkyl) or alkyl (affording the phenoxy-modified alkylidene). The resultant alkylidenes (**2a,b**) further react with ArOH to afford the bis(phenoxy) complexes, and it has been demonstrated that these reactions also proceed via coordination of ArOH. These results should be useful not only for the preparation of various vanadium-alkyl and alkylidene complexes but also for a better understanding especially in the field of organometallic chemistry of vanadium and of the basic reaction mechanism in vanadium-catalyzed organic synthesis.

■ EXPERIMENTAL SECTION

Figure 4. ^{51}V NMR spectra for monitoring the reaction of $V(CHSiMe_3)(NAd)(O\text{-}2,6\text{-}Me_2C_6H_3)(PMe_3)_2$ (**2a**) with $2,6\text{-}Me_2C_6H_3OH$ (1 equiv) in C_6D_6 at 25 °C. Right: The reaction in the presence of PMe_3 (5 equiv to **2a**).

Scheme 5

Synthesis of V(NAd)(CHSiMe₃)(CH₂SiMe₃)(PMe₃)₂ (1). Into a 50 mL scale sealed Schlenk tube in the drybox were added *n*-hexane (10 mL), V(NAd)(CH₂SiMe₃)₃ (762 mg, 1.65 mmol), and PMe₃ (1.51 g, 19.8 mmol) at room temperature. The solution was then stirred upon heating at 70 °C for 4 days. After the reaction, the solution was passed through a Celite pad, and the filter cake was washed with *n*-hexane. The combined filtrate and wash was then placed in a rotary evaporator to remove volatiles. The resultant solid was then dissolved in a

minimum amount of *n*-hexane, and the chilled solution placed in the freezer gave a yellow-green solid. Yield: 217 mg (25%). ^{1}H NMR (C_6D_6): δ 0.32 (s, 9H, $SiCH_3$), 0.38 (s, 9H, $SiCH_3$), 1.16 (br, 18H, PMe_3), 1.55−2.00 (m, total 6H, Ad-H), 13.0, 15.3 (br, 1H, VCH−). ^{31}P NMR (C_6D_6): δ −0.93, −2.24 (broad). ^{13}C NMR (C_6D_6): δ 2.85, 3.23, 5.90, 18.6, 30.6, 30.8, 36.8, 47.5, 48.5, 316.4. ^{51}V NMR (C_6D_6): δ −77.7, 43.3 ($\Delta\nu_{1/2}$ = 658 Hz). Anal. Calcd for $C_{24}H_{54}NP_2Si_2V$: C, 54.83; H, 10.35; N, 2.66. Found: C, 54.76; H, 9.96; N, 2.60.

Synthesis of V(CHSiMe₃)(NAd)(O-2,6-Me₂C₆H₄)(PMe₃)₂ (2a). An *n*-hexane solution (20 mL) containing V(CHSiMe₃)(NAd)(CH₂SiMe₃)-(PMe₃)₂ (**1**, 565 mg, 1.07 mmol) was added to 2,6-Me₂C₆H₃OH (131 mg, 1.07 mmol) at −30 °C. The solution was stirred at room temperature for 30 min. The reaction mixture was then placed in a rotary evaporator to remove volatiles. The resultant solid was dissolved in a minimum amount of *n*-hexane, and the chilled solution placed in the freezer gave a yellow solid. Yield: 311 mg (52%). ^{1}H NMR (C_6D_6): δ 0.38 (s, 9H, $SiCH_3$), 0.90 (br, 18 H, PMe_3), 1.60 (br, 6H, Ad), 2.04 (s, 3H, Ad), 2.11 (s, 6H, CH_3), 2.40 (br, 6H, Ad), 6.98 (t, 1H, J = 7.4 Hz, Ar-H), 7.29 (d, 2H, J = 7.4 Hz, Ar-H), 16.1 (br, 1H, VCH−). ^{31}P NMR (C_6D_6): δ −11.6, −15.7 (broad). ^{13}C NMR (C_6D_6): δ 2.91, 16.75, 18.51, 30.49, 36.76, 47.03, 48.34, 115.86,

Figure 5. ^{51}V NMR spectra for monitoring the reaction of (a) $V(CHSiMe_3)(NAd)(OC_6F_5)(PMe_3)_2$ (**2b**) with $2,6\text{-}Me_2C_6H_3OH$ (1 equiv) and (b) $V(CHSiMe_3)(NAd)(O\text{-}2,6\text{-}Me_2C_6H_3)(PMe_3)_2$ (**2a**) with C_6F_5OH (1 equiv) in C_6D_6 at 25 °C.

124.50, 128.57, 166.26, 328.0. ^{51}V NMR (C_6D_6): δ −176.6 ($\Delta\nu_{1/2} = 648$ Hz). Anal. Calcd for $C_{28}H_{52}NOP_2SiV$: C, 60.09; H, 9.36; N, 2.50. Found: C, 60.27; H, 9.44; N, 2.50.

Typical NMR Experiments: The Reaction of V(CHSiMe₃)(NAd)-(CH₂SiMe₃)(PMe₃)₂ (1) with C₆F₅OH in C₆D₆. A typical procedure is as follows. Into a frozen C_6D_6 solution (ca. 0.4 mL) containing **1** (29 mg, 55 μmol) placed in the freezer (−30 °C) was added a C_6D_6 solution (ca. 0.1 mL) containing C_6F_5OH (10 mg, 1.0 equiv) in the drybox. The mixture was then monitored by ^{51}V NMR to estimate the ratio between the starting material and the product by integration ratio of the resonances. The measurements were started in less than 5 min.

Ring-Opening Metathesis Polymerization of Norbornene. The typical reaction procedure (Table 1) is as follows. Into a vial containing a benzene solution (9.30 mL) were added dissolved norbornene (200 mg), a benzene solution (0.25 mL) containing $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(PMe_3)_2$ (**1**, Ad = 1-adamantyl, 0.5 μmol), and a benzene solution containing ArOH (Ar = C_6F_5, 2,6-$F_2C_6H_3$, 2,6-$Me_2C_6H_3$) (0.5 μmol as 13.0 μL of a benzene solution) at room temperature (25 °C). The mixture was stirred for a prescribed time. The polymerization was then quenched by the addition of excess PhCHO, and the solution was stirred for an additional 30 min at room temperature. The mixture was then poured into methanol (ca. 100 mL). The resultant solid was collected by filtration, washed with methanol, and then dried *in vacuo*. The ROMPs of NBE in the absence of ArOH were also performed similarly in the drybox. The ROMPs by **1-NHC** were also conducted similarly except that the reactions were conducted in a sealed Schlenk tube at 80 °C in an oil bath.

Crystallographic Analysis. All measurements were made on a Rigaku XtaLAB mini imaging plate diffractometer with graphite-monochromated Mo Kα radiation. The crystal collection parameters are listed in the Supporting Information (Table S1).[10] All structures were solved by direct methods[14] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, and the rest were refined using the riding model. All calculations were performed using the Crystal Structure[15] crystallographic software package except for refinement, which was performed using SHELXL-97.[16]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional NMR spectra for $V(CHSiMe_3)(NAd)(CH_2SiMe_3)$-$(PMe_3)_2$ (**1**, Ad = 1-adamantyl) and $V(CHSiMe_3)(NAd)(O\text{-}2,6\text{-}Me_2C_6H_3)(PMe_3)_2$ (**2a**) and some reaction chemistry (with phenols, etc.) and crystal and data collection parameters and structural reports including CIF files for **1** and **2a**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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Scheme 6

■ ACKNOWLEDGMENTS

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(10) Crystal and data collection parameters and structural reports including CIF files for $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(PMe_3)_2$ (**1**, Ad = 1-adamantyl) and $V(CHSiMe_3)(NAd)(O-2,6-Me_2C_6H_3)-(PMe_3)_2$ (**2a**) are shown in the Supporting Information.

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