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A Transient Vanadium(III) Neopentylidene Complex. Redox Chemistry and Reactivity of the V=CH^{t}Bu Functionality

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The vanadium(III) bis(neopentyl) complex (PNP)V(CH$_2{}^t$Bu)$_2$ (PNP = N[4-Me-2-(P^{i}Pr$_2$)C$_6$H$_3$]$_2{}^-$), a complex readily prepared from alkylation of (PNP)VCl$_2$ with 2 equiv of LiCH$_2{}^t$Bu, serves as a precursor to the transient vanadium(III) alkylidene complex "(PNP)V=CH^{t}Bu". Two-electron oxidation of the intermediate [(PNP)V=CH^{t}Bu] with chalcogen sources results in formation of the vanadium(V) chalcogenide series (PNP)V=CH^{t}Bu(X) (X = O, S, Se, Te). This family of chalcogenide−alkylidenes has been studied via ^{51}V NMR spectroscopy in combination with DFT computational methods. The redox chemistry of [(PNP)V=CH^{t}Bu] and the reactivity of the alkylidene ligand are explored with the substrates N$_3$SiMe$_3$, N≡C^{t}Bu, N$_2$, and azobenzene. It was discovered that N=N cleavage of the last substrate can be achieved without oxidation of the metal.

Introduction

The utility of high-oxidation-state transition-metal alkylidenes is well-known within the chemical community, as many of these systems are capable of catalyzing important transformations such as olefin metathesis,[1] alkyne polymerization,[2−4] and Wittig-type reactions.[1,5] More recently, high-oxidation-state transition-metal alkylidenes have found a place in alkane metathesis catalytic cycles, combining alkene metathesis and dehydrogenation/hydrogenation catalysts.[6−9] Although significant effort has been dedicated to the development of nucleophilic "Schrock-type" alkylidene complexes containing 4d and especially 5d transition metals belonging to groups 5−7, the chemistry of 3d transition-metal alkylidenes, especially for vanadium, is still in its infancy.

The first vanadium(III) alkylidene complex, CpV=CH^{t}Bu(dmpe) (dmpe = bis(dimethylphosphanyl)ethane),[10] was reported by Teuben and co-workers in 1989. The synthesis of this complex involved treatment of the V(III) bis(alkyl) precursor with the chelating bis-phosphine ligand dmpe to promote α-hydrogen abstraction, furnishing the terminal alkylidene unit. It was not until 1994, however, that the first high-valent vanadium(V) alkylidene complex, CpV(NAr)(CHPh)(PMe$_3$) (Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$), was reported.[11] Unlike the heavier d^0 alkylidene congeners (e.g., Ta(V)), which are typically prepared by α-hydrogen abstraction involving high-valent metal precursors, CpV(NAr)(CHPh)(PMe$_3$) was generated via a two-electron-redox process in which the precursor, CpV(NAr)(PMe$_3$)$_2$, was oxidized by the Wittig reagent Ph$_3$P=CHPh, resulting in an alkylidene group-transfer reaction.[11]

High-oxidation-state alkylidene complexes of vanadium are of particular interest to us, given their potential use in catalytic group transfer chemistry due to the accessible V(V) ↔ V(III) redox shuffle. It has recently been established by Nomura et al. that vanadium(V) alkylidenes can function as highly active ring-opening metathesis polymerization (ROMP) catalysts.[12−14] In addition, silica-supported vanadium (IV) alkylidenes reported in 1998 by Scott and co-workers were shown to be reactive toward olefins, undergoing metathesis with styrene and catalyzing its polymerization.[15,16]

In the context of group 5 metal chemistry, the PNP ligand framework (PNP = N[2-P(CHMe$_2$)$_2$-4-Me-C$_6$H$_3$]$_2{}^-$),[17−19] a

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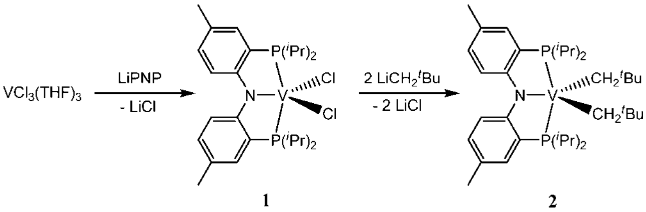
Scheme 1. Synthesis of 1 and 2 from the Precursor $VCl_3(THF)_3$



newer hybrid of the original Fryzuk ligand,[20] has recently been used as an ancillary support for transient Nb(III) fragments capable of activating atmospheric nitrogen and cleaving the N═N bond in azobenzene.[21] Likewise, this scaffold stabilized the first crystallographically characterized examples of terminal niobium bis(alkylidenes)(bistrimethylsilylmethylidene and bisneopentylidene),[22] as well as the first monomeric tantalum bis(methylidene) complex, $(PNP)Ta(CH_2)_2$.[23] In 1989, a related monoanionic PNP ligand was applied to vanadium, and this system was even used to construct some vanadium aryl and alkyl complexes.[24,25] More recently, we have shown the V(III) bis(neopentyl) complex $(PNP)V(CH_2{}^tBu)_2$ to be a ready precursor to a series of terminal vanadium(V) complexes bearing terminal alkylidene ligands when treated with various two-electron oxidants such as N_2CPh_2, oxo sources such as $OPPh_3$ ($O{=}PMe_3$ or N_2O can also be used), and sulfide sources such as S_8 and $S{=}PPh_3$.[26]

Herein, we report further on the reactivity of the V(III) alkyl species, $(PNP)V(CH_2{}^tBu)_2$, a molecule capable of undergoing two-electron-redox processes to generate terminal V(V) alkylidenes as well as other products derived from a transient alkylidene fragment, $[(PNP)V{=}CH^tBu]$. Some of the latter chemistry includes metathesis, atmospheric nitrogen, activation, and azobenzene N═N bond rupture. In addition to reactivity, we also discuss and explore the ^{51}V NMR spectroscopy of chalcogenido alkylidene complexes derived from the two-electron oxidation of $[(PNP)V{=}CH^tBu]$ through a combination of experiment and DFT calculations.

Results and Discussion

Incorporation of the Pincer Ligand and Subsequent Synthesis of the Alkylidene Precursor $(PNP)V(CH_2{}^tBu)_2$. In order to access the $[(PNP)V{=}CH^tBu]$ fragment (**A**), the PNP framework must first be introduced on V(III), followed by preparation of an appropriate vanadium alkyl precursor having α-hydrogens, but ideally lacking β-hydrogens to prevent competing side reactions such as β-hydrogen elimination. Accordingly, the precursor $(PNP)VCl_2$ (**1**) was conveniently synthesized by treatment of $VCl_3(THF)_3$ in toluene/THF (3:1) with 1 equiv of Li(PNP) at room temperature under an inert atmosphere (Scheme 1). It should be noted that complex **1** appears to bind Lewis bases, given that solutions in solvents such as toluene, benzene, and dichloromethane are red while a blue solution is formed in Lewis basic solvents such as THF and pyridine. Although **1** can be isolated and stored for later use, we have found that this is generally unnecessary, as this complex can generally prepared and used in situ en route to the corresponding bis(alkyl) species by performing the subsequent alkylation step in a one-pot reaction (vide infra), in a fashion similar to that described for preparation of the Ti(III) analogue $(PNP)Ti(CH_2{}^tBu)_2$.[27]

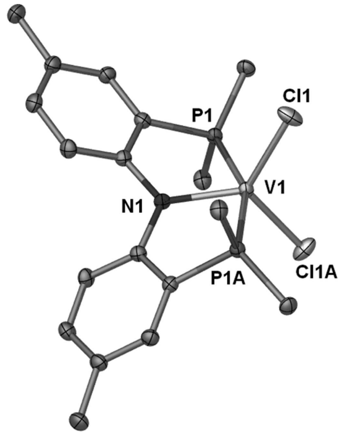


Figure 1. Molecular structure of complex **1** depicting thermal ellipsoids at the 50% probability level, with H atoms and ^{i}Pr methyl groups omitted for clarity. Distances are reported in Å and angles in deg. Selected metrical parameters: V(1)−N(1), 1.950(3); V(1)−Cl(1), 2.2687(7); V(1)−Cl(1A), 2.2687(7); V(1)−P(1), 2.4835(6); V(1)−P(1A), 2.4835(6); P(1)−V(1)−P(1A), 158.42(4); N(1)−V(1)−Cl(1) 121.74(2); N(1)−V(1)−Cl(1A) 121.74(2); Cl(1)−V(1)−Cl(1A), 116.53(5).

Although **1** was typically used as a reactant in situ, we felt compelled to confirm its connectivity by single-crystal X-ray diffraction studies, as the close relatives "$(PNP)TiCl_2$" and "$(PNP)NbCl_2$" eluded crystallographic analysis or isolation.[21,27] Single crystals of **1** were grown by slow diffusion of hexane into a dichloromethane solution at room temperature. The single-crystal X-ray structure of **1** (Figure 1) displays a monomeric $(PNP)VCl_2$ species in a distorted-trigonal-bipyramidal geometry with the N and two Cl atoms defining the base of the pyramid. Half of the formula unit is crystallographically unique; V and N are located on a 2-fold axis ($^3/_4$, y, $^1/_4$). The observed geometrical parameters are within the expected ranges. The identity of **1** is further supported by mass spectral analyses (MS-CI), further suggesting that the molecular ion is indeed the monomeric and unsolvated $(PNP)VCl_2$ fragment.

Synthesis of the bis(neopentyl)vanadium complex $(PNP)V(CH_2{}^tBu)_2$ (**2**) was achieved by treatment of a −36 °C THF/toluene solution of **1** (generated in situ) with 2 equiv of neopentyllithium, $LiCH_2{}^tBu$, in hexane (Scheme 1). Upon addition of the lithium reagent, the red/purple suspension of **1** rapidly becomes green, and after workup of the reaction mixture, complex **2** is collected in ~78% yield as analytically pure green crystals upon cooling a concentrated hexanes solution to −35 °C over 12 h. The complex is exceedingly air and moisture sensitive. Over the course of several days, room-temperature solutions of **2** under an atmosphere of nitrogen are converted to $[(PNP)V{=}CH^tBu]_2(\mu_2,\eta^1{:}\eta^1\text{-}N_2)$ (**3**).[26] The reactivity of **2** contrasts sharply with that of the putative "$(PNP)Nb(CH_2{}^tBu)_2$", a system which presumably undergoes a rapid series of transformations such as α-hydrogen abstraction and dihydrogen elimination steps, resulting in the high-valent bis(neopentylidene) complex $(PNP)Nb(CH^tBu)_2$.[22]

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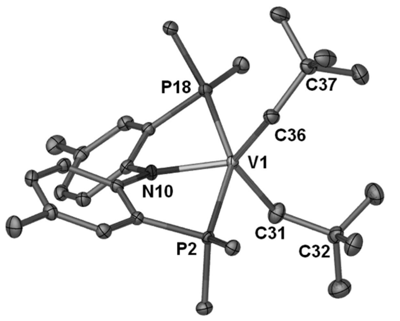
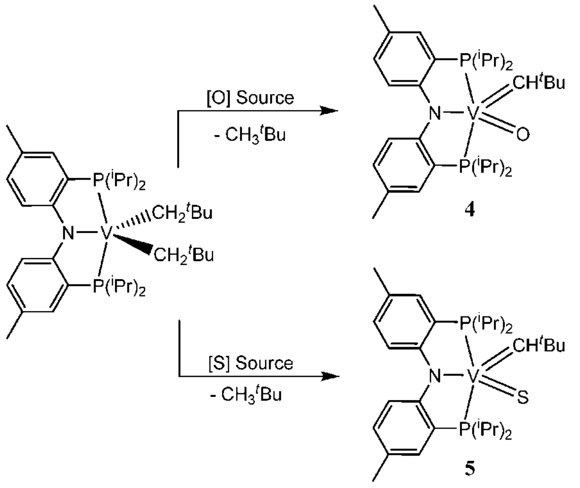


Figure 2. Molecular structure of complex **2** depicting thermal ellipsoids at the 50% probability level, with H atoms and ^{i}Pr methyl groups omitted for clarity. Distances are reported in Å and angles in deg. Selected metrical parameters: V(1)−N(10), 2.0230(11); V(1)−C(36), 2.1085(14); V(1)−C(31), 2.1148(15); V(1)−P(2), 2.5882(4); V(1)−P(18), 2.5947(4); C(36)−V(1)−C(31), 121.46(6); P(2)−V(1)−P(18), 151.750(13); C(32)−C(31)−V(1), 131.03(11); C(37)−C(36)−V(1), 138.85(10).

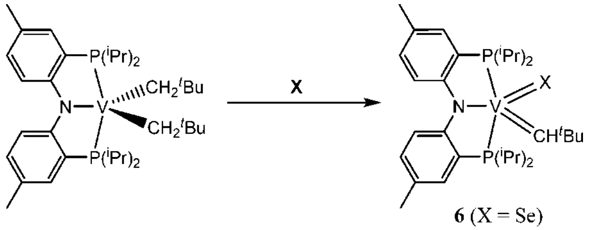
Characterization of **2** was achieved through a combination of solution magnetization measurements (Evans method), X-ray diffraction data, and combustion analysis. The μ_{eff} value for **2** in C_6D_6 at 25 °C was found to be $2.74 \pm 0.07\ \mu_B$. This value is in accord with the expected spin-only value of 2.83 μ_B for the d^2 configuration, thus indicating a high-spin vanadium(III) system. Single crystals of **2** suitable for X-ray diffraction analysis were slowly grown from diethyl ether at room temperature. The crystal structure of **2** revealed the expected monomeric bis(alkyl) species (Figure 2), with the vanadium center confined in a highly distorted trigonal bipyramid when the P−V−P linkage, 151.750(13)°, is treated as the primary axis. Given the meridional constraint imposed by the aryl PNP framework, the alkyl ligands are forced into a cis orientation (121.46(6)°). The V−C distances of 2.1085(14) and 2.1148(15) Å are within the range of other V−C$_{\mathrm{alkyl}}$ distances of 2.062 and 2.061 Å reported for bis(alkyl) V(III) complexes originally synthesized by Budzelaar as well a V(IV) bis(neopentyl) species reported by Gambarotta and co-workers.[28,29] The V−C−C bond angles of 131.03(11) and 138.85(10)° in complex **2** are further indicative of V−C alkyl bonds.

Reactions of 2 To Generate High-Valent and Terminal Vanadium(V) Chalcogenido−Alkylidenes. Previously, we synthesized the chalcogenido−alkylidene species (PNP)V═CH^{t}Bu(O) (**4**) (vide infra) and the analogue (PNP)V═CH^{t}Bu(S) (**5**) via two-electron-redox processes stemming from the precursor **2** and the corresponding chalcogen source (Scheme 2).[26] The oxo−alkylidene species **4** has previously been synthesized via treatment of **2** with Ph$_3$P═O or N$_2$O; we have also confirmed that treatment of **2** with pyridine *N*-oxide or trimethylamine *N*-oxide, with mild heating (50 °C), results in formation of **4** (Scheme 2). While these oxo-transfer type reactions were expected, we have also made the curious discovery that **4** can be generated in 49% yield by treating a hexane solution of **2** with the free radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). After 2 days, the crude reaction mixture of TEMPO and **2** is found by ^{1}H NMR spectra and MS-CI to contain **4** and as yet unidentified paramagnetic products. Complex **4** is separated from the product mixture and isolated in pure form by removing the volatiles in vacuo and extracting with hexamethyldisiloxane (TMS$_2$O). Therefore, it appears that compound **4** is a highly favored thermodynamic product, since reagents such as TEMPO are not typically sought as O atom sources. Complex **5** can be similarly prepared from **2** and sulfide sources such as S$_8$, Ph$_3$P═S, or Me$_3$P═S (Scheme 2).

Scheme 2. Synthesis of 4 and 5 via Treatment of 2 with [O] Sources Such as R$_3$P═O, N$_2$O, TEMPO, R$_3$N═O, and Pyridine *N*-Oxide and [S] Sources Such as S$_8$ and R$_3$P═S, Respectively



Scheme 3. Synthesis of Complexes 6 and 7 via Treatment of 2 with Se^0 and Te^0



6 (X = Se)
7 (X = Te)

Unfortunately, the isolation of the heavier chalcogenide analogues has proven somewhat more difficult. For instance, the selenido alkylidene (PNP)V═CH^{t}Bu(Se) (**6**) can be prepared by heating a dilute mixture of **2** and elemental Se to 60 °C in benzene under an atmosphere of argon for 4 h to afford this complex in 45% yield, as judged by ^{1}H NMR spectroscopy using an internal integration standard (1,4-dioxane) (Scheme 3). Crude powders (judged by ^{1}H NMR spectra)[30] of **6** can be isolated by storing concentrated hexane solutions at −36 °C for several days. While attempts to isolate single crystals of **6** have failed, spectroscopic data strongly support our assignment of the complex in solution as that proposed. MS-CI reveals a molecular ion, [M]$^+$, at *m/z* 629.2007, and the isotopic distribution found experimentally (most abundant ions: *m/z* 625.2005, 626.2046, 627.2021, 629.2007, 630.2033, and 631.2030) is in excellent agreement with the calculated mass distribution (*m/z* 625.205, 626.206, 627.205, 629.202, 630.206, and 631.204).[30] The ^{13}C NMR spectrum contains a broad resonance at 328.4 ppm, which we assign to the alkylidene α-C while the ^{1}H NMR spectrum reveals a singlet at 9.24 ppm assigned to the corresponding alkylidene α-H. These resonances are shown, via an HMQC experiment, to correlate to one another. Due to the broadness of the resonance at 328.4 ppm, NMR spectroscopic coupling constants (J_{CH}) could not be determined with certainty, even

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[30] See the Supporting Information.

when the solution was cooled to −50 °C. The ^{51}V NMR spectrum of **6** evinces one broad signal at 809 ppm ($\Delta\nu_{1/2}$ = 993 Hz, 25 °C, C_6D_6). As a result, the above data, with the support of DFT NMR shift calculations (vide infra), strongly support the identity of **6** as a monomer.

Likewise, attempts to crystallographically characterize (PNP)V=CH^{t}Bu(Te) (**7**) have, thus far, been unsuccessful. To prepare **7**, complex **2** was treated with excess elemental Te powder in THF, resulting in formation of a diamagnetic complex which we propose to be the monomeric tellurido−alkylidene on the basis of a combination of MS-CI, ^{1}H/^{13}C/^{31}P NMR studies, and ^{51}V NMR spectroscopic data (1249 ppm, $\nu_{1/2}$ = 864 Hz). The isotopic distribution and intensities found in the experimental MS-CI spectrum of **7** match those found in the calculated spectrum quite closely, with the most intense ions observed being *m/z* 674.1908, 675.1899, 677.1888, 679.1901 and the most intense ions calculated at *m/z* 674.191, 675.190, 677.193, and 679.192.[30] Further, the ^{1}H NMR spectrum of **7** is consistent with our proposed formulation, while the ^{13}C NMR spectrum of **7** also corroborates our data, revealing an alkylidene carbon resonance at 332.3 ppm (d_8-toluene −28.0 °C). The gHMQC NMR experiments conducted at −13 °C in d_8-toluene clearly reveal a correlation between the downfield carbon peak at 332 ppm and a proton resonance at 6.7 ppm.

Solutions of pure **7** seem to be stable under an inert atmosphere, but the presence of oxidants or traces of Te^0 promote decomposition into as yet unidentified products. Schrock and co-workers also observed a lack of stability in a V=Te multiply bonded species in solution.[31] In their case, solutions of $[N_3N]V{=}Te$ (N_3N^{3-} = $(Me_3SiNCH_2CH_2)_3N$) were often found to decompose via deposition of a Te^0 mirror. To date, the only reported example of a complex bearing a terminal V=Te ligand that is sufficiently stable for structural characterization via X-ray diffraction is [η^4-Me$_8$taa]V=Te ([η^4-Me$_8$taa]$^{2-}$ = octamethyldibenzotetraaza[14]annulene), a species reported by the group of Parkin in 1997.[32]

As with compounds **4** and **5**, we speculate that the heavier alkylidene−chalcogenido derivatives are formed via activation of Se or Te by the transient alkylidene **A.** We propose this mechanism, given that N_2 is activated by transient **A** to afford **3** when no other suitable substrates are present. At this point, however, it is uncertain whether the chalcogen substrate (or N_2) promotes α-hydrogen abstraction in **2** to form the alkylidene prior to oxidation of the metal center (Scheme 4).

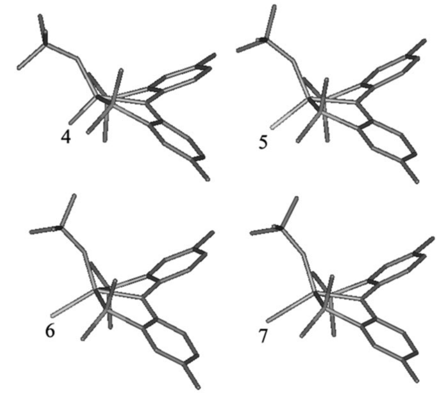


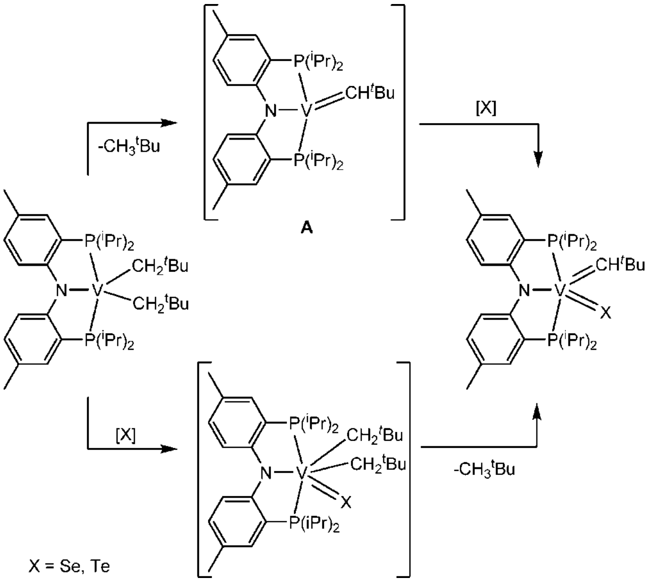
Figure 3. DFT optimized structures (B3LYP, 6-31G**) of (PNP)V=CH^{t}Bu(=X) (complexes **4**−**7**). Isopropyl methyls on phosphorus and hydrogens are omitted for clarity.

Table 1. Selected Calculated (in Italics) and Experimental Structural Data for Chalcogenido−Alkylidenes[a]

complex	V=X bond length	V=C bond length	V=C−C angle
4	1.595/*1.599*	1.894/*1.833*	140.5/*142.4*
5	2.0706/*2.055*	1.826/*1.794*	155.2/*150.6*
6	*2.228*	*1.786*	*153.4*
7	*2.447*	*1.781*	*156.9*

[a] Distances are reported in Å and angles in deg.

Scheme 4. Proposed Formation of Heavier Chalcogenide−Alkylidenes from Se or Te Oxidation



^{51}V NMR Spectra of the Chalcogenide−Alkylidenes. It is well documented that the ^{51}V NMR chemical shifts of high-valent vanadium complexes exhibit inverse electronegativity dependence; ligands bound to vanadium through oxygen or nitrogen atoms induce high shielding, while ligands that are less electronegative and more polarizable (Br$^-$, I$^-$, S^{2-}, Se^{2-}, Te^{2-}) result in deshielding of the ^{51}V nucleus.[33] The ^{51}V NMR spectra for this family of chalcogenide−alkylidene complexes, (PNP)V=CH^{t}Bu(X) (X = O, S, Se, Te), clearly illustrate an inverse electronegativity dependence, as the observed ^{51}V NMR chemical shifts of complexes **4**−**7** follow a trend of increasing chemical shift on proceeding down the chalcogen group. This trend in ^{51}V NMR spectroscopic shifts compares quite favorably with that of a family of vanadium(V) chalcogenide−chalcogenolates prepared by the group of Arnold[34] in 1996 and Gambarotta in 1997,[35] as well as a series of V(V) chalcogenide complexes reported by Schrock in 1994.[31]

As additional support for our contention that **6** and **7** are structurally analogous to complexes **4** and **5,** DFT computational methods were employed. A series of NMR-predictive DFT

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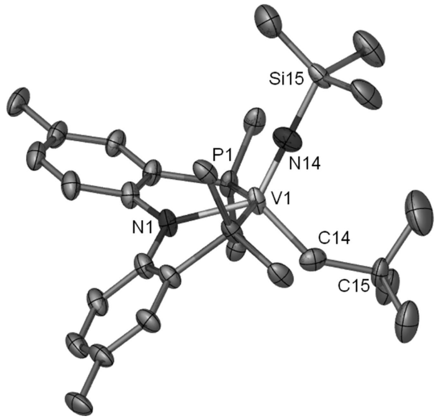

Figure 4. Molecular structure of complex **8** displaying thermal ellipsoids at the 50% probability level with hexanes solvent. H atoms and ^{i}Pr methyl groups are excluded for clarity. Distances are reported in Å and angles in deg. Selected metrical parameters: V(1)−N(14), 1.611(5); V(1)−C(14), 1.928(6); V(1)−N(1), 2.1084(15); V(1)−P(1), 2.4890(3); N(14)−Si(15), 1.732(5); V(1)−N(14)−Si(15), 172.4(3); C(15)−C(14)−V(1), 145.8(5); N(14)−V(1)−C(14), 110.94(19); N(14)−V(1)−N(1), 130.34(18); C(14)−V(1)−N(1), 118.62(18).

calculations of the ^{51}V NMR chemical shifts for geometrically optimized structures of monomeric (PNP)V═CH^{t}Bu(X) complexes **4**−**7** (Figure 3 and Table 1) are in excellent agreement with the experimental data (Table 2). We have also explored the possibility of dimeric forms of **6** and **7**, by either bridging Te or Se or the alkylidene ligands. In both cases the dimeric structures converged into two corresponding monomers during geometry optimization. The optimized structures for complexes **4** and **5** seem to be consistent with experimentally determined structures in that the differences between measured and calculated bond lengths and angles all fall under 5%. The calculated NMR chemical shifts for all chalcogenide−alkylidenes (**4**−**7**) agree within 10% of the experimental values. Calculated shifts for **5**−**7** vary from experiment by less than 5%. We strongly believe that these calculations, in addition to spectroscopic evidence, lend support to our proposed connectivity of **6** and **7** in solution.

Reactivity of 2 with Trimethylsilyl Azide. Treatment of **2** with trimethylsilyl azide led to the expected V(V) imido−alkylidene species concurrent with N_2 evolution. The diamagnetic complex (PNP)V═CH^{t}Bu(NSiMe$_3$) (**8**) was synthesized by treating a thawing hexane solution of **2** with a thawing hexane solution of trimethylsilyl azide and allowing the stirred solution to reach room temperature. Complex **8** was characterized by a combination of X-ray diffraction data, multinuclear NMR spectroscopy, and mass spectroscopy. Multinuclear NMR spectroscopic studies of complex **8** are indicative of a V(V) alkylidene species: in the ^{1}H NMR a diagnostic alkylidene α-H resonance was located at 12.51 ppm, and in the ^{13}C NMR the α-C resonance was found at 321.5 ppm. Mass spectroscopy (CI) yielded the [M]$^+$ value at 636.3340, which is in good agreement with the theoretical value of [M]$^+$, 636.3357.[30] The reaction leading to formation of **8** is not entirely clean, as side products are also observed by ^{1}H and ^{13}C NMR spectra; however, we were fortunate to isolate small yellow, single crystals of **8** grown from concentrated solutions pentane or hexanes at room temperature. Accordingly, the X-ray diffraction analysis of single crystals of **8** reveals the expected pseudo-trigonal-bipyramidal structure (Figure 4). A cursory inspection of the structure of complex **8** indicates that it is geometrically very similar to the molecular structures of **4** and **5**. The vanadium−imide nitrogen bond of 1.611(5) Å is somewhat shorter than those observed for the few crystallographically characterized V(V) imido−alkylidene species;[11,36,37] this is, perhaps, an indication of a strong V−N pseudo triple bond. The V═N−Si angle of 172.4(3)° is additionally supportive of a vanadium−imide nitrogen pseudo triple bond. The vanadium−alkylidene linkage, C(15)−C(14)−V(1), is considerably more distorted than other examples of V(V) imido−alkylidenes with a V−C−C angle of 145.8(5)°.

Table 2. Calculated (cc-pVTZ(-f)) and Experimental NMR Chemical Shifts for Complexes 4−7

complex	^{51}V NMR shift (ppm) exptl	^{51}V NMR shift (ppm) calcd
4	−58	−63
5	570	549
6	809	843
7	1249	1294

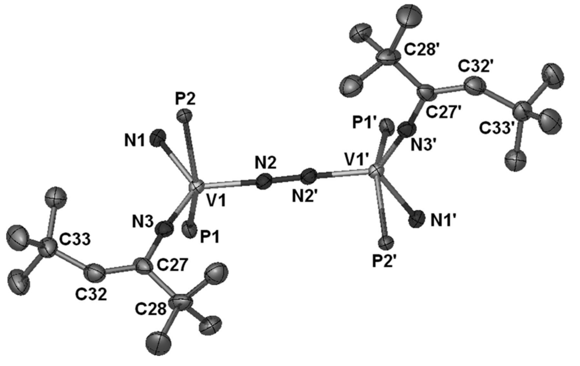

Figure 5. Molecular structure of complex **9** displaying thermal ellipsoids at the 50% probability level, with hexanes solvent and H atoms excluded and the PNP ligand simplified to the first coordination sphere for clarity. Distances are reported in Å and angles in deg. Selected metrical parameters: V(1)−N(1), 2.081(2); V(1)−N(2), 1.845(2); V1−N3, 1.717(2); V(1)−P(1), 2.4987(7); V(1)−P(2), 2.4661(7); N(2)−N(2′), 1.222(4); N(3)−C(27), 1.383(3); C(27)−C(28) 1.551(4); C(27)−C(32), 1.353(4); N(2′)−N(2)−V(1), 178.0(2); N(3)−V(1)−N(2), 122.75(10); N(3)−V(1)−N(1), 118.46(9); N(2)−V(1)−N(1), 118.72(8); P(2)−V(1)−P(1), 152.19(3); C(27)−N(3)−V(1), 173.63(19); C(32)−C(27)−N(3), 127.4(3); C(32)−C(27)−C(28), 118.5(2); C27−C32−C33 135.0(3).

Reactivity of the Transient Alkylidene A with ^{t}BuC≡N. Up to this point, the focus of this report has been on the synthesis of five-coordinate V(V) alkylidenes, which we believe to result from oxidation of the putative alkylidene fragment **A**; however, we have not discussed reactivity at the alkylidene functionality for such a species. It seemed likely that the alkylidene ligand in putative **A** would display Wittig-like behavior in the presence of unsaturated polarized substrates. Accordingly, treatment of **2** with ^{t}BuC≡N under an atmosphere of N_2 produced over 24 h the compound [(PNP)V═NC(^{t}Bu)═CH^{t}Bu]$_2$(μ_2,η^1:η^1-N$_2$) (**9**) (Figure 5). Formation of this complex is proposed to proceed via a [2 + 2] cycloaddition reaction between the alkylidene ligand in transient **A** and ^{t}BuC≡N, resulting in a four-cooordinate vinylimido species, [(PNP)V═NC(^{t}Bu)═CH^{t}Bu], which subsequently binds and reduces N_2 to furnish the end-on bridging dinitrogen as well as a terminal imide ligand (Scheme 5). A similar complex of vanadium was reported by Teuben et al. in 1993; in this example, however, treating the V(III) alkylidene CpV═CH^{t}Bu(dmpe) with ^{t}BuC≡N results in forma-

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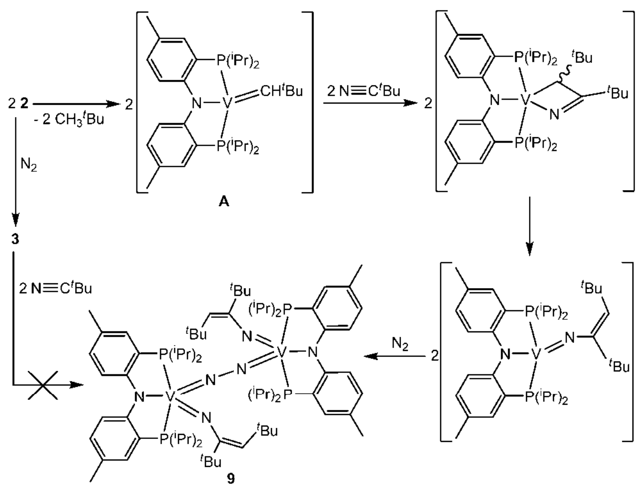
Scheme 5. Proposed Mechanism to Formation of 9 via Intermediate A[a]



[a] Independently, treatment of **3** with ^{t}BuC≡N does not yield **9**, consistent with the proposed mechanism.

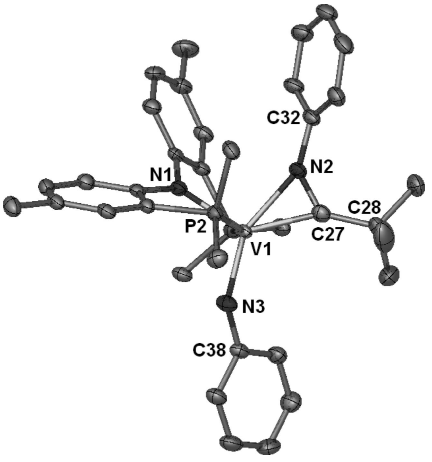


Figure 6. Molecular structure of complex **10** displaying thermal ellipsoids at the 50% probability level. H atoms, ^{i}Pr methyl groups, and hexane solvent are excluded for clarity. Distances are reported in Å and angles in deg. Selected metrical parameters: V(1)–N(3), 1.951(2); V(1)–N(2), 2.111(2); V(1)–C(27), 2.056(3); V(1)–N(1), 2.057(2); V(1)–P(2), 2.5405(8); V(1)–P(1), 2.5500(9); C(27)–N(2), 1.281(3); N(3)–V(1)–C(27), 115.78(11); N(3)–V(1)–N(1), 110.55(9); C(27)–V(1)–N(1), 133.59(10); N(3)–V(1)–N(2), 151.47(10); C(27)–V(1)–N(2), 35.78(9); N(1)–V(1)–N(2), 97.81(8); C(27)–N(2)–V(1), 69.79(16); N(2)–C(27)–V(1), 74.43(17); C(28)–C(27)–V(1), 153.7(2); N(2)–C(27)–C(28), 131.9(3); C(27)–N(2)–C(32), 136.5(3); C(32)–N(2)–V(1), 152.94(19); C(38)–N(3)–V(1), 139.56(19); C(28)–C(27)–N(2)–C(32), −5.8(5).

tion of [CpV=NC(^{t}Bu)=CH^{t}Bu](dmpe) without any evidence of dinitrogen activation.[38] In the formation of [CpV=NC(^{t}Bu)=CH^{t}Bu](dmpe), the starting complex, CpV=CH^{t}Bu(dmpe), is coordinatively saturated; thus, the probablility of N_2 coordinating is diminished. However, in the case of compound **9**, the putative intermediate, [(PNP)V=NC(^{t}Bu)=CH^{t}Bu], is a low-valent and coordinatively unsaturated vinyl–imido fragment, which seems primed for coordination and reduction of a substrate such as N_2. Vanadium(III) has been known to activate N_2 when coordination sites are available.[39−41] However, one cannot refute a different pathway to formation of compound **9**. For instance, intermediate **A** could activate N_2 prior to Wittig-like reactivity of the nitrile with the alkylidene ligand. This pathway would also result in formation of a vanadium complex having both N_2 and alkylidene ligands.

Previously, we reported the synthesis of the alkylidene–dinitrogen complex **3,** by mild heating of **2** under a bed of atmospheric nitrogen over 12 h (vide supra). This prompted an investigation of an alternative mechanism to formation of compound **9** using complex **3**. Accordingly, treatment of **3** with excess ^{t}BuC≡N at room temperature or under mild heating (40 °C) for 48 h did not result in a reaction according to both ^{1}H and ^{31}P NMR spectra of the mixture (Scheme 5). The lack of reactivity in **3** toward nitriles is not entirely unexpected, as this molecule is nearly coordinatively saturated as well as sterically hindered. However, this lack of reactivity of **3** implies that Wittig-like chemistry most likely precedes N_2 activation along the formation of **9**.

Characterization of **9** involved multinuclear NMR studies, combustion analysis, and single-crystal X-ray diffraction studies. Analogous to the structure of **3**,[26] half of the molecule is crystallographically unique with an inversion on the N–N ($-x$, y, $-z + {}^1/_2$) bond. The X-ray structure reveals a topologically linear V=N=N=V bridging unit with a V–N–N angle of 178.0(2)°. The N(2)–N(2′) distance of 1.222(4) Å is indicative of significant reduction in the N≡N bond from that of free dinitrogen (1.098 Å).[42] Each NC(^{t}Bu)=CH^{t}Bu fragment is found with the ^{t}Bu groups trans to one another. Additionally, the imide linkage, C(27)–N(3)–V(1), is virtually linear at 173.63(19)°, thus implying the presence of a strong bond between the imide nitrogen and vanadium. It should be noted that, prior to crystallization, complex **9** appears as a mixture of two isomers according to NMR studies. ^{1}H and ^{13}C NMR spectra of these isomeric mixtures contain twice the number of resonances expected in **9**, with only a slight disparity in chemical shifts. Once isolated as a crystalline material, complex **9** appears as only one isomer, as evidenced by X-ray diffraction and solution NMR studies.

N=N Cleavage of Azobenzene by Transient A. Previously we have demonstrated that a transient and putative Nb(III) species, "(PNP)NbCl$_2$", readily cleaves the N=N bond in azobenzene by an overall 4e reduction, whereby a metal–ligand cooperative process generates (PNP=NPh)NbCl$_2$(NPh) (PNP=NPh$^-$ = N[2-P(CHMe$_2$)$_2$-4-Me-C$_6$H$_3$][2-P=NPh(CHMe$_2$)$_2$-4-Me-C$_6$H$_3$]). In the case of V(III), compound **1** fails to react with azobenzene at room temperature over several days. However, treatment of **2** with 1 equiv of azobenzene results in formation of a V(III) η^2-iminoacyl–amide complex, [(PNP)V(η^2-PhN=C^{t}Bu)(NHPh)] (**10**), which can be isolated in 45% yield as red crystals. Cleavage of the N=N bond in azobenzene by vanadium(III) has precedent, but such a process is rare. The group of Kawaguchi has reported that the vanadium(III) tris(arylthiolato) complex V(SAr)$_3$(THF) (Ar = C$_6$H$_3$-2,6-(Si(CH$_3$)$_3$)$_2$) when treated with azobenzene results in formation of a V(V) imide–sulfenamide complex, V(NPh)(PhNSAr)-

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Scheme 6. Proposed Mechanism of Formation of Compound 10 from N=N Bond Cleavage in Azobenzene

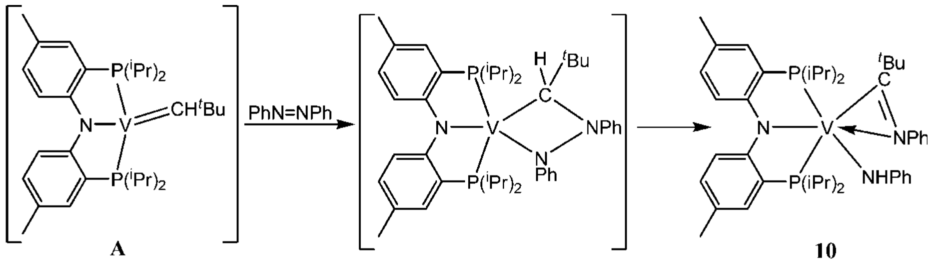

Table 3. Crystal Data and Experimental Parameters for Compounds 1, 2, and 8−10

	1	2	8	9	10
empirical formula	$C_{26}H_{40}Cl_2NP_2V$	$C_{36}H_{62}NP_2V$	$C_{34}H_{59}N_2P_2SiV$	$C_{78}H_{132}N_6P_4V_2$	$C_{46}H_{67}N_3P_2V$
formula wt	550.37	621.75	636.80	1379.66	774.91
cryst color and shape, size (mm^3)	red isometric block, 0.8 × 0.07 × 0.07	black cleaved block, 0.30 × 0.30 × 0.30	yellow plate, 0.05 × 0.05 × 0.005	black block, 0.22 × 0.18 × 0.12	brown plate, 0.18 × 015 × 0.04
T (K)	150(2)	126(2)	15(2)	150(2)	150(2)
λ (Å)	0.710 73	0.710 73	0.442 80	0.710 73	0.710 73
cryst syst, space group	monoclinic, *P*2/*n*	orthorhombic, *Pbca*	monoclinic, *C*2/*c*	monoclinic, *C*2/*c*	triclinic, $P\bar{1}$
unit cell dimens					
a (Å)	11.5013(7)	18.6610(9)	11.6147(7)	28.613(2)	13.1283(10)
b (Å)	9.2139(5)	19.7507(9)	31.6104(19)	14.9540(11)	13.6869(10)
c (Å)	12.9166(7)	19.8391(10)	11.6936(7)	21.963(3)	14.0635(10)
α (deg)					66.438(2)
β (deg)	95.777(1)		95.694(1)	121.997(1)	70.476(2)
γ (deg)					82.018(2)
V (Å^3)	1361.84(13)	7312.1(6)	4272.1(4)	7969.9(13)	2183.1(3)
Z	2	8	4	4	2
ρ_{calcd} (Mg/m^3)	1.342	1.130	0.990	1.150	1.179
μ (mm^{-1})	0.693	0.382	0.187	0.358	0.334
θ range for data collecn (deg)	2.21−26.75	2.05−30.02	0.80−19.93	1.60−26.42	1.62−25.36
no. of rflns collected	15 994	117 358	28 085	48 069	17 379
no. of unique rflns	2855 (R_{int} = 0.0948)	10 692 (R_{int} = 0.0627)	8025 (R_{int} = 0.0447)	8179 (R_{int} = 0.0413)	7943 (R_{int} = 0.0439)
no. of obsd rflns ($I > 2\sigma(I)$)	2091	7888	6045	6700	5231
max and min transmissn	0.9531 and 0.9466	0.8964 and 0.7911	0.9991 and 0.9907	0.9583 and 0.9254	0.9868 and 0.9423
no. of data/restraints/ params	2855/0/150	10 692/0/609	8025/20/220	8179/6/423	7943/3/483
goodness of fit on F^{2a}	1.023	0.993	1.107	1.062	0.996
final R indices ($I > 2\sigma(I)$)^a	R1 = 0.0359, wR2 = 0.0767	R1 = 0.0337, wR2 = 0.0846	R1 = 0.0518, wR2 = 0.1693	R1 = 0.0491, wR2 = 0.1302	R1 = 0.0447, wR2 = 0.1021
R indices (all data)^a	R1 = 0.0631, wR2 = 0.0848	R1 = 0.0543, wR2 = 0.0953	R1 = 0.0651, wR2 = 0.1810	R1 = 0.0625, wR2 = 0.1412	R1 = 0.0885, wR2 = 0.1189
largest diff peak and hole (e Å^{-3})	0.395 and −0.483	0.696 and −0.213	1.108 and −1.094	0.886 and −0.363	0.444 and −0.490

[a] Goodness of fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$, all data. R1 = $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

(SAr).[43] In their studies, the N=N bond of azobenzene has been cleaved in a metal−ligand 4e cooperative process. In our case, we propose that complex **10** derives from a [2 + 2] cycloaddition of azobenzene across the alkylidene moiety in transient **A** to furnish a diazametallacyclobutane intermediate, in which the proton originating from the alkylidene unit then undergoes a 1,3-shift to promote cleavage of the weak N−N bond (Scheme 6). The magnetic moment of complex **10** (by the Evans method) is consistent with an $S = 1$ vanadium(III) ion ($\mu_{eff} = 2.98\ \mu_B$, 25 °C, C_6D_6). Mass spectroscopy (MS-CI) also corroborates the identity of **10**, yielding the ion $[M - H]^+$, found at m/z 730.3608 (calculated $[M - H]^+$ m/z 730.3618). As depicted in Figure 6, the solid-state structure of **10** clearly exposes a three-membered azametallacycle (η^2-acylimine), V(1)−C(27)−N(2), as well as a primary anilide ligand. This η^2-acylimine feature is manifested in the V(1)−C(27) distance of 2.056(3) Å, consistent with the V−C$_{alkyl}$ as well as a dative bond to an iminoacyl nitrogen (V(1)−N(2), 2.111(2) Å).[44−48] The C(27)−N(2) bond length of 1.281(3) Å is consistent with a C=N moiety, thus further supporting our designation of **10** as having an η^2-iminoacyl fragment. Additionally, the torsion angle of the iminoacyl fragment (C(28)−C(27)−N(2)-−(32)) is −5.8(5)°, and C(28) deviates 0.038 Å while C(32) is 0.133 Å from the plane defined by the atoms V(1), C(27), and N(2), suggesting that a proton is highly unlikely to be present on either C(27) or N(2). Overall, the gross metrical parameters about the V−C−N ring system in **10** are comparable to those of other known vanadium

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(49) An analysis of over 180 entries containing more than 425 V−N amide linkages found in the CSD, via Conquest V1.10 on 10/10/08, suggests an average V−N amide bond distance of approximately 2.0 Å.

iminoacyl complexes reported in the literature.[44−48] Finally, the V(1)−N(3) bond length of 1.951(2) Å[49] and the angle C(38)−N(3)−V(1) of 139.56(19)° are indicative of a vanadium primary anilide ligand. The formation of complex **10** contrasts with all our other previous chemistry in that N═N rupture does not occur by a reductive cleavage process, since the oxidation state on vanadium is unchanged.

Conclusions

The bis(neopentyl)vanadium(III) complex **2** has been shown to be a versatile precursor to high-valent vanadium alkylidenes as well as derivatives originating from the transformation of the alkylidene functionality. Specifically, two-electron -redox chemistry of the transient alkylidene complex **A** allows for the isolation of novel high-valent vanadium alkylidene complexes bearing terminal chalcogenides ranging from O^{2-} to Te^{2-}. While the sulfide and oxo complexes are thermally stable, the selenide and telluride derivatives undergo decomposition in solution to, as yet, unidentified products. To assist in the characterization of the heavier chalcogenide−alkylidenes, we have conducted a combination of experimental and DFT-based computational studies, which provide excellent agreement between our experimental and calculated ^{51}V NMR spectroscopic data. Computed structures corroborate well with the latter data and lend strong support to our proposed connectivity of monomeric (PNP)V═CH^{t}Bu)(X) (X = O, S, Se, Te) complexes.

While the reactivity of the transient alkylidene fragment **A** is seemingly dominated by such 2e redox chemistry with chalcogen sources or oxidants such as N_3SiMe_3, the alkylidene motif itself has been demonstrated to be a participant in [2 + 2] cycloaddition chemistry, as evidenced by the products of reactions with the substrates ^{t}BuC≡N and azobenzene. The product resulting from treatment of **2** with ^{t}BuC≡N derives from cycloaddition with a transient alkylidene fragment as well as reduction of dinitrogen, while azobenzene leads to a η^2-iminoacyl product thought to be derived from cycloaddition and a 1,3-hydrogen shift resulting in N−N bond cleavage.

The ability of **A** to reduce N_2 or other substrates, as well as perform [2 + 2] cycloaddition chemistry, provides a unique opportunity to study two important transformations taking place at one metal center. Likewise, such a system might provide clues on how to activate atmospheric nitrogen and subsequently perform cycloaddition chemistry with this substrate. Other current efforts in our laboratories include further exploration of the redox chemistry and metathesis reactivity of the alkylidene unit resulting from **2**.

Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Laboratory Master double-drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere. Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in Sure-Seal reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column.[50] Diethyl ether and CH_2Cl_2 were dried by passage through two columns of activated alumina.[50] THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal (thin cuts). Distilled THF was transferred under vacuum into glass bombs before being brought into a drybox. C_6D_6 was purchased from Cambridge Isotope Laboratory (CIL), degassed, and then vacuum-transferred to 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Complexes **3**−**5**,[26] Li(PNP),[51] LiCH$_2{}^t$Bu,[52] and VCl$_3$(THF)$_3$[53] were prepared according to the literature. Complex **2** was prepared with slight modifications to the procedure initially reported.[26] CHN analyses were performed by Midwest Microlabs, Indianapolis, IN. ^{1}H, ^{51}V, ^{31}P, and ^{13}C NMR spectra were recorded on Varian 500, 400, and 300 MHz NMR spectrometers. ^{1}H and ^{13}C NMR are reported with reference to residual solvent resonances: for ^{1}H NMR residual C_6H_6 in C_6D_6 at 7.16 ppm and for ^{13}C NMR C_6D_6 at 128 ppm. ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (0.0 ppm). ^{51}V NMR chemical shifts are reported with respect to $VOCl_3$ (0.0 ppm). Values of $\nu_{1/2}$ in ^{51}V spectra are reported with the line-broadening parameter set to 20. Solution magnetic moments measurements were obtained by the method of Evans.[54,55] X-ray diffraction data were collected on a SMART6000 (Bruker) system or a Bruker APEX Kappa DUO using Mo radiation under a stream of N_2 (g) at low temperatures, except for compound **9** data, which were collected on a Bruker APEX II detector on a D8 platform at ChemMatCARS, APS, Chicago. CI mass spectra were collected with a MAT-95 XP mass spectrometer. Peak matching was done with the CMASS and LIST subroutines of XCalibur.

Preparation of (PNP)VCl$_2$ (1). To a stirred suspension of VCl$_3$(THF)$_3$ (86 mg, 0.23 mmol) in THF was added a solution of Li(PNP) (100 mg, 0.230 mmol) in toluene. The red suspension quickly gave way to a purple suspension, which was stirred overnight to ensure complete reaction. Generally, when (PNP)VCl$_2$ was used as a reactant, it was prepared in situ, assuming 100% conversion. X-ray-diffraction-quality crystals were grown by slow diffusion of hexanes into a saturated CH_2Cl_2 solution (~1 mL) of (PNP)VCl$_2$ in an NMR tube.

^{1}H NMR (25 °C, 300.06 MHz, CD_2Cl_2): paramagnetic δ 23.22 ($\Delta\nu_{1/2}$ = 214 Hz), 11.08 ($\Delta\nu_{1/2}$ = 211 Hz), 7.17 ($\Delta\nu_{1/2}$ = 71 Hz), 3.42 ($\Delta\nu_{1/2}$ = 39 Hz), 2.34 ($\Delta\nu_{1/2}$ = 64 Hz), 1.27 ($\Delta\nu_{1/2}$ = 25 Hz), 1.16 ($\Delta\nu_{1/2}$ = 25 Hz), 0.88 ($\Delta\nu_{1/2}$ = 75 Hz), −1.46 ($\Delta\nu_{1/2}$ = 56 Hz), −2.57 ($\Delta\nu_{1/2}$ = 174 Hz). Evans magnetic moment (25 °C, 399.97 MHz, CD_2Cl_2): $\mu_{\text{eff}} \approx 2.4$; we propose the low μ_{eff} is likely due to very low solubility of **1** in most common organic solvents. MS-CI: theoretical [M]$^+$, *m/z* 549.1447; experimental [M]$^+$, *m/z* 549.1451.

One-Pot Preparation of (PNP)V(CH$_2{}^t$Bu)$_2$ (2). To a stirred room-temperature THF/toluene solution of VCl$_3$(THF)$_3$ (1.73 g, 4.63 mmol) was slowly added Li(PNP) (2.02 g, 4.64 mmol) suspended in toluene. The mixture was stirred overnight, resulting in a red-purple suspension. The suspension was then cooled to −36 °C, and to it was slowly added a solution of LiCH$_2{}^t$Bu (743 mg, 9.52 mmol) in hexanes at −36 °C. Rapidly the purple suspension gave way to a green solution, which was stirred for 4 h at room temperature. Solvent was removed in vacuo, and the remaining green solid was extracted with hexane (~75 mL). The resulting green solution was filtered and concentrated. Small green crystals were grown by cooling the hexane solution to −36 °C overnight (76.1% yield in three crystal crops, 2.19 g, 3.52 mmol). The identity of the compound was confirmed by comparison of its ^{1}H NMR spectrum with that of an authentic sample of **2** as well as magnetic moment measurements (Evans method).

Synthesis of (PNP)V═CH^{t}Bu(O) (4) via Treatment of 2 with TEMPO. To a stirred room-temperature toluene solution of **2** (150 mg, 0.241 mmol) was added 1 equiv of TEMPO in toluene. Stirring for 2 days led to formation of a brown solution which was

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stripped of volatiles in vacuo. Complex **4** was extracted from the crude mixture using hexamethyldisiloxane (TMS$_2$O), and the extract was filtered and dried under vacuum. The identity of the yellow product was confirmed by comparing the ^{1}H NMR and ^{31}P NMR spectra and MS-CI spectrum with those of an authentic sample of **4**. The yield was 49.0% based on **2** (66.7 mg, 0.118 mmol).

Synthesis of 4 via Treatment of 2 with Pyridine *N*-Oxide. To a room-temperature C_6D_6 solution of **2** (28 mg, 0.045 mmol) in an NMR tube with a J. Young screw top was added 1 equiv of pyridine *N*-oxide (4.6 mg, 0.048 mmol). This mixture was then heated to 50 °C for 8 h, over which time the color of the solution became significantly lighter. The identity of the product was confirmed to be **4** by comparison of the ^{1}H NMR and ^{31}P NMR spectra and MS-CI spectrum with those of an authentic sample.[26] The yield of **4** as determined by use of a 5 μL 1,4-dioxane NMR internal integration standard was 43%.

Synthesis of 4 via Treatment of 2 with Trimethylamine *N*-Oxide. To a room-temperature C_6D_6 solution of **2** (29 mg, 0.047 mmol) NMR tube with a J. Young screw top was added 1 equiv of trimethylamine *N*-oxide (3.6 mg, 0.048 mmol). This mixture was then heated to 50 °C for 8 h. This was accompanied by a change in color to yellow. The identity of the product was confirmed by comparing the ^{1}H NMR and ^{31}P NMR spectra and MS-CI spectrum with those of an authentic sample of (PNP)V=CH^{t}Bu(=O).[26] The yield of **4** as determined by use of a 5 μL 1,4-dioxane NMR internal integration standard was 20%.

Synthesis of (PNP)V=CH^{t}Bu(Se) (6). To a room-temperature C_6D_6 solution of **2** (75 mg, 0.12 mmol) in a NMR tube with a J. Young screw top was added 2 equiv of Se (19 mg, 0.24 mmol). The tube was sealed, and this mixture was then heated to 60 °C for 5 h. The yield of **6** was 45%, as determined by as an internal NMR integration standard (1,4-dioxane, 5 μL). The NMR solution was then dried, extracted with pentane, filtered through Celite, and concentrated in vacuo. Storage of this solution at −36 °C allowed for isolation of green microcrystalline clumps, which were dried and collected in 69% yield (52.2 mg, 0.083 mmol).

^{1}H NMR (25 °C, 400.1 MHz, C_6D_6): δ 9.24 (s, 1H, =C*H*^{t}Bu), 7.20 (d of d, 1H, Ar *H*), 7.10 (d of d, 1H, Ar *H*), 6.91 (d, 1H, Ar *H*), 6.83 (d, 2H, Ar *H*), 6.74 (d, 1H, Ar *H*), 2.37 (overlapped septets, 2H, C*H*(CH$_3$)$_2$), 2.24 (m (obscured), 1H, C*H*(CH$_3$)$_2$), 2.17 (m (obscured), 1H, C*H*(CH$_3$)$_2$), 2.16 (s, 3H, Ar C*H$_3$*), 2.09 (s, 3H, Ar C*H$_3$*), 1.58 (s, 9H, CH^t*Bu*), 1.55 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 1.40 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$),; 1.34 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 1.28 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 1.13 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 1.07 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 0.99 (m, 6H, CH(C*H$_3$*)$_2$). ^{13}C{^{1}H} NMR (6.0 °C, 125.7 MHz, C_6D_6): δ 328.4 (V=*C*H^{t}Bu), 161.3 (Ar), 160.9 (Ar), 132.7 (Ar), 132.4 (Ar), 131.9 (Ar), 127.3 (Ar), 125.3 (Ar), 120.4 (Ar), 119.8 (Ar), 118.5 (Ar), 115.6 (Ar), 48.5 (*C*^{t}Bu), 35.2 (C^t*Bu*), 29.8 (CMe$_2$), 26.4 (CMe$_2$), 20.8 (Ar *Me*), 20.7 (Ar *Me*), 20.4 (CMe$_2$), 19.5 (CMe$_2$), 19.3 (CMe$_2$), 18.8 (CMe$_2$), 18.4 (CMe$_2$), 18.0 (CMe$_2$), 17.7 (CMe$_2$), 17.6 (CMe$_2$), 17.1 (CMe$_2$), 16.1 (CMe$_2$); one aryl resonance not located, likely obscured by solvent resonances. ^{31}P NMR (25 °C, 121.5 MHz, C_6D_6): δ 73.0 (broad). ^{51}V NMR (25 °C, 131.5 MHz, C_6D_6): δ 809 ($\Delta\nu_{1/2}$ = 993 Hz). MS-CI: theoretical [M]$^+$, *m/z* 629.2018; found [M]$^+$, *m/z* 629.2007.

Synthesis of (PNP)V=CH^{t}Bu(Te) (7). In a glovebox, to a room-temperature THF solution of **2** (285 mg, 0.458 mmol) in a side-arm reaction tube was added 7 equiv of Te powder (409 mg 3.21 mmol). The reaction tube was sealed, placed under vacuum, and then removed from the glovebox. This mixture was heated to 50 °C with stirring in an oil bath for 2 days. The reaction mixture was then dried in vacuo and then reintroduced into the glovebox under vacuum. To the residue was added *n*-hexanes. The resulting brown solution was filtered through a pad of Celite, concentrated in vacuo, and stored at −36 °C. Storage overnight allows for isolation of crude brown powders of **7** in ~27% yield (85 mg, 0.126 mmol).

^{1}H NMR (25 °C, 400.1 MHz, C_6D_6): δ 7.24 (m, 1H, Ar *H*), 7.07 (m, 1H, Ar *H*), 6.90 (m, 2H, Ar *H*), 6.80 (s, 1H, C*H*^{t}Bu), 6.79 (m, 1H, Ar *H*), 6.72 (m, 1H, Ar *H*), 2.35 (overlapped septets, 2H, C*H*(CH$_3$)$_2$), 2.25 (m (obscured by Ar C*H$_3$* resonance), 2H, C*H*(CH$_3$)$_2$), 2.17 (s, 3H, Ar C*H$_3$*), 2.05 (s, 3H, Ar C*H$_3$*), 1.65 (s, 9H, CH^t*Bu*), 1.62 (m, 3H, CH(C*H$_3$*)$_2$), 1.35 (doublet of doublets, 6H, CH(C*H$_3$*)$_2$), 1.25 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 1.17 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 1.10 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 0.98 (m, 6H, CH(C*H$_3$*)$_2$). ^{13}C{^{1}H} NMR (25.0 °C, 125.7 MHz, C_6D_6): 332.3 (V=*C*H^{t}Bu), 160.4 (Ar), 160.2 (Ar), 132.7 (Ar), 132.3 (Ar), 132.2 (Ar), 127.0 (Ar), 125.5 (Ar), 120.9 (Ar), 119.4 (Ar), 117.9 (Ar), 116.6 (Ar), 116.0 (Ar), 45.3 (*C*^{t}Bu), 36.2 (C^t*Bu*), 28.1 (CMe$_2$), 26.6 (CMe$_2$), 21.8 (CMe$_2$), 21.1 (Ar*Me*), 20.9 (Ar*Me*), 19.8 (CMe$_2$), 19.2 (CMe$_2$), 18.7 (CMe$_2$), 18.2 (CMe$_2$), 17.6 (CMe$_2$), 17.4 (CMe$_2$), 17.2 (CMe$_2$), 16.6 (CMe$_2$), 16.3 (CMe$_2$); one aryl resonance not located, likely obscured by solvent peak. ^{31}P NMR (25 °C, 121.5 MHz, C_6D_6): δ 95 (doublet, broad). ^{51}V NMR (25 °C, 131.5 MHz, C_6D_6): δ 1249 ppm ($\nu_{1/2}$ = 864 Hz). gHMQC (−13 °C, C_7H_8): a strong correlation between peaks at 332 ppm (^{13}C dimension) and 6.68 ppm (^{1}H dimension) is observed. MS-CI: theoretical [M]$^+$, *m/z* 679.1915; found [M]$^+$, *m/z* 679.1901.

Synthesis of (PNP)V=N(SiMe$_3$)(CH^{t}Bu) (8). To a stirred −76 °C hexane solution of **2** (100 mg, 0.161 mmol) was slowly added a −76 °C hexane solution of trimethylsilyl azide (19 mg, 0.16 mmol). The mixture was slowly warmed to room temperature and stirred overnight, followed by removal of the volatiles in vacuo. The red residue was taken up into hexane (~5 mL) and filtered. From the filtrate, yellow powder was obtained by concentration and storage of this solution (~1 mL). X-ray-quality crystals suitable for diffraction studies can be manually separated from the powder. The yellow powder and crystals are collected in approximately 24% yield (25 mg, 0.039 mmol) as crude material.

^{1}H NMR (25 °C, 400.1 MHz, C_6D_6): δ 12.51 (s, 1H, V=C*H*^{t}Bu), 7.26 (m, 2H, Ar *H*), 6.84 (m, 2H, Ar *H*), 6.78 (m, 2H, Ar *H*), 2.30 (overlapped septets, 2H, C*H*(CH$_3$)$_2$), 2.22 (septet, 1H, C*H*(CH$_3$)$_2$), 2.18 (s, 3H, Ar C*H$_3$*), 2.13(s, 3H, Ar C*H$_3$*), 2.08 (septet, 1H, C*H*(CH$_3$)$_2$), 1.41 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$), 1.27 (m, 12 H, CH(C*H$_3$*)$_2$), 1.05 (m, 6H, CH(C*H$_3$*)$_2$), 0.88 (m, 3H, CH(C*H$_3$*)$_2$), 0.32 (s, 9H, Si*Me$_3$*). ^{13}C{^{1}H} NMR (25 °C, 125.7 MHz, C_6D_6): δ 322.5 (V=*C*H^{t}Bu), 162.1 (Ar), 161.5 (Ar), 132.4 (Ar), 132.1 (Ar), 131.7 (Ar), 125.5 (Ar), 124.6 (Ar), 120.4 (Ar), 118.1 (Ar), 117.7 (Ar), 117.5 (Ar), 116.4 (Ar), 45.7 (*C*^{t}Bu), 34.4 (C^t*Bu*), 26.6 (CMe$_2$), 26.5 (CMe$_2$), 20.8 (Ar *Me*), 20.7 (Ar *Me*), 20.3 (CMe$_2$), 19.5 (CMe$_2$), 19.4 (CMe$_2$), 19.1 (CMe$_2$), 18.9 (CMe$_2$), 18.7 (CMe$_2$), 18.6 (CMe$_2$), 18.1 (CMe$_2$), 16.3 (CMe$_2$), 16.1 (CMe$_2$), 4.3 (Si*Me$_3$*). ^{31}P NMR (25 °C, 121.5 MHz, C_6D_6): δ 52.4. ^{51}V NMR (25 °C, 131.5 MHz, C_6D_6): δ −123 ($\Delta\nu_{1/2}$ = 1014 Hz). MS-CI: theoretical [M]$^+$, *m/z* 636.3357; found [M]$^+$, *m/z* 636.3340.

Synthesis of [(PNP)V=NC(^{t}Bu)=CH^{t}Bu]$_2$(μ_2,η^1:η^1-N$_2$) (9). To a stirred hexane solution of **2** (123 mg, 0.198 mmol) was added N≡C^{t}Bu at room temperature. The solution was stirred for 24 h, and the volatiles were removed in vacuo. The red residue was taken up into diethyl ether (~5 mL) and the solution then filtered. X-ray-diffraction-quality crystals were grown by concentration and storage of a diethyl ether solution at room temperature. Storage of a concentrated hexane solution at −36 °C allowed for isolation of the complex as brown-red crystals in 30.7% yield (39.3 mg, 0.030 mmol). The crystalline material appeared to consist of only one isomer. Over time in solution, complex **9** decomposed into an as yet unidentified species.

^{1}H NMR (25 °C, 400.1 MHz, C_6D_6): δ 7.23 (m, 1H, Ar *H*), 7.19 (m, 1H, Ar *H*), 7.03 (m, 2H, Ar *H*), 6.83 (m, 2H, Ar *H*), 4.37 (s, 1H, N(^{t}Bu)C=C*H*(^{t}Bu)), 2.71 (septet, 1H, C*H*(CH$_3$)$_2$), 2.61 (septet, 2H, C*H*(CH$_3$)$_2$), 2.33 (septet, 2H, C*H*(CH$_3$)$_2$), 2.24 (s, 3H, Ar C*H$_3$*), 2.23 (s, 3H, Ar C*H$_3$*), 1.54 (m, 3H, CH(C*H$_3$*)$_2$), 1.50 (s, 9H, N (^{t}*Bu*)C=CH(^{t}Bu)), 1.46 (doublet of doublets, 3H, CH(C*H*$_3$)$_2$), 1.41 (doublet of doublets, 3H, CH(C*H*$_3$)$_2$), 1.33 (m, 3H, CH(C*H*$_3$)$_2$), 1.25 (m, 6H, CH(C*H*$_3$)$_2$), 1.12 (m, 3H, CH(C*H*$_3$)$_2$), 1.07 (s, 9H, N(^{t}Bu)C=CH(^{t}*Bu*)), 0.98 (doublet of doublets, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 167.5 (N−*C*), 160.9 (Ar), 160.3 (Ar), 131.8 (Ar), 130.9 (Ar), 127.1 (Ar), 126.4 (Ar), 125.9 (Ar), 124.4 (Ar), 122.8 (Ar),119.8 (NC(^{t}Bu)=*C*H(^{t}Bu)), 118.9 (Ar), 115.4 (Ar), 40.1 (*C*^{t}Bu), 34.1 (*C*^{t}Bu), 32.4 (C^t*Bu*), 31.4 (C^t*Bu*), 28.6 (*C*Me$_2$), 25.6 (*C*Me$_2$), 24.4 (*C*Me$_2$), 23.2 (*C*Me$_2$), 21.0 (Ar *Me*), 20.9 (Ar *Me*), 20.5 (C*Me*$_2$), 20.1 (C*Me*$_2$), 19.9 (C*Me*$_2$), 19.8 (C*Me*$_2$), 19.7 (C*Me*$_2$), 18.5 (C*Me*$_2$), 17.0 (C*Me*$_2$); one methyl resonance and aryl resonance were not located, aryl resonance likely obscured by solvent. ^{31}P NMR (25 °C, 121.5 MHz, C$_6$D$_6$): δ 51.8. ^{51}V NMR (25 °C, 131.5 MHz, C$_6$D $_6$): δ 7 ($\Delta\nu_{1/2}$ = 1480 Hz). Anal. Calcd (C$_{72}$H$_{118}$N$_6$P$_4$V$_2$): C, 66.85; H, 9.19; N, 6.5. Found: C, 67.19; H, 9.46; N, 6.46.

Synthesis of (PNP)V(C(^{t}Bu)=NPh)(NHPh) (10). To a stirred hexane solution of **1** (50 mg, 0.080 mmol) was added 1 equiv of azobenzene (14.6 mg, 0.080 mmol) at room temperature. The red solution was stirred overnight, followed by removal of the volatiles in vacuo. The residue was extracted with diethyl ether (~5 mL) and the solution filtered. From the filtrate, red crystals can be grown by concentration (~1 mL) and storage of this solution at room temperature in 45% yield (26.5 mg in two crops, 0.036 mmol). Magnetic moment (Evans method) (25 °C, 400.1 MHz, C$_6$D$_6$): μ_{eff} = 2.98 ± 0.03 $\mu_{\mathrm{B}.}$ ^{1}H NMR (25 °C, 400.1 MHz, C$_6$D$_6$): δ 23.8 ($\nu_{1/2}$ = 1300 Hz), 21.9 ($\nu_{1/2}$ = 870 Hz), 20.4 ($\nu_{1/2}$ = 1300 Hz), 17.6 ($\nu_{1/2}$ = 290 Hz), 14.8 ($\nu_{1/2}$ = 126 Hz), 3.7 ($\nu_{1/2}$ = 113 Hz), 0.07 ($\nu_{1/2}$ = 109 Hz), −0.95 ($\nu_{1/2}$ = 84 Hz), −5.4 ($\nu_{1/2}$ = 213 Hz), −11.9 ($\nu_{1/2}$ = 360 Hz), −17.6 ($\nu_{1/2}$ = 210 Hz), −24.3 ($\nu_{1/2}$ = 420 Hz). MS-CI: theoretical [M − H]$^+$, *m/z* 730.3618; found [M − H]$^+$, *m/z* 730.3608.

Computational Details. All calculations were carried out using density functional theory as implemented in the Jaguar 6.0 suite[56] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[57−60] and the 6-31G** basis set with no symmetry restrictions. Transition metals were represented using the Los Alamos LACVP basis.[61−63] The NMR chemical shift calculation was computed by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ζ basis set cc-pVTZ(-f) that includes a double set of polarization functions. For all transition metals, we used a modified version of LACVP, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with the triple-ζ quality basis.

The models used in this study consist of up to ~100 atoms,[30] which represent the nontruncated molecules that were also used in the related experimental work. These calculations challenge the current state of computational capabilities, and the numerical efficiency of the Jaguar program allows us to accomplish this task in a bearable time frame.

Structural Studies. Crystal data and experimental parameters for all structures are given in Table 3. Complete structural details for each molecule are reported in the Supporting Information.

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Supporting Information Available: Text, figures, tables, and CIF files giving additional spectroscopic data and structural and theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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