

# Reactivity Studies of a Masked Three-Coordinate Vanadium(II) Complex\*\*

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Dedicated to Professor Herbert W. Roesky

The ability of vanadium to exist in various oxidation states renders this ion ideal for multielectron reactions, and therefore, a suitable metal for incorporation into novel ligand frameworks. An archetypal example of a low-valent vanadium species is vanadocene,  $[\text{V}(\text{Cp})_2]$  ( $\text{Cp}^- = \eta^5\text{-C}_5\text{H}_5$ ),<sup>[1]</sup> and its hindered relative decamethylvanadocene,  $[\text{V}(\text{Cp}^*)_2]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ).<sup>[2]</sup> Despite these complexes being known for quite some time, and being  $S = 3/2$  systems, their reactivity is often restricted given the coordinatively saturated metal ion. Prototypical among mononuclear  $\text{V}^{\text{II}}$  species are other coordinatively saturated complexes,  $[\text{VCl}_2(\text{L})_2]$  ( $\text{L} = \text{Me}_2\text{XCH}_2\text{CH}_2\text{XMe}_2$ ,  $\text{X} = \text{N}$  or  $\text{P}$ )<sup>[3]</sup> as well as complexes with a three-legged piano stool geometry such as  $[\text{V}(\text{Cp})(\text{dmpe})(\text{X})]$  ( $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ,  $\text{X} = \text{monoanionic ligand}$ ).<sup>[4]</sup> However, one approach to preparing a more reactive, low-valent metal fragment is by masking its coordination sphere with an arene, analogous to that of Rothwell et al. 15 years ago.<sup>[5]</sup> Reminiscent of this strategy are other masked, low-valent arene complexes having metals such as Zr, V, Fe, Ni, Co, Cu, Cr, and U.<sup>[6]</sup> Of these examples, the work by Tsai et al. has demonstrated facile access to monovalent vanadium through the isolation of an inverted sandwich

divanadium(I) species supported by the ubiquitous nacnac ligand ( $\text{nacnac}^- = [\text{Ar}] \text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[\text{Ar}]$ ,  $\text{Ar} = 2,6\text{-(CHMe}_2)_2\text{C}_6\text{H}_3$ ).<sup>[6f]</sup> What is striking about this system is the presence of a highly reducing metal center supported by an innocent nacnac scaffold. The innocence of the nacnac ligand is atypical in the context of electron-rich early transition metals given the vulnerability of the imine functionality of nacnac to engage in two-electron reductive cleavage.<sup>[7]</sup> The stability of this low-valent vanadium nacnac scaffold suggested that hemilabile arenes, in combination with an appropriate ligand, could mask low-coordinate and thus reactive vanadium fragments.

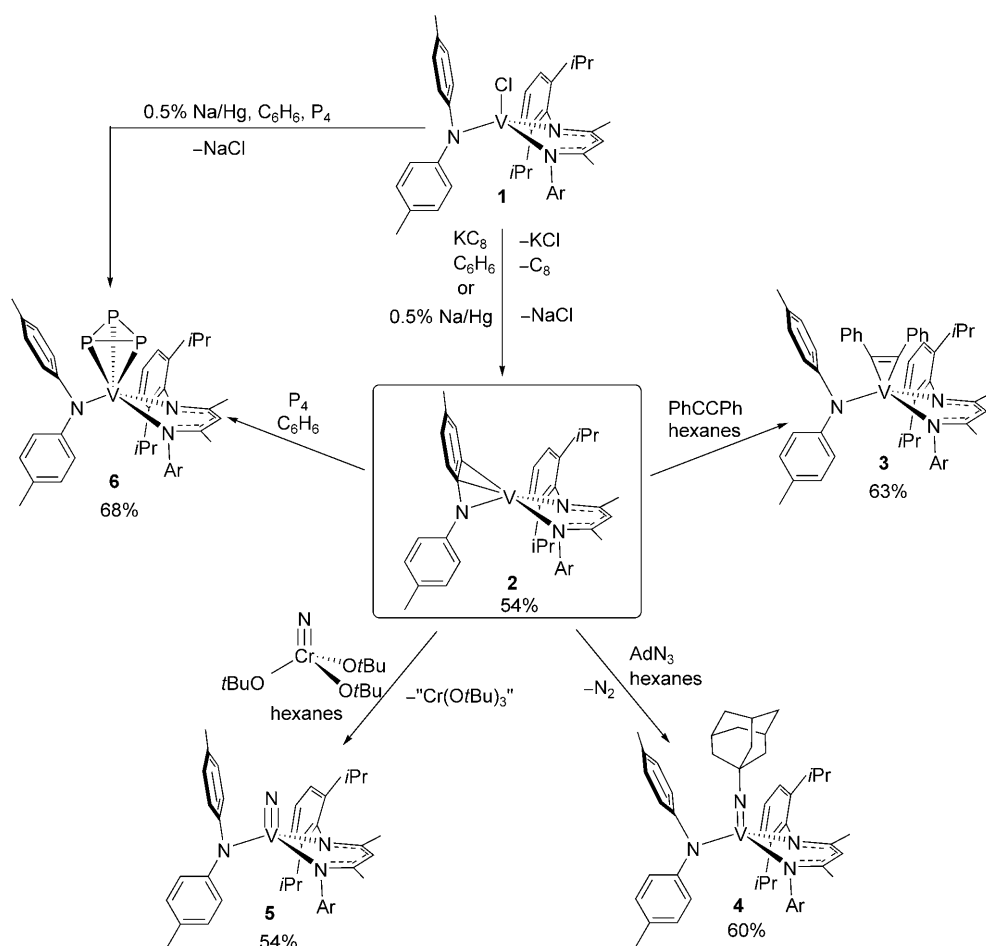
Described herein is the isolation and characterization of a masked three-coordinate vanadium(II) complex, whereby a tethered arene moiety protects the unsaturated and highly reducing metal center. We investigate the electronic structure of the  $\text{V}^{\text{II}}$  complex and through a series of reactivity studies, we demonstrate it to be a suitable three-coordinate template for two- and three-electron chemistry including the formation of the first *cyclo*- $\text{P}_3$  complex of vanadium.

We reasoned that direct reduction of the  $\text{V}^{\text{III}}$  complex,  $[(\text{nacnac})\text{VCl}(\text{Ntol}_2)]$  (**1**),<sup>[8]</sup> should provide access to a mononuclear vanadium(II) species, given the unique ability of nacnac in stabilizing vanadium(I) and (II) complexes.<sup>[6c,9,10]</sup> Electrochemical studies of  $[(\text{nacnac})\text{VCl}(\text{Ntol}_2)]$  showed irreversible anodic and reversible cathodic waves at +0.47 and −1.30 V, respectively (referenced vs.  $[\text{Fe}(\text{Cp}_2)]^{0/+}$  couple at 0.0 V in THF).<sup>[10]</sup> Chemical reduction of **1** with  $\text{KC}_8$  or 0.5 % Na/Hg in benzene produced dark red solids obtained in 54 % yield after crystallization from *n*-pentane at −37 °C (Scheme 1). <sup>1</sup>H NMR spectroscopic data revealed extremely shifted and broadened resonances consistent with a paramagnetic metal center, while single crystal X-ray diffraction (XRD) measurements confirmed loss of chloride ligand concurrent with formation of the  $\text{V}^{\text{II}}$  complex,  $[(\text{nacnac})\text{V}(\text{Ntol}_2)]$  (**2**) (Figure 1).<sup>[10]</sup> Taking into account only the nitrogen interactions, the vanadium center in the molecular structure of **2** adopts a distorted trigonal geometry in which the V center lies 0.47 Å above the  $\text{N}_3$  plane. However, the most salient structural feature is the presence of  $\text{V}-\text{C}(\textit{ipso})$  (2.505(6) Å) and  $\text{V}-\text{C}(\textit{ortho})$  interactions (2.441(5) Å) with one of the aryl moieties of the  $\text{Ntol}_2$  ligand. Similar  $\eta^3$  bonding interactions are commonly observed for the benzyl ligand and have been structurally observed with bulky anilide ligands coordinated to three-coordinate Ti, V, and U complexes.<sup>[11]</sup> Solid-state magnetization measurements (SQUID) of two independently prepared samples of **2** over a 2–300 K temper-

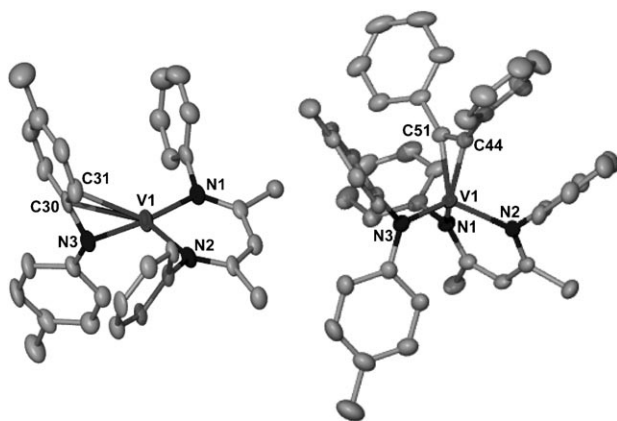
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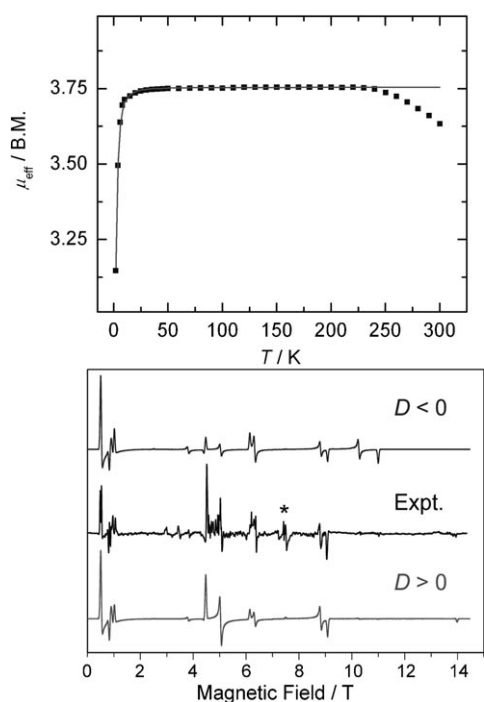
**Scheme 1.** Synthesis of complexes **2–6**.



**Figure 1.** The molecular structures of  $[(\text{nacnac})\text{V}(\text{Ntol}_2)]$  (**2**) and  $[(\text{nacnac})\text{V}(\eta^2\text{-C}_2\text{Ph}_2)(\text{Ntol}_2)]$  (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and isopropyl groups on the nacnac ligand have been excluded for clarity. Selected bond lengths [Å] and angles [°] for **2**: V1–N1 2.016(5), V1–N2 1.999(4), V1–N3 1.980(4), V1–C30 2.441(4), V1–C31 2.505(6); N3–V1–N2 127.0(2), N3–V1–N1 125.18(19), N2–V1–N1 90.47(19), N3–V1–C30 34.67(18), N2–V1–C30 144.2(2), N1–V1–V1–C30 125.35(19), N3–V1–C31 62.52(19), N2–V1–C31 119.63(19), N1–V1–C31 136.4(2), C30–V1–C31 33.67(17). For **3**: V1–N1 2.0378(15), V1–N2 2.0468(15), V1–N3 1.9169(16), V1–C44 2.0009(19), V1–C51 2.0063(18); N1–V1–N4 99.47(10), N1–V1–N2 91.89(8), N1–V1–N3 128.00(8), N3–V1–N4 105.62(9).

ature range confirmed the presence of a  $\text{V}^{\text{II}}$  ion with three unpaired electrons (Figure 2).<sup>[10]</sup> The average magnetic moment of  $\mu_{\text{eff}}$  ( $3.76 \mu_{\text{B}}$ ) is invariable over the range 20–250 K. There is a slight decrease above 250 K, which at this point we cannot fit or explain. Below 20 K, the magnetic moment sharply decreases in accord with zero-field splitting (zfs) effects. Fitting of the magnetization data using a standard spin Hamiltonian for  $S=3/2$  with axial zfs ( $D \neq 0$ ,  $E=0$ ) and an isotropic  $g$  value yielded  $g_{\text{iso}} = 1.94(4)$  and  $|D| = 2.9(5) \text{ cm}^{-1}$  (Figure 2). Additionally, room temperature magnetic susceptibility measurement (300 K) of **2** in  $\text{C}_6\text{D}_6$  by the Evans method ( $\mu_{\text{eff}} = 4.05 \mu_{\text{B}}$ ) is consistent with an  $S=3/2$  system in solution. Despite the fact that **2** is EPR silent at 298 K in an X-band EPR experiment (9 GHz, perpendicular mode), and which was also the case for  $[\text{Cp}_2\text{V}]$ ,<sup>[11]</sup> high-frequency and -field EPR (HF-EPR)

measurements of polycrystalline samples over the temperature range 10–50 K at 208 GHz were also consistent with a mononuclear complex having a quartet ground state (Figure 2).<sup>[12]</sup> Simulations of the HF-EPR spectra of **2** yielded the following spin Hamiltonian parameters:  $g_{\text{iso}} = 1.98(1)$ ,  $D = +2.99(2)$ ,  $E = +0.11(2) \text{ cm}^{-1}$ . The absolute value of  $D$  is in excellent agreement with magnetometry, while its positive sign (determined by comparing the relative amplitudes of particular turning points with simulations) and the value of the rhombic component  $E$  could be established thanks to superiority of a resonance technique over a bulk measurement. The zfs for **2**, determined here by two independent methods, is significantly larger than that reported for mononuclear  $\text{V}^{\text{II}}$  complexes, with the closest being vanadocene, for which the zfs was indirectly determined by X- and Q-band EPR to be  $|D| = 2.3 \text{ cm}^{-1}$ .<sup>[14]</sup> The zfs of  $\text{V}(\text{II})$  has been reported for a number of systems in which the ion is coordinated in homoleptic, six-coordinate environments with N,<sup>[12a]</sup> O,<sup>[12b]</sup> or halide<sup>[12c]</sup> donors. In these highly symmetric cases,  $|D| < 0.2 \text{ cm}^{-1}$ , and is often  $< 0.01 \text{ cm}^{-1}$ , which allowed its facile measurement by X-band EPR. Of greater relevance to **2**, we note two  $\text{V}^{\text{II}}$  molecular complexes of lower symmetry: *trans*- $[\text{VCl}_2(\text{dmpe})_2]$ , for which  $D \approx 0.46 \text{ cm}^{-1}$ ,<sup>[13a]</sup> and an organovanadium(II) complex,



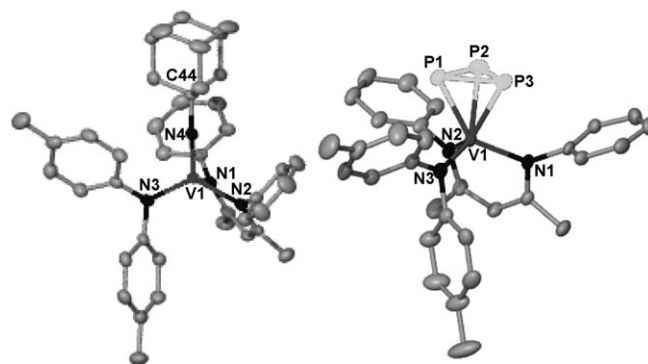
**Figure 2.** Upper: DC susceptibility of a powder of **2** measured at 1 T (squares) with a simulation (black line) based on a best fit of the data points in the range 2–200 K, and using the following parameters:  $S = 3/2$ ,  $g_{\text{iso}} = 1.938$ ,  $|D| = 2.934 \text{ cm}^{-1}$ ,  $\text{TIP} = 145 \times 10^{-6} \text{ emu}$ . Lower: HFEPR spectra of a polycrystalline sample of **2** recorded at 10 K and 208 GHz (middle trace). Simulated traces are given above and below, employing the parameters:  $S = 3/2$ ,  $|D| = 2.99$ ,  $|E| = 0.11 \text{ cm}^{-1}$ ,  $g_{\text{iso}} = 1.98$ ,  $\Delta B_{\text{iso}} = 250 \text{ G}$ ; for the upper trace,  $(D, E) < 0$  was used; for the lower trace,  $(D, E) > 0$  was used. The asterisk indicates a minor  $\text{V}^{\text{IV}}$  impurity which is not simulated.

$[\text{V}(\text{dipp})_4]^{2-}$  (dipp = 2,6-diisopropylphenylate), with approximate square-planar geometry, which exhibits a rhombic EPR spectrum at X-band and 77 K that is indicative of  $D \gg h\nu$  ( $> 0.3 \text{ cm}^{-1}$ ).<sup>[13b]</sup> HFEPR of this complex (and of vanadocene) would be instructive by allowing direct measurement of zfs (sign as well as magnitude) for comparison with **2**.<sup>[13c]</sup>

Compound **2** is a  $[\text{V}^{\text{II}}(\text{N}_2\text{N}')]^+$  template for two- and three-electron reactions, since the arene interaction of the anilide is readily disrupted upon treatment with various small molecules. Accordingly, mixing of diphenylacetylene with **2** results in two-electron reduction of the acetylene C–C triple bond to afford the metallacyclopentadiene complex,  $[(\text{nacnac})\text{V}(\eta^2\text{-C}_2\text{Ph}_2)(\text{Ntol}_2)]$  (**3**), in 63 % isolated yield. Solution susceptibility measurement (300 K, Evans method,  $\mu_{\text{eff}} = 1.92 \mu_{\text{B}}$ ) is consistent with oxidation to  $\text{V}^{\text{IV}}$  ( $S = 1/2$ ) as result of two-electron reduction of the alkyne moiety. The presence of a  $\text{V}^{\text{IV}}$  ion is further corroborated by the room temperature X-band EPR spectrum in toluene solution ( $g_{\text{iso}} = 1.97$ ), which reveals an eight line pattern arising from hyperfine coupling to  $^{51}\text{V}$  ( $I = 7/2$ ; 99.6 %) of  $A_{\text{iso}} = 166 \text{ MHz}$ ,<sup>[10]</sup> and in the range reported for  $[\text{V}(\text{Cp})_2]^{2+}$  complexes ( $A_{\text{iso}} = 120\text{--}210 \text{ MHz}$ ).<sup>[1e]</sup> Furthermore, XRD studies unambiguously reveal formation of a metallacyclopentadiene ( $\text{V}\text{--C}44$ ,  $2.0009(19) \text{ \AA}$ ;  $\text{V}\text{--C}51$ ,  $2.0063(18) \text{ \AA}$ ;  $\text{C}51\text{V}\text{--C}44$ ,  $38.10(8)^\circ$ ) moiety derived from two-electron reduction of the alkyne (Figure 1). This reaction

of **2** with an alkyne is reminiscent of the reaction of vanadocene and diphenylacetylene.<sup>[1e]</sup>

In an analogous two-electron reaction, treating **1** with an equivalent of  $\text{N}_3\text{Ad}$  ( $\text{Ad} = 1\text{-adamantyl}$ ) at room temperature leads to rapid extrusion of  $\text{N}_2$  with concomitant formation of  $[(\text{nacnac})\text{V}=\text{NAd}(\text{Ntol}_2)]$  (**4**) in 60 % isolated yield from recrystallization in diethyl ether at  $-37^\circ\text{C}$  (Scheme 1). Formation of  $\text{V}^{\text{IV}}$  in **4** is again confirmed by room temperature susceptibility (Evans method,  $\mu_{\text{eff}} = 1.84 \mu_{\text{B}}$ ) as well as X-band EPR ( $g_{\text{iso}} = 1.97$  and  $A_{\text{iso}}(^{51}\text{V}) = 74 \text{ MHz}$ ).<sup>[10]</sup> This hyperfine coupling value is low compared to that of  $[\text{V}(\text{Cp})_2]^{2+}$  complexes<sup>[1e]</sup> and may reflect greater delocalization of the unpaired electron onto the imido ligand. XRD studies reveal formation of a terminal imido ( $\text{V}=\text{N}$ ,  $1.654(2) \text{ \AA}$ ,  $\text{V}=\text{N}\text{--C}$ ,  $177.4(2)^\circ$ ). Complex **4** resembles reported tetrahedral  $\text{V}^{\text{IV}}$  imido complexes.<sup>[14]</sup> As with **3**, and in contrast to **2**, no arene interactions are observed in the molecular structure of **4** (Figure 3).



**Figure 3.** The molecular structures of  $[(\text{nacnac})\text{V}(\text{=NAd})(\text{Ntol}_2)]$  (**4**) (left) and  $[(\text{nacnac})\text{V}(\text{cyclo-P}_3)(\text{Ntol}_2)]$  (**6**) (right) with thermal ellipsoids at the 50 % probability level. Hydrogen atoms and isopropyl groups on the nacnac ligand have been excluded for clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **4**:  $\text{V1}\text{--N1}$   $2.047(2)$ ,  $\text{V1}\text{--N2}$   $2.054(2)$ ,  $\text{V1}\text{--N3}$   $1.956(2)$ ,  $\text{V1}\text{--N4}$   $1.654(2)$ ;  $\text{N1}\text{--V1}\text{--N4}$   $106.99(10)$ ,  $\text{N1}\text{--V1}\text{--N2}$   $88.30(9)$ ,  $\text{N1}\text{--V1}\text{--N3}$   $120.64(10)$ ,  $\text{N3}\text{--V1}\text{--N4}$   $107.64(11)$ . For **6**:  $\text{V1}\text{--N1}$   $1.988(2)$ ,  $\text{V1}\text{--N2}$   $2.030(2)$ ,  $\text{V1}\text{--N3}$   $1.911(2)$ ,  $\text{V1}\text{--P1}$   $2.4300(9)$ ,  $\text{V1}\text{--P2}$   $2.4388(9)$ ,  $\text{V1}\text{--P3}$   $2.4328(9)$ ;  $\text{P1}\text{--V1}\text{--P2}$   $52.07(3)$ ,  $\text{P1}\text{--V1}\text{--P3}$   $51.80(3)$ ,  $\text{N1}\text{--V1}\text{--N2}$   $96.17(9)$ ,  $\text{N1}\text{--V1}\text{--N3}$   $112.7(1)$ ,  $\text{P1}\text{--V1}\text{--N1}$   $138.43(7)$ ,  $\text{P1}\text{--V1}\text{--N3}$   $87.07(7)$ .

Complex **2** can also promote three-electron reactions. For example, the reaction of **2** and  $[(t\text{BuO})_3\text{Cr}\equiv\text{N}]$ <sup>[15]</sup> in hexanes at room temperature over 3 h results in complete intermetal N-atom transfer with quantitative conversion to the recently reported  $\text{V}^{\text{V}}$  nitride  $[(\text{nacnac})\text{V}\equiv\text{N}(\text{Ntol}_2)]$ <sup>[8]</sup> (**5**). This result is based on comparison of  $^1\text{H}$  NMR and FT-IR spectra of **5** to authentic samples (Scheme 1).<sup>[10]</sup> To our knowledge, formation of **5** from **2** and  $[(t\text{BuO})_3\text{Cr}\equiv\text{N}]$  represents the first example of complete intermetal N-atom transfer involving a group 5 metal.<sup>[16]</sup> The fact that **2** can engage in three-electron reactions prompted the pursuit of other substrates that could form unusual ligand frameworks on the  $[(\text{nacnac})\text{V}(\text{Ntol}_2)]$  scaffold.

When complex **2** is treated with 1 equivalent of  $\text{P}_4$  at room temperature, the first *cyclo-P*<sub>3</sub> complex of vanadium, namely diamagnetic  $[(\text{nacnac})\text{V}(\text{cyclo-P}_3)(\text{Ntol}_2)]$  (**6**), is isolated as a

golden brown solid in 68 % yield subsequent to recrystallization (Scheme 1). Moreover, **6** can also be generated independently, and in a one-pot synthesis, through the reduction of **1** with 0.5 % Na/Hg in the presence of 1 equivalent of P<sub>4</sub> in 40 % isolated yield. The other reaction products, which presumably would give the fate of the fourth equivalent of P from P<sub>4</sub>, have not yet been characterized. XRD studies of the major product unambiguously revealed the formation of **6**.<sup>[17]</sup> The molecular structure of **6** is shown in Figure 3 and features a *cyclo*-P<sub>3</sub> moiety coordinated in a η<sup>3</sup> coordination mode to render a tetrahedral vanadium(V) center with a V–P<sub>3</sub> centroid distance of 2.10 Å. The average V–P distance of **6** at 2.44 Å coupled with the internuclear P–P distances (≈2.13 Å) is consistent with a *cyclo*-P<sub>3</sub><sup>3–</sup> ligand. Complex **6** can thus be viewed both as a P<sub>3</sub>V core where the vanadium center represents one vertex of the tetrahedron, or as a pseudo tetrahedral vanadium center with three N donors where the *cyclo*-P<sub>3</sub><sup>3–</sup> ligand occupies the fourth site. Solution state <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic measurements at room temperature of this diamagnetic complex revealed a broad resonance at δ = 85.0 ppm (Δν<sub>1/2</sub> = 234 Hz), which is significantly downfield shifted compared to related heavier congeners.<sup>[18]</sup> <sup>1</sup>H NMR spectroscopic data of compound **6** indicates C<sub>s</sub> symmetry in solution as all four *i*Pr methyl resonances associated with the nacnac ligand are well-resolved doublets (J<sub>HH</sub> = 7.0 Hz). However, the resonance associated with the methyl groups on the ditolylamide ligand is broad (Δν<sub>1/2</sub> = 63.0 Hz) suggesting dynamic behavior of complex **6** at room temperature.<sup>[10]</sup> Variable-temperature <sup>1</sup>H NMR spectroscopy (25 to –60 °C) was performed on **6** in [D<sub>8</sub>]toluene to gain insight into this fluxionality, and spectra reveal two well-resolved singlets at δ = 2.29 and 1.92 ppm for the tolyl methyls as well as inequivalent aryltolyl environments.<sup>[10]</sup> In contrast, the <sup>31</sup>P{<sup>1</sup>H} spectrum of **6** at –60 °C still evinces a rapidly rotating P<sub>3</sub><sup>3–</sup> framework with a broad singlet shifted upfield at δ = 76 ppm (Δν<sub>1/2</sub> = 123 Hz). <sup>51</sup>V NMR spectrum of **6** recorded in [D<sub>8</sub>]toluene at 25 °C revealed a broad resonance extremely downfielded at δ = 2798 ppm (Δν<sub>1/2</sub> = 596 Hz).

In summary, we have demonstrated that combining a monoanionic bidentate ligand (nacnac) with a sterically demanding ditolylamide results in formation of a reactive [V<sup>II</sup>{N<sub>2</sub>N'}] scaffold reminiscent of the masked three-coordinate complex, [(H)Mo(η<sup>2</sup>-*i*PrC=NAr){N(*i*Pr)Ar}<sub>2</sub>] reported by Cummins et al. in 1998.<sup>[16g]</sup> Although there is a diagonal relationship between V and Mo, complex **2** fails to activate and split N<sub>2</sub> under normal conditions therefore hinting that the aryl interaction might be inhibiting such a process. This behavior is in contrast to work by Cloke et al.<sup>[19]</sup> in which a V<sup>II</sup> complex generated in situ from V<sup>III</sup> cleaves N<sub>2</sub> to give a nitrido-bridged dimer. We are currently trying to understand these significant differences by both experimental and theoretical approaches. In particular, the large zfs of **2**, in contrast to that found for six-coordinate V<sup>II</sup> complexes,<sup>[12]</sup> needs to be investigated computationally, as has been done for certain V<sup>III</sup> complexes of less common geometry.<sup>[20]</sup>

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