

Low-Coordinate and Neutral Nitrido Complexes of Vanadium

Ba L. Tran, Maren Pink, Xinfeng Gao, Hyunsoo Park, and Daniel J. Mindiola*

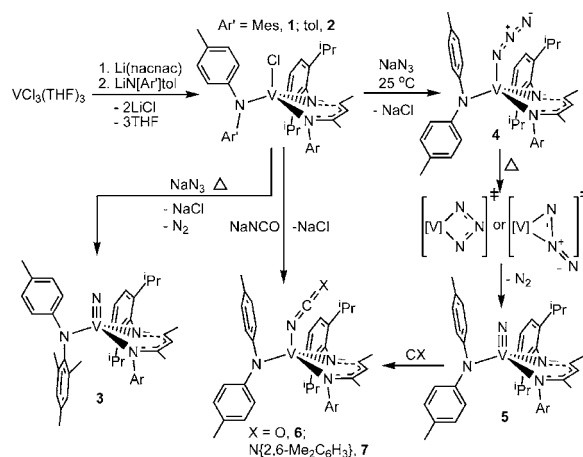
Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Received September 30, 2009; E-mail: mindiola@indiana.edu

Terminal nitrido complexes of early, first-row transition metals such as Sc, Ti, and V are rare entities despite their implications in N-atom transfer chemistry and single source molecular precursors to metal nitride films.¹ In fact, monomeric groups III and IV nitride complexes are virtually nonexistent, while group V,² specifically neutral vanadium nitrides are exceedingly rare. To date, the only reported synthesis and structural characterization of a coordinatively saturated and neutral vanadium(V) nitrido was stabilized by pyridine and quinuclidine donors.² However, the caveat to the construction of the nitride product involved an extremely volatile, metastable precursor, $\text{Cl}_3\text{V}\equiv\text{NSiMe}_3$, rendering access to the nitride product somewhat nontrivial. Yet, grafting anionic nitrides onto V is slightly more prevalent with such examples being reported by Gambarotta,^{3a} Cummins,^{3b} and Sobota.^{3f} Surprisingly, the neutral vanadium(V) nitride is a rare functional group presumably because of the unavailability of electron rich V(III) starting materials having only one good leaving group (i.e. halide or pseudohalide). Given our interest in metal–ligand multiple-bond chemistry, we sought a facile entry to such a species, but confined to a low-coordination environment to render it reactive. Also, the accessibility of the $\text{V}^{\text{III}}/\text{V}^{\text{V}}$ redox couple could render these systems good N-atom transfer reagents. We postulated that two-electron chemistry may be the most suitable route for attaining a neutral vanadium(V) nitrido complex from a vanadium(III) halide precursor upon treatment with an azide source. Here, we delineate the synthesis of two novel, neutral vanadium(V) nitrido complexes confined in a four-coordinate environment and the redox nature of the $\text{V}\equiv\text{N}$ multiple bond toward two-electron redox chemistry.

To graft the nitride ligand in a low coordination environment, we utilized the precursor $[(\text{nacnac})\text{VCl}_2]^4$ ($\text{nacnac} = [\text{ArNC}(\text{CH}_3)_2\text{CH}]^-$, $\text{Ar} = 2,6\text{-}(\text{CHMe}_2)_2\text{C}_6\text{H}_3$) in combination with a sterically imposing anilide ligand to lock all aryl groups for the purpose of steric crowding and prevent cyclometalation pathways with the proximal *i*Pr groups. Accordingly, Scheme 1 summarizes the preparation of the two precursors by means of salt metathesis of $[(\text{nacnac})\text{VCl}_2]$ with 1 equiv of $\text{Li}(\text{N}[\text{Ar}'\text{tol}])$ (where $\text{Ar}' = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ [Mes] or $4\text{-CH}_3\text{C}_6\text{H}_4$ [tol]) to render the complexes $(\text{nacnac})\text{VCl}(\text{N}[\text{Ar}'\text{tol}])$ ($\text{Ar}' = \text{Mes}$, **1**; tol, **2**) in 60% and 61% isolated yield,⁵ respectively. As expected for an $S = 1$ system, rt magnetization measurements by the method of Evans gave $\mu_{\text{eff}} = 2.90 \mu_{\text{B}}$ for **1** and $2.79 \mu_{\text{B}}$ for **2**. Subsequent treatment of **1** with a slight excess of sodium azide resulted in evolution of N_2 concomitant with formation of the nitride, $(\text{nacnac})\text{V}\equiv\text{N}(\text{N}[\text{Mes}]\text{tol})$ (**3**). To ensure complete formation of **3**, the reaction was performed in THF at rt for 12 h, all volatiles were removed, and the mixture was thermolyzed in toluene solution at 100°C for 8 h to eventually afford pure, diamagnetic **3** in 54% yield.⁵ Single crystal X-ray diffraction (XRD) studies of **3** confirmed the proposed molecular connectivity featuring a mononuclear pseudotetrahedral V center having a short $\text{V}\equiv\text{N}$ distance of $1.573(2) \text{ \AA}$, comparable to the neutral monomeric vanadium nitride ($1.568(19) \text{ \AA}$)² but also similar to the few known anionic forms, $1.565(5)\text{--}1.582(3) \text{ \AA}$.³ The nitride

Scheme 1. Synthesis of Complex **1–7**. [V] represents the scaffold $(\text{nacnac})[(\text{Ar}'\text{tol})\text{N}]\text{V}$ and $\text{Ar}' = 2,6\text{-Pr}_2\text{C}_6\text{H}_3$



ligand has classical H-bonding with a cocrystallized $\text{HN}[\text{Mes}]\text{tol}$ ($0.98(3) \text{ \AA}$) and with symmetry equivalent at $-x+3/2, y+1/2, -z+1/2$.

In solution at rt, the ^1H NMR spectrum of **3** suggests pseudo C_3 symmetry, but given the line broadening for some of the nacnac resonances we cannot rule out the presence of two isomers in solution.⁵ Another salient feature of **3** is the ^{51}V NMR spectrum displaying a broad resonance at 66.9 ppm ($\Delta\nu_{1/2} = 1770 \text{ Hz}$), while the ^{15}N NMR spectrum of ^{15}N nitride enriched **3**- ^{15}N (prepared analogously from **1** and excess Na^{15}N_3) confirmed a highly deshielded terminal nitride moiety at 1035 ppm ($\Delta\nu_{1/2} = 121 \text{ Hz}$). The infrared spectrum of **3** also revealed a strong stretch at 1027 cm^{-1} , which is characteristic of a terminal nitride functionality,⁶ and the isotopologue, **3**- ^{15}N , presented a red-shifted stretch at 1000 cm^{-1} in accord with the value predicted using the harmonic oscillator approximation.

Although the formation of **1** is proposed to occur via a putative vanadium(III) azide, $(\text{nacnac})\text{V}(\text{N}_3)(\text{N}[\text{Mes}]\text{tol})$, our initial attempts at trapping such an intermediate and monitoring its decay to **3** were unsuccessful. Fortunately, we circumvented this issue by opting for a less sterically demanding environment in compound **2**. Accordingly, the reaction of **2** and NaN_3 (6 equiv) in THF at rt over 0.5 h rendered green solids of $(\text{nacnac})\text{V}(\text{N}_3)(\text{Ntol}_2)$ (**4**) in 30% yield after recrystallization from hexane at -37°C . Formation of **4** has been formulated on the basis of its rt magnetic moment measurement by Evans' method ($\mu_{\text{eff}} = 2.85 \mu_{\text{B}}$), infrared spectrum ($\nu_{\text{NNN}} 2082 \text{ cm}^{-1}$), and combustion analysis.⁷ Moreover, single crystal XRD analysis revealed a bent azide ligand ($\text{V}-\text{N}=\text{N} = 106.56(12)^\circ$) coordinated to a V(III) center confined to a pseudo tetrahedral geometry (Figure 1). Monitoring the thermolysis of a green solution of **4** in C_6D_6 at 100°C for 12 h via ^1H NMR spectroscopy evinced complete transformation to a new diamagnetic and orange species assigned as $(\text{nacnac})\text{V}\equiv\text{N}(\text{Ntol}_2)$ (**5**).⁵ Kinetic measurements monitored by UV–vis spectroscopy ($60\text{--}90^\circ\text{C}$)

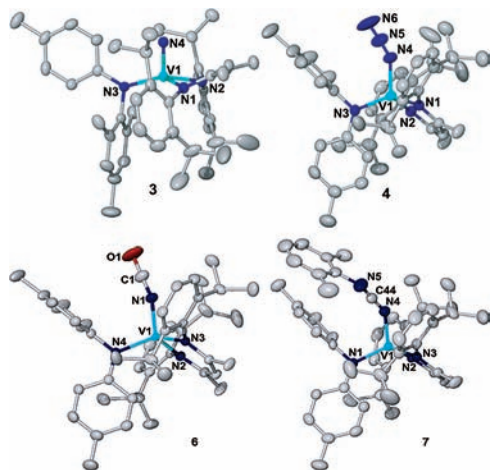


Figure 1. Structures of **3**, **4**, **6**, and **7** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and cocrystallizing HN[Mes]tol (for **3**) are excluded for clarity.

revealed first-order dependence on the **4**→**5** conversion, which allowed for extraction of the activation parameters $\Delta H^\ddagger = 18.4(4)$ kcal/mol and $\Delta S^\ddagger = -29(5)$ eu from the Eyring plot.⁵ The negatively large ΔS^\ddagger value suggests a very early transition state with respect to **5** and a highly ordered system in which the azide ligand plausibly forms a three- or four-membered ring with the V(III) center (Scheme 1), via chelation at the β or γ positions. Preliminary kinetic data also suggest the **4**→**5** conversion to be solvent dependent since the reaction is 16 times slower in THF than in toluene at 60 °C ($k = 1.95 \times 10^{-7}$ vs 3.06×10^{-6} s⁻¹).⁵ Therefore, our proposed rearrangement could parallel imide formation from metastable azide precursors of the type MN₃R⁸ but could also involve an associate-dissociative type mechanism. Complex **5** displays ¹H NMR solution spectroscopic features nearly identical to those of **3**. For example, there are two distinct singlets at 2.14 and 2.10 ppm for the inequivalent tolyl methyls in accord with a pseudo C₃ symmetric system and a broad resonance at -138 ppm ($\Delta\nu_{1/2} = 787$ Hz) as established by ⁵¹V NMR spectroscopy.⁵ The ¹⁵N NMR spectrum of an isotopically enriched nitride, **5**-¹⁵N, has a resonance at 1049 ppm ($\Delta\nu_{1/2} = 145$ Hz), while an intense stretch in the IR can be observed at 1006 cm⁻¹ (blue-shifted to 1031 cm⁻¹ for the unlabeled isotopologue **5**).⁵

Although **3** or **5** failed to react with PPh₃, PMe₃, CO₂, and N₂CPh₂ at 25 or 45 °C, treatment of **5** with π -acids such as CO (1 atm) and CN{2,6-Me₂C₆H₃} promoted reduction at the V metal center concurrent with formation of a N=C bond by virtue of an incomplete N-atom transfer. When treated with 1 atm of CO, the ¹H NMR spectrum evinced diagnostic resonances akin to those of other V(III) precursor complexes such as **1**, **2**, and **4**, while the IR spectrum unambiguously confirmed a strong ν_{NCO} stretch centered at 2208 cm⁻¹,⁵ identical to the assigned isocyanate value in the complex (OCN)V(N[*t*-Bu]Ar)₃ (Ar = 3,5-Me₂C₆H₃) reported by Cummins.^{3c} These results, in addition to single crystal XRD studies (Figure 1), were consistent with the product of such a reaction being (nacnac)V(NCO)(Ntol₂) (**6**, Scheme 1). For comparative purposes, it was found that **6** can be independently synthesized from the salt metathesis of **1** and NaNCO in THF in 65% isolated yield (Scheme 1).⁵ Analogously, treatment of **5** with the isonitrile C≡N{2,6-Me₂-C₆H₃} elicited reduction at the metal center to form a carbodiimide complex (nacnac)V(NCN{2,6-Me₂-C₆H₃})(Ntol₂) (**7**, Scheme 1), based on ¹H NMR spectroscopy (broad resonances in accord with formation of a V(III) center), IR spectroscopy (ν_{NCN} at 2154 cm⁻¹),⁹ and a solid state structure. The structural features of **7** are overall

similar to those of **6**, having a bent carbodiimide ligand and a pseudotetrahedral V(III) platform enforced by the nacnac and anilide ligands (Figure 1).

In the latter two cases we attribute these reactions to the nucleophilic nature of the nitride ligand and the accessible V(III) redox couple.^{3e} Although similar behavior toward π -acids has been observed for strained hydrazido complexes¹⁰ and sterically congested trimethylsilylimide complexes of uranium(V)¹¹ or anionic vanadium nitrides,^{3e} our study demonstrates that neutral nitride ligands can also engage in such transformations. Our proposed transition states to N₂ extrusion suggests that the microscopic reverse reaction for CO and CNR reductive coupling could be operating via [2+2] or [1+2] addition pathways.

In conclusion, the work presented here reveals that neutral, low-coordinate vanadium nitrides can be readily assembled and the nitride ligand can mitigate electron transfer to V therefore setting the stage for delivery of the N-atom. We are currently exploring more detailed mechanistic work to the formation of **5** and whether the reactivity of **3** and **5** can likely promote analogous reactions to nitride complexes of precious and heavier metals such as Os, Ru, and, more recently, Ir.¹²

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Supporting Information Available: Experimental procedures, X-ray crystallographic information, and spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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