Article

Tale of Three Molecular Nitrides: Mononuclear Vanadium (V) and (IV) Nitrides As Well As a Mixed-Valence Trivanadium Nitride Having a V₃N₄ Double-Diamond Core

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ABSTRACT: Transmetallation of $[VCl_3(THF)_3]$ and $[TlTp^{tBu,Me}]$ afforded $[(Tp^{tBu,Me})VCl_2]$ (**1**, $Tp^{tBu,Me}$ = hydro-tris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate), which was reduced with KC_8 to form a C_{3v} symmetric V^{II} complex, $[(Tp^{tBu,Me})VCl]$ (**2**). Complex **1** has a high-spin ($S = 1$) ground state and displays rhombic high-frequency and -field electron paramagnetic resonance (HFEPR) spectra, while complex **2** has an $S = 3/2$ $^4A_2$ ground state observable by conventional EPR spectroscopy. Complex **1** reacts with NaN_3 to form the V^V nitride-azide complex $[(Tp^{tBu,Me})V≡N(N_3)]$ (**3**). A likely V^{III} azide intermediate *en route* to **3**, $[(Tp^{tBu,Me})VCl(N_3)]$ (**4**), was isolated by reacting **1** with N_3SiMe_3. Complex **4** is thermally stable but reacts with NaN_3 to form **3**, implying a bis-azide intermediate, $[(Tp^{tBu,Me})V(N_3)_2]$ (**A**), leading to **3**. Reduction of **3** with KC_8 furnishes a trinuclear and mixed-valent nitride, $[\{(Tp^{tBu,Me})V\}_2(\mu_4\text{-}VN_4)]$ (**5**), conforming to a Robin−Day class I description. Complex **5** features a central vanadium ion supported only by bridging nitride ligands. Contrary to **1**, complex **2** reacts with NaN_3 to produce an azide-bridged dimer, $[\{(Tp^{tBu,Me})V\}_2(1,3\text{-}\mu_2\text{-}N_3)_2]$ (**6**), with two antiferromagnetically coupled high-spin V^{II} ions. Complex **5** could be independently produced along with $[(\kappa_2\text{-}Tp^{tBu,Me})_2V]$ upon photolysis of **6** in arene solvents. The putative $\{V^{IV}≡N\}$ intermediate, $[(Tp^{tBu,Me})V≡N]$ (**B**), was intercepted by photolyzing **6** in a coordinating solvent, such as tetrahydrofuran (THF), yielding $[(Tp^{tBu,Me})V≡N(THF)]$ (**B-THF**). In arene solvents, **B-THF** expels THF to afford **5** and $[(\kappa_2\text{-}Tp^{tBu,Me})_2V]$. A more stable adduct (**B-OPPh₃**) was prepared by reacting **B-THF** with OPPh₃. These adducts of **B** are the first neutral and mononuclear V^{IV} nitride complexes to be isolated.
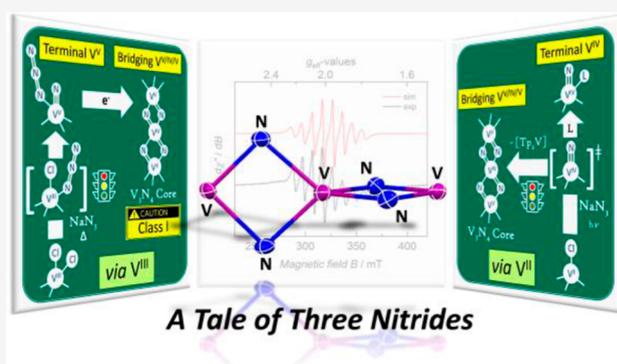
INTRODUCTION

The nitride functional group can derive from N_2 reduction and splitting by low-valent metal coordination complexes.[1] In biochemistry, the existence of a nitrogenase enzyme with vanadium in the active-site cofactor (FeV-co) is further impetus for research into vanadium coordination chemistry with ligands related to or derived from dinitrogen.[2] In solid-state chemistry, vanadium nitride surfaces may promote catalytic reduction[3] or oxidation[4] reactions and even exhibit superconductivity[5] at low temperatures. This promising material composed of a base metal is also attractive as an electrochemical capacitor given its high electronic conductivity, thermal stability,[6] high density, and high specific capacitance.[7] Although mononuclear anionic and neutral V^V nitride complexes are known (Figure 1),[1o,w,8] very little, if any, is known about mononuclear V^{IV} nitrides, given their propensity to bridge and form oligomeric structures.[9] This is rather surprising given how the close derivative, vanadyl

($[V≡O]^{2+}$),[10] is ubiquitous in coordination chemistry, energy storage technologies (*e.g.*, redox-flow batteries),[11] and biological systems.[12] Moreover, molecular vanadium nitride complexes offer the enticing possibility of serving as well-defined precursors for vanadium nitride films.[13] However, there is currently a lack of atomically precise systems that demarcate how the transformation from molecules to a bulk material might proceed. In particular, a system in which a vanadium center is surrounded by only nitride ligands (and *vice versa*), while preserving a discrete architecture, remains unknown.
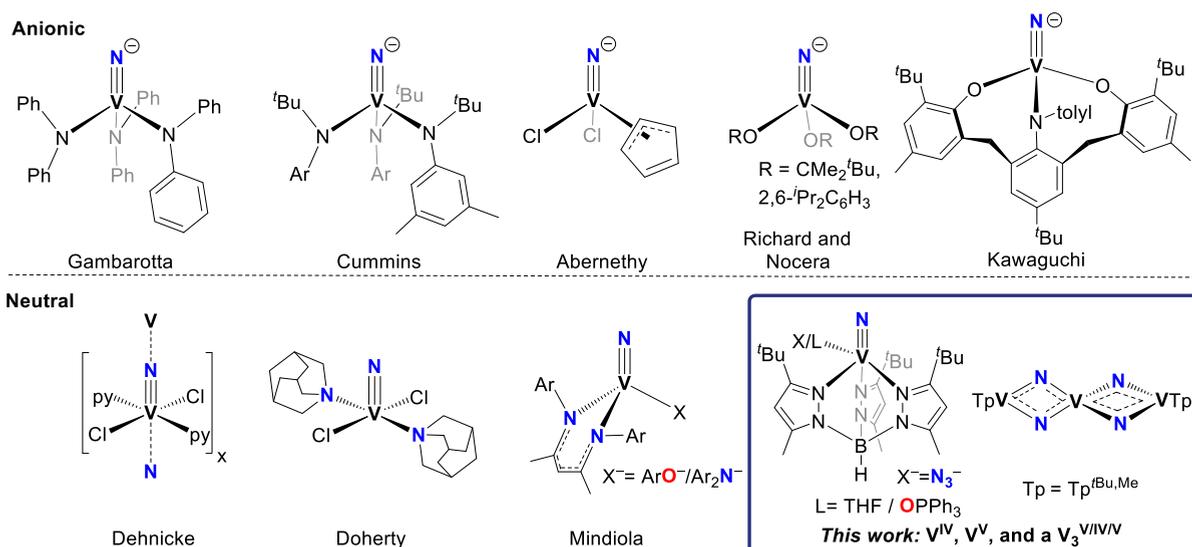
Figure 1. Examples of mononuclear vanadium nitrides. Counterions and solid-state aggregations are excluded for clarity. X and L represent a monoanionic and a neutral ligand, respectively. Specific details are provided in each case. Tp represents $Tp^{tBu,Me}$.

Scheme 1. Synthesis of Chloride Precursors 1 and 2, along with THF/DMAP Adducts of 2, 2-THF, and 2-DMAP, Demonstrating Lewis Acidity of the V^{II} Center[a]
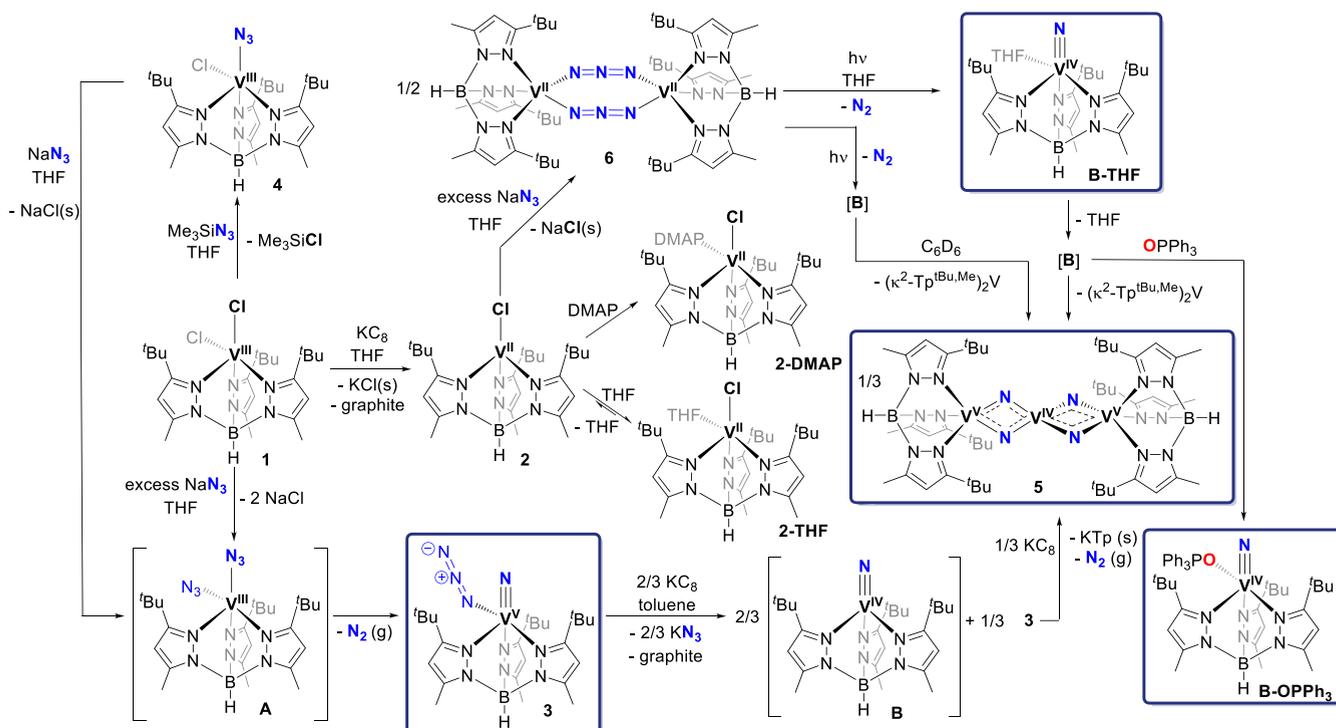
[a]Metathesis of **1** with NaN_3 and Me_3SiN_3 produces azide and/or nitride species **3** and **4**, respectively. Complex **3** likely forms *via* intermediates **4** and **A** as reaction of **4** with either NaN_3 or excess Me_3SiN_3 (at elevated temperatures) generates **3**. Metathesis of **2** with NaN_3 produces bis-azide complex **6**. One-electron reduction of **3** produces trinuclear **5** *via* intermediate **B**; an alternative route commences with photolysis of **6** in arene solvents. Photolysis of **6** in THF stabilizes intermediate **B** by generating the adduct **B-THF**. **B-THF** gradually releases THF to form **5** and $[(\kappa^2\text{-}Tp^{tBu,Me})_2V]$. Reaction of **B-THF** with $OPPh_3$ forms the more stable adduct **B-OPPh_3**.

In this study (Scheme 1), we demonstrate synthetic entries to a rare, pseudo-tetrahedral, high-spin V^{II} complex, $[(Tp^{tBu,Me})VCl]$ (**2**), which is readily prepared by one-electron reduction of the V^{III} precursor, $[(Tp^{tBu,Me})VCl_2]$ (**1**, $Tp^{tBu,Me}$ = hydro-tris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate). We showcase how these V^{II} or V^{III} precursors can yield mononuclear V^{IV} and V^{V} nitrides as well as a unique trinuclear and mixed-valent

vanadium system with a central vanadium ion ligated only by bridging nitrides. We also show how a reactive mononuclear V^{IV} nitride can be generated by three independent routes and under the right conditions can be isolated and fully characterized. These nitride products, along with intercepted intermediates leading to the nitride functionality, have been isolated and structurally and spectroscopically characterized. The para-
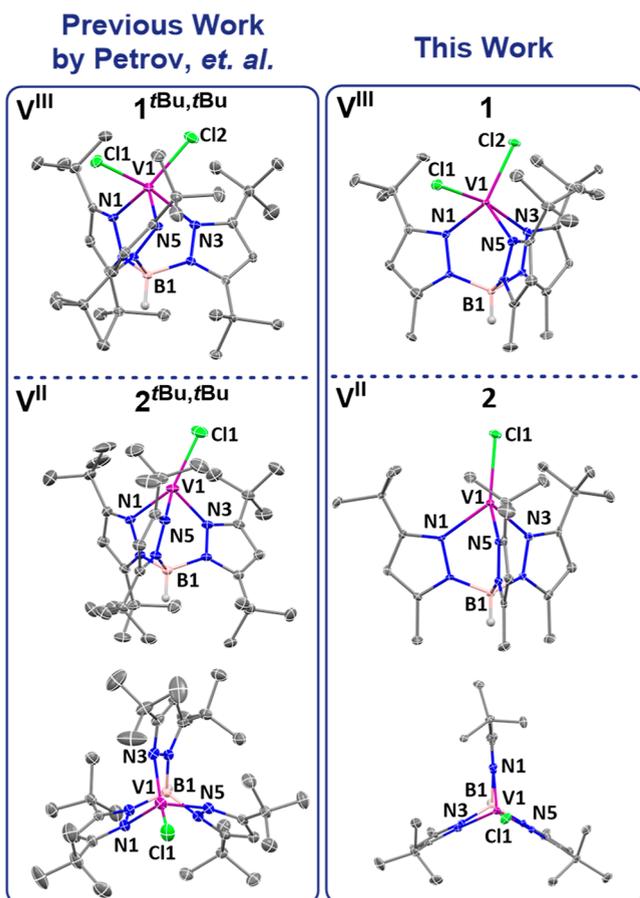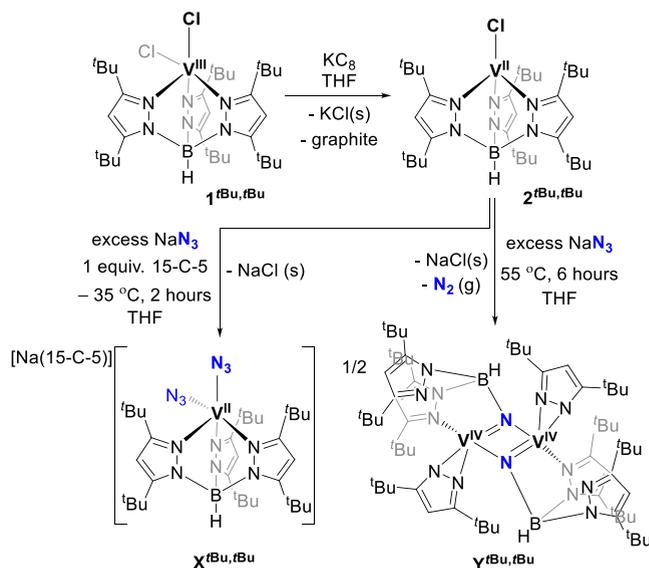
magnetic vanadium systems have been studied by solution- and solid-state magnetometry. Conventional continuous wave (CW) X-band electron paramagnetic resonance (EPR) has been applied to half-integer (*i.e.*, V^{IV}) species. In the case of complex **1**, which has an $S = 1$ electronic ground state and, thus, is less suited for conventional EPR spectroscopy, we have applied high-frequency and -field EPR (HFEPR) to better understand its electronic structure. Theoretical studies performed in parallel with experiments have also yielded a detailed picture of the bonding and electronic structure for this family of vanadium complexes and their respective nitrides.

■ RESULTS AND DISCUSSION

Tri- and Divalent Vanadium Complexes Supported by a Tripodal Monoanionic Ligand. Recently, Petrov and co-workers reported the synthesis of a pseudo-tetrahedral divalent V^{II} complex, $[(Tp^{tBu,tBu})VCl]$ (**2**^{tBu,tBu}, $Tp^{tBu,tBu}$ = hydro-tris(3,5-di(*tert*-butyl)pyrazol-1-yl)borate),[14] but did not explore its reactivity. Our own reaction studies revealed that the steric encumbrance imposed by the two ^{t}Bu groups on the pyrazolyl moieties imparted too much strain on the B−N bonds for this chemistry to flourish. The degree of twisting of the sterically encumbered pyrazolyl groups in both **1**^{tBu,tBu} and **2**^{tBu,tBu} (Figure 2, left) may be taken as a portent of this system to decompose *via* ligand degradation. As a result, attempts to explore the chemistry

Figure 2. Structural representation of $[(Tp^{tBu,tBu})VCl_2]$ (**1**^{tBu,tBu}) and $[(Tp^{tBu,tBu})VCl]$ (**2**^{tBu,tBu}) (left) along with **1** and **2** (right; 50% thermal ellipsoid probability). Only one of the two molecules in the asymmetric unit (for **1** and **2**) is shown for simplicity. Disorder and hydrogen atoms (except B−H's) are excluded for clarity.

of **2**^{tBu,tBu} *via* transmetallation reactions with NaN_3 led to undesired decomposition pathways, such as borotropic rearrangements that are common for early-transition metals bearing Tp ligand(s) (Scheme 2).[15] When excess NaN_3 was

Scheme 2. Reactivity Studies of Petrov's $[(Tp^{tBu,tBu})VCl]$ (2^{tBu,tBu}) with Excess NaN_3 with or without Crown Ether

added to **2**^{tBu,tBu} in the presence of the crown ether, 15-C-5, the bis-azide ate complex $[Na(15\text{-}C\text{-}5)][(Tp^{tBu,tBu})V(N_3)_2]$ (**X**^{tBu,tBu}) was isolated in 92% yield (Scheme 2) and characterized by single-crystal X-ray diffraction (sc-XRD). On the other hand, performing the reaction in the absence of 15-C-5 under thermolytic conditions led to the dimeric $(V^{IV})_2$ complex $[\{hydro\text{-}bis(3,5\text{-}di(tert\text{-}butyl)pyrazol\text{-}1\text{-}yl)boraneimide\}V(3,5\text{-}di(tert\text{-}butyl)pyrazol\text{-}1\text{-}yl)]_2$ (**Y**^{tBu,tBu}) in 47% yield, which was characterized by sc-XRD studies and multinuclear NMR spectroscopy. The latter complex is likely to form *via* the intermediacy of a reactive V^{IV} nitride, $[(Tp^{tBu,tBu})V\equiv N]$, which then undergoes ligand degradation and dimerization steps.

The molecular structure of **X**^{tBu,tBu} (Figure 3A) reveals the lack of threefold symmetry for the $Tp^{tBu,tBu}$ ligand owing to significant skewing of the pyrazolyl arms to the same extent, if not greater, as in **1**^{tBu,tBu}. The torsion angle, $\angle V-N_{1,pz1}-N_{2,pz1}-B$, for the most twisted pyrazolyl arm (pz1), defined as ξ_{twist}, provides a measure of the extent of skewing (a perfectly threefold symmetric Tp ligand would have $\xi_{twist} = 0°$; *cf.* Table S20 for the full list of ξ_{twist} angles of all pyrazolyl arms of all compounds discussed herein). In the case of **X**^{tBu,tBu}, the ξ_{twist} value is 52.0(1)°. In complex **Y**^{tBu,tBu} (Figure 3B), the average V−N and V≡N bond distances are 1.986(3) Å and 1.735(3) Å, respectively, which are reminiscent of Cloke's $[(L)V(\mu_2\text{-}N)_2V(L)]$ complex (L^{2-} = $(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2$), where the average V−N and V≡N bond distances are 1.886 Å and 1.740 Å, respectively.[9b]

Based on the aforementioned results, we examined the less sterically encumbered, methyl-derivatized ligand, $Tp^{tBu,Me}$, reported originally by Trofimenko[16] and popularized by Theopold,[17] Parkin,[18] Takats,[19] and Anwander,[20] among others.[21] Accordingly, transmetallation of $[VCl_3(THF)_3]$ with $[TlTp^{tBu,Me}][22]$ in toluene at 65 °C afforded $[(Tp^{tBu,Me})VCl_2]$ (**1**) in 75% yield as brick-orange plates after workup (Scheme 1). Single crystals of **1** could be obtained by Et_2O/toluene vapor
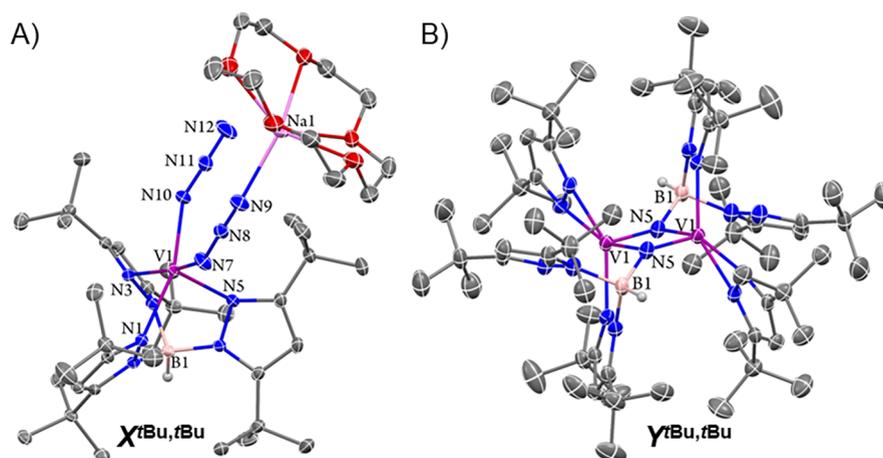
Figure 3. Structural representations (thermal ellipsoids at 50% probability) of (A) $X^{tBu,tBu}$ and (B) $Y^{tBu,tBu}$. Hydrogen atoms (except B−H's), the second molecule in the asymmetric unit, and the co-crystallized solvent (in B) are excluded for clarity.
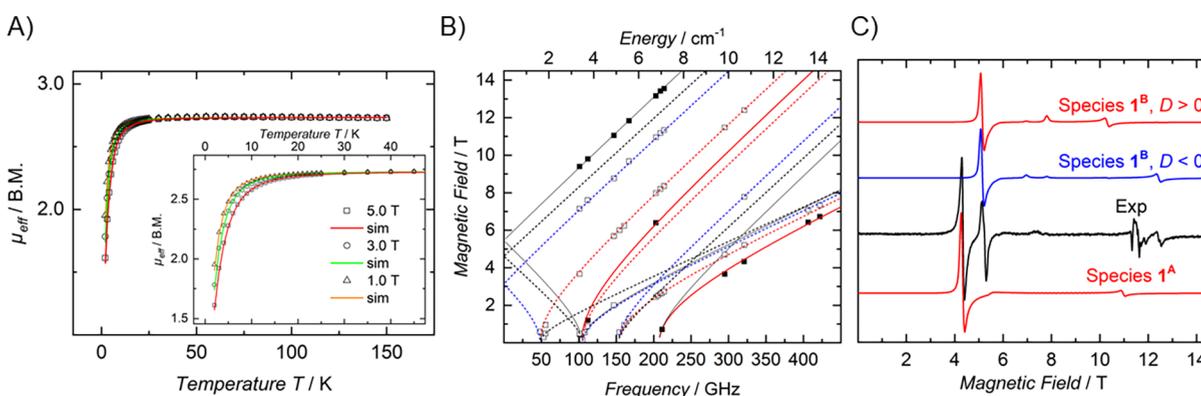

Figure 4. (A) VT-VF SQUID magnetization data of **1** with applied magnetic fields of 1, 3, and 5 T. (B) 2D plot of turning points in the powder spectra of **1** as a function of frequency (energy), marked as squares. **1^A**: full squares, **1^B**: empty squares. The curves (**1^A**: solid, **1^B**: dashed) were simulated using spin Hamiltonian parameters as in Table S1. Red curves: turning points with the magnetic field parallel to the x-axis of the zfs tensor; blue: $B_0 \| y$; black: $B_0 \| z$. (C) HFEPR spectrum of **1** at 4.5 K and 321 GHz (black trace). The colored traces are simulations using spin Hamiltonian parameters of species **1^B** (top) and species **1^A** (bottom). For species **1^B**, simulations use positive D (red) and negative D (blue). For species **1^A**, the sign of D is undefined due to maximum rhombicity of the zero-field splitting (zfs) tensor. Simulation: **1^A**, $|D|$ = 5.4 cm^{-1}, E = 1.8 cm^{-1}, g_{iso} = 1.96; **1^B**, D = −4.3 cm^{-1}, $|E|$ = 0.81 cm^{-1}, and g_{iso} = 1.96; the resonances at g = 1.96 (11.7 T) most likely originate from a V^{IV} oxidation product.

diffusion at −35 °C. An sc-XRD study confirmed a five-coordinate V^{III} complex supported by a κ^3-Tp^{tBu,Me} chelate. With a τ_5 value[23] of 0.53 (Figure 2, top right), compound **1** falls midway between the limiting square pyramidal (SP) and trigonal bipyramidal (TBP) geometries,[23] whereas the chloride ligands are essentially orthogonal to each other (Cl−V−Cl$_{avg}$, 95.8(8)°). Complex **1** crystallizes with two crystallographically independent, but chemically equivalent, molecules in the asymmetric unit (space group Cc), having B−V−Cl$_{anti}$ angles of 149.5(1) and 150.2(3)°. The V−Cl$_{avg}$ bond distance of 2.249 Å in **1^{tBu,tBu}** is similar to the V−Cl$_{avg}$ bond distance of 2.264 Å in **1**. Figure 2 shows a side-by-side comparison of **1^{tBu,tBu}** and **1**, which clearly reveals less twisting of the pyrazolyl arms in the methyl-substituted complex: ξ_{twist} = 62.0(5)° in **1^{tBu,tBu}** and 31.0(2)° in **1**. This structural difference is even more pronounced for the four-coordinate V^{II} species (*vide infra*).

The UV−vis spectrum of **1** shows two absorption bands with maxima at 521 and 720 nm (d−d transitions: ε = 229, 79 M^{-1} cm^{-1}) with the first band showing a shoulder at 589 nm (ε = 153 M^{-1} cm^{-1}), *cf.* Supporting Information, Section S12.1, for more detailed discussion. The solution magnetic moment of complex **1** (μ_{eff} = 2.71 μ_B; Evans' method, 300 K, C$_6$D$_6$) corresponds to the spin-only value for S = 1, appropriate for a d^2 ion. Solid-state superconducting quantum interference device (SQUID) magnetization measurements of **1** (two independently prepared samples) were conducted in the temperature range of 2−150 K with applied magnetic fields of 1, 3, and 5 T (Figure 4A; only the first sample shown for clarity; *cf.* Supporting Information, Section S7.1). In agreement with solution data, both samples give μ_{eff} = 2.72 μ_B at 300 K, while below 10 K, the magnetic moment begins to decrease, ultimately reaching μ_{eff} = 1.95 μ_B at 2 K due to zero-field splitting (zfs). Fitting the magnetic data to a spin Hamiltonian for an S = 1 species yielded the parameters D = 5.9 cm^{-1}, E/D = 0.33, and g_{avg} = 1.93 (averaged fit values of the two independent batches).

Given the even number of unpaired electrons in **1**, we subjected a sample to HFEPR spectroscopy at 4.5 K. The frequency dependence of the HFEPR spectra (Figure 4B)[24] reveals two distinct species in the solid state, labeled **1^A** and **1^B**, with slightly different spin Hamiltonian parameters. This observation correlates with two crystallographically independent molecules of **1** in the crystal structure analysis (*vide supra*). Species **1^A** is characterized by a larger D-value of 5.2 cm^{-1} and the maximum rhombicity of the zfs tensor (E = 1.73 cm^{-1}),
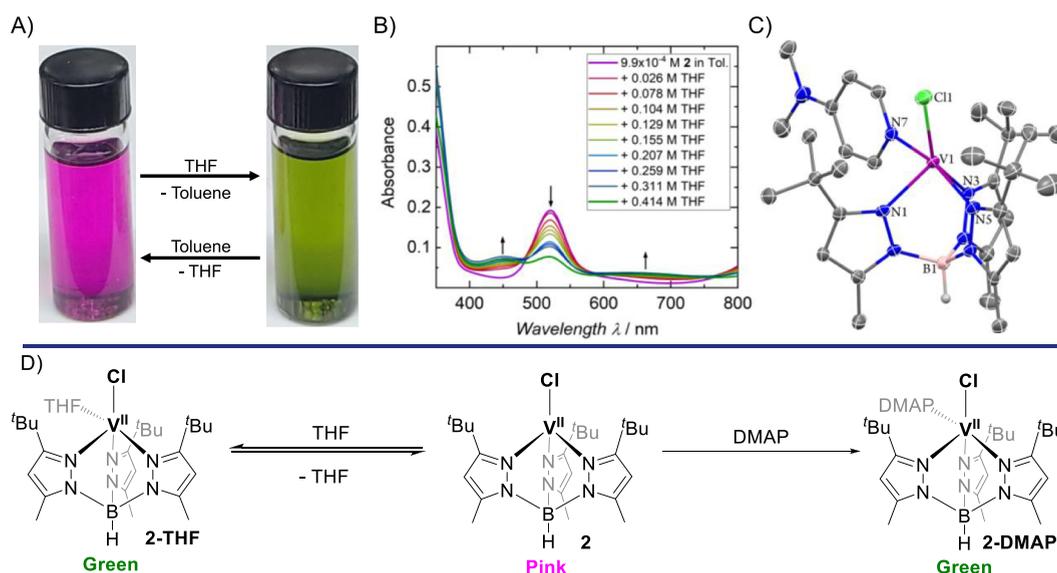
Figure 5. (A) Reversible color change of **2** when dissolved in non-coordinating (pink, *e.g.*, in toluene) and coordinating solvents (green, *e.g.*, in THF). (B) Titration (with THF) of **2** in toluene. (C) Structural representation of **2-DMAP** (thermal ellipsoids at 50% probability). Hydrogens (except B—H) are omitted for clarity. (D) Reversible coordination between **2** and THF (left) and the formation of **2-DMAP** (right).

while species $\mathbf{1^B}$ has a smaller $|D|$ value of 4.3 cm^{-1} and moderate rhombicity of the zfs tensor ($|E| = 0.81$ cm^{-1}). Simulations of single-frequency spectra, such as those shown in Figure 4C, proved that the sign of D for species $\mathbf{1^B}$ is negative, while that of species $\mathbf{1^A}$ is spectroscopically undefined because of the maximum rhombicity condition ($|E/D| \approx 1/3$). However, since the magnitudes of the spectroscopic D values for $\mathbf{1^A}$ and $\mathbf{1^B}$ are similar to each other as well as to the D value determined for the bulk sample of **1** from SQUID magnetization, species $\mathbf{1^A}$ and $\mathbf{1^B}$ could conceivably have the same sign of D. The magnitude of D for **1** is less than that observed for six-coordinate, approximately octahedral V^{III} complexes ($D \approx 7$ cm^{-1} for homoleptic complexes with O donors but larger for heteroleptic ones).[25] Four-coordinate, approximately tetrahedral d^2 complexes (*e.g.*, V^{III}, Cr^{IV}) have very small (ideally zero) zfs.[26] We are not aware of zfs being determined for a five-coordinate V^{III} complex, so at present, the significance of the magnitude of zfs in **1** cannot be put into much context.[a] A possible structural origin for the difference in zfs parameters between $\mathbf{1^A}$ and $\mathbf{1^B}$ may be the slightly different metrics for the two molecules seen by sc-XRD (*cf.* Supporting Information, Section S12.1). This high sensitivity of HFEPR spectroscopy to structural changes is underlined by the failure of infrared (IR) ($\nu_{BH} = 2563$ cm^{-1}, solid state) spectroscopy to distinguish crystallographic conformers of **1**. In solution (300 K, C$_6$D$_6$), ^{1}H NMR of complex **1** gives a single BH resonance and a single ^{1}H NMR chemical environment for the pyrazolyl groups, suggesting rapid fluctuation of the molecule in solution (*cf.* Supporting Information, Section S4.3, Figure S14) and thus an ideally trigonal average structure.

Despite showing only non-reversible features, cyclic voltammetry (CV) studies of **1** (using 0.1 M [^{n}Bu$_4$N][PF$_6$] in THF) revealed both anodic and cathodic processes, thus suggesting chemical accessibility of oxidized and reduced derivatives of **1** (*cf.* Supporting Information, Section S10.1, Figure S106). Thus, chemical reduction of **1** with KC$_8$ in THF generates a green solution, presumably containing five-coordinate [(Tp^{tBu,Me})-VCl(THF)] (**2-THF**). Upon removal of THF *in vacuo*, putative **2-THF** converts to four-coordinate [(Tp^{tBu,Me})VCl] (**2**),

isolated as pink crystals in 62% yield (Scheme 1, and Figure 5A). sc-XRD studies of **2** established a slightly distorted tetrahedral geometry ($\tau_4 = 0.72$)[27] around the V^{II} center with a tridentate grip of the Tp^{tBu,Me} ligand (Figure 2, bottom right). Akin to **1**, complex **2** has two crystallographically independent molecules in the asymmetric unit, with slightly different metrics. The average B—V—Cl angle of 168.4(5)° reveals some deviation of Cl from the B—V vector, presumably stemming from a Jahn—Teller effect, which is operative in a d^3 ion in tetrahedral symmetry ($^4T_1$ ground state; $e^2t_2^1$). The B—V—Cl angle is closer to linearity in **2** than in Petrov's $\mathbf{2^{tBu,tBu}}$ complex (157.7(9)°), most likely due to the lesser steric encumbrance of the Tp ligand. In $\mathbf{2^{tBu,tBu}}$ and **2**, ξ_{twist} equals 46.6(1) and 7.1(7)°, respectively, revealing a distorted Tp^{tBu,tBu} ligand in $\mathbf{2^{tBu,tBu}}$ as opposed to a near-ideal threefold symmetric Tp^{tBu,Me} ligand in **2**. It is also notable that [(Tp^{tBu,R})VCl] (R = ^{t}Bu or Me) has roughly a T$_d$ geometry when for a d^3 system, ideal SP would be of lower energy than ideal T$_d$ (*cf.* Supporting Information, Section S12.2). Indeed, a four-coordinate V^{II} complex with homoleptic monodentate ligands, [V(OAr)$_4${Li(THF)}$_2$] (Ar = 2,6-di-isopropylphenyl), has an SP geometry.[28] Due to the larger ionic radius of V^{II} *versus* V^{III}, the average V—Cl bond distance in **2** exceeds that in **1** (V—Cl$_{avg}$: 2.356(1) Å in **2** and 2.264(3) in **1**). An Et$_2$O solution of **2** retains the pink color of the solid, indicative of a four-coordinate structure in solution. The vis—near IR (NIR) spectrum of **2** can be assigned and semi-quantitatively analyzed by ligand-field theory (LFT) as described in the Supporting Information (see Section S12.2). However, as discussed before, complex **2** readily binds THF to form **2-THF** (Scheme 1 and Figure 5D, left) as manifested by a reversible color change from pink (Et$_2$O) to green (THF). When changing solvents from Et$_2$O to THF, the electronic absorption for **2** at 520 nm ($\varepsilon = 160$ M^{-1} cm^{-1}) undergoes a blue shift to 457 nm ($\varepsilon = 65$ M^{-1} cm^{-1}). In addition, the intense absorptions extending into the NIR region [893 (infl), 924 (max), and 960 nm (infl), with $\varepsilon = 130$, 150, and 130 M^{-1} cm^{-1}, respectively] are replaced by weaker and broader features at 668 and 855 nm ($\varepsilon = 32$, 19 M^{-1} cm^{-1}). Along these lines, titration of a toluene solution of **2** with THF (0—0.414 M) reveals three
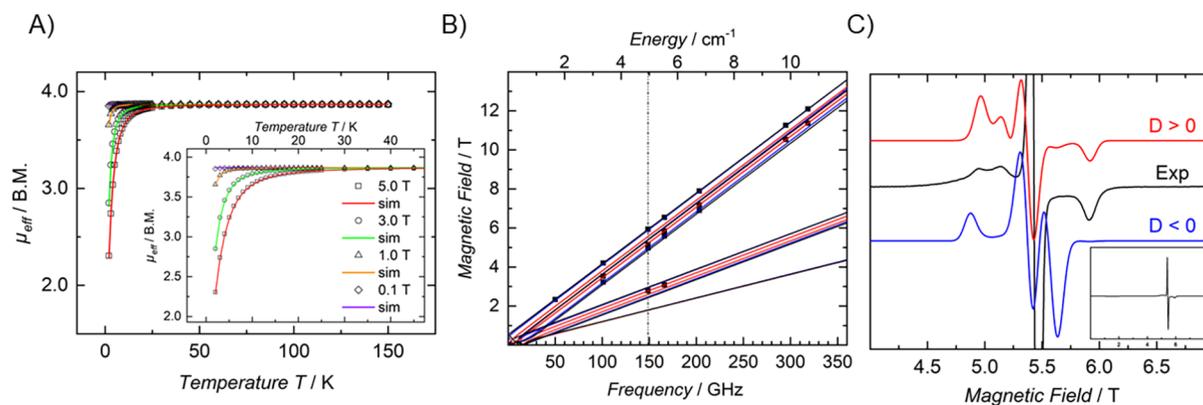
Figure 6. (A) VT-VF SQUID magnetization data of **2** at 5.0, 3.0, 1.0, and 0.1 T; experimental data are shown as squares, circles, triangles, and diamonds, respectively, and simulations are shown as red, blue, green, and purple traces, respectively. Simulation: $S = 1.5$, $D = 0.01$ cm^{-1}, $E/D = 0.33$, $g_{avg} = 2.00$. (B) 2D plot of turning points in the powder spectra of **2** as a function of frequency (energy), marked as squares. The curves were simulated using spin Hamiltonian parameters: $S = 3/2$, $|D| = 0.25(1)$ cm^{-1}, $|E| = 0.058(5)$ cm^{-1}, and $g = [2.000(3), 1.96(1), 1.967(5)]$. Red curves: turning points with the magnetic field parallel to the x-axis of the zfs tensor; blue: $B_0\|y$; black: $B_0\|z$. The vertical dashed line represents the frequency (149 GHz) at which the spectrum in (C) was recorded. (C) Main plot: EPR spectrum of **2** at 4.5 K and 149 GHz (black trace). Colored traces are simulations using spin Hamiltonian parameters, where D is positive (red) or negative (blue): $S = 3/2$, $|D| = 0.24$ cm^{-1}, $|E| = 0.026$ cm^{-1}, $g = [1.97, 2.00, 1.97]$. The experimental spectrum is dominated by a high-amplitude signal at $g = 1.96$ from an $S = 1/2$ impurity (V^{IV}, not simulated). *Inset:* the full experimental spectrum in the same conditions, indicating the absence of any V^{III} species.

clear isosbestic points and an association constant (K) between **2** and THF on the order of 1.2–3.6 M^{-1} (Figure 5B, *cf.* Supporting Information, Section S8.4.1). Thus, in neat THF (12.3 M), **2** exists mainly as the five-coordinate adduct **2-THF** (94–98%). Notably, **2** displays a lower affinity toward THF than isostructural $[(Tp^{tBu,Me})TiCl]$ ($K_{ass} = 5$–8 M^{-1}), highlighting the stronger Lewis acidity of a Ti^{II} *versus* V^{II} ion.[29] Similarly, cyclic voltammetry (CV) data for **2** dissolved in 1,2-difluorobenzene or THF (*cf.* Supporting Information, Section S10.2, Figure S107) show only a slight variation in oxidation and reduction potentials, possibly due to the reversible formation of **2-THF** in the latter case. In the cathodic scans, the reduction potentials for **2** in THF are anodically shifted by +0.02 V compared to **2** in 1,2-difluorobenzene, which readily converts to an equilibrium constant for the association of **2** with THF of 2.2 M^{-1}, in good agreement with UV–vis titrations. Despite multiple attempts at crystallization, we were unable to isolate **2-THF**, presumably due to the low association constant and/or volatility of the Lewis base. We therefore examined a stronger Lewis base such as DMAP. Accordingly, treatment of **2** with DMAP quantitatively produces green crystals of $[(Tp^{tBu,Me})$-VCl(DMAP)]$ (**2-DMAP**; Scheme 1 and Figure 5C). The solution magnetic moment of adduct **2-DMAP** ($\mu_{eff} = 3.67$ μ_B; Evans' method, 300 K, C$_6$D$_6$) is consistent with a high-spin d^3 system ($S = 3/2$, $g = 1.90$). The UV–vis spectra of **2-DMAP** and **2-THF** are qualitatively similar, whereas both differ markedly from the UV–vis spectrum of **2** (*cf.* Supporting Information, Sections S8.4 and 8.5, Figures S82 and S84). Most notably, the near-IR absorption band of **2** (924 nm) is absent for **2-DMAP** and **2-THF**, while the absorption band at 520 nm in **2** falls at a higher energy (394 nm) in **2-DMAP**.

Given the paramagnetic nature of **2**, magnetization studies were conducted. In solution, the magnetic moment of **2** indicates a mononuclear V^{II} ion with $S = 3/2$ ($\mu_{eff} = 3.78$ μ_B; Evans' method, 300 K, C$_6$D$_6$). Similarly, SQUID magnetometry for two independently prepared samples (**2**−300, **2**−150 K shown in Figure 6A) showed the magnetic moment to be relatively constant between 10 and 300 K (3.87 and 3.84 μ_B at 300 K), in accord with solution state data. However, below 10 K

and in an applied field of 1.0 T, the magnetic moment starts decreasing and reaches $\mu_{eff} = 3.65$−3.61 μ_B at 2 K due to zfs (*cf.* Supporting Information, Section S7.2, Figures S66 and S67). At higher fields, the decrease becomes steeper, for example, leading to a magnetic moment of 2.31 μ_B at 2 K and 5.0 T (Figure 6A). Simulation of the magnetization data for **2** with an $S = 3/2$ spin Hamiltonian yields $D = +0.01$ cm^{-1}. Petrov's **2**^{tBu,tBu} complex has a magnetic moment of 3.78 μ_B at 300 K and 3.52 μ_B at 2 K, thereby displaying essentially the same magnetic behavior as **2**.[14] As a spectroscopic complement to the magnetometric data, X- and Q-band EPR spectral data of **2** in glassy toluene (12 K) indicate a rhombic $S = 3/2$ system with $g_{avg} = 1.97$ (*cf.* Supporting Information, Section S5.1, Figure S43). Based on simulation of the X-band data, D and E are 0.33 and 0.03 cm^{-1}, respectively. On the other hand, Q-band spectra yield slightly different D and E (0.28 and 0.075 cm^{-1}, respectively). The variation between X- and Q-band data reflects the challenging nature of deconvoluting numerous anisotropic linewidths simultaneously with features that potentially arise from various m_s transitions. To resolve this ambiguity, we studied a powdered sample of **2** by HFEPR spectroscopy at 4.5 K, obtaining the frequency dependence of the resonances (Figure 6B,C; more details in the Supporting Information, Section S6.2). Here, the inter-Kramers transitions converge to a small energy of ∼0.56 cm^{-1}, which equals 2D^* for $S = 3/2$ ($D^* = (D^2 + 3E^2)^{1/2}$). The complete set of frequency-independent spin Hamiltonian parameters is $D = +0.25(1)$ cm^{-1}, $E = 0.058(5)$ cm^{-1}, and $g = [2.000(3), 1.96(1), 1.967(5)]$. The single-frequency spectra could be simulated using this set of parameters and prove that the sign of D is positive, and with the magnitude consistent with the values from frozen solution X- and Q-band EPR studies. This zfs is consistent with a simple LFT analysis (*cf.* Supporting Information, Section S12.2).

The frontier molecular orbitals of **2** (Figure 7) reveal an idealized C_{3v} symmetric system, where the energetic ordering for the vanadium 3d orbitals, $d_{x^2-y^2} \approx d_{xy} < d_{z^2} < d_{xz} \approx d_{yz}$, essentially can be rationalized as the result of the chloride ligand being a stronger σ- and π-donor ligand than the weak-field $[Tp^{tBu,Me}]$ ligand. This might hint that the $[Tp^{tBu,Me}]$ ligand is bound
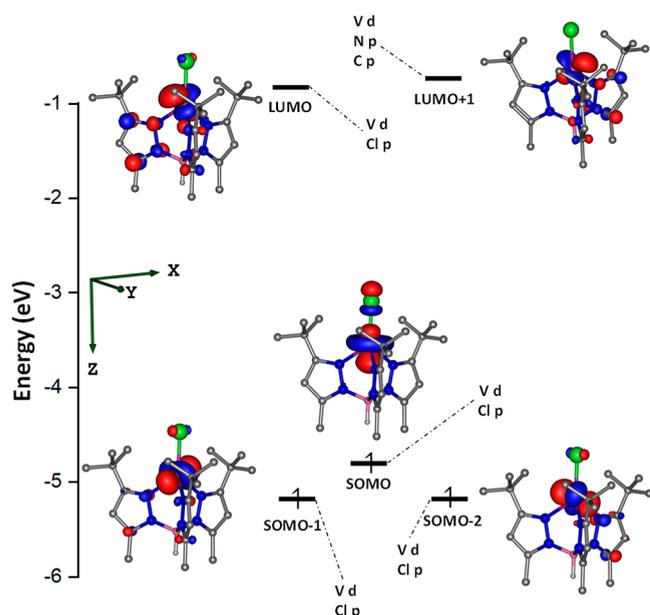
Figure 7. Calculated MO diagram for **2**. Orbital energies are in eV (B3LYP/TZVP).

relatively weakly to the vanadium center, and indeed, the tendency for the $[\text{Tp}^{tBu,Me}]$ ligand to dissociate has a remarkable impact on the reactivity of its derivatives (*vide infra*). In the case of **2-DMAP** (*cf.* Supporting Information, Section S11, Figure S117), coordination of a Lewis base breaks the threefold symmetry, and consequently, the degeneracy of the singly-occupied molecular orbital (SOMO) − 2 and SOMO − 1 orbitals computationally observed in **2** is broken.

High-Valent Vanadium Nitrides and Intermediates Stemming from Complex 1. At room temperature, complex **1** slowly reacts (overnight) with 2 equiv of NaN_3 in THF to afford the azide-nitride complex $[(\text{Tp}^{tBu,Me})V\equiv N(N_3)]$ (**3**) in 61% yield. After filtration of insoluble sodium salts, the reaction mixture must then be heated at 50 °C for an additional hour to ensure full conversion to **3** prior to workup (Scheme 1 and Figure 8B). Monitoring the reaction mixture by ${}^1H$ NMR shows a new paramagnetic species that forms but then decays to **3**. We propose this intermediate to be either the mono-azide complex $[(\text{Tp}^{tBu,Me})V(\text{Cl})(N_3)]$ (**4**, *vide infra*) or the bis-azide complex $[(\text{Tp}^{tBu,Me})V(N_3)_2]$ (**A**). sc-XRD of **3** confirmed the terminal nature of the nitride moiety ($V\equiv N_7$: 1.558(2) Å and 1.565(5) Å), non-linear coordination of the azide ligand ($V-N_8-N_9$: 126.1(1) and 137.5(6)°), and a geometry confined between SP and TBP (τ_5: 0.59 and 0.54) for the two polymorphs (Figure 8A and Table 1). Preparing the four ${}^{15}N$-enriched isotopomers, $[(\text{Tp}^{tBu,Me})V\equiv N({}^{15}N=N=N)]$, $[(\text{Tp}^{tBu,Me})V\equiv N(N=N={}^{15}N)]$, $[(\text{Tp}^{tBu,Me})V\equiv{}^{15}N({}^{15}N=N=N)]$, and $[(\text{Tp}^{tBu,Me})\text{-}V\equiv{}^{15}N(N=N={}^{15}N)]$ (collectively denoted as **3-${}^{15}N$**) from complex **1** and $Na({}^{15}N=N=N)$ revealed a characteristic, highly deshielded ${}^{15}N$ NMR nitride resonance at 1035.8 ppm along with the expected two azide resonances at 212.2 and 243.9 ppm, corresponding to ${}^{15}N$-enriched α- and γ-azide positions. IR spectral data of **3** (in KBr plates) show the prototypical signature of the azide group at 2079 and 2063 cm^{-1} (in-phase/out-of-phase asymmetric stretching vibrations),[30] which red-shift to 2039 and 2054 cm^{-1} for isotopomer **3-${}^{15}N$**, respectively (*cf.* Supporting Information, Section S9.6, Figure S99). The ${}^1H$-$\{{}^{11}B\}$ NMR spectrum of **3** shows one broad B*H* resonance at
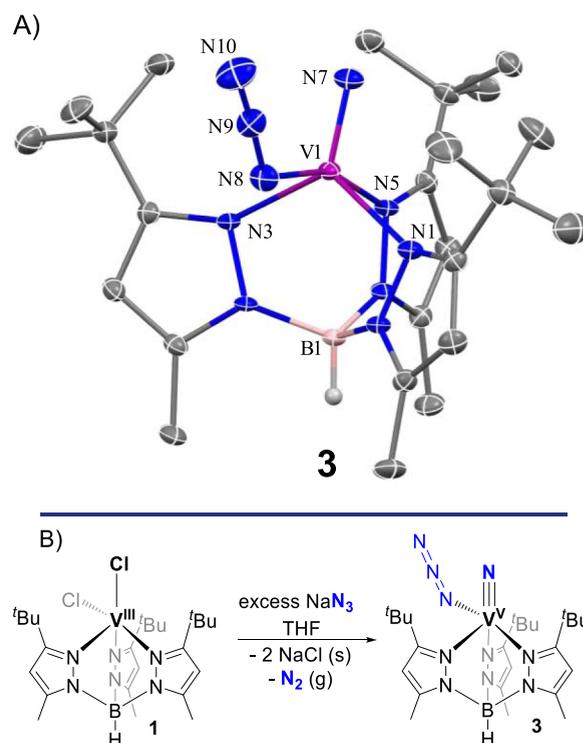
Figure 8. (A) Structural representation of nitride-azide complex **3** with thermal ellipsoids at 50% probability level. Hydrogen atoms (except the B−H) are omitted for clarity. (B) Synthesis of **3**.

Table 1. Salient Metric Parameters, NMR, and IR Spectroscopic Features of Vanadium Nitrides 3, 5, B-THF, and B-OPPh₃

Complex	**3**	**5**	**B-THF**	**B-OPPh₃**
$VN_{nitride}$ (Å)	1.558(2)	1.676(2)^a	1.578(2)	1.587 (2)
		1.825(2)		
		1.872(2)		
		1.786(3)		
τ_5	0.59	0.76^b	0.52	0.48
${}^{15}N$ NMR (δ)	1035.8	n/a	n/a	n/a
${}^{51}V$ NMR (δ)	−246.3	n/a	n/a	n/a
${}^{11}B$ NMR (δ)	−35.9	−8.9	−19.3	−22.7
ν_{BH} (cm^{-1})	2555	2550	2546	2558

^{a}Only one half of the molecule is included for $VN_{nitride}$ distances; *cf.* Figure 10B. $^b\tau_4$ for the central VN_4 fragment is measured as 0.79.

4.16 ppm along with three resonances from the C*H₃*, C*H*, and ${}^tBu$ groups. This indicates the equivalence of the three pyrazolyl arms, consistent with rapid fluctuation of the molecule in solution at room temperature. As expected for a V^V complex, the UV−vis spectrum of **3** in pentane reveals no d−d transitions but only charge-transfer/ligand-centered bands at 388 (infl.), 310 (infl.), and 236 nm (max.) (ε = 1660, 3060, and 4940 M^{-1} cm^{-1}, respectively).

As mentioned previously, thermolysis is necessary to fully convert **1** and NaN_3 into **3**. To our surprise, treatment of **1** with 1.05 equiv Me_3SiN_3 produces the mono-azide complex $[(\text{Tp}^{tBu,Me})V(N_3)\text{Cl}]$ (**4**) in 67% yield (Scheme 1 and Figure 9B), which was confirmed by a combination of structural (Figure 9A), spectroscopic (ν_{N_3} = 1991 and 2074 cm^{-1}, *cf.* Supporting Information, Section S9.7, Figure S100), and
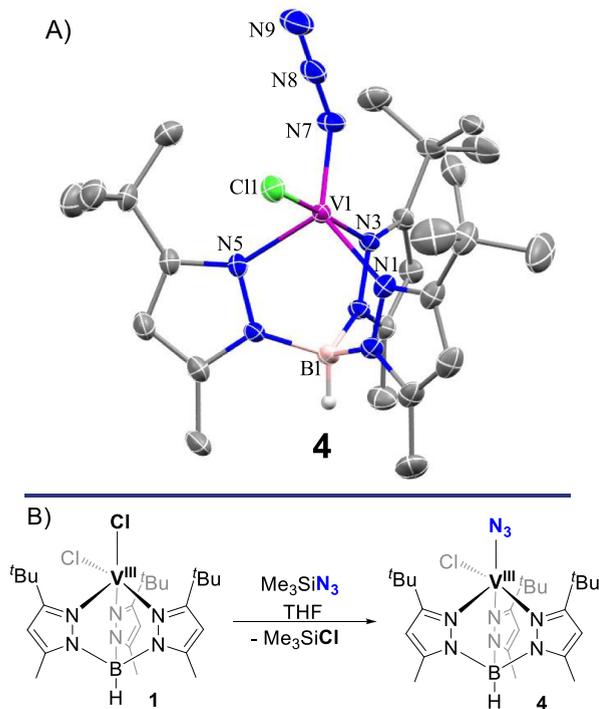
Figure 9. (A) Structural representation of complex **4** (thermal ellipsoids at 50% probability). Hydrogen atoms (except B−H) are omitted for clarity. (B) Synthesis of **4**.

magnetic studies (μ_{eff} = 2.68 μ_B; Evans' method, 300 K, C_6D_6; μ_{eff} = 2.77 μ_B; SQUID, 300 K; corresponding to the spin-only moment for S = 1 with g = 1.93(3)). In terms of metrics, the V−Cl (2.327(9) Å) and V_1−N_7 (1.896(3) Å) bonds in **4** are essentially orthogonal (Cl_1−V_1−N_7 = 94.0(4)°), and the τ_5 value of 0.69 suggests a geometry midway between SP and TBP. Although complex **4** shows all the features of a high-spin d^2 ion, it is surprisingly stable to thermolysis (decomposition above 50 °C, *cf.* Supporting Information, Section S8.7, Figure S87) as well as photolysis. However, treatment of **1** with excess Me_3SiN_3 (or treatment of **4** with NaN_3), followed by heating to 45 °C overnight, leads to nitride-azide complex **3**. This points to **A** being a common intermediate in the conversion of **1** and **4** to nitride complex **3** (Scheme 1). It further suggests that the reaction of **1** with NaN_3 traverses two transmetallation steps before N_2 extrusion ensues. We have no definitive reason why complex **4**, as opposed to **A**, would be reluctant to undergo N_2 elimination, but based on previous studies, we speculate that an azide ligand bridging across two V centers might play a critical role.[8k,31]

Vanadium^{IV} Nitrides from V^V and V^{II} Precursors. As opposed to the ubiquitous vanadyl ion ([VO]$^{2+}$), terminal V^{IV} nitrides are exceedingly rare with the only crystallographically characterized example being dinuclear $[Na]_2[(nacnac)(ArO)$-$V\equiv N]_2$ (nacnac$^-$ = [ArNC(CH$_3$)]$_2$CH$^-$, Ar = 2,6-$^iPr_2C_6H_3$), in which the vanadium centers are bridged by alkoxide and Na^+−arene interactions.[8m] In the above V^{IV} example, other ligands than nitride are bridging, but there is however a tendency for nitride ligands themselves to bridge and form $[LM(\mu_2$-$N)_2ML]$ core structures, where M is a high-valent metal. Representative d-block examples involve V, Nb, Ta, Cr, and W.[11,9b,32] We therefore inquired if compound **3** could be reduced by one electron to yield a putative four-coordinate, neutral V^{IV} nitride, $[(Tp^{tBu,Me})V\equiv N]$ (**B**). In our case, treatment of **3** with KC_8

furnishes an unprecedented trinuclear complex with four bridging nitride ligands, $[\{(Tp^{tBu,Me})V\}_2(\mu_4$-$VN_4)]$ (**5**) in 54% isolated yield, where the central $[VN_4]^{8-}$ unit could be considered analogous to the ubiquitous vanadate ion, $[VO_4]^{3-}$ (Scheme 1 and Figure 10D, route 1). The connectivity of **5** was established by sc-XRD studies (Figure 10A,B), which reveal three vanadium centers arranged in a linear, double-diamond core fashion (V1−V3−V2 = 177.45(3)°). The central vanadium (V3) is supported by only bridging nitride ligands, resulting in an approximately tetrahedral geometry, which is elongated along the V−V−V vector ($\tau_4 = \tau_4' = 0.79$, Table 1). This unique complex with a V_3N_4 core (two diamond cores oriented orthogonally) has a similar tetrahedral geometry around the central vanadium, which has previously been computationally predicted for the metastable V^{IV} nitride.[33] Within each $\{V(\mu$-$N)_2V\}$ fragment of **5**, the V−N bond distances are alternately short (1.676(3)−1.786(3) Å) and long (1.825(2)−1.884(3) Å, Figure 10B), which parallels Cloke's dinuclear $[\{N(N'')V\}_2(\mu$-$N)_2]$ complex[9b] $((N(N'')_2)^{2-}$: $[(Me_3Si)N(CH_2CH_2N$-$(SiMe_3))_2]^{2-})$, where the average V−N and V≡N bond distances are 1.87 and 1.74 Å, respectively. The V_{distal}−$V_{central}$ distances in **5** are 2.605(1) and 2.594(1) Å, which results in a separation of the two V_{distal} of 5.198(1) Å. Notably, and given its composition, the formation of **5** requires expulsion of a $Tp^{tBu,Me}$ ligand. When preparing **5** from **3** and KC_8, a lustrous black solid appears (graphite); we also observe KN_3 (by IR spectroscopy) as well as $[KTp^{tBu,Me}]$ (by ^1H NMR spectroscopy). Mass balance therefore suggests 2/3 KN_3 and 1/3 $[KTp^{tBu,Me}]$ (and 1/3 N_2) to form for each 1/3 equiv of **5**. From this complex reaction mixture, $[KTp^{tBu,Me}]$ could be removed *via* fractional crystallization. Alternatively, addition of 1/3 equiv of $[VCl_3(THF)_3]$ generates **1**, and this could be readily separated from **5** due to the low solubility of **1** in alkanes (41% yield with respect to $[KTp^{tBu,Me}]$, Scheme 3). In a third approach, $[KTp^{tBu,Me}]$ can be removed by extracting **5** into cold hexamethyldisiloxane and filtering the solution through Celite. This allows $[KTp^{tBu,Me}]$ to be recovered, while isolating **5** in ∼51% yield. Complex **5** can tantalizingly be thought of as an antiferromagnetically coupled adduct of an electron-deficient nitridyl "VN_2" fragment and two units of putative **B**, overall leading to a doublet spin state. Therefore, **5** should be paramagnetic, and we indeed show how this species represents a trinuclear system with a mixed-valent $\{V^V(\mu_4$-$V^{IV}N_4)V^V\}$ core. Solution magnetic measurements (μ_{eff} = 1.89 μ_B; Evans' method, 300 K, C_6D_6) corroborate this formulation, while X-band EPR (Figure 10C) shows the characteristic features of an S = 1/2 species with hyperfine coupling to a single ^{51}V center (A = 91.4 × 10^{-4} cm^{-1}, I = 7/2, 99.75%). Overall, the confinement of the unpaired electron to a single vanadium center is in line with a Robin−Day class I system.[34]

The calculated MO diagram of **5** suggests contribution of $d_{x^2-y^2}$ orbitals on all three V centers in SOMO, but the unpaired electron is largely localized around the central V^{IV} ion given that the SOMO is composed of orthogonal vanadium $d_{x^2-y^2}$ orbitals which lack any constructive interactions (Figure 11). Notably, the SOMO is approximately 1.2 eV higher in energy than the other occupied orbitals as shown by restricted open (RO) B3LYP calculations, and the natural bond orbital analysis indicates that approximately 78% of the electron density in the SOMO is localized on the central vanadium atom, in accord with **5** having an eight-line EPR spectrum.

In pursuing the putative V^{IV} nitride intermediate **B**, we turned to **2** and treated it with NaN_3 in THF (in the dark) to form the
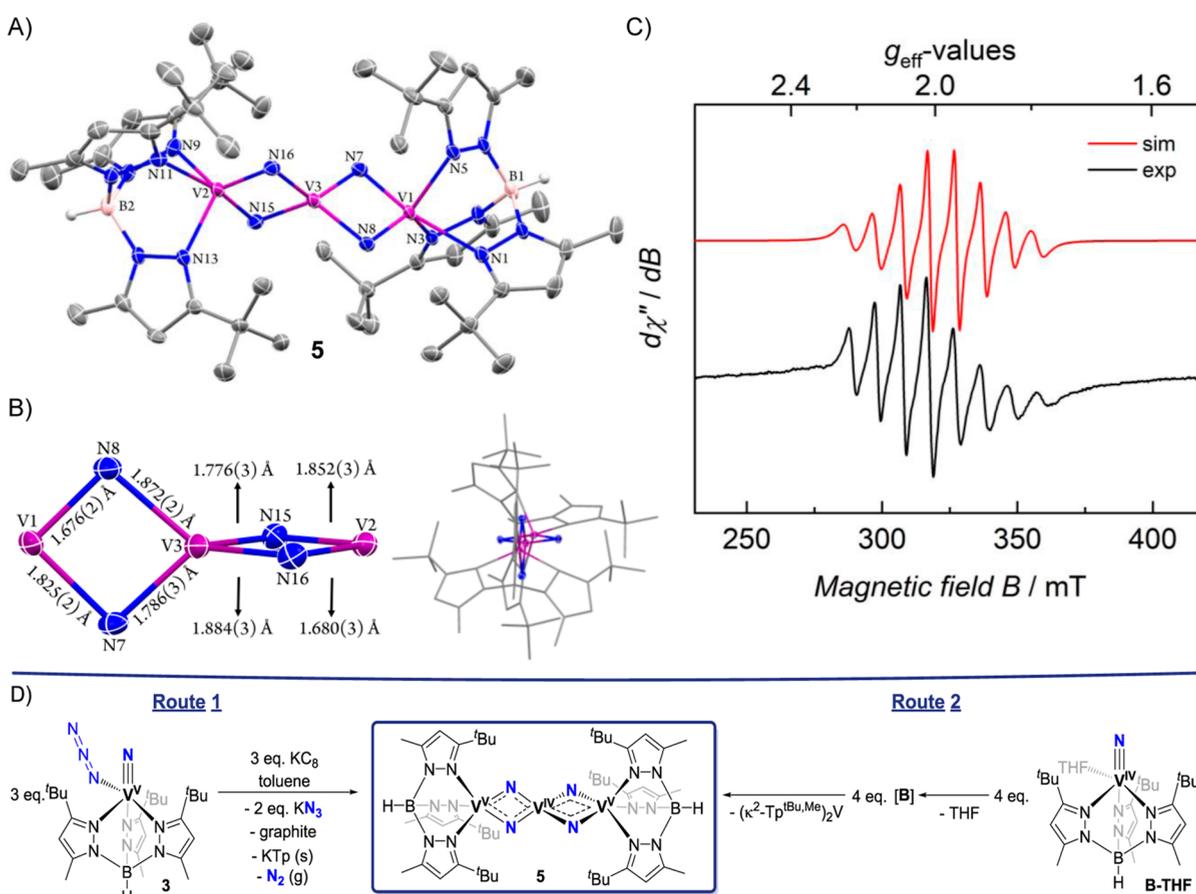
Figure 10. (A) Structural representation of complex **5** (thermal ellipsoids at 50% probability). Hydrogen atoms (except B−H's) and the co-crystallized solvent are omitted for clarity. (B) $\{V^V(\mu_4\text{-}V^{IV}N_4)V^V\}$ core of **5** viewed from the side and along the V_3 axis. (C) CW X-band EPR spectrum of **5** in toluene at 293 K. Experiment (black trace). Simulation (red trace): $g_{iso} = 1.98$, $W_{FWHM,iso} = 2.03 \times 10^{-4}$ cm^{-1}/GHz, $a_{iso} = 91.4 \times 10^{-4}$ cm^{-1} ($I = 7/2$ (^{51}V), 99.75% nat. abundance). (D) Two independent syntheses of **5**.

Scheme 3. Synthesis of Complex 5 from the Reduction of 3, Followed by Treatment with $[VCl_3(THF)_3]$ to Form 1, Which Can Be Separated More Conveniently but Also Recycled
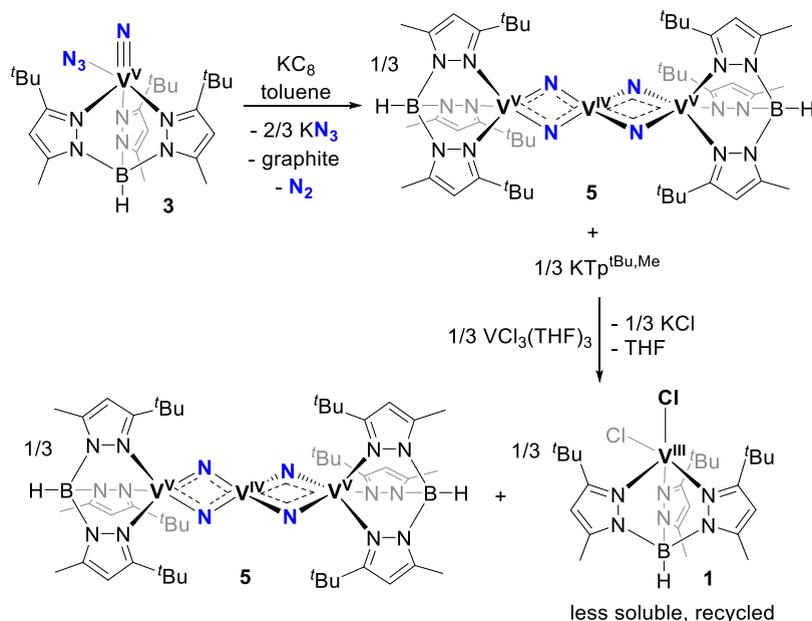
azide-bridged dimer $[\{(Tp^{tBu,Me})V\}_2(1,3\text{-}\mu_2\text{-}N_3)_2]$ (**6**) in 95% isolated yield (Scheme 1 and Figure 12D). The dimeric nature of

6 was confirmed by sc-XRD (Figure 12A). As opposed to most mononuclear five-coordinate species presented above, complex
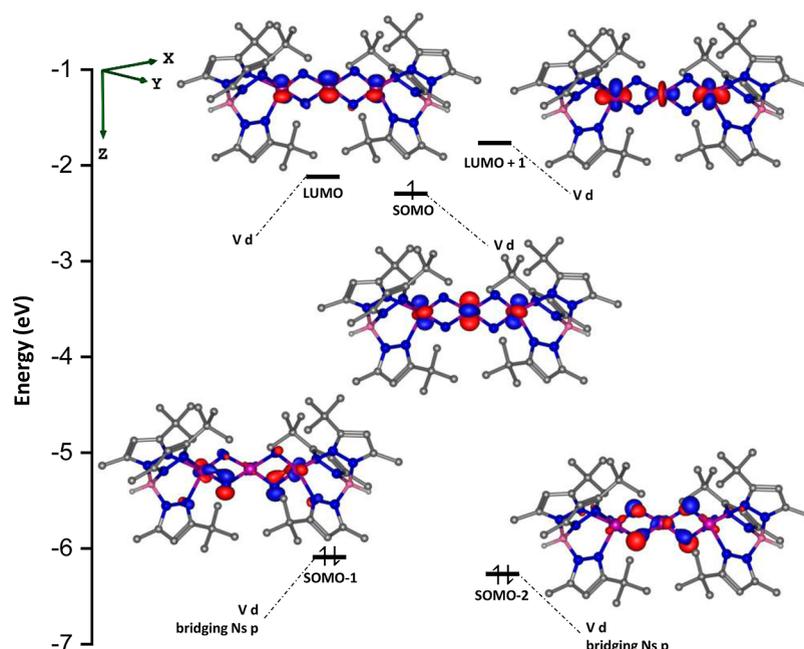
Figure 11. Calculated MO diagram of **5**. Orbital energies in eV (RO-B3LYP/TZVP).
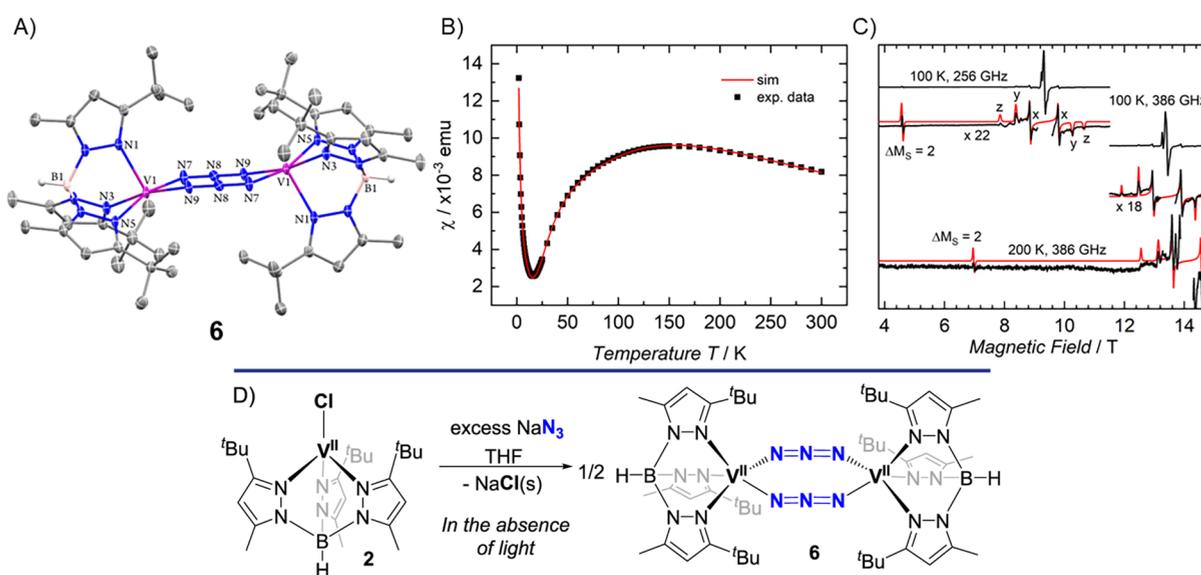

Figure 12. (A) Thermal ellipsoid plot of complex **6** (50% probability). Hydrogen atoms (except B–H) and co-crystallized toluene are omitted for clarity. (B) Magnetic susceptibility plot for a powder sample of **6** (at 1 T, black squares). Simulation (red trace): $g_{ave} = 1.932$, $J = -29.8$ cm^{-1}, $j = -1.80$ cm^{-1}, TIP = 360×10^{-6} cgs emu (for each V), and paramagnetic impurity (*i.e.*, monomeric V^{II}) = 0.72%. (C) Black: HFEPR spectra of **6** recorded at conditions indicated. Red: simulations of the (total spin) $S = 1$ state spectra using $g_x = 1.954$, $g_y = 1.957$, $g_z = 1.976$, $D_{S=1} = -1.293$ cm^{-1}, and $E_{S=1} = -0.145$ cm^{-1}. A strong central transition is cut off in the 386 GHz spectrum and in the magnified 256 and 368 GHz spectra. The "forbidden" $\Delta m_S = 2$ transition is labeled. Labels x, y, and z indicate the molecular orientations at which the respective transitions occur. (D) Synthesis of **6**.

6 has a τ_5 value of 0.09, indicative of a nearly ideal SP geometry in which one of the pyrazolyl arms occupies the apical position. Notably, a similar SP geometry ($\tau_5 = 0.06$) is observed in the bis-azide ate complex, $[\text{Na}(15\text{-C-5})][(\text{Tp}^{tBu,tBu})\text{V}(\text{N}_3)_2]$ (X^{tBu,tBu}).

Solid-state SQUID magnetization measurements (2–300 K) are consistent with a d^3-d^3 dimeric species with moderate antiferromagnetic coupling between the V^{II} centers (Figure 12B). μ_{eff} of the dimeric species is 4.42 μ_B at 300 K, which corresponds to 3.12 μ_B per one V ion. At lower temperatures, the effective magnetic moment decreases steadily to reach 0.45 μ_B at 2 K. The effective magnetic moment determined by SQUID

magnetometry at 300 K is consistent with the value extracted by Evans' method ($\mu_{eff} = 4.48$ μ_B per dimer or 3.16 per V, 300 K, C$_6$D$_6$) at the same temperature. Both values are lower than expected for an uncoupled spin-only (d^3)$_2$ system ($\mu_{eff} = 3.87$ μ_B per one V). and notably, the consistency of the magnetic moments suggests **6** to remain dimeric in solution.

Antiferromagnetic exchange coupling of the form $H = -2JS_1S_2$ in this system results in a diamagnetic ground state with a total spin of $S = 0$. States with $S = 0$, 1, 2, and 3 have energies of 0, $-2J$, $-6J$, and $-12J$, respectively. All paramagnetic states are EPR-active, but only the $S = 2$ state is observed in X-

band EPR as states $S = 1$ and $S = 3$ exhibit large zfs requiring higher field/frequencies. HFEPR spectra of **6** were recorded at 120−386 GHz. Spectral quality (Figure 12C) was sufficient to determine the spin Hamiltonian parameters of the $S = 1$ state. The zfs parameters for $S = 1$ of the dimer imply the zfs parameters of each V^{II} ion as $D_V = +0.54$ cm^{-1} and $E_V = +0.06$ cm^{-1}. The magnetic susceptibility data were then fitted using the "microscopic" spin Hamiltonian with D_V and E_V fixed as found from EPR (*cf.* Supporting Information, Section S6.3). It was found that the biquadratic exchange term, $j(S_1 S_2)^2$,[35] must be included to simulate the experimental magnetic data. This term appears very often in Cr^{III} dimers with the same $d^3−d^3$ configuration as our V^{II} dimer.[36]

We propose complex **6** to extrude N$_2$ both thermolytically and photolytically, with photolysis giving the cleanest conversion. Accordingly, irradiation of **6** in toluene with a Xe or a 390 nm LED lamp over 2 h generated the trinuclear species **5**. The requisite release of Tp^{tBu,Me} was traced to a new paramagnetic species, $[V(\kappa^2\text{-Tp}^{tBu,Me})_2]$, identified on the basis of an sc-XRD study. Due to the similar solubilities of **5** and the divalent V^{II} complex, spectroscopically pure $[V(\kappa^2\text{-Tp}^{tBu,Me})_2]$ could not be isolated (Scheme 1 and Figure 13). The Tp^{tBu,Me} ligands in
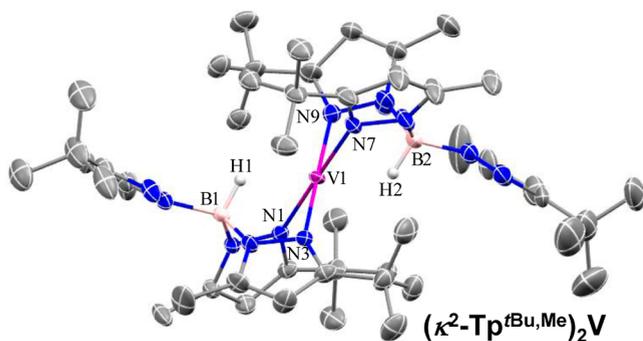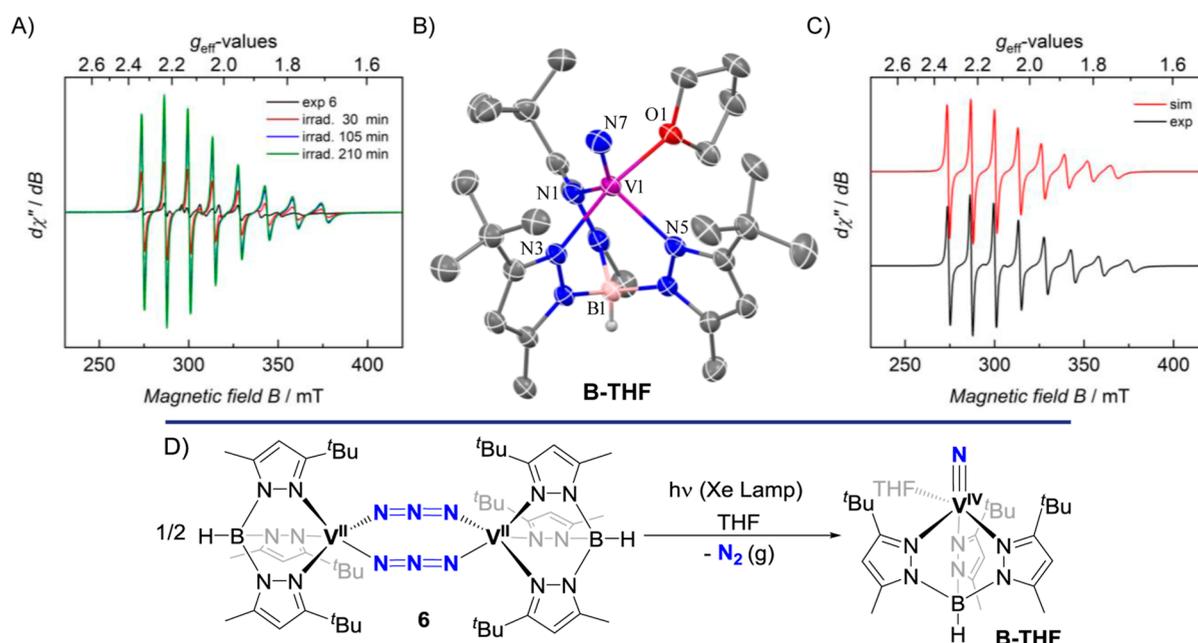

Figure 13. Structural representation of the complex $[(\kappa^2\text{-Tp}^{tBu,Me})_2V]$ (thermal ellipsoids at 50% probability). Hydrogen atoms (except B−H) and co-crystallized toluene and pentane are omitted for clarity.

$[V(\kappa^2\text{-Tp}^{tBu,Me})_2]$ seemingly bind in a bidentate fashion, which defines a square planar motif around vanadium (N−V−N = 85.5(7) and 85.6(5)°, $\tau_4 = 0.04$). However, $[V(\kappa^2\text{-Tp}^{tBu,Me})_2]$ is more appropriately seen as an octahedral complex containing *transoid* BH donor groups (V−H = 1.984(1) and 1.967(1) Å). Returning to the formation of **5** from **6**, a V^{II} ion sequesters the excess equivalent of Tp^{tBu,Me}, which stands apart from the reduction of compound **3** to generate **5** and $[KTp^{tBu,Me}]$. We propose **6** to photolytically extrude N$_2$ by forming **B**, which then undergoes a series of ligand-exchange reactions with three more equivalents of **B**. The Lewis acidity of **B** and the ability of the nitride and pyrazolyl groups to bridge between vanadium centers are most likely reasons why a unique complex such as **5** forms. Attempts at preparing $[V(\kappa^2\text{-Tp}^{tBu,Me})_2]$ independently from **2** and 1 equiv $[TlTp^{tBu,Me}]$ or from $[VCl_2(tmeda)_2]$ and 2 equiv $[TlTp^{tBu,Me}]$ were unsuccessful (*cf.* Supporting Information, Section S3.13), which lends support for a mechanism in which several units of **B** aggregate prior to releasing **5** and $[V(\kappa^2\text{-Tp}^{tBu,Me})_2]$.

Trapping of the Mononuclear V^{IV} Nitride B. Given the photochemical formation of **5** upon photolysis of **6** in toluene, we conducted the same experiment in a coordinating solvent. Irradiation of **6** in THF at 293 K over 30 min to several hours (Figure 14D) resulted in gradual decay of the X-band EPR

signals from the precursor concurrent with growth of a new signal consistent with a new radical distinct from **5** (Figure 14A). Gratifyingly, photolysis of **6** on a preparative scale quantitatively afforded the new paramagnetic species, which was identified as the Lewis base adduct of the elusive terminal V^{IV} nitride **B**, namely, $[(Tp^{tBu,Me})V\equiv N(THF)]$ (**B-THF**), on the basis of an sc-XRD study (Scheme 1 and Figure 14B). The solid-state structure of **B-THF** exhibits some disorder of the ^{t}Bu groups and THF ligands. As expected, based on the larger ionic radius of V^{IV} compared to V^V, the V≡N bond in **B-THF** (1.580(2) Å) is slightly longer than in **3** (1.561(5) Å). On the other hand, the V≡N bond distance is somewhat shorter in **B-THF** than in the only other reported V^{IV} nitride complex, namely, dinuclear $[Na]_2[(nacnac)(ArO)V\equiv N]_2$ (V≡N: 1.624(2) and 1.614(3) Å). Like most other five-coordinate species in this work, **B-THF** falls midway between the limiting TBP and SP geometries ($\tau_5 = 0.52$, Table 1). Despite being stable for days at −35 °C in THF, the complex **B-THF** slowly decomposes at room temperature in the solid state (*vide infra*). The X-band EPR spectrum of **B-THF** (Figure 14C) shows the signature eight-line pattern from hyperfine coupling of the unpaired electron to the ^{51}V center ($a_{iso} = 123 \times 10^{-4}$ cm^{-1}, 369 MHz). This ^{51}V isotropic hyperfine coupling is ∼15% greater than that observed for vanadyl with five exclusively O-donor ancillary ligands (318−328 MHz)[37] and is much larger than in vanadyl porphyrins (263 MHz).[38] Clearly, **B-THF** is a vanadium-centered paramagnet. This character of complex **B-THF** was also established by solution magnetometry ($\mu_{eff} = 1.95 \mu_B$; Evans' method, 300 K, THF-d_8), corresponding to $S = 1/2$. Last, preparing the 50% ^{15}N enriched isotopomer $[(Tp^{tBu,Me})V\equiv^{15}N(THF)]$ (**B-THF−^{15}N**), *via* photolysis of **6-^{15}N**, did not alter the X-band EPR spectral features, further indicating the nitride group to have minimal nitridyl character. This is likely the result of the unpaired electron residing in a d-orbital with delta symmetry with respect to the V−N$_{nitride}$ axis.[39] This result is consistent with Bendix' studies of isoelectronic Cr^V terminal nitride complexes with an SP or octahedral geometry; here, hyperfine coupling to the axial nitride ^{14}N is obscured by unresolved coupling to equatorial ligands such as ^{35,37}Cl ($I = 3/2$, 100%), whereas coupling to the nitride is resolved when the equatorial ligands are ^{16}O (from the dibenzoylmethane ligand, dbm; modeled as acac for calculations).[40] In **B-THF−^{15}N**, unresolved hyperfine coupling to pyrazolyl ^{14}N (three coordinated, three not) prevents resolution of the small coupling to nitride ^{14,15}N.[41]

When dissolving the complex **B-THF** in C$_6$D$_6$ for NMR spectroscopic characterization, the V^{IV} nitride rapidly transforms to **5** and $[V(\kappa^2\text{-Tp}^{tBu,Me})_2]$ (Scheme 1, and Figure 10D). In general, **B-THF** is quite unstable in weakly coordinating solvents. Presumably, the lack of a Lewis base allows the unsaturated V^{IV} center in **B** to oligomerize via bridging nitride and/or pyrazolyl moieties. As a result, we propose that dissolution of **B-THF** in hydrocarbon solvents results in dissociation of THF that is accompanied with bimolecular reactions, eventually disproportionating to **5** and $[V(\kappa^2\text{-Tp}^{tBu,Me})_2]$. Surprisingly, there is no structurally characterized example of a neutral $[V(Tp)_2]$ despite many reports on analogous $[M(Tp)_2]^0$ complexes that exist in the literature.[42] Based on the above studies, it is clear that **B** is highly reactive, probably because it has a d-electron count of only 13 valence electrons. Due to the instability of **B-THF**, we turned to a stronger Lewis base that could trap **B** without compromising the nitride ligand, namely, OPPh$_3$. Photolysis of **6** in THF in the presence of 2 equiv of OPPh$_3$ generated the **B-OPPh$_3$** adduct in

Figure 14. (A) CW X-band EPR spectra of pristine **6**-^{14}**N** in THF at 293 K (black trace) and after irradiation. (B) Structural representation of the complex **B-THF** (thermal ellipsoids at 35% probability). Hydrogen atoms (except B−H), the co-crystallized solvent, and disorder on THF and ^{t}Bu groups are omitted for clarity. (C) CW X-band EPR spectrum of **B-THF** in THF at 293 K (black trace). Simulation (red trace): S = 1/2, g_{iso} = 1.99, and $W_{FWHM,iso}$ = 2.00 × 10^{-4} cm^{-1}/GHz. Hyperfine coupling to one ^{51}V (I = 7/2, 99.75%) a_{iso} = 123 × 10^{-4} cm^{-1}. (D) Photolysis of **6** leading to **B-THF**.

near-quantitative yield (94%, Scheme 1 and Figure 16B). The complex **B-OPPh$_3$** resembles **B-THF** structurally with a τ_5 value
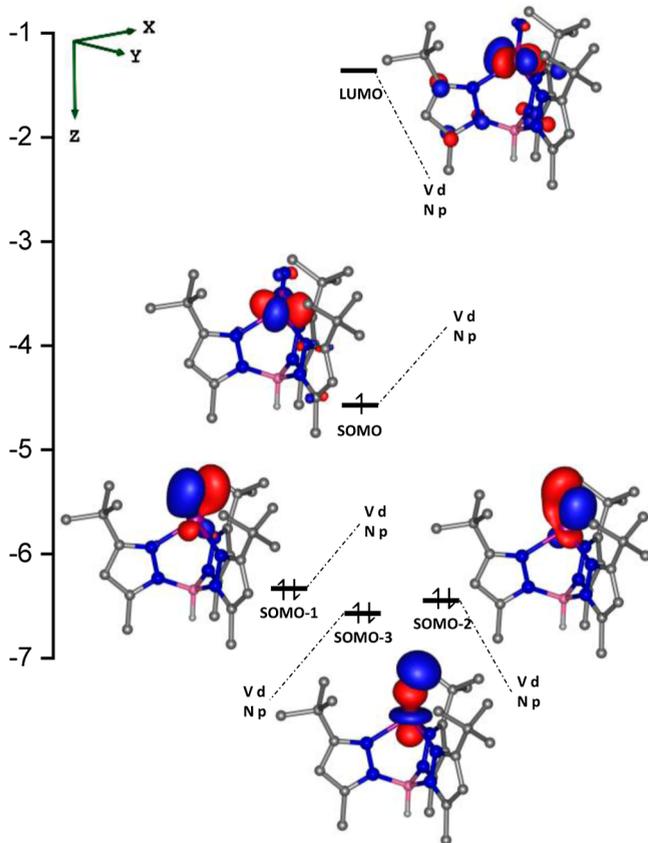
Figure 15. MO diagrams of **B**. Orbital energies reported in eV (B3LYP/TZVP).
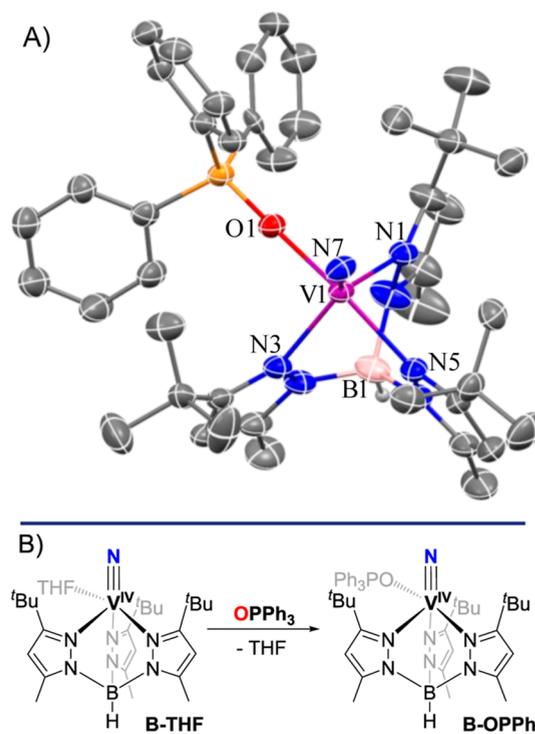
Figure 16. (A) Structural representation of the complex **B-OPPh$_3$** (thermal ellipsoids at 50% probability). Hydrogen atoms (except B−H) are omitted for clarity. (B) Reaction between **B-THF** and OPPh$_3$ to furnish **B-OPPh$_3$**.

of 0.48 (Table 1). The V≡N bond distance in **B-OPPh$_3$** (1.587(2) Å) is slightly longer than that in **B-THF** (Figure 16A, Table 1), most likely the result of OPPh$_3$ being a stronger σ-donor ligand than THF. The cyclic voltammograms of **B-THF** and **B-OPPh$_3$** reveal a reversible one-electron anodic event for

each complex. The reduction potentials are +0.38 and +0.08 eV for **B-THF** and **B-OPPh₃**, respectively, suggesting oxidation of these species to a terminal V^V nitride to be reversible as well as highly tunable through the choice of a Lewis base (*cf.* Supporting Information, Sections S10.4 and S10.5, Figures S110 and S113). The voltammogram of **B-OPPh₃** further reveals a multi-electron cathodic process at a negative potential (−1.53 eV, Figure S112).

Figure 15 shows the calculated MO diagram of **B** (geometry optimized after removing L from the sc-XRD structure of **B−L**); MO diagrams of the adducts **B-OPPh₃** and **B-THF** are presented in Figures S122 and S123, respectively. The most salient bonding features for **B** are a V≡N triple bond, composed of the SOMO − 3 (σ-symmetric combination of V 3d_{z^2}/N 2p_z atomic orbitals), SOMO − 2, and SOMO − 1 (orthogonal, π-symmetric combinations of V 3d_{yz}/N 2p_y and the V 3d_{xz}/N 2p_x atomic orbitals). The SOMO essentially consists of a V 3d_{xy} orbital, which is δ-symmetric along the V≡N direction (z-axis) and, therefore, interacts insignificantly with 2s and 2p orbitals of the nitride ligand. This is in accordance with the minimal ^{14,15}N hyperfine coupling observed by EPR (vide supra, Figure 14C and Supporting Information, Section S5.4). In analogy to **B**, the adducts, **B-THF** and **B-OPPh₃**, each displays a V≡N triple bond and has an unpaired electron in a d_{xy} orbital. However, while the lowest unoccupied molecular orbital (LUMO) of **B** is largely confined to the metal center, the LUMOs of **B-OPPh₃** and **B-THF** are instead ligand-based (*cf.* Supporting Information, Section S11, Figures S122 and S123).

CONCLUSIONS

We have used a sterically demanding hydro-tris(pyrazolyl)-borate ligand, [Tp^{tBu,Me}]⁻, to synthesize the spin triplet V^{III} complex [(Tp^{tBu,Me})VCl₂] (**1**). Replacement of the pyrazoles' 5-^{t}Bu groups with less bulky Me substituents resolved the propensity for the previously reported [(Tp^{tBu,tBu})VCl₂] to undergo ligand degradation, while preserving a sterically encumbering environment. Reduction of **1** affords a high-spin (S = 3/2) and mononuclear V^{II} complex, [(Tp^{tBu,Me})VCl] (**2**) with a ^{4}A₂ electronic ground-state, established by solution- and solid-state magnetometry as well as EPR and HFEPR spectroscopy. The affinity of **2** toward THF and 4-dimethylaminopyridine (DMAP) reveals its Lewis acidity and proclivity to attain five-coordination. Two-step transmetallation of **1** with NaN₃, followed by N₂ extrusion, affords a diamagnetic V^V nitride, **3**. Using Me₃SiN₃ as an azide source, we isolated and characterized an unexpected intermediate, the V^{III} azide-chloride complex, **4**, which converts to **3** upon exposure to additional azide. Attempts at reducing **3** to a V^{IV} nitride affords the unprecedented trinuclear tetra-nitride **5**. Solution magnetometry and EPR studies of complex **5** reveal one unpaired electron confined to a single vanadium center, in accord with a Robin−Day class I system. In an alternative approach, we explored photolysis of the dinuclear V^{II} azide **6**. In toluene, this affords **5** and [V(κ²-Tp^{tBu,Me})₂], while in THF, this furnishes a neutral, mononuclear V^{IV} nitride, **B-THF**, where **B** is the still elusive four-coordinate [(Tp^{tBu,Me})V(≡N)]. Use of a stronger Lewis base, such as OPPh₃, led to the kinetically stable V^{IV} nitride, **B-OPPh₃**. Notably, the unpaired electron in the V^{IV} nitride species is metal-centered as seen from the vanishing hyperfine coupling to the nitride ligand and the typical ^{51}V coupling. We thus report the first example (as **B−L**, **B** = (Tp^{tBu,Me})V(≡N), **L** = THF, or OPPh₃) of a neutral mononuclear [V≡N]⁺ (azavanadyl) analogue to the many such [V≡O]$^{2+}$ (vanadyl) species.

Overall, we have demonstrated how the [Tp^{tBu,Me}]⁻ ligand can accommodate low-valent vanadium centers but also support high-valent V^V and V^{IV} nitrides in mononuclear or trinuclear forms. The latter, compound **5**, forms upon loss of the [Tp^{tBu,Me}]⁻ ligand, which has allowed us to study, for the first time, a well-defined tri-vanadium tetra-nitride motif, where the central V center is supported *only* by bridging nitride ligands, [{(Tp^{tBu,Me})V}₂(μ₄-VN₄)], thus exhibiting a double-diamond core. This is the first example of a [VN₄]$^{8-}$ analogue of the ubiquitous vanadate ion, [VO₄]$^{3-}$. We are currently exploring the reactivity of complex **5** since its central V ion could act as a molecular mimic of vanadium nitride surfaces. We are also investigating the reactivity of the terminal V^{IV} nitrides **B** and **B−L**.

ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c00276.

Synthetic procedures, NMR, IR, UV−vis, EPR, HFEPR, SQUID, computational, electrochemical, and X-ray crystallographic data (PDF)

Computational data of coordinates (PDF)

5-SOMO rotation (ZIP)

Accession Codes

CCDC 1971914−1971922 and 2126109−2126113 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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https://pubs.acs.org/10.1021/jacs.2c00276

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

On the occasion of the 90th anniversary of his birth, we dedicate this paper to the memory of Swiatoslaw ("Jerry") Trofimenko (1931−2007), the great Ukrainian-American chemist who invented the "scorpionate" (pyrazolylborate) ligand. We would also like to thank Prof. Jesper Bendix (Copenhagen University) for the Ligfield software and Prof. Brian M. Hoffman (Northwestern University) for use of EPR/ENDOR spectrometers in his laboratory and helpful comments about vanadium nitrogenase.

■ ABBREVIATIONS

$Tp^{tBu,Me}$	hydro-tris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate
$Tp^{tBu,tBu}$	hydro-tris(3,5-di-*tert*-butylpyrazol-1-yl)borate
CV	cyclic voltammetry
T_d	tetrahedral
SP	square planar (four-coordinate)
TBP	trigonal bipyramidal
SP	square pyramidal (five-coordinate)
DMAP	4-dimethylaminopyridine
sc-XRD	single-crystal X-ray diffraction
ENDOR	electron nuclear double resonance
HFEPR	high-frequency and -field electron paramagnetic resonance

■ ADDITIONAL NOTE

[a] A homoleptic five-coordinate V^{III} complex, $[NBu_4]_2[V^{III}(C_6F_5)_5]$, has been reported, which has a slightly distorted TBP geometry.[26b] The complex is EPR-silent at X- and Q-bands (in contrast to nearly tetrahedral V^{III} in $[Li(thf)_4][V(C_6Cl_5)_4]$, which has $|D| = 0.513$ cm^{-1}), so it is likely that its zfs is on the order of several cm^{-1}.

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