

# A Tale of Three Molecular Nitrides: Mononuclear Vanadium(V) and (IV) Nitrides, as well as a Mixed-Valence Trivanadium Nitride Having a V<sub>3</sub>N<sub>4</sub> Double Diamond-Core.

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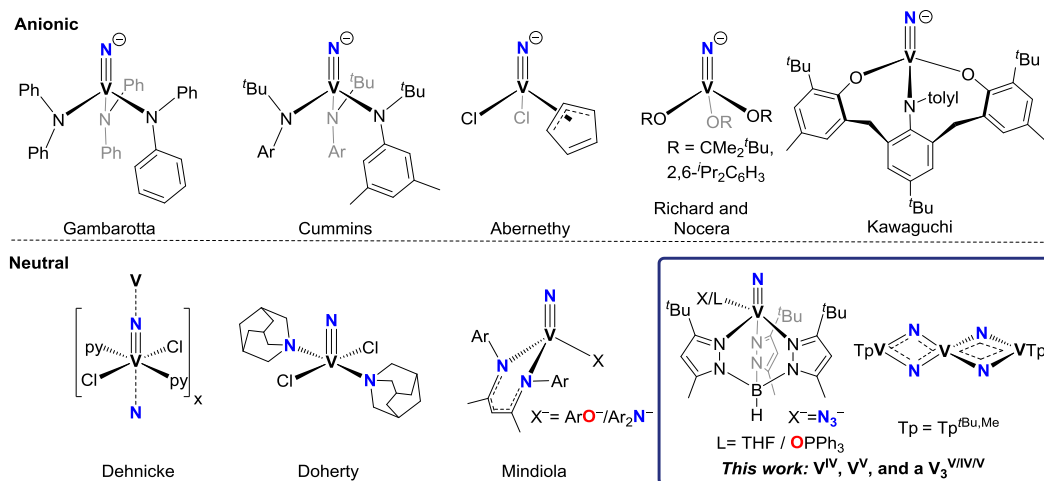
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**ABSTRACT:** Transmetalation of [VCl<sub>3</sub>(THF)<sub>3</sub>] and [TiTp<sup>tBu,Me</sup>] afforded [(Tp<sup>tBu,Me</sup>)VCl<sub>2</sub>] (**1**, Tp<sup>tBu,Me</sup> = hydro-tris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate), which was reduced with KC<sub>8</sub> to afford a C<sub>3v</sub> symmetric V<sup>II</sup> complex, [(Tp<sup>tBu,Me</sup>)VCl] (**2**). Complex **1** has a high-spin (*S* = 1) ground state and displays rhombic high-frequency and -field EPR spectra, while complex **2** has an *S* = 3/2 <sup>4</sup>A<sub>2</sub> ground state observable by conventional EPR. Complex **1** reacts with NaN<sub>3</sub> to form V<sup>V</sup> nitride-azide complex [(Tp<sup>tBu,Me</sup>)V≡N(N<sub>3</sub>)] (**3**). A likely V<sup>III</sup> azide intermediate *en route* to **3**, [(Tp<sup>tBu,Me</sup>)VCl(N<sub>3</sub>)] (**4**), was isolated by reacting **1** with N<sub>3</sub>SiMe<sub>3</sub>. Complex **4** is thermally stable but reacts with NaN<sub>3</sub> to form **3**, implying a bis-azide intermediate, [(Tp<sup>tBu,Me</sup>)V(N<sub>3</sub>)<sub>2</sub>] (**A**), leading to **3**. Reduction of **3** with KC<sub>8</sub> furnishes a trinuclear and mixed-valent nitride, [{(Tp<sup>tBu,Me</sup>)V}(μ<sub>4</sub>-VN<sub>4</sub>)] (**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<sub>3</sub> to produce an azide-bridged dimer, [{(Tp<sup>tBu,Me</sup>)V}<sub>2</sub>(1,3-μ<sub>2</sub>-N<sub>3</sub>)<sub>2</sub>] (**6**), with two antiferromagnetically coupled high-spin V<sup>II</sup> ions. Complex **5** could be independently produced along with [(κ<sub>2</sub>-Tp<sup>tBu,Me</sup>)<sub>2</sub>V], upon photolysis of **6** in arene solvents. The putative {V<sup>IV</sup>≡N} intermediate, [(Tp<sup>tBu,Me</sup>)V≡N] (**B**), was intercepted by photolyzing **6** in a coordinating solvent, such as THF, yielding [(Tp<sup>tBu,Me</sup>)V≡N(THF)] (**B-THF**). In arene solvents, **B-THF** expels THF to afford **5** and [(κ<sub>2</sub>-Tp<sup>tBu,Me</sup>)<sub>2</sub>V]. A more stable adduct (**B-OPPh<sub>3</sub>**) was prepared by reacting **B-THF** with OPPh<sub>3</sub>. These adducts of **B** are the first neutral and mononuclear V<sup>IV</sup> nitride complexes to be isolated.

## INTRODUCTION

The nitride functional group can derive from N<sub>2</sub> reduction and splitting by low-valent metal coordination complexes.<sup>1</sup> 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.<sup>2</sup> In solid state chemistry, vanadium nitride surfaces may promote catalytic reduction<sup>3</sup> or oxidation<sup>4</sup> reactions, and even exhibit superconductivity<sup>5</sup> 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,<sup>6</sup> high density and high specific capacitance.<sup>7</sup> Although mononuclear anionic and neutral V<sup>V</sup> nitride complexes are known (Figure 1),<sup>10, 1w, 8</sup> very little, if any, is known about mononuclear V<sup>IV</sup> nitrides, given their propensity to bridge and form oligomeric structures.<sup>9</sup> This is rather surprising given how the close derivative, vanadyl ([V=O]<sup>2+</sup>),<sup>10</sup> is ubiquitous in coordination chemistry, energy storage technologies (*e.g.*, redox-flow batteries),<sup>11</sup> and biological systems.<sup>12</sup> Moreover, molecular vanadium nitride complexes offer the enticing possibility of serving as well-

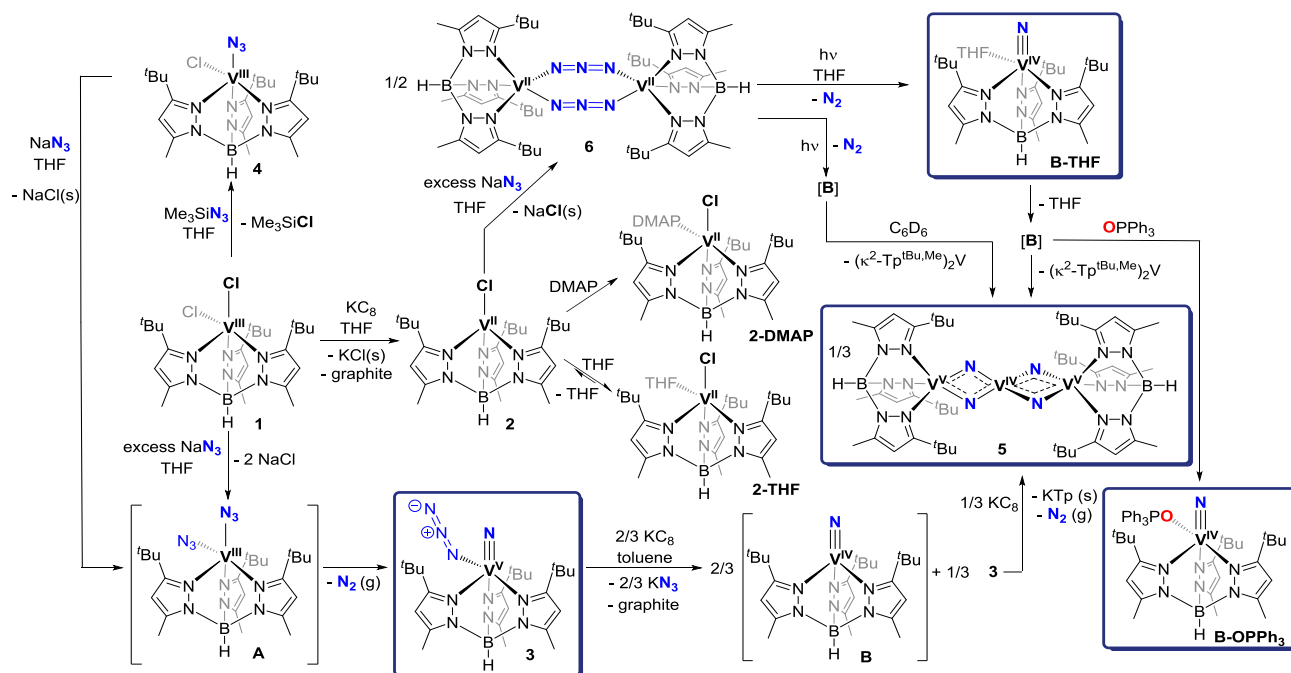
defined precursors for vanadium nitride films.<sup>13</sup> However, there is currently a lack of atomically precise systems that demarcate how the transformation from molecule to bulk material might proceed. In particular, a system in which a vanadium center is surrounded by only nitride ligands (and *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  $\text{Tp}^{t\text{Bu},\text{Me}}$ .

In this study (Scheme 1), we demonstrate synthetic entries to a rare, pseudo-tetrahedral, high-spin  $\text{V}^{\text{II}}$  complex,  $[(\text{Tp}^{t\text{Bu},\text{Me}})\text{VCl}]$  (**2**), which is readily prepared by one-electron reduction of the  $\text{V}^{\text{III}}$  precursor,  $[(\text{Tp}^{t\text{Bu},\text{Me}})\text{VCl}_2]$  (**1**,  $\text{Tp}^{t\text{Bu},\text{Me}}$  = hydrotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate). We showcase how these  $\text{V}^{\text{II}}$  or  $\text{V}^{\text{III}}$  precursors can yield mononuclear  $\text{V}^{\text{IV}}$  and  $\text{V}^{\text{V}}$  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  $\text{V}^{\text{IV}}$  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

clear and mixed-valent vanadium system with a central vanadium ion ligated only by bridging nitrides. We also show how a reactive mononuclear  $\text{V}^{\text{IV}}$  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

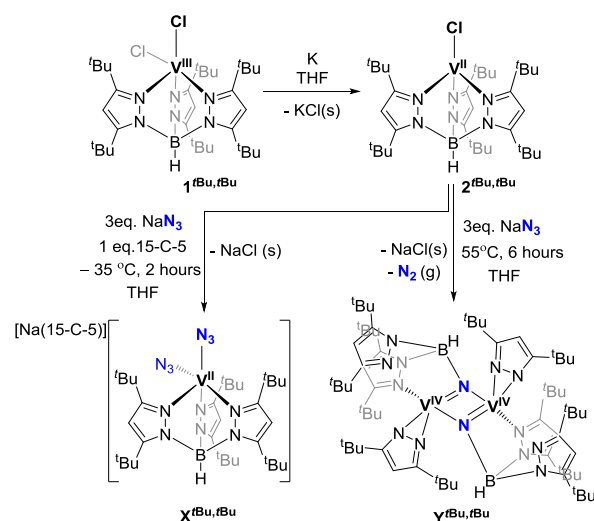


**Scheme 1.** Synthesis of chloride precursors **1** and **2**, along with THF/DMAP adducts of **2**, **2-THF** and **2-DMAP**, demonstrating Lewis-acidity of the  $\text{V}^{\text{II}}$  center. Metathesis of **1** with  $\text{NaN}_3$  and  $\text{Me}_3\text{SiN}_3$  produces azide and/or nitride species **3** and **4**, respectively. Complex **3** likely forms *via* intermediates **4** and **A** as reaction of **4** with either  $\text{NaN}_3$  or excess  $\text{Me}_3\text{SiN}_3$  (at elevated temperatures) both generate **3**. Metathesis of **2** with  $\text{NaN}_3$  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 adduct **B-THF**. **B-THF** gradually releases THF to form **5** and  $[(\kappa^2\text{-Tp}^{t\text{Bu},\text{Me}})_2\text{V}]$ . Reaction of **B-THF** with  $\text{OPPh}_3$  forms the more stable adduct, **B-OPPh**<sub>3</sub>.

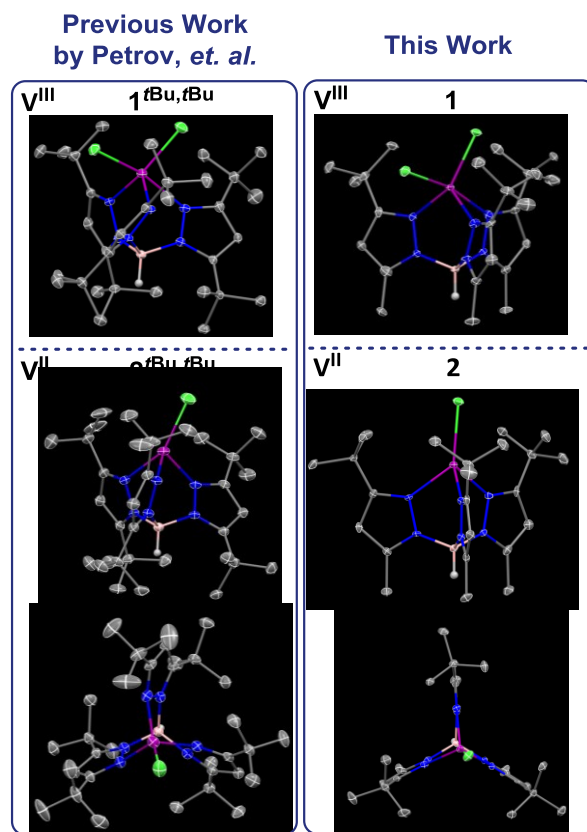
spectroscopically characterized. The paramagnetic vanadium systems have been studied by solution- and solid-state magnetometry. Conventional CW X-band EPR has been applied to half-integer (*i.e.*,  $V^{IV}$ ) species. In the case of complex **1**, which has an  $S = 1$  electronic ground state and, thus, 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 experiment 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,  $[(Tp^{tBu,tBu})VCl]$  ( $Tp^{tBu,tBu}$  = hydro-tris(3,5-di(*tert*-butyl)pyrazol-1-yl)borate),<sup>14</sup> but did not explore its reactivity. Our own reaction studies revealed that the steric encumbrance imposed by the two <sup>t</sup>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  $[(Tp^{tBu,tBu})VCl_2]$  and  $[(Tp^{tBu,tBu})VCl]$  (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 of  $[(Tp^{tBu,tBu})VCl]$  *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).<sup>15</sup> When excess  $NaN_3$  was added to  $[(Tp^{tBu,tBu})VCl]$  in the presence of the crown-ether, 15-C-5, the bis-azide ate complex  $[Na(15-C-5)][(Tp^{tBu,tBu})V(N_3)_2]$  ( $X^{tBu,tBu}$ ) 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 ( $V^{IV}$ )<sub>2</sub> complex  $\{[hydro-bis(3,5-di(*tert*-butyl)pyrazol-1-yl)boraneimide]V(3,5-di(*tert*-butyl)pyrazol-1-yl)]_2$  ( $Y^{tBu,tBu}$ ) in 47% yield, which was characterized by single crystal X-ray diffraction studies (sc-XRD) and multinuclear NMR spectroscopy. The latter complex is likely to form *via* the intermediacy of a reactive  $V^{IV}$  nitride,  $[(Tp^{tBu,tBu})V=N]$ , which then undergoes ligand degradation and dimerization steps.



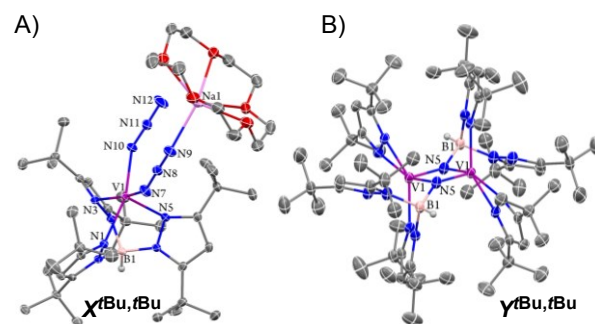
**Scheme 2.** Reactivity studies of Petrov's  $[(Tp^{tBu,tBu})VCl]$  (**2<sup>tBu,tBu</sup>**) with excess  $NaN_3$  with or without crown-ether.



**Figure 2.** Structural representation of  $[(Tp^{tBu,tBu})VCl_2]$  (**1<sup>tBu,tBu</sup>**) and  $[(Tp^{tBu,tBu})VCl]$  (**2<sup>tBu,tBu</sup>**) (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.

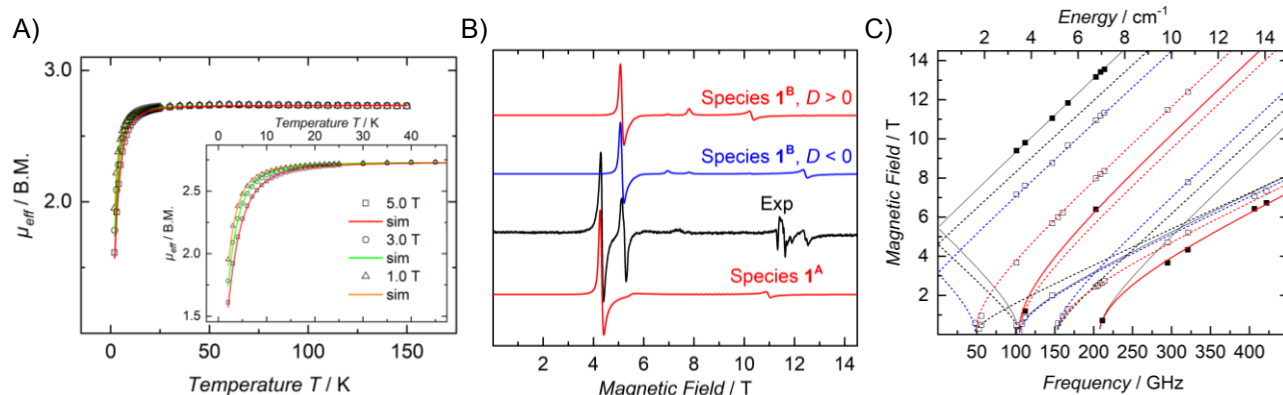
tyl)pyrazol-1-yl)]<sub>2</sub> (**Y<sup>tBu,tBu</sup>**) in 47% yield, which was characterized by single crystal X-ray diffraction studies (sc-XRD) and multinuclear NMR spectroscopy. The latter complex is likely to form *via* the intermediacy of a reactive  $V^{IV}$  nitride,  $[(Tp^{tBu,tBu})V=N]$ , which then undergoes ligand degradation and dimerization steps.

The molecular structure of **X<sup>tBu,tBu</sup>** (Figure 3A) reveals the



**Figure 3.** Structural representations (thermal ellipsoids at 50% probability) of **A)** **X<sup>tBu,tBu</sup>** and **B)** **Y<sup>tBu,tBu</sup>**. Hydrogen atoms (except B–H's), the second molecule in the asymmetric unit, and co-crystallized solvent (in **B**) are excluded for clarity.

lack of three-fold symmetry for the  $Tp^{tBu,tBu}$  ligand owing to

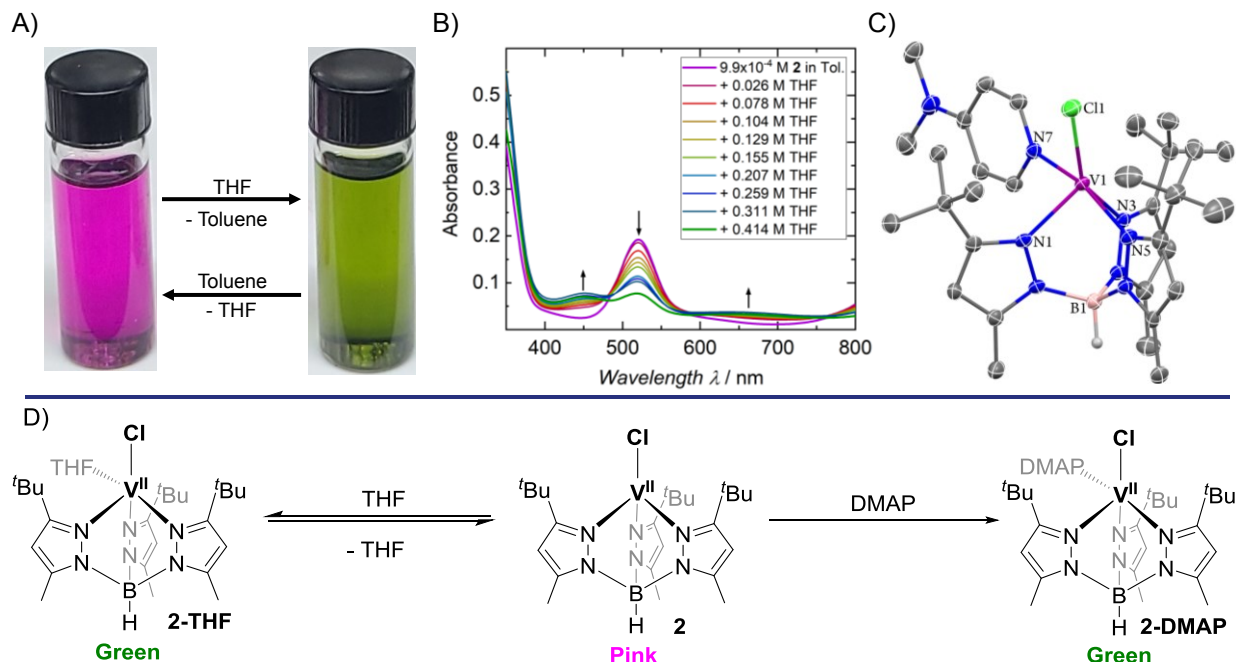


**Figure 4.** **A)** VT-VF SQUID magnetization data of **1** with applied magnetic fields of 1, 3, and 5 T. **B)** HFEPR spectrum of **1** at 4.5 K and 321 GHz (black trace). The colored traces are simulations using spin Hamiltonian parameters of species **1<sup>B</sup>** (top) and species **1<sup>A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

significant skewing of the pyrazolyl arms to the same extent, if not greater, as in  $[(\text{Tp}^{\text{tBu,tBu}})\text{VCl}_2]$ . The torsion angle,  $\angle \text{V-N}_{1,\text{pz1}}-\text{N}_{2,\text{pz1}}-\text{B}$ , for the most twisted pyrazolyl arm (pz1), defined as  $\xi_{\text{twist}}$ , provides a measure of the extent of skewing (a perfectly 3-fold symmetric Tp ligand would have  $\xi_{\text{twist}} = 0^\circ$ ; *c.f.* Table S20 for the full list of  $\xi_{\text{twist}}$  angles of all pyrazolyl arms of all compounds discussed herein). In the case of  $\text{X}^{\text{tBu,tBu}}$ , the  $\xi_{\text{twist}}$  value is  $52.0(1)^\circ$ . In complex  $\text{Y}^{\text{tBu,tBu}}$  (Figure 3B), the average V–N and V=N bond distances are  $1.986(3) \text{ \AA}$  and  $1.735(3) \text{ \AA}$ , respectively, which are reminiscent of Cloke’s  $[(\text{L})\text{V}(\mu_2\text{-N})_2\text{V}(\text{L})]$  complex ( $\text{L}^{2-} = (\text{Me}_3\text{Si})\text{N}\{\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)_2\}$ ) where the average V–N and V=N bond distances are  $1.886 \text{ \AA}$  and  $1.740 \text{ \AA}$ , respectively.<sup>9b</sup> Based on the aforementioned results, we examined the less sterically encumbered, methyl-derivatized ligand,  $\text{Tp}^{\text{tBu,Me}}$ , reported originally by Trofimenko<sup>16</sup> and popularized by Theopold,<sup>17</sup> Parkin,<sup>18</sup> Takats,<sup>19</sup> Anwander,<sup>20</sup> among others.<sup>21</sup> Accordingly, transmetalation of  $[\text{VCl}_3(\text{THF})_3]$  with  $[\text{TiTp}^{\text{tBu,Me}}]^{22}$  in toluene at  $65^\circ \text{C}$  afforded  $[(\text{Tp}^{\text{tBu,Me}})\text{VCl}_2]$  (**1**) in 75% yield as brick-orange plates after workup (Scheme 1). Single crystals of **1** could be obtained by  $\text{Et}_2\text{O}$ /toluene vapor diffusion at  $-35^\circ \text{C}$ . A sc-XRD study confirmed a five-coordinate  $\text{V}^{\text{III}}$  complex supported by a  $\kappa^3\text{-Tp}^{\text{tBu,Me}}$  chelate. With a  $\tau_5$  value<sup>23</sup> of 0.53 (Figure 2, top right), compound **1** falls midway between the limiting square pyramidal (SP) and trigonal bipyramidal (TBP) geometries,<sup>23</sup> whereas the chloride ligands are essentially orthogonal to each other ( $\text{Cl-V-Cl}_{\text{avg}}$ ,  $95.8(8)^\circ$ ). Complex **1** crystallizes with two crystallographically independent, but chemically equivalent, molecules in the asymmetric unit (space group  $Cc$ ), having  $\text{B-V-Cl}_{\text{anti}}$  angles of  $149.5(1)$  and  $150.2(3)^\circ$ . The V–Cl<sub>avg</sub> bond distance of  $2.249 \text{ \AA}$  in  $[(\text{Tp}^{\text{tBu,tBu}})\text{VCl}_2]$  is similar to the V–Cl<sub>avg</sub> bond distance of  $2.264 \text{ \AA}$  in **1**. Figure 2 shows a side-by-side comparison of  $[(\text{Tp}^{\text{tBu,tBu}})\text{VCl}_2]$  and **1**, which clearly reveals less twisting of the pyrazolyl arms in the methyl-substituted complex:  $\xi_{\text{twist}} = 62.0(5)^\circ$  in  $[(\text{Tp}^{\text{tBu,tBu}})\text{VCl}_2]$  and  $31.0(2)^\circ$  in **1**. This structural difference is even more pronounced for the four-coordinate  $\text{V}^{\text{II}}$  species (*vide infra*).

The UV-Vis spectrum of **1** shows two absorption bands with maxima at 521 and 720 nm (d-d transitions:  $\epsilon = 229, 79 \text{ M}^{-1} \text{ cm}^{-1}$ ) with the first band showing a shoulder at 589 nm ( $\epsilon = 153 \text{ M}^{-1} \text{ cm}^{-1}$ ), *cf.* SI, Section 12.1, for more detailed discussion. The solution magnetic moment of complex **1** ( $\mu_{\text{eff}} = 2.71 \text{ \mu_B}$ ; Evans’ method, 300 K,  $\text{C}_6\text{D}_6$ ) corresponds to the spin-only value for  $S = 1$  with  $g = 1.92$ , appropriate for a  $d^2$  ion. Solid-state SQUID magnetization measurements of **1** (two independently prepared samples) were conducted in the temperature range 2–150 K with applied magnetic fields of 5, 3, and 1 T (Figure 4A; only first sample shown for clarity; *cf.* SI, Section 7.1). In agreement with solution data, both samples give  $\mu_{\text{eff}} = 2.72 \text{ \mu_B}$  at 300 K, while below 10 K, the magnetic moment begins to decrease, ultimately reaching  $\mu_{\text{eff}} = 1.95 \text{ \mu_B}$  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:  $D = 5.9 \text{ cm}^{-1}$ ,  $E/D = 0.33$ , and  $g_{\text{avg}} = 1.93$ , (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)<sup>24</sup> reveals two distinct species in the solid state, labeled **1<sup>A</sup>** and **1<sup>B</sup>**, with slightly different spin Hamiltonian parameters. This observation correlates with two crystallographically independent molecules of **1** in the crystal structure analysis. Species **1<sup>A</sup>** is characterized by a larger  $D$ -value of  $5.2 \text{ cm}^{-1}$  and maximum rhombicity of the zfs tensor ( $E = 1.73 \text{ cm}^{-1}$ ) while species **1<sup>B</sup>** has a smaller  $|D|$  value of  $4.3 \text{ cm}^{-1}$  and moderate rhombicity of the zfs tensor ( $|E| = 0.81 \text{ cm}^{-1}$ ). Simulations of single-frequency spectra, such as those shown in



**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 formation of **2-DMAP** (right).

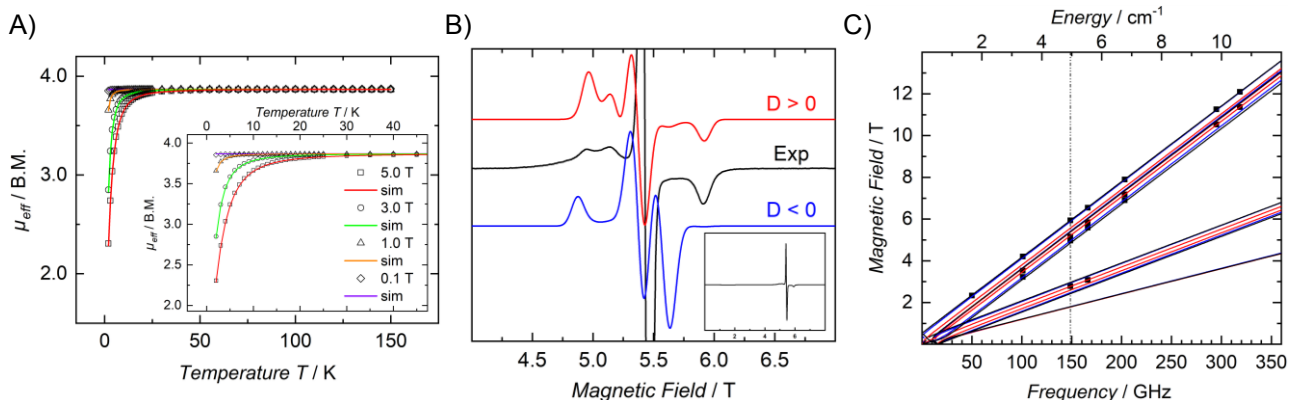
Figure 4C, proved that the sign of  $D$  for species **1<sup>B</sup>** is negative while that of species **1<sup>A</sup>** is spectroscopically undefined because of the maximum rhombicity condition ( $|E/D| \approx 1/3$ ). However, since the magnitudes of the spectroscopic  $D$  values for **1<sup>A</sup>** and **1<sup>B</sup>** are similar to each other as well as to the  $D$  value determined for the bulk sample of **1** from SQUID magnetization, species **1<sup>A</sup>** and **1<sup>B</sup>** 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<sup>III</sup> complexes ( $D \approx 7 \text{ cm}^{-1}$  for homoleptic complexes with 0 donors, but larger for heteroleptic ones).<sup>25</sup> Four-coordinate, approximately tetrahedral  $d^2$  complexes (*e.g.*, V<sup>III</sup>, Cr<sup>IV</sup>) have very small (ideally zero) zfs.<sup>26</sup> We are not aware of zfs being determined for a five-coordinate V<sup>III</sup> complex, so at present the significance of the magnitude of zfs in **1** cannot be put into much context.<sup>§</sup> A possible structural origin for the difference in zfs parameters between **1<sup>A</sup>** and **1<sup>B</sup>** may be the slightly different metrics for the two molecules seen by sc-XRD (*cf.* SI, Section 12.1). This high sensitivity of HFEPR spectroscopy to structural changes is underlined by the failure of IR ( $\nu_{\text{BH}} = 2563 \text{ cm}^{-1}$ , solid state) spectroscopy to distinguish crystallographic conformers of **1**. In fluid solution (300 K, C<sub>6</sub>D<sub>6</sub>), <sup>1</sup>H NMR of complex **1** gives a single BH resonance and a single <sup>1</sup>H NMR chemical environment for the

pyrazolyl groups, suggesting rapid fluctuation of the molecule in solution (*cf.* SI, Section 4.3, 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 [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] in THF), revealed both anodic and cathodic processes, thus suggesting chemical accessibility of oxidized and reduced derivatives of **1** (*cf.* SI, Section 10.1, Figure S106). Thus, chemical reduction of **1** with KC<sub>8</sub> in THF generates a green solution, presumably containing five-coordinate [(Tp<sup>tBu,Me</sup>)VCl(THF)] (**2-THF**). Upon removal of THF *in vacuo*, putative **2-THF** converts to four-coordinate [(Tp<sup>tBu,Me</sup>)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 ( $\tau_4 = 0.72$ )<sup>27</sup> around the V<sup>III</sup> center with a tridentate grip of the Tp<sup>tBu,Me</sup> 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  $168.4(5)^\circ$  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 (<sup>4</sup>T<sub>1</sub> ground state;  $e^2t_2^1$ ). The B–V–Cl angle is closer to linearity in **2** than in Petrov's [(Tp<sup>tBu,tBu</sup>)VCl] complex

<sup>§</sup> A homoleptic five-coordinate V<sup>III</sup> complex, [NBu<sub>4</sub>]<sub>2</sub>[V<sup>III</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>5</sub>], has been reported, which has a slightly distorted TBP geometry.<sup>26b</sup> The complex is EPR-silent at X- and Q-bands (in contrast to nearly tetrahedral V<sup>III</sup> in [Li(thf)<sub>4</sub>][V(C<sub>6</sub>Cl<sub>5</sub>)<sub>4</sub>], which has  $|D| = 0.513 \text{ cm}^{-1}$ ), so it is likely that its zfs is on the order of several  $\text{cm}^{-1}$ .





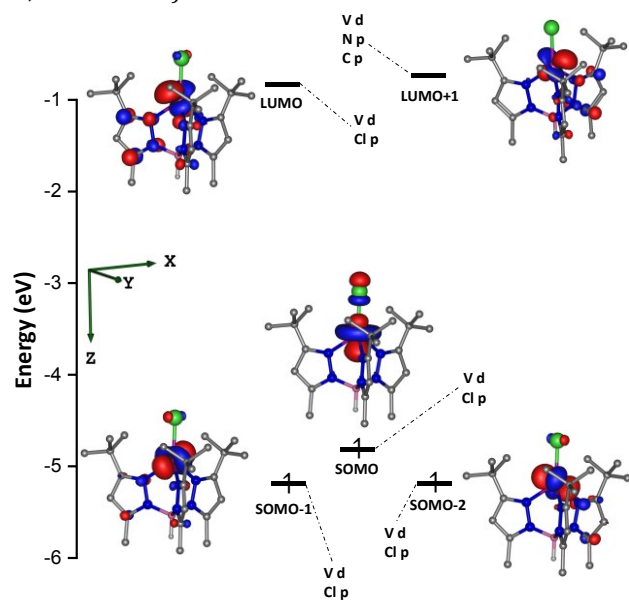
**Figure 6.** **A)** VT-VF SQUID magnetization data of **2** at 5.0, 3.0, 1.0, and 0.1 T; experimental data shown as squares, circles, triangles, and diamonds, simulations shown as red, blue, green, and purple traces, respectively. Simulation:  $S = 1.5$ ,  $D = 0.01 \text{ cm}^{-1}$ ,  $E/D = 0.33$ ,  $g_{\text{avg}} = 2.00$ . **B)** 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):  $S = 3/2$ ,  $|D| = 0.24 \text{ cm}^{-1}$ ,  $|E| = 0.026 \text{ cm}^{-1}$ ,  $g = [1.97, 2.00, 1.97]$ . The experimental spectrum is dominated by a high-amplitude signal at  $g = 1.96$  from an  $S = 1/2$  impurity ( $\text{V}^{\text{IV}}$ , not simulated). *Inset:* the full experimental spectrum in the same conditions, indicating the absence of any  $\text{V}^{\text{III}}$  species. **C)** 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:  $S = 3/2$ ,  $|D| = 0.25(1) \text{ cm}^{-1}$ ,  $|E| = 0.058(5) \text{ cm}^{-1}$ ,  $g = [2.000(3), 1.96(1), 1.967(5)]$ . Red curves: turning points with magnetic field parallel to the x-axis of the zfs tensor; blue:  $B_0 \parallel y$ ; black:  $B_0 \parallel z$ . The vertical dashed line represents the frequency (149 GHz) at which the spectrum in Figure 6B was recorded.

(157.7(9)°), most likely due to the lesser steric encumbrance of the Tp ligand. In  $[(\text{Tp}^{\text{tBu,tBu}})\text{VCl}]$  and **2**,  $\xi_{\text{twist}}$  equals 46.6(1)° and 7.1(7)°, respectively, revealing a distorted  $\text{Tp}^{\text{tBu,tBu}}$  ligand in  $[(\text{Tp}^{\text{tBu,tBu}})\text{VCl}]$  as opposed to a near-ideal three-fold symmetric  $\text{Tp}^{\text{tBu,Me}}$  ligand in **2**. It is also notable that  $[(\text{Tp}^{\text{tBu,R}})\text{VCl}]$  ( $R = \text{tBu}$  or  $\text{Me}$ ) has roughly Td geometry when for a  $d^3$  system, ideal SP would be of lower energy than ideal Td (*cf.* SI, section 12.2). Indeed, a four-coordinate  $\text{V}^{\text{II}}$  complex with homoleptic monodentate ligands,  $[\text{V}(\text{OAr})_4\{\text{Li}(\text{THF})_2\}_2]$  ( $\text{Ar} = 2,6\text{-di-isopropylphenyl}$ ), has SP geometry.<sup>28</sup> Due to the larger ionic radius of  $\text{V}^{\text{II}}$  versus  $\text{V}^{\text{III}}$ , the average V–Cl bond distance in **2** exceeds that in **1** ( $V\text{--}Cl_{\text{avg}}$ : 2.356(1) Å in **2** and 2.264(3) in **1**). Solutions of **2** in Et<sub>2</sub>O retain the pink color of the solid, indicative of a 4-coordinate structure in solution. The Vis-NIR spectrum of **2** can be assigned and semi-quantitatively analyzed by ligand-field theory (LFT) as described in the SI (see Section 12.2). 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<sub>2</sub>O) to green (THF). When changing solvents from Et<sub>2</sub>O to THF, the electronic absorption for **2** at 520 nm ( $\epsilon = 160 \text{ M}^{-1} \text{ cm}^{-1}$ ) undergoes a blueshift to 457 nm ( $\epsilon = 65 \text{ M}^{-1} \text{ cm}^{-1}$ ). In addition, the intense absorptions extending into the NIR region [893 (infl.), 924 (max.), 960 nm (infl.), with  $\epsilon = 130, 150$ , and  $130 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively], are replaced by weaker and broader features at 668 and 855 nm ( $\epsilon = 32, 19 \text{ M}^{-1} \text{ cm}^{-1}$ ). Along these lines, titration of a toluene solution of **2** with THF (0–0.414 M), reveals an association constant ( $K$ ) between **2** and THF on the order of 1.2–3.6 M<sup>−1</sup> (Figure 5B, *cf.* SI, Section 8.4.1). 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  $[(\text{Tp}^{\text{tBu,Me}})\text{TiCl}]$  ( $K_{\text{ass}} = 5\text{--}8 \text{ M}^{-1}$ ), highlighting the stronger Lewis acidity of a  $\text{Ti}^{\text{III}}$  vs.  $\text{V}^{\text{II}}$  ion.<sup>29</sup> Likewise, CV data for **2** dissolved in 1,2-difluorobenzene or THF (*cf.* SI, Section 10.2, 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, 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  $2.2 \text{ M}^{-1}$ , 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 4-dimethylaminopyridine (DMAP). Accordingly, treatment of **2** with DMAP quantitatively produces green crystals of  $[(\text{Tp}^{\text{tBu,Me}})\text{VCl}(\text{DMAP})]$  (**2-DMAP**; Scheme 1 and Figure 5C). The solution magnetic moment of adduct **2-DMAP** ( $\mu_{\text{eff}} = 3.67 \mu_{\text{B}}$ ; Evans' method, 300 K, C<sub>6</sub>D<sub>6</sub>) 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.* SI, Sections 8.4 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 higher energy (394 nm) in **2-DMAP**.

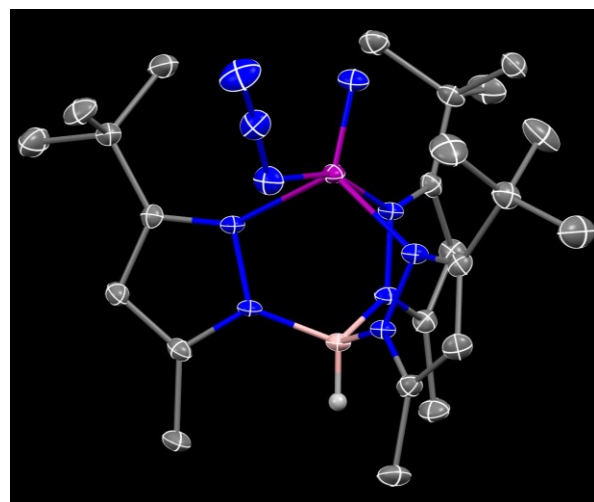
Given the paramagnetic nature of **2**, magnetization studies were conducted. In solution, the magnetic moment of **2** indicates a mononuclear  $\text{V}^{\text{II}}$  ion with  $S = 3/2$  ( $\mu_{\text{eff}} = 3.78 \mu_{\text{B}}$ ; spin-only value with  $g = 1.95$ ; Evans' method, 300 K, C<sub>6</sub>D<sub>6</sub>). Likewise, SQUID magnetometry for two independently prepared samples (2–300 K, 2–150 K shown in Figure 6A) showed the magnetic moment to be relatively constant between 10–300 K (3.87 and  $3.84 \mu_{\text{B}}$  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  $\mu_{\text{eff}} = 3.65\text{--}3.61 \mu_{\text{B}}$  at 2 K due to zfs (*cf.* SI, Section 7.2, Figures S66 and S67). At higher fields, the decrease becomes steeper, *e.g.*, leading to a magnetic moment of  $2.31 \mu_{\text{B}}$  at 2 K and 5.0 T (Figure 6A). Simulation of the magnetization

data for **2** with an  $S = 3/2$  spin Hamiltonian yields  $D = +0.01 \text{ cm}^{-1}$ . Petrov's  $[(\text{Tp}^{\text{tBu},\text{tBu}})\text{VCl}]$  complex has a magnetic moment of  $3.78 \mu_{\text{B}}$  at 300 K and  $3.52 \mu_{\text{B}}$  at 2 K, thereby displaying essentially the same magnetic behavior as **2**.<sup>14</sup> 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  $g_{\text{avg}} = 1.97$  (cf. SI, Section 5.1, Figure S43). Based on simulation of the X-band data,  $D$  and  $E$  are  $0.33$  and  $0.03 \text{ cm}^{-1}$ , respectively. On the other hand, Q-band spectra yield slightly different  $D$  and  $E$  ( $0.28$  and  $0.075 \text{ cm}^{-1}$ , respectively). The variation between X- and Q-band data reflects the challenging nature of deconvoluting numerous anisotropic linewidths simultaneous 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 (Figures 6B and 6C; more details in the SI, Section 6.2). Here, the inter-Kramers transitions converge to a small energy of  $\sim 0.56 \text{ cm}^{-1}$ , which equals  $2D^*$  for  $S = 3/2$  ( $D^* = (D^2 + 3E^2)^{1/2}$ ). The complete set of frequency-independent spin Hamiltonian parameters are:  $D = +0.25(1) \text{ cm}^{-1}$ ,  $E = 0.058(5) \text{ cm}^{-1}$ , 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 magnitude consistent with the values from frozen solution X- and Q- band EPR studies. This zfs is consistent with a simple LFT analysis (cf. SI, Section 12.2).

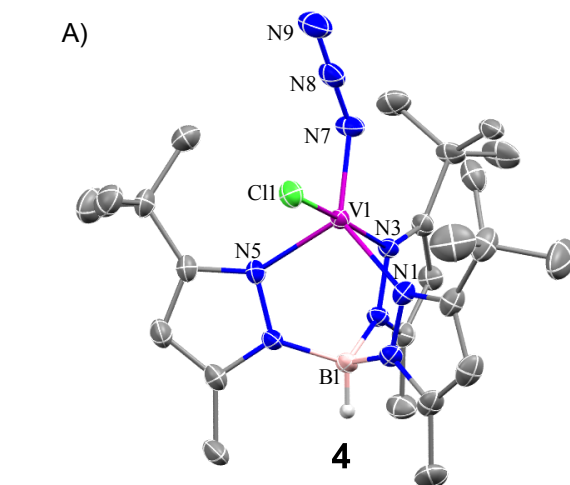


**Figure 7.** Calculated MO diagram for **2**. Orbital energies are in eV (B3LYP/TZVP).

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 and being a stronger  $\sigma$ - and  $\pi$ -donor ligand than the weak-field  $[\text{Tp}^{\text{tBu},\text{Me}}]$  ligand. This might hint that the  $[\text{Tp}^{\text{tBu},\text{Me}}]$  ligand is bound relatively weakly to the vanadium center, and indeed, the tendency for the  $[\text{Tp}^{\text{tBu},\text{Me}}]$  ligand to dissociate has remarkable impact on the reactivity of its derivatives (*vide infra*). In the case of **2-DMAP** (cf. SI, Section 11, Figure



**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**.



**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**.

S117), coordination of a Lewis base breaks the three-fold symmetry and consequently, the degeneracy of the SOMO-2 and SOMO-1 orbitals computationally observed in **2** is broken.

### High-Valent Vanadium Nitrides and Intermediates Stemming from Complex **1**.

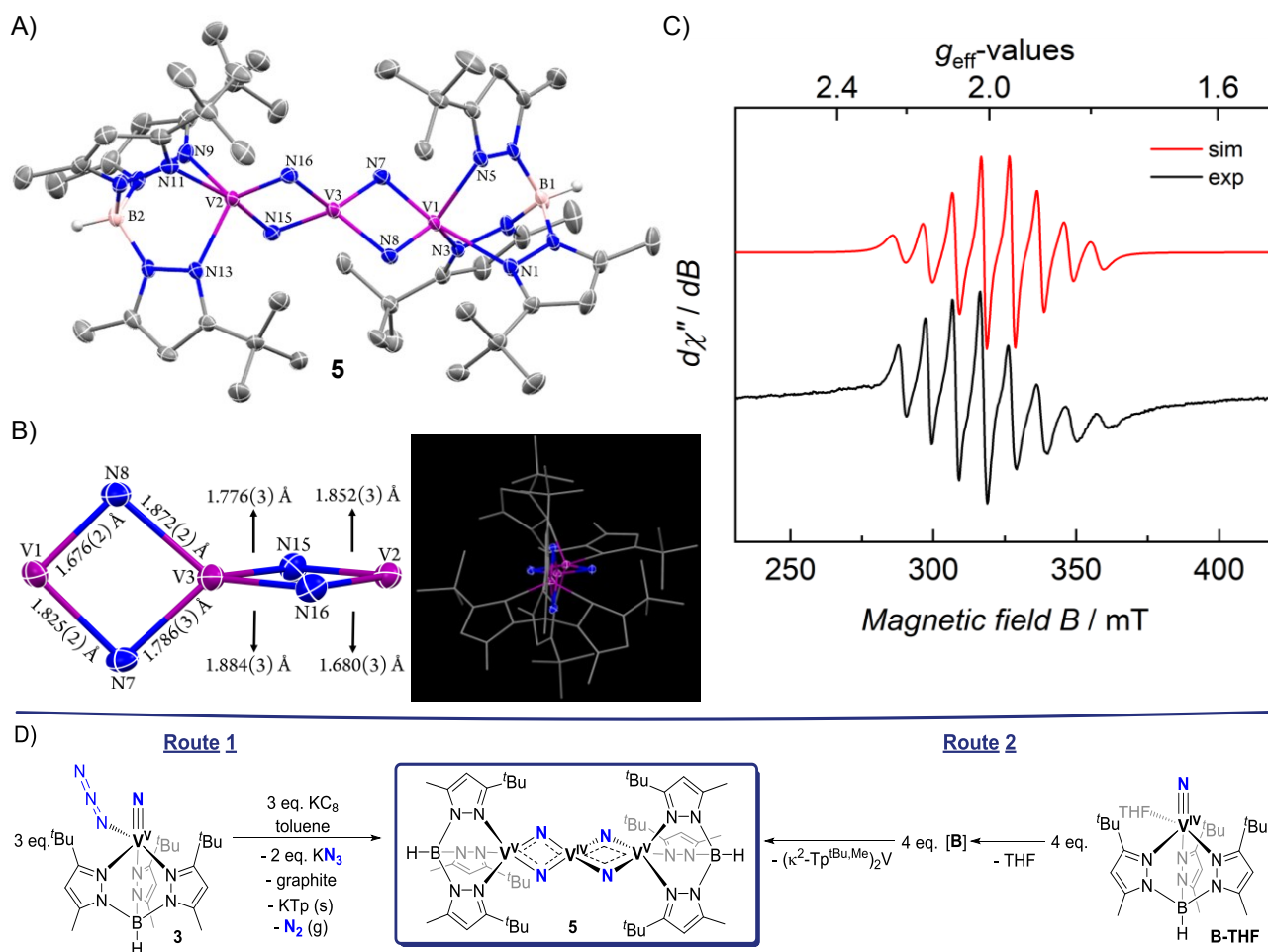
At room temperature, complex **1** slowly reacts (overnight) with two equiv. of  $\text{NaN}_3$  in THF to afford the azide-nitride complex  $[(\text{Tp}^{\text{tBu,Me}})\text{V}=\text{N}(\text{N}_3)]$  (**3**) in 61% yield. After filtration of insoluble sodium salts, the reaction mixture must then be 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  $^1\text{H}$  NMR shows a new paramagnetic species that forms but then decays to **3**. We propose this intermediate to be either the mono-azide complex  $[(\text{Tp}^{\text{tBu,Me}})\text{V}(\text{Cl})(\text{N}_3)]$  (**4**, *vide infra*) or the bis-azide complex  $[(\text{Tp}^{\text{tBu,Me}})\text{V}(\text{N}_3)_2]$  (**A**). sc-XRD of **3** confirmed the terminal nature of the nitride moiety ( $\text{V}=\text{N}_7$ : 1.558(2) Å and 1.565(5) Å), non-linear coordination of the azide ligand ( $\text{V}-\text{N}_8-\text{N}_9$ : 126.1(1)° and 137.5(6)°), and a geometry confined between SP and TBP ( $\tau_5$ : 0.59 and

**Table 1.** Salient metric parameters, NMR, and IR spectroscopic features of the vanadium nitrides **3**, **5**, **B-THF**, and **B-OPPh<sub>3</sub>**.

Complex	<b>3</b>	<b>5</b>	<b>B-THF</b>	<b>B-OPPh<sub>3</sub></b>
$\text{VN}_{\text{nitride}}$ (Å)	1.558(2)	1.676(2) <sup>a</sup> 1.825(2) 1.872(2) 1.786(3)	1.578(2)	1.587(2)
$\tau_5$	0.59	0.76 <sup>b</sup>	0.52	0.48
$^{15}\text{N}$ NMR ( $\delta$ )	1035.8	n/a	n/a	n/a
$^{51}\text{V}$ NMR ( $\delta$ )	-246.3	n/a	n/a	n/a
$^{11}\text{B}$ NMR ( $\delta$ )	-35.9	-8.9	-19.3	-22.7
$\nu_{\text{BH}}$ ( $\text{cm}^{-1}$ )	2555	2550	2546	2558

<sup>a</sup>Only one half of the molecule is included for  $\text{VN}_{\text{nitride}}$  distances; cf. Figure 10B.

<sup>b</sup> $\tau_4$  for the central  $\text{VN}_4$  fragment is measured as 0.79.



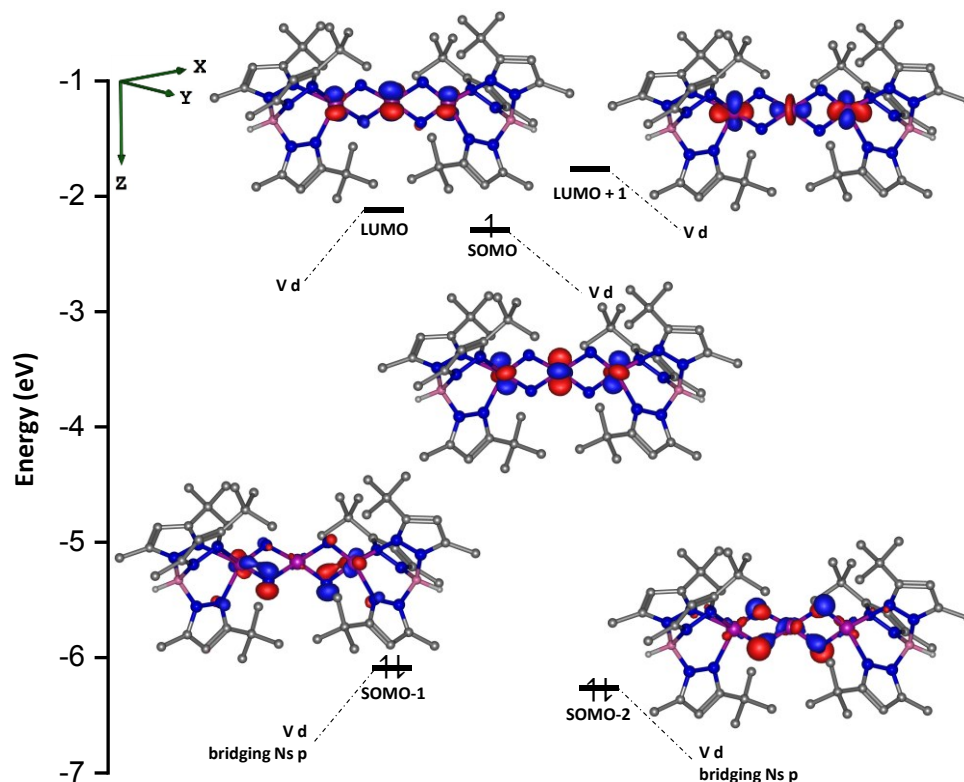
**Figure 10.** **A)** Structural representation of complex **5** (thermal ellipsoids at 50% probability). Hydrogen atoms (except B-H's) and co-crystallized solvent are omitted for clarity. **B)** The  $\{\text{V}(\mu_4\text{-V}^{\text{I}}\text{N}_4)\text{V}\}$  core of **5** viewed from the side and along the  $\text{V}_3$  axis. **C)** CW X-band EPR spectrum of **5** in toluene at 293 K. Experiment (black trace). Simulation (red trace):  $g_{\text{iso}} = 1.98$ ,  $W_{\text{FWHM,iso}} = 2.03 \times 10^{-4} \text{ cm}^{-1} / \text{GHz}$ ,  $a_{\text{iso}} = 91.4 \times 10^{-4} \text{ cm}^{-1}$  ( $I = 7/2$  ( $^{51}\text{V}$ ), 99.75% nat. abundance). **D)** Two independent syntheses of **5**.



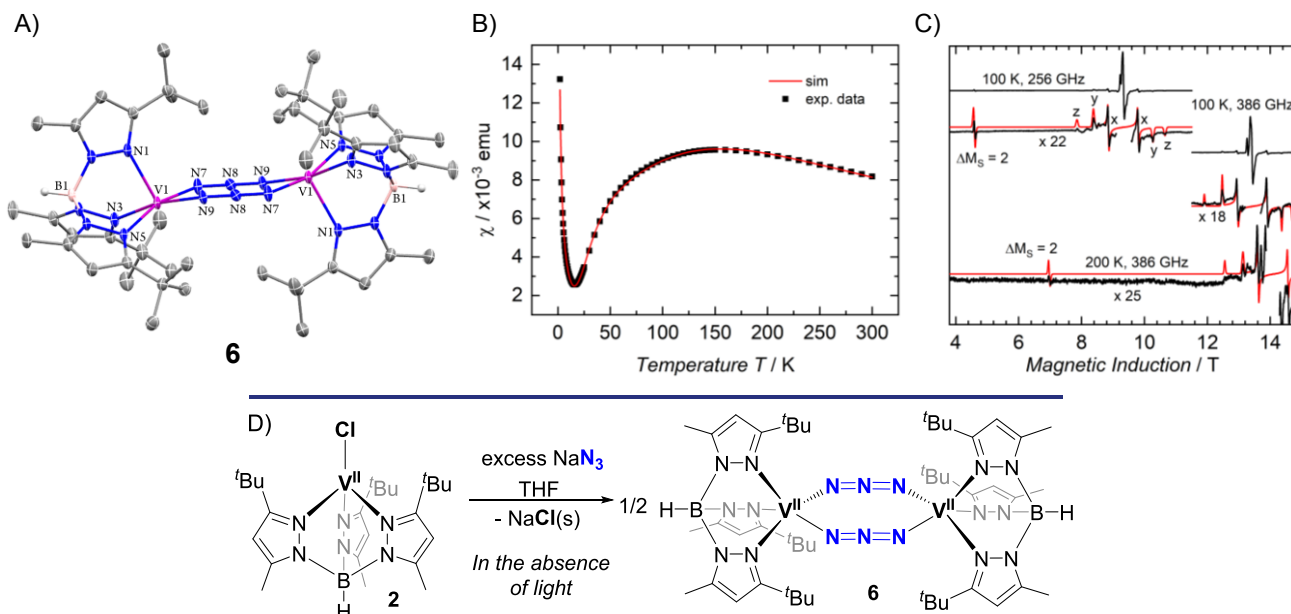
0.54) for the two polymorphs (Figure 8A and Table 1). Preparing the four  $^{15}\text{N}$ -enriched isotopomers,  $[(\text{Tp}^{\text{tBu,Me}})\text{V}\equiv\text{N}(^{15}\text{N}=\text{N}=\text{N})]$ ,  $[(\text{Tp}^{\text{tBu,Me}})\text{V}\equiv\text{N}(\text{N}=\text{N}=^{15}\text{N})]$ ,  $[(\text{Tp}^{\text{tBu,Me}})\text{V}\equiv^{15}\text{N}(^{15}\text{N}=\text{N}=\text{N})]$ , and  $[(\text{Tp}^{\text{tBu,Me}})\text{V}\equiv^{15}\text{N}(\text{N}=\text{N}=^{15}\text{N})]$ , (collectively denoted  $\mathbf{3}\text{-}^{15}\text{N}$ ) from complex  $\mathbf{1}$  and  $\text{Na}(^{15}\text{N}=\text{N}=\text{N})$ , revealed a characteristic, highly deshielded  $^{15}\text{N}$  NMR nitride resonance at 1035.8 ppm along with the expected two azide resonances at 212.2 and 243.9 ppm, corresponding to  $^{15}\text{N}$ -enriched  $\alpha$ - and  $\gamma$ -azide positions. IR spectral data of  $\mathbf{3}$  (in KBr plates) show the prototypical signature of the azide group at 2079 and 2063  $\text{cm}^{-1}$  (in-phase/out-of-phase asymmetric stretching vibrations),<sup>30</sup> which redshift to 2039 and 2054  $\text{cm}^{-1}$  for isotopomer  $\mathbf{3}\text{-}^{15}\text{N}$  (cf. SI, Section 9.6, Figure S99). The  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of  $\mathbf{3}$  shows one broad BH resonance at 4.16 ppm along with three resonances from the  $\text{CH}_3$ , CH and  $^t\text{Bu}$  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  $\text{V}^{\text{V}}$  complex, the UV-Vis spectrum of  $\mathbf{3}$  in pentane reveals no d-d transitions but only charge transfer / ligand-centered bands at 388 (infl.), 310 (infl.) and 236 nm (max.) ( $\epsilon = 1660, 3060, 4940 \text{ M}^{-1} \text{ cm}^{-1}$ ).

As mentioned previously, thermolysis is necessary to fully convert  $\mathbf{1}$  and  $\text{NaN}_3$  into  $\mathbf{3}$ . To our surprise, treatment of  $\mathbf{1}$  with 1.05 equiv.  $\text{Me}_3\text{SiN}_3$  produces the mono-azide complex  $[(\text{Tp}^{\text{tBu,Me}})\text{V}(\text{N}_3)\text{Cl}]$  ( $\mathbf{4}$ ) in 67% yield (Scheme 1 and Figure 9B), which was confirmed by a combination of structural (Figure 9A), spectroscopic ( $\nu_{\text{N}_3} = 1991$  and 2074  $\text{cm}^{-1}$ , cf. SI, Section 9.7, Figure S100) and magnetic studies ( $\mu_{\text{eff}} = 2.68 \mu_{\text{B}}$ ; Evans' method, 300 K,  $\text{C}_6\text{D}_6$ ;  $\mu_{\text{eff}} = 2.77 \mu_{\text{B}}$ ; 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  $\text{V}_1\text{-N}_7$  (1.896(3) Å) bonds in  $\mathbf{4}$  are essentially orthogonal ( $\text{Cl}_1\text{-V}_1\text{-N}_7 = 94.0(4)^\circ$ ), and the  $\tau_5$  value of 0.69 suggests a geometry midway between SP and TBP. Although complex  $\mathbf{4}$  shows all the features of a high-spin  $d^2$  ion, it is surprisingly stable to thermolysis (decomposition above 50 °C, cf. SI, Section 8.7, Figure S87) as well as photolysis. However, treatment of  $\mathbf{1}$  with excess  $\text{Me}_3\text{SiN}_3$  (or treatment of  $\mathbf{4}$  with  $\text{NaN}_3$ ) followed by heating to 45 °C overnight, leads to nitride-azide complex  $\mathbf{3}$ . This points to  $\mathbf{A}$  being a common intermediate in the conversion of  $\mathbf{1}$  and  $\mathbf{4}$  to nitride complex  $\mathbf{3}$  (Scheme 1). It further suggests that the reaction of  $\mathbf{1}$  with  $\text{NaN}_3$  traverses two transmetalation steps, before  $\text{N}_2$  extrusion ensues. We have no definitive reason why complex  $\mathbf{4}$ , as opposed to  $\mathbf{A}$ , would be reluctant to undergo  $\text{N}_2$  elimination, but, based on previous studies, we speculate that an azide ligand bridging across two V centers might play a critical role.<sup>8k,31</sup>



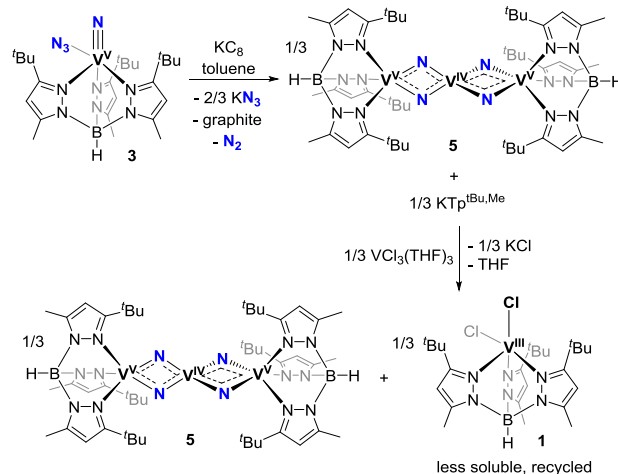
**Figure 11.** Calculated MO diagram of  $\mathbf{5}$ . Orbital energies in eV (RO-B3LYP/TZVP).



**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):  $g_{\text{ave}} = 1.932$ ,  $J = -29.8 \text{ cm}^{-1}$ ,  $j = -1.80 \text{ cm}^{-1}$ ,  $\text{TIP} = 360 \times 10^{-6} \text{ cgs emu}$  (for each V), paramagnetic impurity (*i.e.*, monomeric  $\text{V}^{\text{II}}$ ) = 0.72 %. **C)** Black: HFEPR spectra of **6** recorded at conditions indicated. Red: simulations of the (total spin)  $S = 1$  state spectra using  $g_x = 1.954$ ,  $g_y = 1.957$ ,  $g_z = 1.976$ ,  $D_{S=1} = -1.293 \text{ cm}^{-1}$ ,  $E_{S=1} = -0.145 \text{ cm}^{-1}$ . 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, z indicate the molecular orientations at which the respective transitions occur. **D)** Synthesis of **6**.

**Vanadium<sup>IV</sup> Nitrides from  $\text{V}^{\text{V}}$  and  $\text{V}^{\text{II}}$  Precursors.** As opposed to the ubiquitous vanadyl ion ( $[\text{VO}]^{2+}$ ), terminal  $\text{V}^{\text{IV}}$  nitrides are exceedingly rare with the only crystallographically characterized example being dinuclear  $[\text{Na}]_2[(\text{nacnac})(\text{ArO})\text{V}\equiv\text{N}]_2$  ( $\text{nacnac}^- = [\text{ArNC}(\text{CH}_3)]_2\text{CH}^-$ ,  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ), in which the vanadium centers are bridged by alkoxide and  $\text{Na}^+$ –arene interactions.<sup>8m</sup> In the above  $\text{V}^{\text{IV}}$  example, other ligands than nitride are bridging, but there is however a tendency for nitride ligands themselves to bridge and form  $[\text{LM}(\mu_2\text{-N})_2\text{ML}]$  core structures, where M is a high-valent metal. Representative d block examples involve V, Nb, Ta, Cr, and W.<sup>11, 9b, 32</sup> We therefore inquired if compound **3** could be reduced by one electron to yield a putative four-coordinate, neutral  $\text{V}^{\text{IV}}$  nitride,  $[(\text{Tp}^{\text{tBu,Me}})\text{V}\equiv\text{N}]$  (**B**). In our case, treatment of **3** with  $\text{KC}_8$  furnishes an unprecedented trinuclear complex with four bridging nitride ligands,  $[\{(\text{Tp}^{\text{tBu,Me}})\text{V}\}_2(\mu_4\text{-VN}_4)]$  (**5**) in 54% isolated yield, where the central  $[\text{VN}_4]^{8-}$  unit could be considered analogous to the ubiquitous vanadate ion,  $[\text{VO}_4]^{3-}$  (Scheme 1 and Figure 10D, route 1). The connectivity of **5** was established by sc-XRD studies (Figure 10A and 10B), which reveal three vanadium centers arranged in a linear, double diamond core fashion ( $\text{V1}–\text{V3}–\text{V2} = 177.45(3)^\circ$ ). 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  $\text{V}_3\text{N}_4$  core (two diamond cores oriented orthogonally) has a similar tetrahedral geometry around the central vanadium, which has previously been computationally predicted for the metastable  $\text{V}^{\text{IV}}$  nitride.<sup>33</sup> Within each  $\{\text{V}(\mu\text{-N})_2\text{V}\}$  fragment of **5**, the V–N bond distances are alternatingly short (1.676(3)–1.786(3) Å) and

long (1.825(2)–1.884(3) Å, Figure 10B), which parallels Cloke’s dinuclear  $[\{(\text{N}(\text{N}''')\text{V})_2(\mu\text{-N})_2\}]$  complex<sup>9b</sup> ( $(\text{N}(\text{N}''')_2)^{2-}$ :  $[(\text{Me}_3\text{Si})\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)_2)_2]^{2-}$ ), where the average V–N and V=N bond distances are 1.87 and 1.74 Å, respectively. The  $\text{V}_{\text{distal}}–\text{V}_{\text{central}}$  distances in **5** are 2.605(1) and 2.594(1) Å, which results in a separation of the two  $\text{V}_{\text{distal}}$  of 5.198(1) Å. Notably, and given its composition, the formation of **5** requires expulsion of a  $\text{Tp}^{\text{tBu,Me}}$  ligand. When preparing **5** from **3** and  $\text{KC}_8$ , a lustrous black solid appears (graphite); we also observe  $\text{KN}_3$  (by IR spectroscopy) as well as  $[\text{KTp}^{\text{tBu,Me}}]$  (by



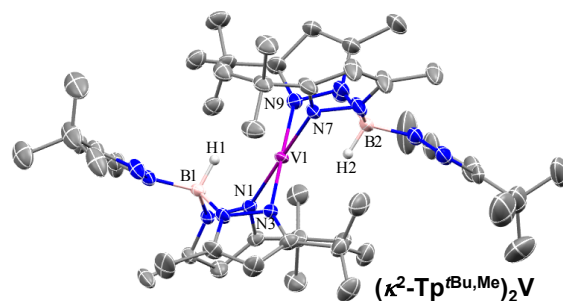
**Scheme 3.** Synthesis of complex **5** from the reduction of **3** followed by treatment with  $[\text{VCl}_3(\text{THF})_3]$  to form **1**, which can be separated more conveniently but also re-

$^1\text{H}$  NMR spectroscopy). Mass balance therefore suggests 2/3  $\text{KN}_3$  and 1/3  $[\text{KTp}^{\text{tBu,Me}}]$  (and 1/3  $\text{N}_2$ ) to form for each 1/3 equiv. of **5**. From this complex reaction mixture  $[\text{KTp}^{\text{tBu,Me}}]$  could be removed *via* fractional crystallization. Alternatively, addition of 1/3 equiv. of  $[\text{VCl}_3(\text{THF})_3]$  generates **1**, and this could be readily separated from **5** due to the low solubility of **1** in alkanes (41% yield with respect to  $[\text{KTp}^{\text{tBu,Me}}]$ , Scheme 3). In a third approach,  $[\text{KTp}^{\text{tBu,Me}}]$  can be removed by extracting **5** into cold hexamethyldisiloxane and filtering the solution through Celite. This allows  $[\text{KTp}^{\text{tBu,Me}}]$  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 “ $\text{VN}_2$ ” 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  $\{\text{V}^{\text{V}}(\mu_4\text{-V}^{\text{IV}}\text{N}_4)\text{V}^{\text{V}}\}$  core. Solution magnetic measurements ( $\mu_{\text{eff}} = 1.89 \mu_{\text{B}}$ ; Evans’ method, 300 K,  $\text{C}_6\text{D}_6$ ) 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  $^{51}\text{V}$  center ( $A = 91.4 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $I = 7/2$ , 99.75%). Overall, the confinement of the unpaired electron to a single vanadium center is in line with a Robin-Day class I system.<sup>34</sup>

The calculated MO diagram of **5** suggests contribution of  $\text{d}_{x^2-y^2}$  orbitals on all three V centers in SOMO, but the unpaired electron is largely localized around the central  $\text{V}^{\text{IV}}$  ion given that the SOMO is comprised of orthogonal vanadium  $\text{d}_{x^2-y^2}$  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 (NBO) 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  $\text{V}^{\text{IV}}$  nitride intermediate **B**, we turned to **2** and treated it with  $\text{NaN}_3$  in THF (in the dark) to form the azide-bridged dimer  $[(\text{Tp}^{\text{tBu,Me}}\text{V})_2(1,3\text{-}\mu_2\text{-N}_3)_2]$  (**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 **6** has a  $\tau_5$  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,  $[\text{Na}(15\text{-C-5})][(\text{Tp}^{\text{tBu,tBu}}\text{V}(\text{N}_3)_2)]$  (**X**<sup>*tBu,tBu*</sup>).

Solid-state SQUID magnetization measurements (2–300 K) are consistent with a  $\text{d}^3\text{-d}^3$  dimeric species with moderate antiferromagnetic coupling between the  $\text{V}^{\text{II}}$  centers (Figure 12B).  $\mu_{\text{eff}}$  of the dimeric species is  $4.42 \mu_{\text{B}}$  at 300 K, which corresponds to  $3.12 \mu_{\text{B}}$  per one V ion. At lower temperatures, the effective magnetic moment decreases steadily to reach  $0.45 \mu_{\text{B}}$  at 2 K. The effective magnetic moment determined by SQUID magnetometry at 300 K is consistent with the value extracted by Evans’ method ( $\mu_{\text{eff}} = 4.48 \mu_{\text{B}}$  per dimer, or  $3.16 \mu_{\text{B}}$  per V, 300 K,  $\text{C}_6\text{D}_6$ ) at the same temperature. Both values are lower than expected for an uncoupled spin-only ( $\text{d}^3$ )<sub>2</sub> system ( $\mu_{\text{eff}} = 3.87 \mu_{\text{B}}$  per one V) and, notably, the consistency of the magnetic moments suggests **6** to remain dimeric in solution.



**Figure 13.** Structural representation of complex  $[(\kappa^2\text{-Tp}^{\text{tBu,Me}})_2\text{V}]$  (thermal ellipsoids at 50% probability). Hydrogen atoms (except B–H) and co-crystallized toluene and pentane are omitted for clarity.

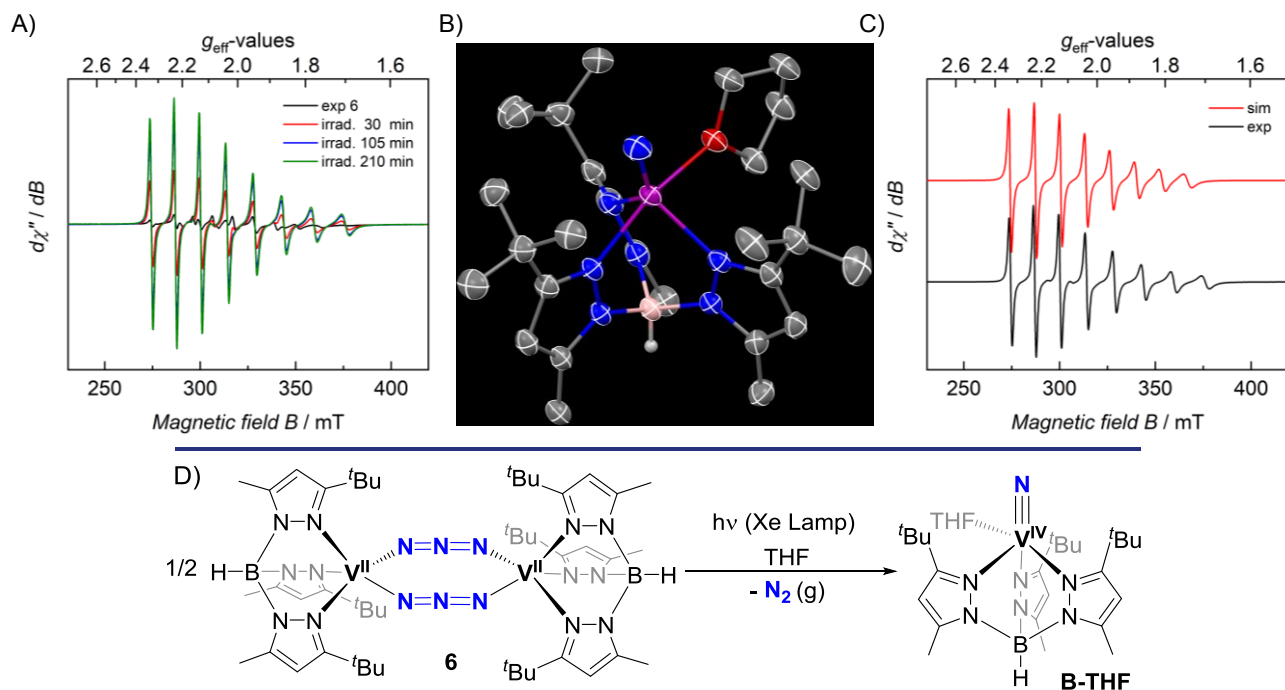
Antiferromagnetic exchange coupling of the form  $H = -2J\text{S}_1\text{S}_2$  in this system results in a diamagnetic ground state with a total spin  $S = 0$ . States with  $S = 0, 1, 2$ , and  $3$  have energies  $0, -2J, -6J$ , and  $-12J$ , respectively. All paramagnetic states are EPR-active, but only the  $S = 2$  state is observed in X-Band EPR, as states  $S = 1$  and  $S = 3$  exhibit large zero-field splitting requiring higher field/frequencies. HFEP 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  $\text{V}^{\text{II}}$  ion as  $D_{\text{V}} = +0.54 \text{ cm}^{-1}$  and  $E_{\text{V}} = +0.06 \text{ cm}^{-1}$ . The magnetic susceptibility data were then fitted using the “microscopic” spin Hamiltonian with  $D_{\text{V}}$  and  $E_{\text{V}}$  fixed as found from EPR (*cf.* SI, Section 6.3). It was found that the biquadratic exchange term,  $j(\text{S}_1\text{S}_2)^2$ ,<sup>35</sup> must be included to simulate the experimental magnetic data. That term appears very often in  $\text{Cr}^{\text{III}}$  dimers with the same  $\text{d}^3\text{-d}^3$  configuration as our  $\text{V}^{\text{II}}$  dimer.<sup>36</sup>

We propose complex **6** to extrude  $\text{N}_2$  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  $\text{Tp}^{\text{tBu,Me}}$  was traced to a new paramagnetic species,  $[\text{V}(\kappa^2\text{-Tp}^{\text{tBu,Me}})_2]$ , identified on the basis of a sc-XRD study. Due to the similar solubilities of **5** and the divalent  $\text{V}^{\text{II}}$  complex, spectroscopically pure  $[\text{V}(\kappa^2\text{-Tp}^{\text{tBu,Me}})_2]$  could not be isolated (Scheme 1 and Figure 13). The  $\text{Tp}^{\text{tBu,Me}}$  ligands in  $[\text{V}(\kappa^2\text{-Tp}^{\text{tBu,Me}})_2]$  seemingly bind in a bidentate fashion, which defines a square planar motif around vanadium ( $\text{N-V-N} = 85.5(7)^\circ$  and  $85.6(5)^\circ$ ,  $\tau_4 = 0.04$ ). However,  $[\text{V}(\kappa^2\text{-Tp}^{\text{tBu,Me}})_2]$  is more appropriately seen as an octahedral complex containing *transoid* BH donor groups ( $\text{V-H} = 1.984(1)$  and  $1.967(1) \text{ \AA}$ ). Returning to the formation of **5** from **6**, a  $\text{V}^{\text{II}}$  ion sequesters the excess equivalent of  $\text{Tp}^{\text{tBu,Me}}$ , which stands apart from the reduction of compound **3** to generate **5** and  $[\text{KTp}^{\text{tBu,Me}}]$ . We propose **6** to photolytically extrude  $\text{N}_2$  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  $[\text{V}(\kappa^2\text{-Tp}^{\text{tBu,Me}})_2]$  independently from **2** and 1 equiv.  $[\text{TiTp}^{\text{tBu,Me}}]$  or from  $[\text{VCl}_2(\text{tmeda})_2]$  and 2 equiv.  $[\text{TiTp}^{\text{tBu,Me}}]$  were unsuccessful (*cf.* SI, Section 3.13), which lends support for a mechanism

in which several units of **B** aggregate prior to releasing **5** and  $[V(\kappa^2\text{-Tp}^{t\text{Bu},\text{Me}})_2]$ .

**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  $[(\text{Tp}^{t\text{Bu},\text{Me}})_2\text{V}\equiv\text{N}(\text{THF})]$  (**B-THF**), on the basis of a 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  $\text{V}\equiv\text{N}$  bond in **B-THF** (1.580(2) Å) is slightly longer than in **3** (1.561(5) Å). On the other hand, the  $\text{V}\equiv\text{N}$  bond distance is somewhat shorter in **B-THF** than in the only other reported  $V^{IV}$  nitride complex, namely dinuclear  $[\text{Na}]_2[(\text{nacnac})(\text{ArO})\text{V}\equiv\text{N}]_2$  ( $\text{V}\equiv\text{N}$ : 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  $-35^\circ\text{C}$  in THF, 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 8-line pattern from hyperfine coupling of the unpaired electron to the  $^{51}\text{V}$  center ( $a_{\text{iso}} = 123 \times 10^{-4} \text{ cm}^{-1}$ , 369 MHz). This

$^{51}\text{V}$  isotropic hyperfine coupling is  $\sim 15\%$  greater than that observed for vanadyl with five exclusively O-donor ancillary ligands (318–328 MHz)<sup>37</sup> and is much larger than in vanadyl porphyrins (263 MHz).<sup>38</sup> Clearly, **B-THF** is a vanadium centered paramagnet. This character of complex **B-THF** was also established by solution magnetometry ( $\mu_{\text{eff}} = 1.95 \mu_{\text{B}}$ ; Evans' method, 300 K, THF-*d*<sub>8</sub>), corresponding to  $S = 1/2$ . Lastly, preparing the 50%  $^{15}\text{N}$  enriched isotopomer  $[(\text{Tp}^{t\text{Bu},\text{Me}})_2\text{V}\equiv^{15}\text{N}(\text{THF})]$  (**B-THF- $^{15}\text{N}$** ), *via* photolysis of **6- $^{15}\text{N}$** , 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  $\text{V-N}_{\text{nitride}}$  axis.<sup>39</sup> This result is consistent with Bendix' studies of isoelectronic  $\text{Cr}^V$  terminal nitride complexes with SP or octahedral geometry; here, hyperfine coupling to the axial nitride  $^{14}\text{N}$  is obscured by unresolved coupling to equatorial ligands such as  $^{35,37}\text{Cl}$  ( $I = 3/2$ , 100%), whereas coupling to the nitride is resolved when the equatorial ligands are  $^{16}\text{O}$  (from dibenzoylmethane ligand, dbm; modeled as acac for calculations).<sup>40</sup> In **B-THF- $^{15}\text{N}$** , unresolved hyperfine coupling to pyrazolyl  $^{14}\text{N}$  (three coordinated, three not) prevents resolution of the small coupling to nitride  $^{14,15}\text{N}$ .<sup>41</sup>



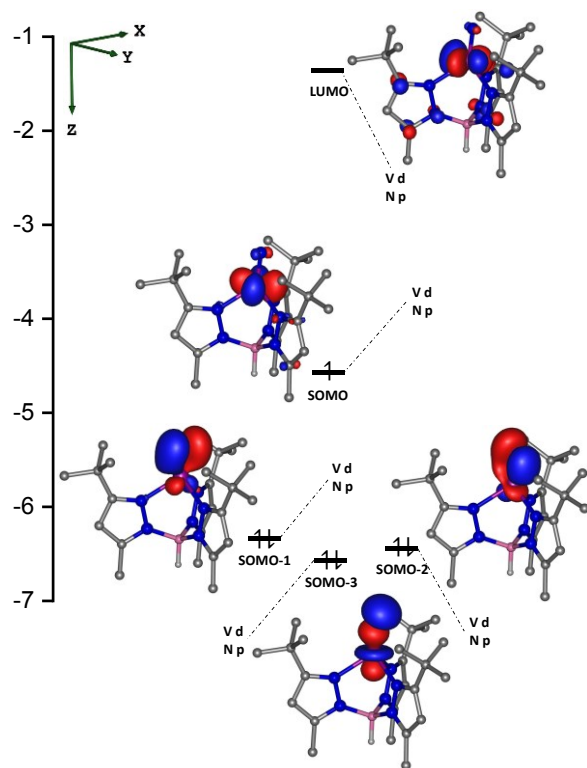
**Figure 14.** **A)** CW X-band EPR spectra of pristine **6- $^{14}\text{N}$**  in THF at 293 K (black trace) and after irradiation. **B)** Structural representation of complex **B-THF** (thermal ellipsoids at 35% probability). Hydrogen atoms (except B-H), co-crystallized solvent, and disorder on THF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



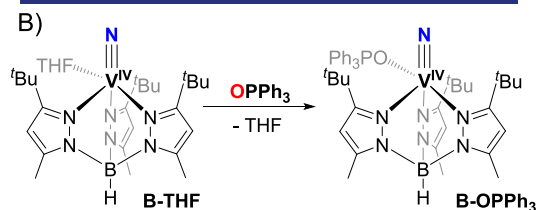
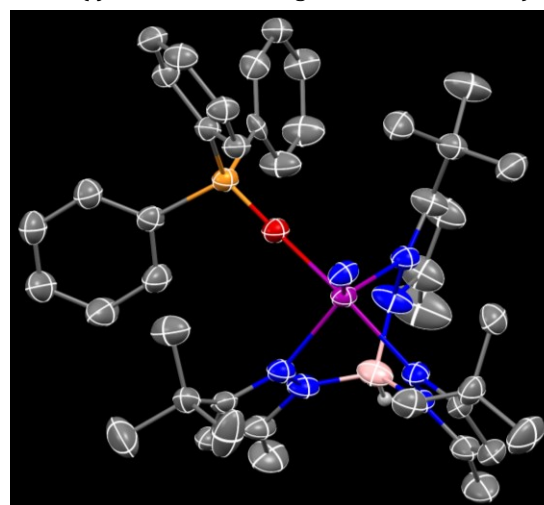
When dissolving complex **B**-THF in C<sub>6</sub>D<sub>6</sub> for NMR spectroscopic characterization, the V<sup>IV</sup> nitride rapidly transforms to **5** and [V( $\kappa^2$ -Tp<sup>*t*Bu,Me</sup>)<sub>2</sub>] (Scheme 1, and Figure 10D). In general, **B**-THF is quite unstable in weakly coordinating solvents. Presumably, the lack of a Lewis base allows the unsaturated V<sup>IV</sup> 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( $\kappa^2$ -Tp<sup>*t*Bu,Me</sup>)<sub>2</sub>]. Surprisingly, there is no example of a neutral [V(Tp)<sub>2</sub>] despite many reports on analogous [M(Tp)<sub>2</sub>]<sup>0</sup> complexes that exist in the literature.<sup>42</sup> 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<sub>3</sub>. Photolysis of **6** in THF in the presence of two equiv. of OPPh<sub>3</sub> generated the **B**-OPPh<sub>3</sub> adduct in near-quantitative yield (94%, Scheme 1, and Figure 16B). Complex **B**-OPPh<sub>3</sub> resembles **B**-THF structurally with a  $\tau_5$  value of 0.48 (Table 1). The V $\equiv$ N bond distance in **B**-OPPh<sub>3</sub> (1.587(2) Å) is slightly longer than in **B**-THF (Figure 16A, Table 1), most likely the result of OPPh<sub>3</sub> being a stronger  $\sigma$ -donor ligand than THF. The cyclic voltammograms of **B**-THF and **B**-OPPh<sub>3</sub> 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**-OPPh<sub>3</sub>, respectively, suggesting oxidation of these species to a terminal V<sup>V</sup> nitride to be reversible as well as highly tunable through the choice of Lewis base (*cf.* SI, Sections 10.4 and 10.5, Figures S110 and S113). The voltammogram of **B**-OPPh<sub>3</sub> 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 sc-XRD structure of **B**-L); MO diagrams of adducts **B**-OPPh<sub>3</sub> and **B**-THF are presented in Figures S122 and S123, respectively. The most salient bonding features for **B** are a V $\equiv$ N triple bond, comprised of the SOMO-3 ( $\sigma$ -symmetric combination of V 3d<sub>z<sup>2</sup></sub>/N 2p<sub>z</sub> atomic orbitals), SOMO-2, and SOMO-1 (orthogonal,  $\pi$ -symmetric combinations of V 3d<sub>yz</sub>/N 2p<sub>y</sub> and the V 3d<sub>xz</sub>/N 2p<sub>x</sub> atomic orbitals). The SOMO essentially consists of a V 3d<sub>xy</sub> orbital, which is  $\delta$ -symmetric along the V $\equiv$ N direction (*z* axis) and, therefore, interacts insignificantly with 2s and 2p orbitals of the nitride ligand. This is in accordance with the minimal <sup>14,15</sup>N hyperfine coupling observed by EPR (*vide supra*, Figure 14C and SI, Section 5.4). In analogy to **B**, the adducts, **B**-THF and **B**-OPPh<sub>3</sub>, each displays a V $\equiv$ N triple bond and has an unpaired electron in a d<sub>xy</sub> orbital. However, while the LUMO of **B** is largely confined to the metal center, the LUMOs of **B**-OPPh<sub>3</sub> and **B**-THF are instead ligand-based (*cf.* SI, Section 11, Figures S122 and S123).



**Figure 15.** MO diagrams of **B**. Orbital energies reported in eV (B3LYP/TZVP).



**Figure 16.** A) Structural representation of complex **B**-OPPh<sub>3</sub> (thermal ellipsoids at 50% probability). Hydrogen atoms (except B-H) are omitted for clarity. B) Reaction between **B**-THF and OPPh<sub>3</sub> to furnish **B**-OPPh<sub>3</sub>.

## CONCLUSION

We have used a sterically demanding hydro-tris(pyrazolyl)borate ligand, [Tp<sup>*t*Bu,Me</sup>]<sup>−</sup>, to synthesize the spin triplet V<sup>III</sup> complex [(Tp<sup>*t*Bu,Me</sup>)VCl<sub>2</sub>] (**1**). Replacement of the pyrazoles' 5-*t*Bu groups with less bulky Me substituents resolved the propensity for the previously reported [(Tp<sup>*t*Bu,Me</sup>)VCl<sub>2</sub>] to undergo ligand degradation, while preserving a sterically encumbering environment. Reduction of **1** affords a high-spin (*S* = 3/2) and mononuclear V<sup>II</sup> complex, [(Tp<sup>*t*Bu,Me</sup>)VCl]

(2) with a  $^4A_2$  electronic ground-state, established by solution and solid-state magnetometry as well as EPR and HFEPN spectroscopy. The affinity of **2** toward THF and DMAP reveals its Lewis acidity and proclivity to attain five-coordination. Two-step transmetallation of **1** with  $\text{NaN}_3$  followed by  $\text{N}_2$  extrusion affords a diamagnetic  $V^V$  nitride, **3**. Using  $\text{Me}_3\text{SiN}_3$  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  $[\text{V}(\kappa^2\text{-Tp}^{t\text{Bu},\text{Me}})_2]$ , while in THF, this furnishes a neutral, mononuclear  $V^{IV}$  nitride (*i.e.*  $V^{IV}$  nitride), **B-THF**, where **B** is the still elusive four-coordinate  $[(\text{Tp}^{t\text{Bu},\text{Me}})\text{V}(\equiv\text{N})]$ . Use of a stronger Lewis base, such as  $\text{OPPh}_3$ , led to the kinetically stable  $V^{IV}$  nitride, **B-OPPh<sub>3</sub>**. 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  $^{51}\text{V}$  coupling. We thus report the first example (as **B-L**, **B** =  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{V}(\equiv\text{N})$ , **L** = THF, or  $\text{OPPh}_3$ ) of a neutral mononuclear  $[\text{V}\equiv\text{N}]^+$  (vanadazyl) analog to the many such  $[\text{V}\equiv\text{O}]^{2+}$  (vanadyl) species.

Overall, we have demonstrated how the  $[\text{Tp}^{t\text{Bu},\text{Me}}]$ -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  $[\text{Tp}^{t\text{Bu},\text{Me}}]$ -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,  $[(\text{Tp}^{t\text{Bu},\text{Me}})\text{V}]_2(\mu_4\text{-VN}_4)]$ , thus exhibiting a double-diamond core. This is the first example of a  $[\text{VN}_4]^{8-}$  analog of the ubiquitous vanadate ion,  $[\text{VO}_4]^{3-}$ . 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

**Supporting Information.** Supporting information is available free of charge on the ACS publication website at DOI: XXX. Supporting Information (PDF) contains synthetic procedures, NMR, IR, UV-Vis, EPR, HFEPN, SQUID, computational, electrochemical, and X-ray crystallographic data.

## 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](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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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All authors have given approval to the final version of the manuscript.

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On the occasion of the 90<sup>th</sup> 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<sup>tBu,Me</sup>, hydro-tris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate;  
 Tp<sup>tBu,tBu</sup>, hydrotris(3,5-di-*tert*-butylpyrazol-1-yl)borate;  
 CV, cyclic voltammetry;  
 Td, tetrahedral;  
 SP, square planar (4-coordinate);  
 TBP, trigonal bipyramidal;  
 SP, square pyramidal (5-coordinate);  
 DMAP, 4-dimethylaminopyridine;  
 sc-XRD, single crystal X-ray diffraction;  
 ENDOR, electron nuclear double resonance;  
 HFEP, high-frequency and field electron paramagnetic resonance.

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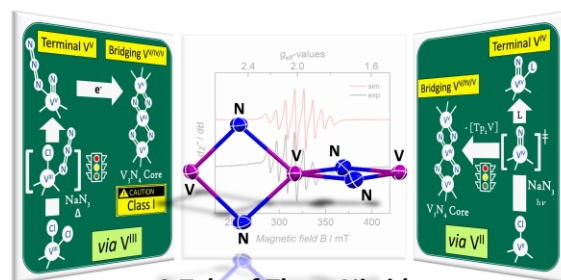
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