



Dalton
Transactions

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Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-ART-11-2019-004544.R1
Article Type:	Paper
Date Submitted by the Author:	14-Dec-2019
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Synthesis, Characterization, DFT Calculations, and Reactivity Study of a Nitrido-Bridged Dimeric Vanadium(IV) Complex†

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Two vanadium(III) complexes, $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{Pr}})_2\text{VCl}_2$ (**1**) and $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{Pr}})_2\text{V}(\text{N}_3)_2$ (**2**), were synthesized and characterized. Chemical reduction of both **1** and **2** gives the thermally stable nitrido-bridged vanadium(IV) dimer complex, $[\{\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{Pr}})_2\text{V}\}_2(\mu\text{-N})_2]$ (**3**), which is a rare example of a dimeric vanadium(IV) complex bridged by two nitrido ligands. The nitride ligands of **3** are unreactive due to the well-protected environment provided by the pincer ligand and its substituents, as is supported by its X-ray crystal structure and further described by DFT calculations.

Introduction

The process of dinitrogen reduction in nitrogenase enzymes is an essential natural process, yet not very well understood. To better understand the process by which these types of enzymes catalyze dinitrogen reduction, relevant intermediate species, such as metal nitrides, need to be synthesized and characterized. To satisfy the need to efficiently generate large quantities of ammonia, the nitrogenase-equivalent industrial Haber-Bosch (H-B) process is used. To match the catalytic efficiency of nitrogenase, the H-B process utilizes a heterogeneous catalyst bed and elevated temperatures and pressures to form ammonia. Given nitrogenase's inherent ability to perform this transformation at ambient temperature, investigating the reaction mechanism of dinitrogen reduction via nitrogenase by using synthetic model compounds may provide interesting information useful in designing efficient and homogeneous transition-metal catalysts based on metal nitride species. Recently, new structural information about the Fe-V cofactor (FeVco) of nitrogenase and its ability to catalyze both CO and N_2 reduction was reported,^{1,2,3,4} Although this information is valuable, understanding the role that vanadium in FeVco plays during dinitrogen reduction is yet to be understood.

Previous literature indicates that metal nitrides are key intermediates in the process of N_2 reduction,⁵ yet the development of vanadium complexes bearing terminal⁶⁻¹¹ or

bridging¹¹⁻¹⁹ nitrido has been rather slow. Although the formation of nitride species has been implied by several examples of nitrogen fixation and activation by vanadium complexes,²⁰ the production of ammonia by the protonation of a nitride-bridged V^{V} dimer complex has only recently been discovered by Nishibayashi *et al.*²¹ As of now, many isolable vanadium nitride complexes have metal centers in the 5+ oxidation state. Smith proposed that the oxidation states of vanadium in FeVco range from 2+ to 4+,^{22,23} so understanding the role of vanadium in V-nitrogenase calls for the design and synthesis of vanadium nitride complexes with these oxidation states. To the best of our knowledge, there are only two reported examples of dimeric vanadium-nitride complexes with oxidation states of 3+ to 4+.^{12,24} Herein, we present the synthesis and characterization of two V^{III} complexes and one nitride-bridged V^{IV} dimer, which are supported by a mono-anionic NNN pincer ligand, $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{Pr}})_2^-$.

Experimental Section

Materials and Methods

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or in an M. Braun UNILab Pro glovebox. Glassware was dried at 150 °C overnight. Diethyl ether, *n*-pentane, tetrahydrofuran, and toluene were purified using a Pure Process Technology solvent purification system. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. All reagents were purchased from commercial vendors and used as received. $\text{HCz}^{\text{tBu}}(\text{Pyr}^{\text{Pr}})_2$ was prepared according to a modified literature procedure.²⁵ ^1H NMR data were recorded on a Varian Inova 500 MHz spectrometer at 22 °C. Resonances in the ^1H NMR spectra are referenced either to residual $\text{C}_6\text{D}_5\text{H}$ at $\delta = 7.16$ ppm or $\text{C}_4\text{D}_7\text{HO}$ at $\delta = 3.58$ ppm. Solution magnetic susceptibilities were determined using the Evans method.²⁶ Continuous-wave (CW) EPR spectrum was recorded at 77 K on a Bruker EMX plus X-band EPR spectrometer equipped with a liquid N_2 cold-

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† Electronic Supplementary Information (ESI) available: Additional X-ray crystallographic data, ^1H NMR spectra, EPR spectrum and computational results. CCDC 1906128-1906131 for complexes **1-4**.

finger Dewar flask. Fourier transform-infrared (FTIR) spectroscopy was performed using a Shimadzu IRAffinity-1S, FTIR spectrometer. Magnetic properties measurement of **3** was carried out on a Quantum Design MPMS 3 equipped with a superconducting quantum interference device (SQUID) detector. Elemental analysis was conducted by Midwest Microlab, LLC (Indianapolis, IN).

Warning: Sodium azide is explosive under appropriate conditions, and should be handled carefully.

Synthesis of $Cz^{tBu}(Pyr^{iPr})_2VCl_2$ (1). Yield: 93%. Under an N_2 atmosphere and at ambient temperature, a tetrahydrofuran solution (THF) (10 mL) of $HCz^{tBu}(Pyr^{iPr})_2$ (300 mg, 0.61 mmol) and lithium diisopropylamide (68 mg, 0.63 mmol) was stirred for 1 hour. The resulting fluorescent yellow solution was transferred to a slurry of VCl_3 (105 mg, 0.67 mmol) in THF (5 mL). The reaction was stirred overnight. Volatiles were removed under reduced pressure, and the remaining solid was extracted with toluene and filtered through Celite. The filtrate was dried *in vacuo* to yield a dark red solid. Crystals suitable for X-ray diffraction were grown by slow evaporation of a toluene solution at ambient temperature. 1H NMR (500 MHz, C_6D_6 , δ): 15.2 ($\Delta\nu_{1/2} = 410$ Hz), 10.2 ($\Delta\nu_{1/2} = 108$ Hz), 4.59 ($\Delta\nu_{1/2} = 177$ Hz), 0.95 ($\Delta\nu_{1/2} = 37$ Hz), -26.5 ($\Delta\nu_{1/2} = 896$ Hz). μ_{eff} (C_6D_6): $3.0 \pm 0.2 \mu_B$. Anal. Calcd for $C_{32}H_{40}Cl_2N_5V \cdot 0.25(C_7H_8)$: C, 63.38; H, 6.62; N, 10.95. Found: C, 63.25; H, 7.05; N, 11.00.

Synthesis of $Cz^{tBu}(Pyr^{iPr})_2V(N_3)_2$ (2). Yield: 86%. To a stirred solution of $Cz^{tBu}(Pyr^{iPr})_2VCl_2$ (260 mg, 0.42 mmol) in THF (11 mL) under N_2 atmosphere, a suspension of sodium azide (68.5 mg, 1.05 mmol) in THF (15 mL) was added. The resulting slurry was stirred overnight at 75 °C. Volatiles were removed under reduced pressure, and the remaining solid was extracted with toluene and filtered through Celite. The filtrate was dried *in vacuo* to yield an orange solid. Crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a toluene solution at ambient temperature. 1H NMR (500 MHz, C_6D_6 , δ): 17.2 ($\Delta\nu_{1/2} = 393$ Hz), 11.2 ($\Delta\nu_{1/2} = 152$ Hz), 5.24 ($\Delta\nu_{1/2} = 430$ Hz), 1.08 ($\Delta\nu_{1/2} = 66$ Hz), -28.0 ($\Delta\nu_{1/2} = 1247$ Hz). μ_{eff} (C_6D_6): $3.2 \pm 0.3 \mu_B$. FT-IR (THF, cm^{-1}): ν 2060 (N_3 , strong). Anal. Calcd for $C_{32}H_{40}N_{11}V$: C, 61.04; H, 6.40; N, 24.47. Found: C, 61.32; H, 6.07; N, 24.52. Note: An identical procedure was adopted to generate ^{15}N enriched (from 50% enriched NaN_3) $Cz^{tBu}(Pyr^{iPr})_2V(N_3)_2$, $2-^{15/14}N$ by treating **1** with $Na^{15}N^{14}N_2$. FT-IR (THF, cm^{-1}): ν 2053 (N_3 , strong).

Synthesis of $\{[Cz^{tBu}(Pyr^{iPr})_2]_2V\}_2(\mu-N)_2$ (3). Method A. Yield: 84%. To a stirred solution of $Cz^{tBu}(Pyr^{iPr})_2VCl_2$ (30 mg, 0.048 mmol) in 10 mL toluene at ambient temperature and under an N_2 atmosphere was added a slurry of potassium graphite (KC_8) (16 mg, 0.12 mmol) in 5 mL toluene. The resulting brown suspension was stirred for 24 h. The solution was filtered through a Celite pad and solvent was removed under reduced pressure to yield a dark brown solid. *Method B.* Yield: 89%. To a stirred solution of $Cz^{tBu}(Pyr^{iPr})_2V(N_3)_2$ (75 mg, 0.12 mmol) in toluene (20 mL) at ambient temperature under N_2 atmosphere, a suspension of potassium graphite (40.2 mg, 0.30 mmol) in THF (2 mL) was added. The resulting slurry was stirred overnight at ambient temperature. The solution was filtered through Celite

and dried *in vacuo* to yield a dark brown solid. Crystals suitable for X-ray diffraction were grown by slow evaporation of an Et_2O solution at ambient temperature. 1H NMR (500 MHz, C_6D_6 , δ): 9.98 ($\Delta\nu_{1/2} = 16$ Hz), 8.81 ($\Delta\nu_{1/2} = 36$ Hz), 7.81 ($\Delta\nu_{1/2} = 29$ Hz), 1.68 ($\Delta\nu_{1/2} = 25$ Hz), -0.03 ($\Delta\nu_{1/2} = 53$ Hz), -0.76 ($\Delta\nu_{1/2} = 73$ Hz). μ_{eff} (C_6D_6): $2.8 \pm 0.2 \mu_B$. Anal. Calcd for $C_{64}H_{80}N_{12}V_2$: C, 68.68; H, 7.20; N, 15.02. Found: C, 68.52; H, 7.10; N, 15.33.

Electrochemistry

Cyclic voltammetry was conducted via a CH-Instruments electrochemical analyzer (model 620E), employing a 3 mm glassy carbon working electrode, a silver wire pseudo reference electrode, and a platinum coiled wire counter electrode. All measurements were performed using either THF or dichloromethane solutions containing 1 mM analyte and 0.1 M (*n*-Bu) $_4$ NPF $_6$ as the supporting electrolyte. The potentials were referenced to a ferrocene/ferrocenium redox couple.

Crystallography

Data for **1** and **4** were collected using a Rigaku Rapid II curved image plate diffractometer employing Cu-K α radiation ($\lambda = 1.54178$ Å). Data for **2** and **3** were measured using a Bruker Kappa APEXII diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). A single crystal of each compound was mounted on a MiTeGen micromesh mount using a trace of mineral oil and cooled *in situ* to 100 or 120 K for data collection. Data for **1** and **4** were collected using the dteck option of CrystalClear-SM Expert 2.1 b32.²⁷ Data were processed using HKL3000 and data were corrected for absorption and scaled using Scalepack.²⁸ Data for **2** and **3** were collected using Apex2^{29,30} and the intensity data were corrected for absorption using multi-scan techniques (SADABS).³¹ The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs and refined by full matrix least squares against F^2 with all reflections using Shelxl2014 or 2016 using the graphical interface Shelxle or OLEX2.^{29,32,33} H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for alkene and aromatic C–H, and 1.00, 0.99 and 0.98 Å for aliphatic CH, CH $_2$ and CH $_3$ moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C)$ with 1.5 for CH $_3$ and 1.2 for CH $_2$ and CH units, respectively. Additional experimental details for all structures are given in the SI. Structures, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1906128-1906131. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods

Density functional calculations employed the Gaussian 09 package,³⁴ the B3LYP functional, and a mix of Pople basis sets to accommodate the large size of the target complexes. For V and N atoms, the 6-311+G(d) basis set was utilized and for C and H the 6-31G(d) basis set was utilized. Geometry optimizations were performed in the gas phase with single-point corrections

utilizing the GD3BJ³⁵ dispersion correction, solvent effects (SMD, THF)³⁶ and a larger basis set (6-311++G(d,p) for all atoms). For each stationary point, singlet (closed- and open-shell), triplet and quintet spin states were evaluated to identify the lowest free energy calculated spin state. All closed-shell singlet wavefunctions were tested for stability with the Stable=Opt command in Gaussian 09.

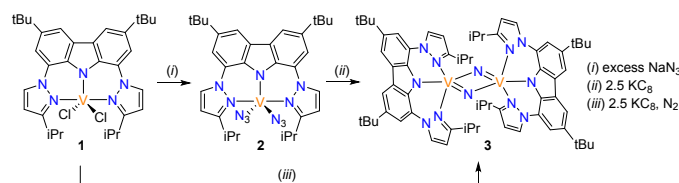
Results and Discussion

Synthesis and characterization of 1–3

The synthetic procedure for complexes 1–3 is summarized in Scheme 1. Complex 1 was prepared by combining HCz^tBu(PyrrⁱPr)₂, lithium diisopropylamide, and VCl₃ in THF at ambient temperature. Work-up and recrystallization from toluene gave large, dark red crystals. One set of resonances observed in the paramagnetic ¹H NMR spectrum suggests a C₂ symmetry (Fig. S1). In agreement with an *S* = 3/2 system, magnetization measurement by the method of Evans gave μ_{eff} of 3.6(2) μ_B.

The reaction of 1 and excess NaN₃ in THF at 75 °C over 18 h rendered orange solids of [Cz^tBu(PyrrⁱPr)₂]V(N₃)₂ (2) in 86% yield. Formation of 2 was indicated by a new set of resonances observed in the ¹H NMR spectrum (Fig. S2) and a distinct ν_{N3} asymmetric stretching frequency observed in the infrared spectrum (2060 cm⁻¹). The spin state of *S* = 3/2 for 2 was confirmed by the room temperature magnetic moment measurement by the Evans method (μ_{eff} = 3.7(3) μ_B).

Prior to this work, several vanadium nitride complexes have been prepared by thermolysis,^{6, 9, 37} but 2 is unreactive upon prolonged heating. Alternatively, attempts to photolyze 2 also proved unsuccessful.³⁸ Indeed, metal nitrido complexes can be generated by chemical reduction of either M–N₂ or M–N₃ complexes.^{39, 40} Therefore, by treating 1 with 2.5 equiv of KC₈ in toluene under N₂ atmosphere, a new species [Cz^tBu(PyrrⁱPr)₂]V(μ–N)₂ (3) is generated. Interestingly, reduction of 1 using KC₈ in THF yielded different paramagnetic species, and one of the products, [Cz^tBu(PyrrⁱPr)₂]VCl(μ–O)[Cz^tBu(PyrrⁱPr)₂]VO (4), was crystallized in THF. While we have not been able to generate 4 in bulk, its identity was confirmed by XRD. Although disorder and poor data quality (R1 = 10.87%) precludes a meaningful discussion of the structural parameters of 4, the atom connectivity has revealed an unexpected dimeric vanadium complex (Fig. S4), which is bridged by an oxo ligand. This could be due to the oxophilic character of vanadium, which upon reduction of 1 with concomitant loss of a Cl atom, would yield a coordinatively unsaturated metal center that may react with trace amounts of



Scheme 1. Synthesis of vanadium complexes 2 and 3.

water⁴¹ or THF.⁴²

Alternatively, reacting 2 with 2.5 equiv of KC₈ under N₂ also yielded 3 with obvious gas evolution upon mixing. To fully rule out the possibility of the nitrogen atom of nitride stemming from the N₂ atmosphere, treatment of 2 with KC₈ under an argon atmosphere was conducted, and 3 was successfully generated in high yield. Additionally, we synthesized 2-¹⁵N which was then reacted with KC₈ to yield 3-¹⁵N, as confirmed by ¹H NMR spectroscopy. Unfortunately, assignment of bands attributable to the ν_{VN} vibrations of both 3 and 3-¹⁵N, which are expected to appear from 940 to 1030 cm⁻¹,^{6, 7, 11, 43} is not possible owing to strong ligand absorptions in the same region.

3 was characterized by ¹H, ⁵¹V NMR, EPR spectroscopy, elemental analysis, and X-ray crystallography. In C₆D₆ at room temperature, compound 3 is paramagnetic as observed by solution ¹H NMR spectroscopy (Fig. S3) and exhibits an effective magnetic moment of 2.8(2) μ_B, which is in good agreement with the spin-only value of 2.83 μ_B for a system with two unpaired electrons (*S* = 1).²⁴

Paramagnetism of 3 indicates minimal antiferromagnetic spin–spin coupling between the formally V^{IV} centers, despite the relatively short V–V distance of 2.6546(9) Å, which is slightly longer than the single-bond radius of di-vanadium (2.45 Å).⁴⁴ NMR and EPR spectroscopic evidence were used to further validate the identity of 3 as a bona fide {V^{IV}≡N}₂ complex. For instance, no peak was observed in ⁵¹V NMR spectroscopy (vs. externally referenced VOCl₃ at 2 ppm). Indeed, the triplet configuration is observed at room temperature according to results from the Evans method. At 77 K temperature, a silent EPR spectrum and diamagnetic results shown in SQUID measurement are consistent with a dimeric imido vanadium(IV) complex, [(μ–Cl)₂V₂(η⁵–C₅H₅)₂(NⁱC₄H₉)₂] having weak antiferromagnetic coupling.

Crystal structures of 1–3

Single crystals suitable for X-ray structure determination were obtained for complexes 1–3. ORTEP drawings are given in Fig. 1–2, selected bond lengths and angles are found in Table S1, and the crystallographic data are summarized in Table S2. The solid-state structures confirm complexes 1 and 2 as mononuclear vanadium complexes with one Cz^tBu(PyrrⁱPr)₂[–] ligand in associat-

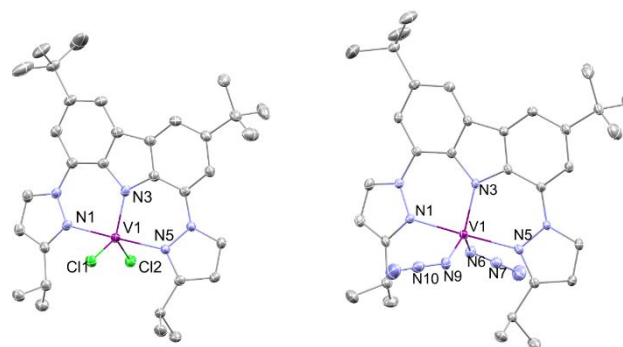


Fig. 1. Molecular structure of 1 (left) and 2 (right) with thermal ellipsoids at the 50% probability level. Hydrogen atoms

and solvent molecules are omitted for clarity. Color key: purple = V, blue = N, gray = C, green = Cl.

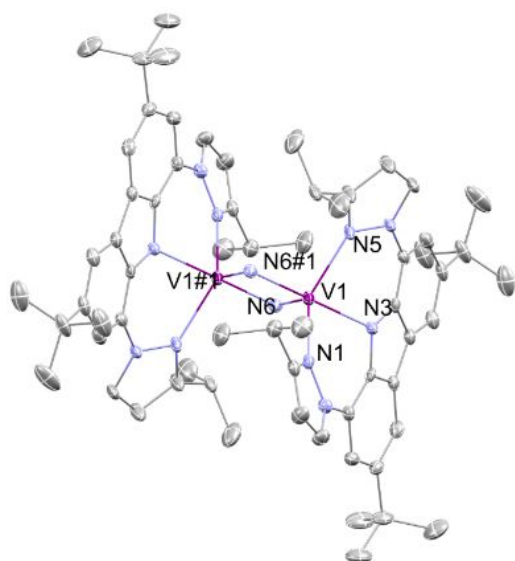


Fig. 2. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Color key: purple = V, blue = N, gray = C.

ion with either two Cl atoms (**1**) or two N₃ groups (**2**). Both **1** and **2** have a slightly distorted trigonal bipyramidal geometry (τ_5 values are 0.74 and 0.83 for **1** and **2**, respectively) with two neutral nitrogen atoms in the axial positions and three anionic atoms in the equatorial plane.⁴⁵ The structural parameters of **1** and **2** agree well with those of closely related pincer-supported V^{III}X₂ (X = Cl and N₃) complexes.^{46, 47} It is noted that **2** is the first well-defined azide-containing mononuclear vanadium complex with a trigonal bipyramidal geometry ($\tau_5 = 0.83$).³⁷

Brown crystals of **3** were grown from slow evaporation of Et₂O solution and the molecular structure was obtained by X-ray diffraction. **3** is a rare example of a dimeric vanadium(IV) complex bridged by two nitrido ligands, [$\{\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\}\text{V}\}_2(\mu\text{-N})_2$. Surprisingly, the two *i*Pr groups on the pincer ligand are not bulky enough to inhibit the formation of the nitride-bridged dimer.

The coordination geometry of **3** is best described as a trigonally distorted rectangular pyramid.⁴⁸ This particular structure could result from heavy distortion around the vanadium center, which could be defined as either a square pyramid or a trigonal bipyramid depending on axial and equatorial assignments. In this case, the five-coordinate vanadium ion is bound to three nitrogen atoms from the supporting ligand, one bridged nitrido nitrogen (N6#1) atom in the equatorial positions, and another bridged nitrido nitrogen (N6) atom in the apical position. The rigid pincer ligand results in the $\angle\text{N1-V1-N5}$ deviating from the ideal trigonal bipyramidal geometry of 120° in the equatorial plane. Therefore, the equatorial plane distortion is significant, with angles of 172.364(10)° (N3-V1-N6#1) and 134.04(10)° (N1-V1-N5), and a V1 deviation of *ca.* 0.471 Å from the plane. The new defined apical V1-N6 bond is then nearly perpendicular (82.41°) to this N1N3N5N6#1 mean plane. The N3-V1 bond length of **3** (2.064(2) Å) is considerably longer

in comparison with those of **1** (1.8961(15) Å) and **2** (1.9097(15) Å), attributed to the *trans* influence of the π -donor nitride ligand.

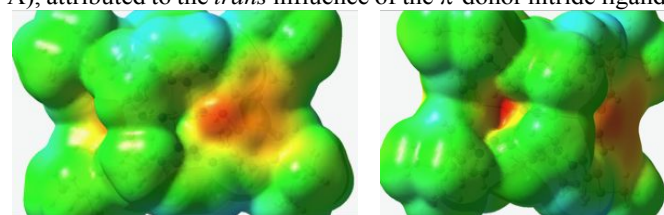


Fig. 3. Molecular electrostatic potential map of **3** at the B3LYP/6-311++G(d,p) level of theory at 0.01 au iso-surface of electron density (red is negative or nucleophilic region, and blue is positive or electrophilic region).

Electrochemistry of 1–3 and synthetic approaches for redox products

Cyclic voltammetry with a glassy carbon electrode in THF with (*n*-Bu)₄NPF₆ was carried out at 100 mV·s⁻¹ for **1–3** (Fig. S5–7), all of which show irreversible oxidation processes. These events can be attributed to metal- or ligand-centered oxidation. However, attempts to isolate the oxidation products by treating **1** or **2** with oxidants were unsuccessful. One quasi-reversible reduction event was observed for **1**, whereas three irreversible events were seen for **2**. The quasi-reversible event for **1** prompted us to isolate this species, which was anticipated to be a one electron reduction product, but instead **4** was unexpectedly obtained. For **3**, several ill-defined anodic voltammetry peaks were observed, but chemical oxidation of **3** and attempts to isolate oxidized products proved unsuccessful (*vide infra*).

Reactivity of 3

Complex **3** is highly stable, despite some other early-transition metal nitride complexes being reported as electrophilic, nucleophilic, or ambiphilic.³⁹ For instance, no reaction occurred in the presence of phosphine ligands such as PMe₃ and PPh₃. Treating **3** with alkylating reagents such as MeI and MeOTf yields methylated pincer ligand, MeCz^{tBu}(Pyr^{iPr})₂, whereas formation of free ligand HCz^{tBu}(Pyr^{iPr})₂ was observed when treating **3** with a proton source, HOTf, or an H atom donor reagent, TEMPOH. In addition, no significant decomposition was observed upon prolonged heating. The molecular electrostatic potential map of **3** (Fig. 3) shows both carbazole and nitride nitrogen atoms are nucleophilic, although the latter is fully protected by *i*Pr and *t*Bu groups of the supporting ligands resulting in low reactivity of the nitride. Treating **3** with oxidants, such as Cp₂FePF₆ or AgOTf, led to an immediate color change of solution, but no well-defined products were isolated. This is surprising, given V^{IV}-V^V and V^V-V^V bridged nitrido complexes, [V^{IV}V^V(Me₃SiN{CH₂CH₂NSiMe₃})₂(μ-N)]₂ and [V^V(Me₃SiN{CH₂CH₂NSiMe₃})₂(μ-N)]₂, being reported as easily prepared and isolated by Cloke *et al.*. Finally, reactions with other substrates including phenylsilane and pinacolborane were unsuccessful.⁸

DFT calculations

The reactivity of **3** was further examined using DFT calculations. The computations suggest that the open-shell singlet (OSS) and triplet states of V₂N₂ are essentially degenerate, with the latter

calculated to be more stable by 1.4 kcal/mol. The geometries are also quite similar in both the V_2N_2 core and the VN bond lengths to the supporting pincer ligand. For the former, VN = 1.63 and 2.02 Å with a VV = 2.67 Å for the OSS and 1.64, 2.02 and 2.67 Å for these same bond lengths for the corresponding triplet **3**. For the OSS, the spin densities computed via a Mulliken population analysis are $\pm 1.1 e^-$ on V and $\pm 0.1 e^-$ on the nitride N with minimal spin density elsewhere for OSS V_2N_2 . The spin density for the triplet has a similar disposition with a bit more localization on to the nitride nitrogens: $1.27 e^-$ for each V and $-0.25 e^-$ for each N. Given the similar geometries and the similar energetics, it is concluded that the ground state of these complexes may be best thought of as weakly coupled V(IV) systems.

Oxidation of neutral V_2N_2 yields a doublet cation via DFT simulations. What is particularly interesting is the asymmetry of the VN bonds in the V_2N_2 core: 1.63, 1.70, 1.83 and 1.97 Å. The spin densities are 1.09 and $0.32 e^-$ for the vanadium atoms, and -0.18 and $-0.19 e^-$ for the nitride nitrogen atoms. It thus appears from the spin densities that oxidation of the neutral $V^{IV}-V^{IV}$ results in a $V^{IV}-V^V$ cation that is Class I (localized) in the Robin-Day system. There is, however, a very small free energy barrier to interconversion. Approximating the transition state as C_{2h} symmetric yields a free energy barrier to interconversion of only 3.6 kcal/mol. The redox properties of V_2N_2 were assessed relative to the ferrocene/ferrocenium couple. At the level of theory used, the DFT calculations indicate the redox reaction is close to thermoneutral, $\Delta G = -5.0$ kcal/mol. Hence, in redox properties, V_2N_2 is akin to ferrocene.

To assess the potential reactivity of the V_2N_2 complex at the vanadium-nitride core with different classes of chemical reagents, the reaction free energies to add a proton, H atom, or hydride to one of the bridging nitride nitrogen atoms were computed; the computed structures of these products are shown in Fig. S8-S12. The computations used the B3LYP functional with single point corrections for dispersion and continuum solvent (SMD-THF) at the basis sets indicated in Computational Methods.

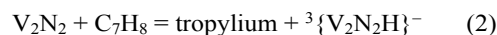
The ΔG for proton transfer to DMSO, eq 1, was endergonic by 24.5 kcal/mol. This corresponds to a pK_a of ~ 3 for $\{V_2N_2H\}^+$ assuming the corrections in a recent paper by Nazemi and Cundari.⁴⁹ As such, it indicates that $\{V_2N_2H\}^+$ is a very strong acid, thus implying that its conjugate base, V_2N_2 , is a very weak base.



Next, the reaction of H^\bullet with V_2N_2 was examined. N–H bond strengths have been implicated as being important in the reactivity of mid- to late-transition metal imide/imidyl/nitrene complexes,⁵⁰ a value that arises from the intrinsic strength of the N–H bond, the geometric relaxation of the involved species upon loss/addition of H^\bullet , and the changes in metal-nitrogen π -bonding as one traverses a reaction coordinate such as $M=N-R \rightarrow M-N(H)-R$. The N–H bond dissociation free energy of $\{V_2N_2H\}$ is 49 kcal/mol, which is a very weak bond, for example, as

compared to organic amine and amide N–H bonds, which are in the range of ~ 80 kcal/mol.⁵¹

Finally, the potential hydricity of the $\{V_2N_2\}$ complex was assessed and the free energy required to abstract H^- from 1,3,5-cycloheptatriene (135Hpt) was computed. As hydride abstraction produces the aromatic tropylium cation, 135Hpt is one of the most hydridic hydrocarbons. The ΔG for this reaction, eq 2, is highly endergonic, + 72.5 kcal/mol. As such, V_2N_2 is indicated to be very weakly hydridic.



Given the aforementioned computed reactivity, and then taking account of the bulky substituents needed to make this complex, it is surmised that the V_2N_2 bimetallic is low in reactivity for chemistry directed at the V_2N_2 core. In relation to monomeric early, high-valent metal nitrides, it is proposed that this lack of reactivity is due to the strong metal-nitrogen π -bonds that would be sacrificed upon any reactivity with typical reagents.

Conclusions

We have prepared and fully characterized three new vanadium complexes supported by a monoanionic NNN-pincer ligand, $Cz^{tBu}(Pyr^{tPr})_2^-$. The rare example of a dimeric nitride-bridged vanadium(IV) complex, **3**, can be produced by chemical reduction of either $Cz^{tBu}(Pyr^{tPr})_2VCl_2$, **1**, under N_2 atmosphere via dinitrogen activation or $Cz^{tBu}(Pyr^{tPr})_2V(N_3)_2$, **2** via azide reduction. The lack of reactivity of the nitrides in **3** was verified by treating **3** with different redox, proton, and hydrogen atom transfer reagents. These results agree with DFT calculations, showing this poor reactivity may be attributed to both the steric protection of the ligands and strong metal-nitrogen π -bonds. Efforts to prepare vanadium nitride complexes with reduced steric bulkiness to improve the reactivity of the nitride ligand are currently underway.

Conflicts of interest

There are no conflicts to declare.

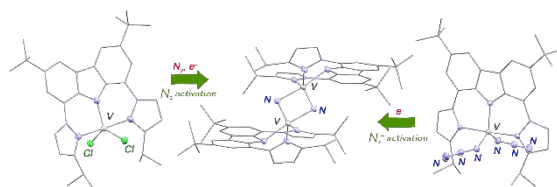
Acknowledgements

This work was supported by start-up funds (Loyola University Chicago). We thank Dr. Daniel J. McElheny (University of Illinois at Chicago) for acquiring ^{51}V -NMR spectra and Airi Kawamura (The University of Chicago) for acquiring SQUID data of **3**. Computations utilized the CASCaM HPC cluster purchased with funds provided by National Foundation Grant CHE-1531468.

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Synthesis and characterization of a rare nitrido-bridged vanadium(IV) dimer complex via both $V^{III}-N_2$ and $V^{III}-N_3$ activation by chemical reduction