Nitrogen Atom Transfer from a Dinitrogen-Derived Vanadium Nitride Complex to Carbon Monoxide and Isocyanide

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S *Supporting Information*

ABSTRACT: Reduction of $[(ONO)V(THF)]$ with KH under an N_2 atmosphere cleaves the $N \equiv N$ bond to afford a bis(μ-nitride) V(IV) dimer. This complex is oxidized to generate a V(V) nitride. The reactions of the V(V) nitride with carbon monoxide and isocyanide led to formation of cyanate and carbodiimide complexes. Following treatment of the cyanate complex with alkyne produces an alkyne adduct along with the release of potassium cyanate. Dissolution of the alkyne adduct in THF regenerates the starting complex $[(ONO)V(THF)]$, thereby closing a synthetic cycle for conversion of N_2 and CO into $[NCO]^-$.

Conversion of atmospheric nitrogen into valuable materials is a challenging problem in chemistry.[1] One approach toward this goal is six-electron reductive N_2 cleavage by transition metal complexes, followed by functionalization of the resulting nitrides and extrusion of N-containing components.[2−4] This methodology is more appealing when combined with soluble metal nitrides capable of mediating the transfer of a nitrogen atom from a metal center to an incoming substrate with concurrent metal reduction.[5] The N_2-derived nitride complexes are known to effect N−X bond formation (X = C or a heteroatom) through nonredox reactions such as alkylation,[3,6] acylation,[4,7] and silylation.[6a,8] However, they are reluctant to engage in redox-coupled nitrogen atom transfer. This is mainly due to thermodynamically stable metal−nitride bonds in high oxidation states, the formation of which compensates for the cleavage of the N_2 bond. One notable exception is a hafnocene μ-nitride complex reported by Chirik et al., which reacted with CO to afford a cyanate-bridging complex.[9] Fryzuk et al. have proposed an electrophilic titanium nitride species as an intermediate for N−P bond formation from phosphine ligands following N_2 scission.[10]

We have reported a triaryloxide-supported diniobium tetrahydride that cleaved N_2 to form a doubly nitride-bridged dinuclear complex.[11] While subsequent conversion into imide complexes and ammonia was achieved by addition of methyl iodide and 2,6-lutidinium chloride,[11a,12] the niobium nitride failed to undergo redox-coupled nitrogen atom transfer. Extending this chemistry to include vanadium is of interest given that redox-coupled nitrogen atom transfer is more feasible with a first row transition metal due to the accessibility of its low oxidation states. The seminal work on carbonylation of vanadium nitride complexes prepared from sodium azide[13,14] is a further inducement to this study. Herein we report N_2 splitting by a

vanadium complex and nitrogen atom transfer from the resulting vanadium nitride to CO and 2,6-xylylisocyanide (XylNC).

Reduction of $[(ONO)V(THF)]$ (**1**) ($[ONO]^{3-}$ = 2,6-(3-^{t}Bu-5-Me-2-OC$_6$H$_2$CH$_2$)-4-^{t}Bu-(p-tolyl)NC$_6$H$_4$)[15] with 2 equiv of KH in THF under N_2 elicited a color change from forest green to dark brown. Following workup in toluene/DME, paramagnetic $[\{K(DME)\}_2\{(ONO)V(\mu\text{-}N)\}]_2$ (**2**) was isolated as a light brown powder in 61% yield (Scheme 1). Formation of H_2 was observed during the reaction, indicating that KH acts as a reductant with elimination of H_2.

Scheme 1. Synthesis and Reactivity of Nitride Complexes
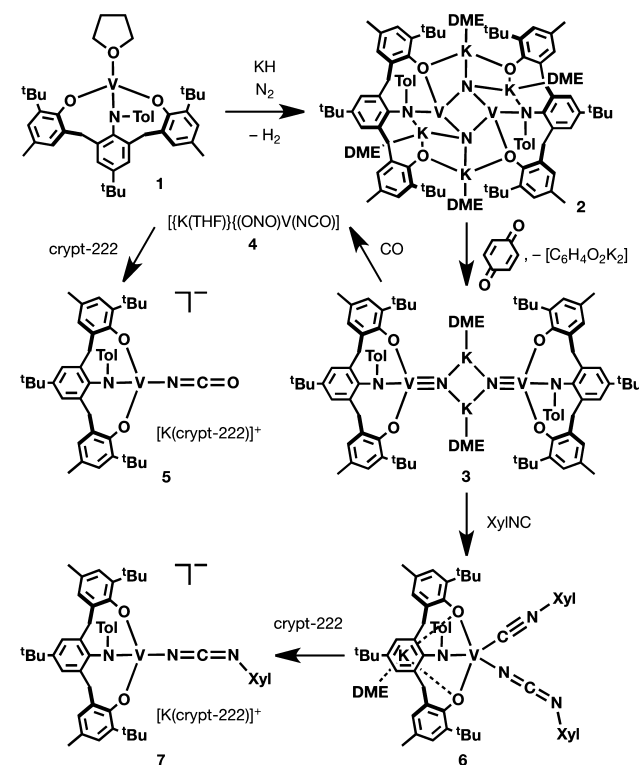
X-ray crystallography revealed **2** to be dimeric with each nitride ligand spanning two K and two V atoms (Figure 1). There is structural change in the coordination mode of the [ONO] ligand, as the ligand is κ^2-N,O-bound to the V atom, whereas one end of the ligand has an aryloxide group unbound to the

Figure 1. Structure of **2** with ellipsoids at the 50% probability level. H atoms are omitted for clarity.
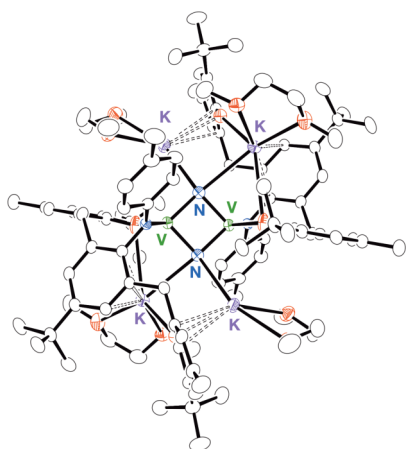

Figure 2. Structure of **3** with ellipsoids at the 50% probability level. H atoms are omitted for clarity.

vanadium center and bridging two K atoms. The coordination geometry at each V center is best described as tetrahedral. The centrosymmetric dimer is held together by the planar V_2N_2 metallacycle, with the V−nitride bond distances (1.794(2) and 1.825(2) Å)[16] comparable to previously reported values for bis(μ-nitride) divanadium complexes.[17,18] The N···N separation of 2.550(3) Å in the V_2N_2 core implies that the N_2 triple bond is completely cleaved. The short V···V distance of 2.5682(8) Å is most likely enforced by two bridging nitrides. The solution magnetic moment of **2** (2.9 μ_B) is therefore consistent with two essentially uncoupled d^1 V(IV) centers.

Intrigued by the possibility that a vanadium(V) nitride species might be accessible, we carried out oxidation of **2** with 1 equiv of benzoquinone in THF. The result was cleavage of the μ-nitride bridge, as evidenced by quantitative generation of [(ONO)-VN]$^-$. Subsequent workup in DME led to isolation of a light yellow powder, which was identified as [{K(DME)}{(ONO)-VN}]$_2$ (**3**) by X-ray diffraction and spectroscopic studies. In contrast, treatment of **2** with AgOTf, I_2, or [Cp$_2$Fe][OTf] did not yield any desired oxidation products.

A tridentate interaction of the [ONO] ligand in **3** is inferred on the basis of the ^{1}H NMR spectrum, which exhibits the number of resonances expected for a C_s symmetric anion with a pair of doublets for the methylene protons. The ^{15}N-enriched isotopologue (**3-^{15}N**), analogously prepared from $^{15}N_2$, shows a large downfield ^{15}N NMR resonance at 958 ppm, as is typical of terminal d^0 metal-nitride functionalities,[13,19a] thereby unequivocally confirming gaseous N_2 as the source of the nitrides in **3**. The ^{51}V NMR spectrum of **3-^{15}N** contains a resonance at −350 ppm, and no detectable coupling of ^{51}V to ^{15}N could be observed due to the broadness of this resonance ($\Delta\nu_{1/2}$ = 2101 Hz). The IR absorption of **3** arising from the V≡N stretch appears at 1007 cm^{-1}, which is appropriately shifted to 974 cm^{-1} in **3-^{15}N**.[13,19] The d^0 vanadium nitride **3** exists as a dimer in the solid state (Figure 2), comprised of a central K_2N_2 metallacycle, in which the two halves are related by crystallographic symmetry. The vanadium−nitride bond distances of 1.591(4) Å are shorter than those of **2** and comparable to those reported for vanadium(V) terminal nitride complexes.[13,19]

Attempts to regenerate **2** by reduction of **3** with KH and KC$_8$ have been unsuccessful. This observation suggests that formation of **2** does not proceed through N_2 scission by the V(II) intermediate followed by reduction of the resulting V(V) nitride species such as **3**. In our case, N_2 scission is presumably
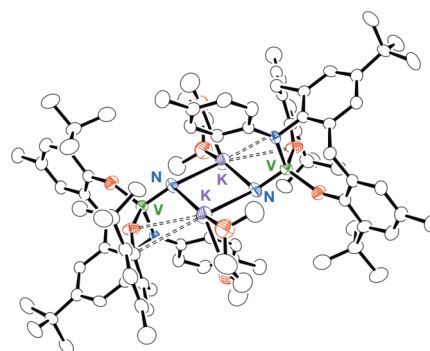
performed by two d^4 V(I) centers. However, we cannot rule out the possibility of cooperative N_2 cleavage involving more than two vanadium ions. Notably, **2** and **3** are rare examples of well-defined vanadium nitride complexes prepared by N_2 splitting.[17,20]

The facile access to V(IV) and V(V) nitride species via N_2 splitting prompts investigation of their potential to undergo nitrogen atom transfer. The bis(μ-nitride) V(IV) dimer **2** was observed to react with CO at ambient pressure for 2 h, resulting in a mixture of a cyanate species [(ONO)V(NCO)]$^-$ and unidentified products. Thus, the discussion will now focus on the reactivity of the vanadium(V) nitride complex **3**. Exposure of **3** in THF to 2.2 MPa of CO at room temperature for 2 days gradually produced a brown solution. Analysis of the reaction mixture suggests the quantitative formation of a crude product, tentatively assigned as [{K(THF)}{(ONO)V(NCO)}] (**4**), which exhibits a strong IR absorption at 2168 cm^{-1} arising from the NCO stretching frequency (2149 cm^{-1} for **4-^{15}N**). During the reaction, C−N bond formation occurs with concomitant reduction from V(V) to V(III). The solution magnetic susceptibility was found to be 2.6 μ_B, in agreement with a high-spin d^2 configuration. Although numerous attempts were made, single crystals suitable for X-ray crystallography were not obtained.

A salt of the [(ONO)V(NCO)]$^-$ anion amenable to X-ray crystallography, [K(cryptand-222)][(ONO)V(NCO)] (**5**), was obtained in 77% yield upon addition of cryptand-222 to **4** in THF. The solid-state structure of **5** (Figure 3) reveals that the compound consists of discrete anions and cations and that a terminally bound cyanate (V−NCO 1.984(3) Å, V−N−C 176.2(3)°) is obtained as a mononuclear, tetrahedral anion.
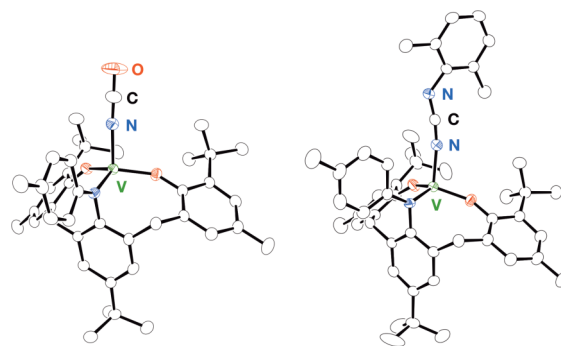

Figure 3. Structures of the anion part of **5** and **7** with ellipsoids at the 50% probability level. H atoms are omitted for clarity.

The cyanate stretching frequency occurs at 2211 cm^{-1} in the IR spectrum (2192 cm^{-1} for **5-^{15}N**). The ion-separated complex **5** is sparingly soluble in nonreactive solvents. The solid-state magnetic moment (2.75 μ_B) is close to the spin-only value for two unpaired electrons. The complex **5** was independently synthesized through the reaction of **1** with KNCO in the presence of cryptand-222 to further confirm the identity of **5**.

This nitrogen atom transfer reactivity can extend to an isocyanide. The reaction of **3** with excess XylNC in THF at 70 °C afforded [{K(THF)}{(ONO)V(NCNXyl)(CNXyl)}] (**6**) in 81% yield. The identity of **6** was established by X-ray diffraction and spectroscopic studies. The solid-state structure reveals a monomeric five-coordinate vanadium center that is bound by an isocyanide, a carbodiimide, and a tridentate [ONO] ligand.[21] Complex **6** occurs in a tight ion-pair form, with a potassium ion residing in the cavity created by three aryl rings of the [ONO] ligand. The IR spectrum features an absorption at 2100 cm^{-1} with a shoulder at 2132 cm^{-1} (2084 and 2113 cm^{-1} for **6-^{15}N**), indicative of carbodiimide and isocyanide coordination. The solution magnetic moment (2.6 μ_B) is in the expected range for a d^2 high-spin complex.

Treatment of **6** in THF with cryptand-222 yielded a THF-soluble salt [K(cryptand-222)][(ONO)V(NCNXyl)] (**7**) in 86% yield with the liberation of XylNC. Complex **7** crystallized as discrete cations and anions, and the solid-state structure (Figure 3) reveals a tetrahedral vanadium center with a nearly linear vanadium−carbodiimide linkage (V−N−C 171.0(3)°, N−C−N 170.2(3)°, V−N 1.968(3) Å). A strong IR absorption at 2125 cm^{-1} is attributed to the NCN stretching frequency (2105 cm^{-1} with a shoulder at 2124 cm^{-1} for **7-^{15}N**). The solution magnetic susceptibility was found to be 2.6 μ_B, consistent with a d^2 high spin complex.

The direct addition of CO/isocyanide to a nitride ligand is rare,[13,22] and subsequent extrusion of the newly formed cyanate/carbodiimide is even more unusual.[14,23] One example closely related to our reactions is carbonylation of an anionic vanadium nitride Na[{Ar(^{t}Bu)N}$_3$VN], in which complete transfer of a nitride nitrogen to CO takes place to produce [{Ar(^{t}Bu)N}$_3$V] along with release of NaNCO.[14] Our results show that nitrogen atom transfer from **3** to CO/XylNC is incomplete, and the functionalized substrate remains bound to the vanadium center. However, we have found that the cyanate ligand in **4** is readily replaced with alkynes, whereas the ion-separated cyanate **5** and the carbodiimide complexes **6** and **7** are unreactive toward alkynes under similar conditions. For **4**, the cyanate ligand departs with the potassium ion, owing to the driving force provided by precipitation of potassium cyanate in toluene. Indeed, the choice of solvent is critical, and the reaction of **4** with alkynes was not found to proceed in THF.

Accordingly, treatment of **4** with excess 2-butyne in toluene liberated potassium cyanate as a colorless precipitate with concomitant formation of diamagnetic [(ONO)V(η^2-MeCCMe)] (**8**)[15] in quantitative yield as judged by ^{1}H NMR spectroscopy. Carried out on a preparative scale, the reaction provided the alkyne adduct **8** in 79% isolated yield, and potassium cyanate was readily separated by centrifugation and characterized by ^{15}N NMR (K^{15}NCO, 68.6 ppm) and IR spectroscopy (ν_{NCO} = 2200 cm^{-1}, $\nu_{^{15}NCO}$ = 2149 cm^{-1}). Finally, the alkyne complex **8** was cleanly transformed into the starting THF adduct **1** upon dissolving **8** in THF followed by removal of volatiles under vacuum. Thus, a synthetic cycle for conversion of N$_2$ and CO into [NCO]$^-$ is completed (Scheme 2).

Scheme 2. Synthetic Cycle for the Conversion of N$_2$ and CO into [NCO]$^-$
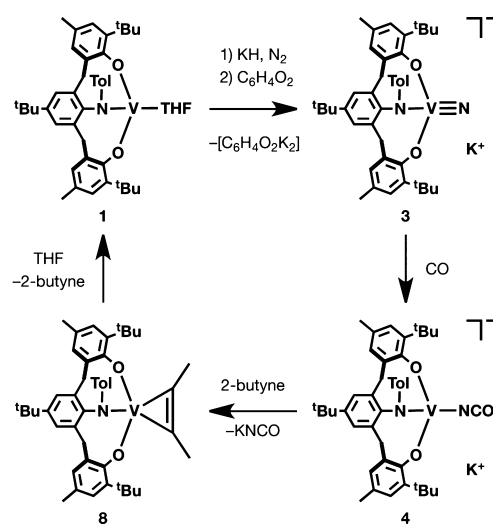
In summary, we have demonstrated N$_2$ splitting by the vanadium [ONO] complex and the ability of the resulting vanadium nitride to transfer a nitrogen atom to CO and XylNC. Redox-coupled nitrogen atom transfer mediated by an N$_2$-derived nitride complex is a challenge due to the strength of its metal−nitride bond. In our system, this problem is circumvented by the robust [ONO] ligation of vanadium and the facile accessibility of low-valent vanadium. The release of the cyanate ion is achieved with the help of alkyne. The use of a more redox-active scaffold for N$_2$ cleavage might lead to the development of synthetic processes for the incorporation of N$_2$-derived nitrogen atoms into substrates. Further synthetic and mechanistic studies are currently in progress.

■ **ASSOCIATED CONTENT**

S **Supporting Information**

Experimental details. This material is free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ **ACKNOWLEDGMENTS**

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