Two-Electron Reduction of a Vanadium(V) Nitride by CO To Release Cyanate and Open a Coordination Site

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Generation of the nitrido functional group is commonly achieved by treatment of metal complexes with azide sources and is fostered by N_2 extrusion.[1] The analogous transformation involving isocyanate and production of CO is less well documented. A previous study by Fickes et al. showed that the 1e reduction of a niobium(IV) isocyanate complex $(OCN)Nb(N[t-Bu]Ar)_3$ (1-Nb(NCO), Ar = 3,5-$Me_2C_6H_3$) results in formation of a nucleophilic, anionic terminal nitride complex $[NNb(N[t-Bu]Ar)_3]^-$ (1-NbN$^-$) with concomitant evolution of CO.[2] This, to the best of our knowledge, is the only example of terminal metal nitride derivation from an isocyanate ligand (Scheme 1A).[2,3] Curious as to the generality of this reductive decarbonylation, we sought to synthesize the analogous vanadium isocyanate complex $(OCN)V(N[t-Bu]Ar)_3$ (1-V(NCO)) to compare its reactivity with that of 1-Nb(NCO).

Scheme 1
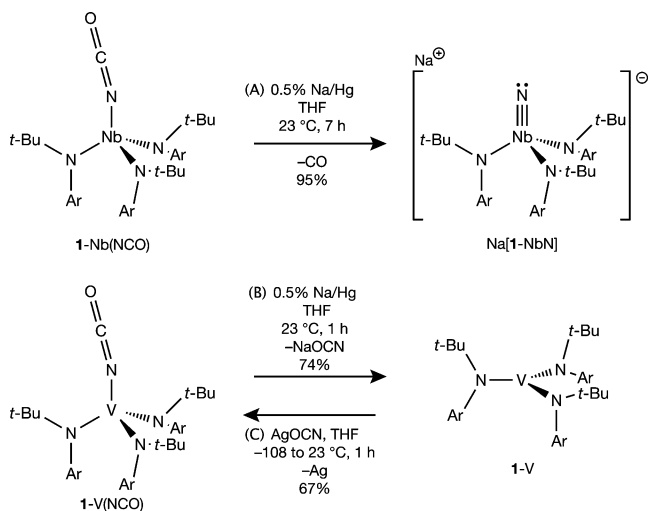
As reported herein, reduction of 1-V(NCO) leads *not* to CO evolution but rather to cyanate dissociation with concomitant opening of a coordination site to produce the known three-coordinate vanadium(III) complex $V(N[t-Bu]Ar)_3$ (1-V, Scheme 1B).[4] This observation suggested in turn that it might be possible to effect N$^-$ transfer from the nitride anion complex $[NV(N[t-Bu]Ar)_3]^-$ (1-VN$^-$) to a molecule of CO, thereby denitrogenating vanadium in a process that is the effective reverse of the reductive decarbonylation seen in the niobium system. Surprisingly, we show that CO not only denitrogenates the vanadium(V) nitride anion complex but also has no observed affinity for the empty coordination site that it thereby generates.

The required vanadium isocyanate complex 1-V(NCO) was prepared by treatment of 1-V with AgOCN in THF (Scheme 1C). Following a standard workup to remove precipitated Ag^0, 1-V(N-CO) was isolated in 67% yield as large black crystals by storing

saturated *n*-pentane solutions of 1-V(NCO) at −35 °C. Complex 1-V(NCO) is characterized by a strong ν_{NCO} at 2207 cm^{-1} in its IR spectrum,[5] an eight line pattern in its EPR spectrum (20 °C, benzene solution) that results from hyperfine coupling to the $I = 7/2$ vanadium nucleus ($g = 1.97$, $a = 6.44 \times 10^{-3}$ cm^{-1}), an effective magnetic moment of 2.0 μ_B (20 °C, benzene solution), and two broad electronic transitions centered at 490 ($\varepsilon = 3200$) and 600 nm ($\varepsilon = 2600$) that span the visible region of the electromagnetic spectrum. The assignment of an *N*-bound isocyanate ligand was supported by a crystallographic study in which refinement statistics for the *N*-bound model ($wR_2 = 0.100$) were markedly better than those for the *O*-bound case ($wR_2 = 0.125$). The solid-state structure of 1-V(NCO) reveals a V−N interatomic distance of 1.955(1) Å for the isocyanate ligand and an average V−N distance of 1.886(1) Å for the anilide ligands (Figure 1). The isocyanate coordination mode is nonlinear with a V−N−C angle of 150.6(1)°, on par with other isocyanate complexes.[6]

With 1-V(NCO) in hand, attention turned to probing the redox chemistry of the complex. When treated with 0.5% Na/Hg in the same manner as that for 1-Nb(NCO), 1-V(NCO) undergoes cyanate dissociation to give 1-V and sodium cyanate (Scheme 1B). Formation of 1-V is also observed when Na/Hg is replaced with KC_8 or $(THF)_3Mg(C_{14}H_{10})$. This result was not entirely unanticipated given the synthetic availability of 1-V and the pseudohalide nature of cyanate.[4] To gain some insight into the contrasting electrochemistry of 1-V(NCO) and 1-Nb(NCO), cyclic voltammetric methods were used to quantify the reduction potentials of the metal complexes. The CV of 1-V(NCO) is marked by two electrochemical events. The first of these is assigned to the V^{5+}/V^{4+} couple with an $E_{1/2} = -0.11$ V vs Fc/Fc$^+$ (Fc = $(C_5H_5)_2$Fe). This event is quasireversible with the ratio i_c/i_a dependent on the sweep rate. The second event appears reversible at sweep rates between 10 and 300
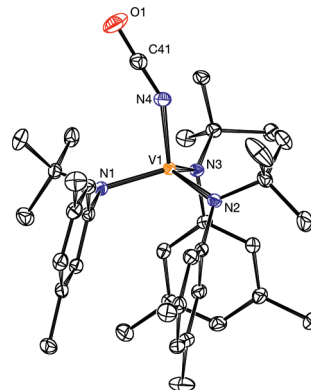

Figure 1. Solid-state structure of 1-V(NCO) with thermal ellipsoids at 50% probability and hydrogens omitted for clarity. Selected bond lengths (Å) and angles (deg): V1−N4 1.955(1), N4−C41 1.182(2), C41−O41 1.889(2), V1−N1 1.870(1), V1−N2 1.882(1), V1−N3 1.906(1), V1−N4−C41 150.6(1).

mV/s and is assigned to the V^{4+}/V^{3+} couple with $E_{1/2} = -1.56$ V vs Fc/Fc^+. Complex **1**-Nb(NCO) likewise displays two redox events in its CV. One event, assigned as the 1e oxidation of **1**-Nb(NCO) (Nb^{5+}/Nb^{4+} couple), has an $E_{1/2} = -1.1$ V vs Fc/Fc^+ and is quasireversible. The other event is centered at -2.9 V vs Fc/Fc^+ and is completely irreversible (see Supporting Information, SI). Assigned to a metal-centered Nb^{4+}/Nb^{3+} reduction, the irreversibility of this process is consistent with 1e reduction resulting in rapid decarbonylation of **1**-Nb(NCO) (*vide supra*), the process of interest.

Given the observed propensity for cyanate dissociation from the vanadium metal center upon reduction of **1**-V(NCO), the question arose as to whether CO could effect N^- transfer from **1**-VN^- with formal 2e reduction of vanadium. No change was observed upon mixing when a solution of Na[**1**-VN] in THF was treated with 1 atm of CO at 23 °C. However, over the course of 24 h, a gradual color change did ensue from bright yellow to dark forest green. After removing the volatile components from the reaction mixture under reduced pressure, the resulting dark green-brown residue was extracted with *n*-hexane and filtered through a sintered glass frit. Concentration and subsequent storage of the filtrate at −35 °C gave dark green crystals of **1**-V, as confirmed by spectroscopic methods,[7] in 71% yield (eq 1). The IR spectrum of an off-white powder collected in the initial filtration revealed it to be the reaction coproduct sodium cyanate ($\nu_{NCO} = 2228$ cm^{-1}). The yield of sodium cyanate was measured to be 77% through gravimetric analysis.[8] To further confirm the formation of sodium cyanate, the treatment was repeated using ^{13}CO. The ^{13}C NMR spectrum of the off-white powder dissolved in D_2O contained a single resonance centered at 129 ppm (see SI), in agreement with the reported chemical shift of cyanate.[9] Additionally, the reaction was monitored via ^{1}H and ^{51}V NMR by carrying it out in flame-sealed NMR tubes. Under a static atmosphere of 1 atm of CO, the reaction proceeds to completion in just over 24 h with complete consumption of Na[**1**-VN], concomitant formation of **1**-V, and no observed intermediates. Furthermore, the addition of 2 equiv of 12-crown-4 as a sodium-sequestering reagent to the reaction mixture had no qualitative effect on the rate of reaction as assayed by NMR.
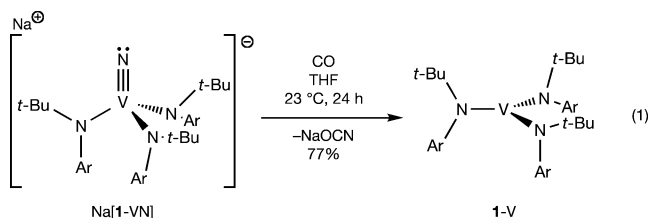
The complete transfer of the N^- ligand can be thought of as an atypical example of metallanitrene chemistry. The reaction of metallanitrenes ($L_nM{=}NR$) with CO to give bound organic isocyanate ligands ($L_nM(RNCO)$) is well documented, but in these examples, the metallanitrene nitrogen atom is often considered electrophilic.[10] The terminal nitride ligand of **1**-VN^- is known to be a competent nucleophile,[11] leading us to suggest that the reaction of eq 1 may proceed via nucleophilic attack on CO. Interestingly, this nitrogen-transfer reactivity does not extend to isonitriles, as evidenced by a lack of any observed reaction between **1**-VN^- and *t*-BuNC (THF, 23 °C, 3 d). Although it does not seem probable that isocyanate formation proceeds through initial coordination of CO to the metal center, due to steric effects of the ancillary ligand

set and the d^0 electron count of vanadium, such a pathway cannot be ruled out. Furthermore, this reaction is effectively the reverse of the decarbonylation observed in the reduction of **1**-Nb(NCO) (Scheme 1A) and can be likened to an isoelectronic reverse reaction of azide oxidation of **1**-V, the method originally used to synthesize **1**-VN^-.[11]

N^- abstraction by CO as documented herein is remarkable and complements previously observed reactivity of metal−ligand multiple bonds with CO. Both terminal imido and bridging nitrido ligands have been shown to combine with CO while effecting 2e reduction of the ligated metal.[12–16] Similarly, discrete metal complexes bearing oxo ligands have been shown to provide CO_2 upon treatment with CO,[17] and heterogeneous catalysis provides many examples of CO acting as a terminal reducing agent on metal oxide materials to produce CO_2.[18] In addition, the newly observed reactivity may shed light on the process of isocyanate formation observed in the reaction of CO with NH_3 over transition metal surfaces.[19,20] Our observation of simple, complete transfer of N^- to CO to generate free $(NCO)^-$ significantly enlarges the precedent for transformations of this type. Furthermore, the generation of an open coordination site that has no observed affinity for CO leaves the door open for the metal center to engage in further chemistry, an attractive feature for catalytic schemes.

Supporting Information Available: Experimental details for the synthesis of **1**-V(NCO) and **1**-V, crystallographic data on **1**-V(NCO), and electrochemical data on **1**-V(NCO) and **1**-Nb(NCO). This material is available free of charge via the Internet at http://pubs.acs.org.

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