

A Nitridoniobium(V) Reagent That Effects Acid Chloride to Organic Nitrile Conversion: Synthesis via Heterodinuclear (Nb/Mo) Dinitrogen Cleavage, Mechanistic Insights, and Recycling

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Abstract: The transformation of acid chlorides (RC(O)Cl) to organic nitriles (RC≡N) by the terminal niobium nitride anion $[\text{N}=\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3]^-$ (**1a-N**⁻), where Np = neopentyl and Ar = 3,5-Me₂C₆H₃) via isovalent N for O(Cl) metathetical exchange is presented. Nitrido anion **1a-N**⁻ is obtained in a heterodinuclear N₂ scission reaction employing the molybdenum trisamide system, Mo(N[R]Ar)₃ (R = *t*-Bu, **2a**; R = Np, **2b**), as a reaction partner. Reductive scission of the heterodinuclear bridging N₂ complexes, (Ar[R]N)₃Mo-(μ-N₂)Nb(N[Np]Ar)₃ (R = *t*-Bu, **3b**; R = Np, **3c**) with sodium amalgam provides 1 equiv each of the salt Na**1a-N** and neutral N≡Mo(N[R]Ar)₃ (R = *t*-Bu, **2a-N**; R = Np, **2b-N**). Separation of **2-N** from Na**1a-N** is readily achieved. Treatment of salt Na**1a-N** with acid chloride substrates in tetrahydrofuran (THF) furnishes the corresponding organic nitriles concomitant with the formation of NaCl and the oxo niobium complex O≡Nb(N[Np]Ar)₃ (**1a-O**). Utilization of ¹⁵N-labeled ¹⁵N₂ gas in this chemistry affords a series of ¹⁵N-labeled organic nitriles establishing the utility of anion **1a-N**⁻ as a reagent for the ¹⁵N-labeling of organic molecules. Synthetic and computational studies on model niobium systems provide evidence for the intermediacy of both a linear acylimido and niobacyclobutene species along the pathway to organic nitrile formation. High-yield recycling of oxo **1a-O** to a niobium triflate complex appropriate for heterodinuclear N₂ scission has been developed. Specifically, addition of triflic anhydride (Tf₂O, where Tf = SO₂CF₃) to an Et₂O solution of **1a-O** provides the bistriflate complex, Nb(OTf)₂(N[Np]Ar)₃ (**1a-(OTf)₂**), in near quantitative yield. One-electron reduction of **1a-(OTf)₂** with either cobaltocene (Cp₂Co) or Mg(THF)₃(anthracene) provided the monotriflate complex, Nb(OTf)(N[Np]Ar)₃ (**1a-(OTf)**), which efficiently regenerates complexes **3b** and **3c** when treated with the molybdenum dinitrogen anions $[\text{N}_2\text{Mo}(\text{N}[\text{t-Bu}]\text{Ar})_3]^-$ (**2a-N₂**⁻) or $[\text{N}_2\text{Mo}(\text{N}[\text{Np}]\text{Ar})_3]^-$ (**2b-N₂**⁻), respectively.

Introduction

Strong chemical bonds introduce an energy barrier to the utilization in synthesis of certain abundant small molecules; the triple NN bond in the dinitrogen molecule, the CO double bonds in carbon dioxide, and the single CH bonds in methane being spotlight examples. This is why “reagents and pathways for breaking into chemical bonds previously considered to be inert,” and “means for converting naturally abundant substances into chemically useful building blocks,” find a nexus on the wish list of grand challenges envisioned by today’s chemists.^{1,2}

In the case of dinitrogen, several reactions in which soluble transition-metal complexes bind the N₂ molecule and effect complete scission of its 226 kcal/mol triple bond to give nitride (N³⁻, alternatively “nitrido”) systems now are recognized for molybdenum,^{3–9} niobium,^{10–12} and vanadium.¹³ Dinitrogen cleavage reactions have frequently been the subject of theoretical

studies.^{14–19} In one instance a heterodinuclear system (Mo/Nb, Scheme 1) has been reported to deliver smooth dinitrogen

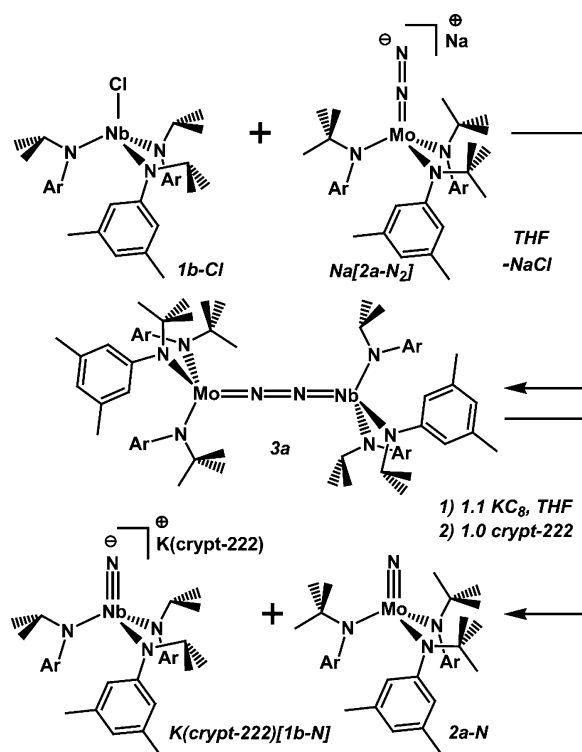
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Scheme 1



cleavage.²⁰ This affords in 1:1 stoichiometry a neutral terminal nitridomolybdenum(VI) complex and an isoelectronic anionic terminal nitridoniobium(V) reagent, as its alkali metal salt (Scheme 1). “Reagent” is used as a descriptor in the preceding sentence with reference to the title RC(O)Cl → RCN transformation, as will become clear shortly.

Organic nitriles (RCN, where R = variable substituent) are attractive organic building blocks for which metal-mediated syntheses are not numerous. Most common are Pd- or Cu-catalyzed aromatic nitrile syntheses that require a source of cyanide ion.^{21–25} Similarly, beginning with the CN bond already intact, a zirconium-based method focusing on carboxamide dehydration (RC(O)NH₂ → RCN) has been reported recently.²⁶ In contrast, metal-mediated methods for CN triple bond *generation* represent a new vista and one that is especially inviting for establishing the connection with dinitrogen cleavage chemistries. A first example of organic nitrile synthesis from corresponding acid chlorides via an N for O(Cl) isovalent exchange process was reported recently;²⁷ it employed the four-coordinate nitridotungsten(VI) complex NW(N[*i*-Pr]Ar)₃ (Ar = 3,5-

C₆H₃Me₂), which is not yet available from N₂. Now we show that the anionic nitridoniobium(V) reagent NNb(N[Np]Ar)₃¹⁻, employed as its sodium salt, is both readily synthesized with dinitrogen as its nitrido nitrogen source *and* serves to smoothly transform acid chlorides into corresponding organic nitriles.

Because dinitrogen can be incorporated stoichiometrically with the chemistry described herein, efficient transfer of an ¹⁵N isotopic label into the organic nitrile product is possible. That the combination of dinitrogen cleavage chemistries with ¹⁵N-isotope labeling strategies is an attractive prospect has been pointed out in the context of a nitridotungsten(VI)-catalyzed ¹⁵N-atom exchange between acetonitrile and benzonitrile.²⁸ Thus, one of the goals of the present work is to provide a reagent for the RC(O)Cl → RC¹⁵N transformation, wherein the isotopic label derives from the economical elemental source, ¹⁵N₂.

While much current research is devoted to the discovery of mild, metal-catalyzed methods for synthesizing ammonia from dinitrogen,^{29–35} there is impetus also for discovery of NH₃-independent methods of N₂-derived nitrogen atom incorporation into organic molecules.³⁶ It is the latter pathway to which the chemistry described herein contributes, being concerned with the interchange of N≡N, N≡M, and finally N≡C triple bonds. In this respect the *cleavage* of organonitrile CN triple bonds by ditungsten systems,³⁷ a key to the synthesis of tungsten(VI) alkylidyne complexes that perform beautifully as alkyne meta-thesis catalysts,³⁸ is relevant background material.

Despite the relative simplicity of the complexes promulgated herein (monodentate secondary amine-derived supporting ligands), a desirable feature would be the ability to reuse them for dinitrogen cleavage following an N-atom transfer operation (e.g., nitrile synthesis). This paper shows accordingly how the oxoniobium(V) byproduct of acid chloride transformation can be recycled in high yield by conversion into its corresponding bistriflate. This is an important and not an intuitive point given the great stability of the oxoniobium(V) functional group.

Also treated herein are mechanistic issues surrounding the acid chloride to nitrile transformation. Acylimido complexes,^{27,39–42} produced by terminal nitride acylation, are implicated as the key intermediates. Stability of the intermediate acylimido complexes is found to be quite sensitive to the choice of ancillary ligand steric attributes. Density functional theory (DFT) computational methods have been brought to bear on the profile of the overall reaction coordinate for acid chloride to organic nitrile transformation by anionic nitridoniobium(V) complexes.

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Experimental Section

General Considerations. Unless otherwise stated, all manipulations were carried out at room temperature, under an atmosphere of purified dinitrogen by use of a Vacuum Atmospheres glovebox or Schlenk techniques. All solvents were obtained anhydrous and oxygen-free according to standard purification procedures. Tetrahydrofuran- d_8 (THF- d_8) was vacuum-transferred from Na metal and stored in the glovebox over 4 Å molecular sieves for at least 3 days prior to use. Benzene- d_6 (C_6D_6) was degassed and stored similarly. Celite 435 (EM Science) and 4 Å molecular sieves (Aldrich) were dried under vacuum at 250 °C overnight and stored under dinitrogen. Gaseous $^{15}N_2$ (99.9% ^{15}N) was purchased from Cambridge Isotope Laboratories in 100 mL break-seal containers. Solid NaOMe was slurried in anhydrous THF under an N_2 atmosphere for 24 h before being dried at ca. 180 °C under vacuum for an additional 24 h. All other reagents were purchased from commercial sources and purified according to standard procedures or prepared as specified in the literature. All glassware was oven-dried at a temperature of 230 °C prior to use.

Solution 1H and ^{13}C NMR spectra were recorded on Varian XL-300 MHz and Varian INOVA 500 MHz spectrometers. 1H and ^{13}C chemical shifts are reported with reference to residual solvent resonances of 7.16 ppm (1H) and 128.3 ppm (^{13}C) for benzene- d_6 or 1.73 ppm (1H) and 67.57 ppm (^{13}C) for THF- d_8 . Solution ^{15}N NMR spectra were recorded on a Bruker Advance-600 spectrometer operating at a resonance frequency of 60.84 MHz. ^{15}N NMR chemical shifts are reported with reference to external formamide- ^{15}N ($H_2^{15}NC(O)H$, 55/45 v/v in dimethyl sulfoxide, DMSO); 113.0 ppm relative to liquid NH_3 (0.0 ppm). Solution IR spectra were recorded on a Perkin-Elmer 1600 series Fourier transform infrared (FTIR) spectrometer. All spectra were recorded in C_6D_6 by use of a solution cell equipped with KBr windows. Solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to that of the sample. Combustion analyses were carried out by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Desilylation of $(Me_3SiN_2)Mo(N[*t*-Bu]Ar)_3$ ($2a-N_2SiMe_3$) with Sodium Methoxide: Optimized Synthesis of $Na[(N_2)Mo(N[*t*-Bu]Ar)_3]$ ($Na[2a-N_2]$). To a THF solution of $2a-N_2SiMe_3$ (3.00 g, 4.13 mmol, 20 mL),⁶ was added anhydrous NaOMe (1.11 g, 20.6 mmol, 5.0 equiv). The reaction mixture was allowed to stir for 24 h while it gradually changed color from orange to magenta. All volatile materials were then removed under reduced pressure and the excess NaOMe was removed by extraction of the resulting purple residue with *n*-pentane (50 mL), followed by filtration through Celite. Concentration of the filtrate to 10 mL and cooling to -35 °C for 1–2 days provided $Na[2a-N_2]$ as orange crystals in 70–80% yield. Spectroscopic data for $Na[2a-N_2]$ prepared by this method were identical to those reported previously.⁶ For the ^{15}N -labeled variant, $Na[2a-^{15}N_2]$, NaOMe and $2a-^{15}N_2SiMe_3$ were allowed to react under static vacuum in order to avoid $^{14}N_2/^{15}N_2$ exchange.

Synthesis of $Mo(H)(\eta^2-t-Bu(H)C=NAr)(N[Np]Ar)_2$ ($2b-H$). To a thawing suspension of $MoCl_3(THF)_3$ ⁴³ (10.0 g, 23.8 mmol) in Et_2O (150 mL) was added solid $(Et_2O)Li(N[Np]Ar)$ ⁴⁴ (13.6 g, 50.1 mmol). The headspace of the reaction flask was evacuated and the reaction was allowed to stir for 6 h. During this time the color of the mixture gradually changed to purple-brown. The mixture was then filtered through Celite to remove LiCl and unreacted $MoCl_3(THF)_3$; the Celite was washed with additional Et_2O (30 mL). The filtrate was dried under vacuum and the resulting purple-brown residue was extracted with *n*-pentane (100 mL) and filtered through Celite, upon which an intractable purple solid remained. The filtrate was concentrated to dryness and the residue was dissolved in Et_2O (75–100 mL). This

solution was stored, under vacuum, at -35 °C for 1–2 days, whereupon purple-brown crystals of $2b-H$ formed and were collected. The mother liquor was reduced to approximately half the original volume and chilled again to produce a second crop of crystals. Yield 7.14 g, 10.7 mmol, 45% (avg) based on multiple syntheses. 1H NMR (500 MHz, C_6D_6 , 20 °C): δ = 2.00 (br) and 1.50 (br) ppm. μ_{eff} (Evans method) = 1.64 μ_B . Anal. Calcd. for $C_{39}H_{60}N_3Mo$: C, 70.24; H, 9.07; N, 6.30. Found: C, 71.01; H, 9.48; N, 6.01.

Synthesis of $Na[(N_2)Mo(N[Np]Ar)_3]$ ($Na[2b-N_2]$). In a dinitrogen-atmosphere glovebox, freshly prepared 1% sodium amalgam (Na; 0.350 g, approximately 10 equiv) was added to a THF solution of $Mo(H)(\eta^2-t-Bu(H)C=NAr)(N[Np]Ar)_2$ ($2b-H$, 1.00 g, 1.50 mmol, 50 mL). The reaction mixture was vigorously stirred for 20 h at room temperature while it was exposed to the N_2 atmosphere through an open gas-adaptor port. The color of the solution was observed to gradually change from purple-brown to dark green. The mother liquor was decanted from the amalgam and evaporated to dryness under vacuum, resulting in a dark green residue. Addition of *n*-pentane (40 mL) resulted in a red-orange solution, which was filtered through Celite and dried under vacuum. Addition of *n*-pentane (15 mL) to the resulting red-orange residue, followed by cooling to -35 °C for 30 min, precipitated essentially pure $Na[2b-N_2]$ (1H NMR, C_6D_6). Yield: 1.933 g, 2.70 mmol, 60% (avg) based on three separate syntheses. Analytically pure, cherry-red single crystals of $Na(Et_2O)[2b-N_2]$ were obtained from a saturated, Et_2O solution stored at -35 °C for 2 days. The ^{15}N -labeled variant, $Na[2b-^{15}N_2]$, was prepared identically under an atmosphere of 99.9% $^{15}N_2$. 1H NMR (500 MHz, C_6D_6 , 20 °C): δ = 6.61 (br s, 6H, *o*-Ar), 6.49 (s, 3H, *p*-Ar), 4.32 (br s, 6H, N-CH₂), 2.19 (s, 18H, Ar-CH₃), and 1.00 (br s, 27H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6 , 20 °C): δ = 159.3.8 (ipso-Ar), 138.9 (*m*-Ar), 122.4 (*p*-Ar), 119.9 (*o*-Ar), 84.9 (N-CH₂), 36.0 (C(CH₃)₃), 29.1 (C(CH₃)₃), and 22.1 (Ar-CH₃) ppm. FTIR (KBr windows, C_6D_6 solution): (ν_{NN}) 1730 cm^{-1} also 2949, 2873, 1584, 1473, 1069, and 681 cm^{-1} . For $Na[2b-^{15}N_2]$, (ν_{NN}) 1784 and 1674 cm^{-1} . Anal. Calcd. for $C_{43}H_{68}N_5OMoNa$ (etherate): C, 65.38; H, 8.68; N, 8.87. Found: C, 65.24; H, 8.80; N, 8.52.

Synthesis of $Nb(I)(N[Np]Ar)_3$ ($1a-I$). To a thawing THF solution of $1a-I_2$ (4.500 g, 4.90 mmol, 75 mL)⁴⁴ was added solid $Mg(THF)_3$ -anthracene (1.128 g, 2.690 mmol, 0.55 equiv). The reaction mixture was allowed to warm to room temperature and was stirred for 1.5 h, during which time it was observed to gradually change in color from orange to purple. All volatile materials were removed in vacuo and the resulting purple-brown residue was extracted with *n*-pentane (40 mL) and filtered through Celite to remove MgI_2 and anthracene. The purple filtrate was then reduced to a volume of 20 mL and frozen. Upon thawing, the solution was quickly cold-filtered through Celite to remove residual anthracene and unreacted $1a-I_2$. The resulting purple filtrate was then reduced to a volume of 15 mL and stored at -35 °C for 2 days, whereupon a purple crystalline solid was obtained and collected. Yield: 1.270 g, 1.61 mmol, 33.0% in two crops. 1H NMR (500 MHz, C_6D_6 , 20 °C): δ = 2.00 (br s) ppm. μ_{eff} (Evans method) = 1.81 μ_B . Anal. Calcd. for $C_{39}H_{60}N_3INb$: C, 59.24; H, 7.65; N, 5.31. Found: C, 59.03; H, 7.60; N, 5.18. Unreacted, orange $1a-I_2$ (contaminated with approximately 25% anthracene) can be recovered by washing the Celite pad with Et_2O (25–30 mL) followed by drying of the filtrate. The resulting orange residue was then slurried in cold *n*-pentane and filtered. Yield of recovered $1a-I_2$: 1.050 g, 1.14 mmol, 23%.

Optimized Synthesis of $ONb(N[Np]Ar)_3$ ($1a-O$) and $Nb(OTf)_2(N[Np]Ar)_3$ ($1a-OTf$). To a thawing Et_2O solution of $ONbCl_3(THF)_2$ (15.0 g, 41.7 mmol, 75 mL) was added solid $(Et_2O)Li(N[Np]Ar)$ (33.9 g, 125.1 mmol, 3 equiv). The reaction mixture was allowed to warm to room temperature and stir for 2.5 h, during which time it gradually became dark brown in color. Removal of the solvent in vacuo followed by extraction with pentane, filtration, and evaporation of the brown filtrate to dryness, provided $1a-O$ as a dark brown residue, which was redissolved in Et_2O (30 mL). Pure $1a-O$ can be obtained as golden-

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yellow blocks in 55% yield from storage of the Et₂O solution at –35 °C for 2 days. However, addition of triflic anhydride (Tf₂O, 17.6 g, 62.5 mmol, 1.5 equiv) directly to the *chilled*, brown filtrate—without isolation of **1a-O**—effected the precipitation of bright-yellow **1a-(OTf)**₂, which was collected by filtration (yield 26.87 g, 27.9 mmol, 67% from ONbCl₃(THF)₂). The spectroscopic properties of **1a-O** and **1a-(OTf)**₂ were identical to those reported previously.⁴⁵

Synthesis of Nb(O₃SCF₃)₂(N[Np]Ar)₃ (1a-OTf**).** The synthesis of **1a-OTf** was performed analogously to that of **1a-I**, employing 1.00 g (1.04 mmol) of **1a-(OTf)**₂ and 0.239 g (0.571 mmol, 0.55 equiv) of Mg(THF)₃(anthracene). Storage of an *n*-pentane solution at –35 °C for 1 day provided purple-green crystals of **1a-OTf**. Yield: 0.338 g, 0.416 mmol, 40%. μ_{eff} (Evans method) = 2.1 μ_{B} . ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 1.789 (br s) and 2.20 (br s) ppm. Anal. Calcd. for C₄₀H₆₀N₃O₃F₃SNb: C, 59.10; H, 7.44; N, 5.17. Found: C, 59.12; H, 7.51; N, 5.07.

Cobaltocene (Cp₂Co) Reduction of Nb(O₃SCF₃)₂(N[Np]Ar)₃ (1a-(OTf)**₂): Alternative Synthesis of **1a-OTf**.** Separately, a 3 mL THF solution of **1a-(OTf)**₂ (1.1 g, 1.14 mmol) and a 2 mL THF solution of Cp₂Co (0.227 g, 1.20 mmol, 1.05 equiv) were frozen in a glovebox cold well (liquid N₂). Upon removal from the cold well, the thawing solution containing Cp₂Co was added dropwise over 3 min to the thawing solution of **1a-(OTf)**₂, eliciting a color change from bright orange to brown-purple. The reaction mixture was allowed to stir at room temperature for 45 min, whereupon all volatile materials were removed in vacuo. The resulting brown residue was extracted with *n*-pentane (3 mL) and filtered through Celite to remove the orange [Cp₂Co][O₃SCF₃] byproduct. Evaporation and redissolution of the filtrate in *n*-pentane provided purple-green crystals of **1a-OTf** when stored at –35 °C. Yield: 0.575 g, 0.707 mmol, 62% in three crops.

Synthesis of Heterodinuclear N₂ Complexes (Ar[Np]N)₃Nb(μ -N₂)-Mo(N[*t*-Bu]Ar)₃ (3b**) and (Ar[Np]N)₃Nb(μ -N₂)/Mo(N[Np]Ar)₃ (**3c**).** Separately, a 10 mL THF solution of **1a-I** (2.50 g, 3.16 mmol) and a 10 mL THF solution of the corresponding molybdenum dinitrogen anion salt (Na[**2a-N**]₂) for **3b**, 2.13 g, 3.16 mmol; Na[**2b-N**]₂) for **3c**, 2.25 g, 3.16 mmol) were frozen in a glovebox cold well cooled externally with liquid nitrogen. Upon removal from the cold well, approximately 4 mL of the thawing solution containing **1a-I** was added dropwise over 1 min to the thawing solution of the molybdenum salt, eliciting a color change from red-orange to green. The reaction mixture was allowed to stir for an additional 3 min, whereupon both solutions were placed back into the cold well. This procedure was repeated two more times until complete addition of **1a-I** was achieved. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 30 min before being evaporated to dryness. The residue obtained was extracted with *n*-pentane (10 mL) and filtered through Celite to remove the NaI byproduct, and the resulting filtrate was evaporated to dryness. The resulting green powders obtained were sufficiently pure for subsequent synthetic applications. However, crystalline material could be obtained by storing Et₂O solutions of either **3b** or **3c** at –35 °C for several days. The monotriflate-Nb(IV) complex, **1a-OTf**, can be readily substituted for **1a-I** in this procedure, resulting in comparable yields of **3b** and **3c**.

3b. Yield 2.24 g, 1.70 mmol, 54%. μ_{eff} (Evans method) = 2.36 μ_{B} . ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 4.4 (br), 2.2 (br), and 1.5 (br) ppm. FTIR (KBr windows, C₆D₆ solution): (ν_{NN}) 1564 cm⁻¹. For **3b**-¹⁵N₂, (ν_{NN}) 1519 cm⁻¹. Anal. Calcd. for C₇₅H₁₁₄N₈NbMo: C, 68.95; H, 8.90; N, 8.25. Found: C, 69.15; H, 9.01; N, 8.49.

3c. Yield 2.06 g, 1.52 mmol, 48%. μ_{eff} (Evans method) = 2.58 μ_{B} . ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 2.1 (br) and 1.5 (br) ppm. FTIR (KBr windows, C₆D₆ solution): (ν_{NN}) 1576 cm⁻¹. For **3c**-¹⁵N₂, (ν_{NN}) 1515 cm⁻¹. Anal. Calcd. for C₇₈H₁₂₀N₈NbMo: C, 68.95; H, 8.90; N, 8.25. Found: C, 68.33; H, 9.12; N, 8.44.

Reductive Cleavage of (Ar[Np]N)₃Nb(μ -N₂)/Mo(N[Np]Ar)₃ (3c**): Synthesis of [Na][NNb(N[Np]Ar)₃] (Na[**1a-N**]) and NMo(N[Np]Ar)₃ (**2b-N**).** To a THF solution of **3c** (2.0 g, 1.47 mmol, 15 mL) was added

an excess of freshly prepared 1% sodium amalgam (Na: 0.135 g, 5.86 mmol, 4 equiv/Nb). The reaction mixture was allowed to stir at room temperature for 2 h, during which time it was observed gradually to change in color from green to orange-brown. The solution was then decanted from the amalgam and evaporated to dryness under reduced pressure. The resulting orange-brown residue was then extracted with *n*-pentane and filtered through Celite. The filtrate was then concentrated to dryness under reduced pressure. The resulting residue was then exposed to two cycles of *n*-pentane (~3 mL) addition and evaporation in order to completely separate THF from Na[**1a-N**]. Dissolving the residue so obtained in *n*-pentane (4 mL), followed by cooling to –35 °C for 30 min, followed by filtration, provided pure Na[**1a-N**] as an off-white powder. Evaporation of the filtrate followed by dissolution of the resulting residue in Et₂O and cooling to –35 °C produced orange single crystals of **2b-N** after 2 days (72%). Complex **3b** can be substituted for **3c** in this procedure, providing Na[**1a-N**] in 80% yield (0.824 g, 1.17 mmol) after precipitation from *n*-pentane and the nitrido molybdenum complex **2a-N**^{3,4,6,8,36,46} in 75% yield (0.704 g, 1.10 mmol) after crystallization from Et₂O.

Na[1a-N**].** Yield 0.824 g, 1.17 mmol, 80%. ¹H NMR (500 MHz, THF-*d*₈, 20 °C): δ = 6.26 (s, 6H, *o*-Ar), 6.11 (s, 3H, *p*-Ar), 4.36 (s, 6H, N-CH₂), 1.90 (s, 18H, Ar-CH₃), and 0.83 (s, 27H, *t*-Bu) ppm. ¹³C{¹H} NMR (125.8 MHz, THF-*d*₈, 20 °C): δ = 159.3 (ipso-Ar), 137.7 (*m*-Ar), 120.9 (*p*-Ar), 119.9 (*o*-Ar), 74.6 (N-CH₂), 36.4 (C(CH₃)₃), 29.9 (C(CH₃)₃), and 21.8 (Ar-CH₃) ppm. ¹⁵N NMR (60.84 MHz, THF-*d*₈, 20 °C): δ = 754 (s) ppm. Anal. Calcd. for C₃₉H₆₀N₄NbNa: C, 66.84; H, 8.63; N, 7.99. Found: C, 67.08; H, 8.94; N, 8.12. Single crystals of yellow [Na(THF)₃][**1a-N**] were obtained by allowing a saturated THF solution of Na[**1a-N**] to stand at –35 °C for several days.

2b-N. Yield 0.720 g, 1.05 mmol, 72%. ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 6.50 (s, 3H, *p*-Ar), 6.26 (s, 6H, *o*-Ar), 4.98 (s, 6H, N-CH₂), 1.94 (s, 18H, Ar-CH₃), and 1.10 (s, 27H, *t*-Bu) ppm. ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 20 °C): δ = 155.8 (ipso-Ar), 138.8 (*m*-Ar), 126.7 (*p*-Ar), 122.7 (*o*-Ar), 85.5 (N-CH₂), 36.0 (C(CH₃)₃), 29.3 (C(CH₃)₃), and 21.7 (Ar-CH₃) ppm. ¹⁵N NMR (60.84 MHz, THF-*d*₈, 20 °C): δ = 870 (s) ppm. Anal. Calcd. for C₃₉H₆₀N₄Mo: C, 68.80; H, 8.88; N, 8.23. Found: C, 68.60; H, 8.95; N, 8.11.

General Procedure for Niobium-Mediated ¹⁵N-Labeled Nitrile Generation from Acid Chloride Substrates. To a THF-*d*₈ solution of Na[¹⁵NNb(N[Np]Ar)₃] (Na[**1a**-¹⁵N]), 0.050 g, 0.071 mmol, 1.5 mL) was added a THF-*d*₈ solution of the appropriate acid chloride substrate (0.95 equiv in all cases, 0.5 mL) at room temperature. A rapid color change from pale brown to yellow orange accompanied the addition. For acid chloride substrates resulting in a volatile organonitrile, the volatile components of the reaction mixture were vacuum-transferred to a flame-sealable NMR tube for analysis. The nonvolatile oxoniobium byproduct, **1a-O**, was liberated from NaCl by extraction with *n*-pentane, followed by filtration of the extract, and set aside for further use. For reactions generating a nonvolatile organonitrile, the reaction mixture was allowed to stir for 20 min after addition of the acid chloride and then evaporated to dryness, after which the dry residue was extracted with *n*-pentane, the extract was filtered, and the filtrate was evaporated to dryness. THF-*d*₈ was then used to dissolve the crude residue immediately prior to spectroscopic analysis. For the latter samples, **1a-O** was present in solution during analysis.

Attempted Observation of Acylimido Intermediates (R(O)CN=Nb(N[Np]Ar)₃; **4a, R = Me, *t*-Bu, **1-Ad**).** To a Teflon-capped NMR tube (J-Young) were added sequentially a THF-*d*₈ solution of Na[**1a-N**] (0.015 g, 0.021 mmol, 0.4 mL), a 0.1 mL buffer zone of neat THF-*d*₈, and a 0.3 mL THF-*d*₈ solution containing 0.95 equiv of pivaloyl chloride (*t*-BuC(O)Cl). After each sequential addition, the sam-

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ple was frozen in a glovebox cold well (liquid N₂) to prevent premature mixing of the layers. The total concentration of Na[**1a-N**] was 2.6 mM. The sample was transported frozen to the spectrometer, whereupon reactants were allowed to mix upon melting of the mixture, immediately prior to ¹H NMR data acquisition. The resulting ¹H NMR spectra contained resonances characteristic exclusively of the reactants and products. No new resonances were observed when additional spectra were intermittently acquired during the process of sample warming to ambient temperature (20 °C, ca. 20 min). Identical results were obtained when 1-adamantoyl or acetyl chloride was employed in this experiment.

Synthesis of *t*-BuC(O)N=Nb(N[*t*-Bu]Ar)₃ (1c-NC(O)-*t*-Bu**).** To a thawing THF solution of Na[**1c-N**]^{47,48} (0.200 g, 0.30 mmol, 3 mL) was added dropwise an equally cold THF solution of *t*-BuC(O)Cl (0.034 g, 0.28 mmol, 0.95 equiv, 2 mL). The resulting pale-yellow reaction mixture was allowed to stir for 45 min before all volatile components were removed under reduced pressure. Extraction of the residue with *n*-pentane, followed by filtration through Celite and evaporation, provided crude **1c-NC(O)-*t*-Bu** as a pale-yellow powder. Near-colorless crystals of **1c-NC(O)-*t*-Bu** were obtained by Et₂O recrystallization at -35 °C (2 days). Yield: 0.131 g, 0.182 mmol, 60%. ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 6.71 (s, 3H, *p*-Ar), 6.02 (s, 6H, *o*-Ar), 2.12 (s, 18H, Ar-CH₃), 1.59 (s, 9H, *t*-Bu-acyl), and 1.42 (s, 27H, *t*-Bu) ppm. ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 20 °C): δ = 149.5 (ipso-Ar), 137.4 (*m*-Ar), 130.5 (*o*-Ar), 128.0 (*p*-Ar), 32.3 (C(CH₃)₃-acyl), 32.2 (C(CH₃)₃), 29.1 (C(CH₃)₃), 21.8 (Ar-CH₃) ppm. FTIR (KBr windows, C₆D₆ solution): ν(C=O) 1640 cm⁻¹. Anal. Calcd. for C₄₁H₆₃N₄NbO: C, 68.31; H, 8.81; N, 7.77; Found: C, 68.44; H, 8.64; N, 7.93.

Crystallographic Structure Determinations. The X-ray crystallographic data collections were carried out on a Siemens Platform three-circle diffractometer mounted with a charge-coupled device (CCD) or APEX-CCD detector and outfitted with a low-temperature, nitrogen-stream aperture. The structures were solved by direct methods, in conjunction with standard difference Fourier techniques, and refined by full-matrix least-squares procedures. A summary of crystallographic data for complexes **2b-H**, Na(THF)₃[**1a-N**], **2b-N**, and **1c-NC(O)-*t*-Bu** is given as Table S3.1, and full crystallographic details for complexes **1a-I** and **1a-OTf** are provided as Supporting Information. Complex Na(THF)₃[**1a-N**] was refined in the trigonal space group *P* $\bar{3}$. The systematic absences in the diffraction data are uniquely consistent with the assigned monoclinic space groups for all other complexes. These choices led to chemically sensible and computationally stable refinements. An empirical absorption correction (SADABS) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically. In most cases, hydrogen atoms were treated as idealized contributions and refined isotropically. The hydrido ligand in complex **2b-H** was located in the electron density difference map and refined isotropically. Complex Na(THF)₃[**1a-N**] cocrystallized with several severely disordered molecules of THF, which could not be reasonably modeled as discrete entities. To account for this disorder, the crystallographic routine SQUEEZE^{49,50} was employed and found a total of 119 electrons in a solvent-accessible void area of 713.5 Å³ (22.5% of unit cell volume), corresponding to 2.94 molecules of THF/unit cell (~1.5 molecules of THF/molecule of Na(THF)₃[**1a-N**]). The final stages of refinement for complex Na(THF)₃[**1a-N**] were performed against the solvent-free reflection file obtained from SQUEEZE and resulted in significant improvements of the final residual values. The residual peak and hole electron density for Na(THF)₃[**1a-N**] were 0.590 and -0.173 e⁻·Å⁻³, respectively. All software used for diffraction data processing and crystal-structure solution and refinement are contained

in the SAINT+ (v6.45) and SHELXTL (v6.14) program suites, respectively (G. Sheldrick, Bruker AXS, Madison, WI).

Computational Details. All DFT calculations were carried out with the Amsterdam Density Functional (ADF) program suite,^{51,52} version 2004.01.⁵³ The all-electron, Slater-type orbital (STO) basis sets employed were of triple- ζ quality augmented with two polarization functions and incorporated relativistic effects by use of the zero-order regular approximation^{54,55} (ADF basis ZORA/TZ2P). The local exchange-correlation potential of Vosko et al.⁵⁶ (VWN) was augmented self-consistently with gradient-corrected functionals for electron exchange according to Becke⁵⁷ and electron correlation according to Perdew.^{58,59} This nonlocal density functional is termed BP86 in the literature and has been shown to give excellent results for the geometries and energetics of transition metal systems.⁶⁰ Crystallographically determined atomic coordinates were used as input where appropriate. Each optimized structure was subjected to a harmonic frequencies calculation to validate characterization as local minima on the potential energy surface (zero imaginary frequencies). All enthalpic values reported were corrected for zero-point and internal energy considerations (SATP: 298.15 K, 1.0 atm).

Results and Discussion

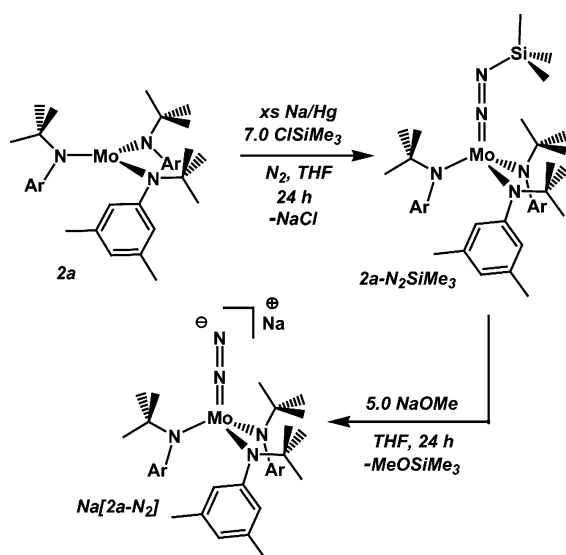
Molybdenum-Based Systems for Dinitrogen Uptake: Improved Syntheses of Mo-N₂ Anions. In our previous report of Nb/Mo heterodinuclear N₂ cleavage,²⁰ the molybdenum dinitrogen anion [**2a-N₂**]⁻ was combined with the chloroniobium(IV) complex Nb(Cl)(N[*i*-Pr]Ar)₃ (**1b-Cl**), as shown in Scheme 1. The resulting Nb/Mo heterodinuclear N₂ complex **3a** was subsequently reduced by KC₈⁶¹ to afford 1 equiv each of the terminal nitrides **2a-N** and [**1b-N**]⁻. Because the synthesis of Na[**2a-N₂**] required an exceedingly long addition time (*t* > 10 h) of trisanilide **2a** to sodium amalgam (Na/Hg), we set out to find a more convenient route to its formation. The corresponding trimethylsilyldiazenido complex, (Me₃SiN₂)Mo(N[*t*-Bu]Ar)₃ (**2a-N₂SiMe₃**), was chosen due to its availability in ¹⁵N-labeled form and facile, one-pot synthesis from **2a**, N₂ and Me₃SiCl.⁶ We have found that treatment of **2a-N₂SiMe₃** with sodium methoxide (NaOMe, 5.0 equiv) readily provides the target salt, Na[**2a-N₂**], in yields of 75–80% after workup and crystallization (Scheme 2). The yields of Na[**2a-N₂**] obtained by this desilylation route are comparable to those reported previously, but the necessity for slow addition of **2a** to Na/Hg is obviated.

In the course of studying the chemistry of molybdaziridine hydride complexes,^{7,62–65} we have discovered another system

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Scheme 2



that provides convenient, one-step access to a molybdenum dinitrogen anion. The molybdaziridine hydride complex Mo(H)-(*i*-Bu(H)C=NAr)(N[Np]Ar)₂ (**2b**-H, Figure 1) is a purple-black, ground-state paramagnet ($\mu_{\text{eff}} = 1.64 \mu_{\text{B}}$) closely related to its diamagnetic niobium analogue.⁴⁴ Complex **2b**-H is readily synthesized on a multigram scale in ca. 45% isolated yield by combination of MoCl₃(THF)₃⁴³ and (Et₂O)Li(N[Np]Ar)⁴⁴ in Et₂O solution. Unlike **2a** and the *N*-isopropylanilide-ligated Mo(H)(Me₂C=NAr)(N[*i*-Pr]Ar)₂ (**2c**-H),⁷ complex **2b**-H has not been observed to effect the six-electron reduction of N₂ in solution at room temperature or below.⁸ Instead, **2b**-H remains unchanged for days under a dinitrogen atmosphere but readily forms the dinitrogen-containing salt, [Na]([N₂)Mo(N[Np]Ar)₃] (Na[**2b**-N₂]), when stirred with excess Na/Hg in the presence of N₂ (Scheme 3).

Diamagnetic Na[**2b**-N₂] is obtained as a cherry-red crystalline solid after crystallization from *n*-pentane and gives rise to an intense ν_{NN} stretch at 1730 cm⁻¹ in C₆D₆ solution ($\nu_{\text{NN}} = 1674 \text{ cm}^{-1}$ for Na[**2b**-¹⁵N₂]). The direct formation of Na[**2b**-N₂]

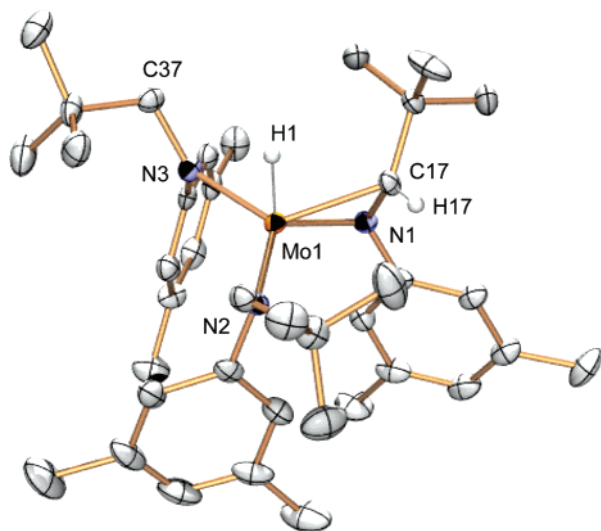
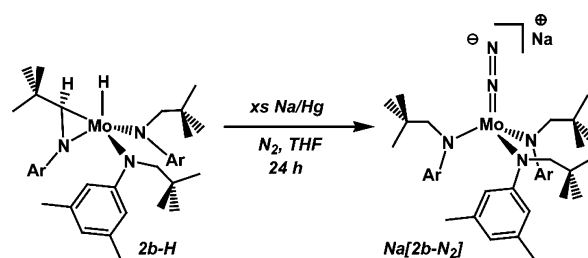


Figure 1. ORTEP drawing of **2b**-H at the 35% probability level. Selected bond distances (in angstroms): Mo1–H1, 1.687(2); Mo1–N1, 1.998(3); Mo1–C17, 2.153(6); Mo1–N2, 1.950(5); N1–C17, 1.383(2); N3–C37, 1.478(5).

Scheme 3



from **2b**-H is notable inasmuch as analogues **2a** and **2c**-H both form their corresponding nitrido complexes (**2a**-N and (μ -N)-[**2c**]) when subjected to an identical synthetic regimen.^{6,8} While the factors governing this fascinating dichotomy are presently unclear, hydrocarbyl substituent variation has been shown previously to greatly influence the small molecule chemistry exhibited by early transition metal anilido complexes.^{6,62,66}

Synthesis of Niobium(IV) Precursors for Heterodinuclear N₂ Cleavage. While the N[*i*-Pr]Ar-ligated niobium(IV) complex **1b**-Cl⁶⁷ was employed previously for heterodinuclear N₂ cleavage,²⁰ for the present study we sought a platform more encouraging of metathetical exchange at the Nb center. Therefore, we chose to pursue the triply *N*-neopentylanilide-ligated (N[Np]Ar) system for this purpose due to its propensity for 5-coordination at Nb.^{44,45,68} Accordingly, reduction of the orange diiodide complex, Nb(I)₂(N[Np]Ar)₃ (**1a**-(I)₂),⁴⁴ with 0.55 equiv of Mg(anthracene)(THF)₃⁶⁹ in THF solution provided the purple-brown monoiodide Nb(I)(N[Np]Ar)₃ (**1a**-I) in 33% yield after crystallization from *n*-pentane. While monoiodide **1a**-I was suitable for reaction with both Na[**2a**-N₂] and Na[**2b**-N₂] (next section), its low overall yield and the multistep nature of its synthesis spurred us to define an alternative niobium(IV) precursor synthesis.

Since the niobium complex **1a**-O is the ultimate product of nitrile formation from [1a-N]⁻ and acid chlorides, it was of interest to develop a quick and efficient synthesis of it from readily accessible starting materials. In this regard, the oxoniobium trichloride complex ONb(Cl)₃(THF)₂⁷⁰ was found to be an ideal synthetic precursor to **1a**-O. Treatment of ONb(Cl)₃(THF)₂ with 3.0 equiv of (Et₂O)Li(N[Np]Ar)⁴⁴ in thawing Et₂O solution provided a dark brown solution rich in **1a**-O after 3 h. Filtration of the reaction mixture, followed by concentration and cooling at -35 °C, provided crystalline **1a**-O in ca. 55% yield. However, isolation of **1a**-O obtained from this synthesis is unnecessary. Addition of triflic anhydride⁷¹ (Tf₂O, Tf = SO₂CF₃, 1.5 equiv) directly to the LiCl-free reaction mixture elicits the precipitation of the bright-orange bistriflate complex Nb(OTf)₂(N[Np]Ar)₃ (**1a**-(OTf)₂),⁴⁵ in 67% overall yield from ONb(Cl)₃(THF)₂ (Scheme 4). The formation of **1a**-(OTf)₂ from **1a**-O and Tf₂O is noteworthy in that the electrophilic potency of the latter incorporates the normally inert oxoniobium(V) function into a common triflate leaving group. Although they

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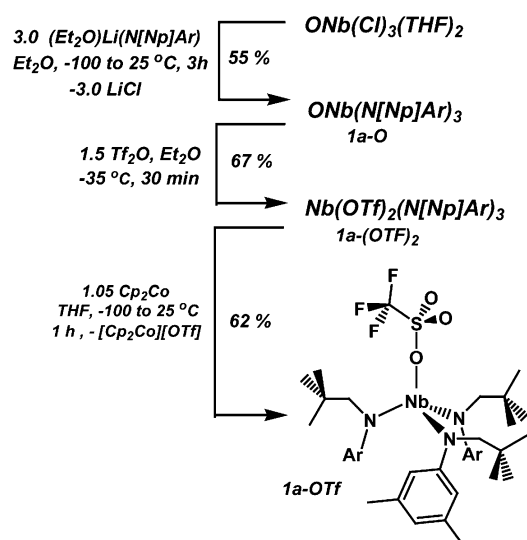
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Scheme 4



are limited in number, examples of conversion of a d^0 early transition metal oxo into a good leaving group have been reported.^{72–74} Subsequent reduction of **1a**-(OTf)₂ with either Mg(anthracene)(THF)₃ or cobaltocene (Cp₂Co) affords the purple-green, niobium(IV) monotriflate complex, Nb(OTf)(N[Np]Ar)₃ (**1a**-OTf) in yields of 40% and 60%, respectively (Scheme 4). Thus, it was gratifying to find a two-step route to a suitable trisanilide niobium(IV) precursor for heterodinuclear N₂ cleavage from ONb(Cl)₃(THF)₂, rather than the four-step procedure from NbCl₃(DME)⁷⁵ (DME = 1,2-dimethoxyethane) as required for **1a**-I.

Synthesis of Dinitrogen-Bridged Mo/Nb Complexes and Heterodinuclear Dinitrogen Cleavage. Dinitrogen anions [**2a**-N₂]⁻ and [**2b**-N₂]⁻ form the heterodinuclear Nb/Mo N₂ complexes (Ar[Np]N)₃Nb(μ -N₂)Mo(N[*t*-Bu]Ar)₃ (**3b**) and (Ar[Np]N)₃Nb(μ -N₂)Mo(N[Np]Ar)₃ (**3c**), respectively, when treated with **1a**-OTf (Scheme 5, reaction i). Paramagnetic **3b** and **3c** are obtained as green-brown crystalline solids after recrystallization from *n*-pentane. Each possesses solution magnetic and spectroscopic properties similar to those reported for the Nb/Mo heterodinuclear N₂ complex **3a**. While both **3b** and **3c** can be isolated in ca. 50% recrystallized yields, we have found the crude materials obtained after removal of NaOTf to be of sufficient purity for subsequent reactions. Accordingly, scission of the dinitrogen units in **3b** and **3c** is effected by addition of excess Na/Hg in THF solution, providing an orange solution containing the Na(THF)_x salt of the niobium nitrido anion [**1a**-N]⁻ and the nitrido molybdenum complexes **2a**-N or **2b**-N, respectively (Scheme 5, reaction ii). Cleavage of the N₂ unit in derivatives **3** upon reduction is readily rationalized by formation of the dinuclear anion [(Ar[Np]N)₃Nb(μ -N₂)Mo(N[R]Ar)₃]⁻. The latter is isoelectronic to the homobimetallic N₂ complex (Ar[R]N)₃Mo(μ -N₂)Mo(N[R]Ar)₃ and similarly possesses an unstable (π_0)⁴(π_1)⁴(π_2)² electronic configuration across the M(μ -N₂)M core with respect to nitrido metal formation.⁴

Consequently, the **3**/Na reaction system exemplifies the only such heterodinuclear N₂ scission process, despite the growing number of reported heterodinuclear N₂ complexes.^{76–84}

Nitrido anion salt Na[**1a**-N] is readily separable from the neutral derivatives **2**-N due to their disparate solubility properties in hydrocarbon solvents. Addition of *n*-pentane to the crude solid obtained from reduction of **3a** solubilizes **2a**-N while precipitating the desolvated salt, Na[**1a**-N], as an off-white powder. Filtration of the mixture affords essentially pure Na[**1a**-N] in 80–85% yield on a scale of up to 2.0 g. The same procedure liberates Na[**1a**-N] from **2b**-N in comparable yield. Subsequent evaporation of the filtrate and recrystallization of the residue from Et₂O, recovers molybdenum complexes **2a**-N and **2b**-N as yellow-orange crystals in 80% and 72% yields, respectively. The molecular structures of Na[**1a**-N] (as its tris-THF solvate) and **2b**-N were determined by X-ray diffraction (Figures 2 and 3, respectively), by way of confirming their formulation. Furthermore, when prepared from ¹⁵N₂, both Na[**1a**-¹⁵N] (δ = 754 ppm) and **2b**-¹⁵N (δ = 870 ppm) exhibit large downfield ¹⁵N NMR chemical shifts, as is typical of terminal triply bound, d^0 nitrido,⁸⁵ phosphido,⁸⁶ and carbido⁸⁷ functionalities.

Metathetical N for O(Cl) Exchange Mediated by [1a-N]⁻: Synthesis of Dinitrogen-Derived Organic Nitriles from Acid Chloride Substrates. Nitrido anion [**1a**-N]⁻ was competent for the conversion of a variety of acid chlorides into corresponding organic nitriles (Scheme 5, reaction iii). For example, treatment of a THF-*d*₈ solution of Na[**1a**-N] with pivaloyl chloride (*t*-BuC(O)Cl, 0.95 equiv) at room temperature elicited a rapid color change from pale yellow to orange. Analysis of the reaction mixture by ¹H NMR spectroscopy after 15 min indicated complete consumption of Na[**1a**-N], concomitant with the formation of **1a**-O and pivalonitrile (*t*-BuC≡N, δ = 1.32 ppm, THF-*d*₈) in nearly quantitative yield. Similar results were obtained for acid chlorides, RC(O)Cl, where R = Ph, 1-Ad (Ad = adamantyl), Me, and HC=CH₂. For the case of R = HC=CH₂, analysis of the reaction mixture by ¹H NMR indicated the formation of dichloride Nb(Cl)₂(N[Np]Ar)₃ in approximately 20% yield relative to **1a**-O, an observation possibly indicative of outer-sphere oxidation of [**1a**-N]⁻ by the electron-withdrawing acid chloride, H₂C=CHC(O)Cl.

The volatile organic nitriles (RCN, where R = *t*-Bu, Me, and HC=CH₂) were isolated from the reaction mixture by simple vacuum transfer, providing THF-*d*₈ solutions of the pure

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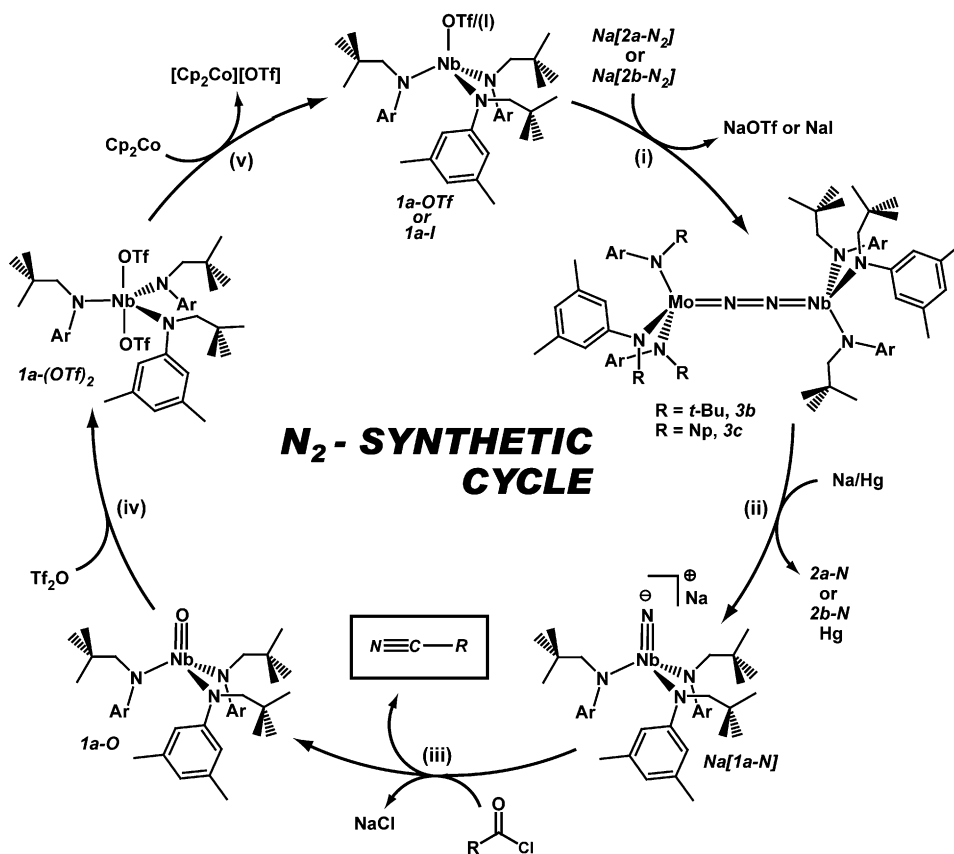
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Scheme 5



compounds in yields of ca. 90% (NMR integration versus Cp_2Fe internal standard) with $\text{Na}[\mathbf{1a-N}]$ as the limiting reagent. Heating was not needed to liberate the newly generated $\text{RC}\equiv\text{N}$ from $\mathbf{1a-O}$, and ^1H NMR gave no indication for the formation of $\text{RC}\equiv\text{N} \rightarrow \mathbf{1a-O}$ Lewis acid/base adducts. While the *tris*- $\text{N}(\text{Np})\text{Ar}$ platform readily permits 5-coordination at Nb,^{44,45,68} evidently enough steric protection is provided to the oxoniobium(V) unit in $\mathbf{1a-O}$ to discourage binding of a nitrile ligand. After vacuum transfer and removal of NaCl , oxo $\mathbf{1a-O}$ was recovered essentially pure as assayed by ^1H NMR. Addition of Tf_2O to $\mathbf{1a-O}$ effected its conversion to bistriflate $\mathbf{1a-(OTf)}_2$, which is subsequently reduced to $\mathbf{1a-OTf}$ by Cp_2Co to close the synthetic cycle for Nb-mediated nitrile formation (Scheme 5, reactions iv and v).

When ^{15}N -labeled $\text{Na}[\mathbf{1a-}^{15}\text{N}]$ was treated with the same acid chlorides, the corresponding ^{15}N -organonitriles were smoothly generated. Vacuum transfer of the volatile ^{15}N -organonitriles into sealable NMR tubes allowed for their analysis by ^{15}N NMR spectroscopy, whereas the ^{15}N NMR spectra of ^{15}N -benzonitrile and ^{15}N -adamantylcarbonitrile ($\text{R} = \text{C}_6\text{H}_5$ and 1-Ad, respectively) were recorded in the presence of oxo $\mathbf{1a-O}$. In all cases, only one resonance was observed over the range 200–900 ppm, highlighting the efficiency of ^{15}N -atom transfer from $\text{Na}[\mathbf{1a-}^{15}\text{N}]$ to acid chloride substrates.

Listed in Table 1 are the experimentally determined solution ^{15}N chemical shifts (δ) for the ^{15}N -labeled organic nitriles generated from $\text{Na}[\mathbf{1a-}^{15}\text{N}]$ in this study. Whereas ^{15}N chemical shift data are available for both ^{15}N -acetonitrile⁸⁸ and ^{15}N -

benzonitrile,^{89,90} to the best of our knowledge chemical shifts for ^{15}N -pivalonitrile, ^{15}N -1-adamantylcarbonitrile, and ^{15}N -acrylonitrile (Figure 4) have not been reported. However, as Table 1 shows, the new ^{15}N chemical shift data reported here exhibit the qualitative trend expected on the basis of inductive effects. Although the ^{31}P nucleus is more sensitive to inductive effects, increasingly electron-releasing substituents promote a similar upfield progression of ^{31}P resonances in phosphalkynes.⁹¹ In addition, treatment of $\text{Na}[\mathbf{1a-}^{15}\text{N}]$ with ^{13}C -labeled acetyl chloride ($\text{H}_3\text{C}^{13}\text{C}(\text{O})\text{Cl}$) afforded doubly labeled ($^{15}\text{N}/^{13}\text{C}$) acetonitrile ($\text{H}_3\text{C}^{13}\text{C}\equiv^{15}\text{N}$), the ^{15}N NMR chemical shift and coupling constants ($^1J_{\text{CN}}$ and $^3J_{\text{HN}}$) of which were in excellent agreement with literature values.

Similar treatment of $\text{Na}[\mathbf{1a-}^{15}\text{N}]$ with ^{13}C -labeled 1-adamantyl chloride ($1\text{-Ad}^{13}\text{C}(\text{O})\text{Cl}$)⁹² produced $^{15}\text{N}/^{13}\text{C}$ -1-adamantylcarbonitrile ($1\text{-Ad}^{13}\text{C}\equiv^{15}\text{N}$, Figure 5), thereby providing another example of a doubly labeled organonitrile from $\text{Na}[\mathbf{1-}^{15}\text{N}]$.

Reaction Sequence Leading to Organonitrile Formation from $\text{Na}[\mathbf{1a-N}]$ and $\text{RC}(\text{O})\text{Cl}$. The reaction between $\text{RC}(\text{O})\text{Cl}$ and $\text{Na}[\mathbf{1a-N}]$ in THF is rapid, proceeding to products $\text{RC}\equiv\text{N}$, $\mathbf{1a-O}$ and NaCl within minutes at room temperature or below. To date, we have not obtained evidence for the presence of intermediate species during the organonitrile formation process. This contrasts with our related tungsten-mediated synthesis of organic nitriles. In that case, treatment of the neutral

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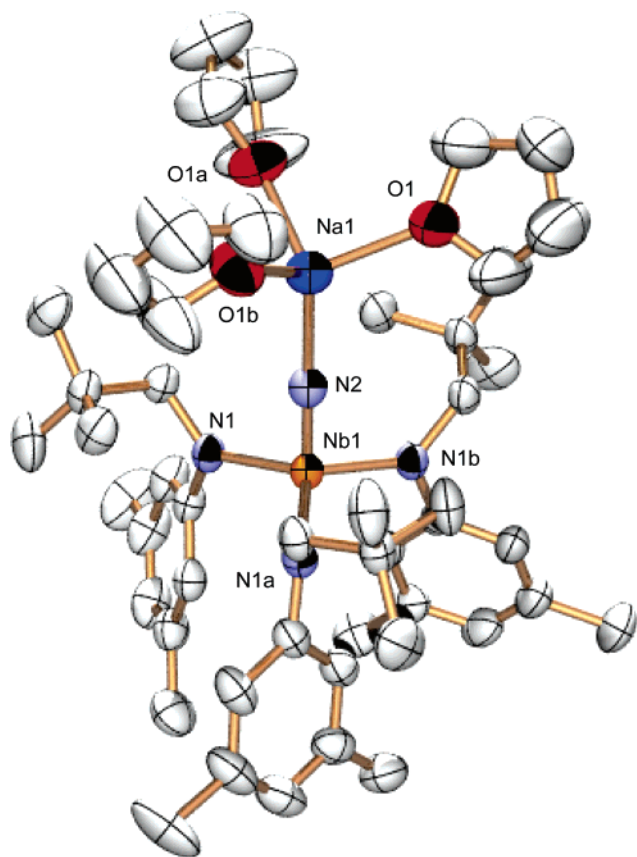


Figure 2. ORTEP drawing of Na(THF)₃[**1a-N**] at the 35% probability level. Selected bond distances (in angstroms) and angles (in degrees): Nb1–N2, 1.718(2); Nb1–N1, 2.084(5); N2–Na1, 2.237(10); N1–Nb1–N2, 100.47(16).

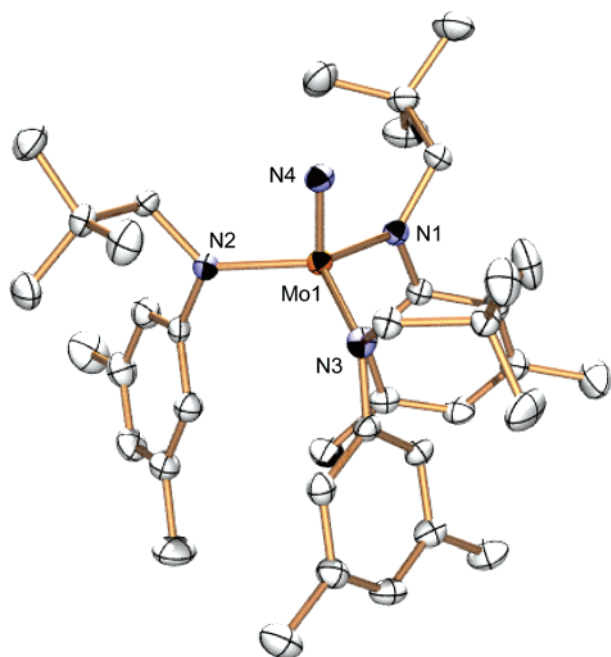


Figure 3. ORTEP drawing of **2b-N** at the 35% probability level. Selected bond distances (in angstroms) and angles (in degrees): Mo1–N4, 1.640(3); Mo1–N1, 1.987(2); Mo1–N2, 1.987(2); Mo1–N3, 1.970(2); N4–Mo1–N1, 100.00(11).

nitrido complex, $\text{N}\equiv\text{W}[\text{N}[\textit{i}\text{-Pr}]\text{Ar}]_3$, with $\text{RC}(\text{O})\text{Cl}$ provided the linear acylimido^{39–42} species $\text{R}(\text{O})\text{CN}=\text{W}(\text{Cl})[\text{N}[\textit{i}\text{-Pr}]\text{Ar}]_3$ as an observable intermediate prior to fragmentation to $\text{RC}\equiv\text{N}$ and

Table 1. Solution ^{15}N NMR Data for ^{15}N -Labeled Organic Nitriles^a ($^{15}\text{N}\equiv\text{CR}$)

nitrile	δ (ppm)	^{15}N coupling constants (Hz)
1-Ad ¹³ C ¹⁵ N ^b	244.1	$^1J_{\text{CN}} = 15.2$
<i>t</i> -BuC ¹⁵ N	244.2	
H ₃ C ¹³ C ¹⁵ N	247.9 ^c	$^1J_{\text{CN}} = 17.0$, $^3J_{\text{HN}} = 1.67$
PhC ¹⁵ N ^b	259.2 ^d	
H ₂ C=C(H)C ¹⁵ N	260.0	$^3J_{\text{HN}} = 1.33$, $^4J_{\text{HN}(\text{trans})} = 0.24$ ^e

^a All spectra were acquired in THF-*d*₈ at 20.1 °C on an instrument operating at 60.84 MHz ($^1\text{H} = 600.2$ MHz). ^b Spectrum acquired in the presence of **1a-O**. ^c Literature value for $^{13}\text{N}\equiv^{13}\text{C}-\text{CH}_3$ $\delta = 245.0$ ppm (neat). ^d Literature value for $^{15}\text{N}\equiv\text{C}-\text{C}_6\text{H}_5 = 258.4$ ppm in CH_2Cl_2 . ^e The $^4J_{\text{HN}(\text{cis})}$ coupling was not resolved.

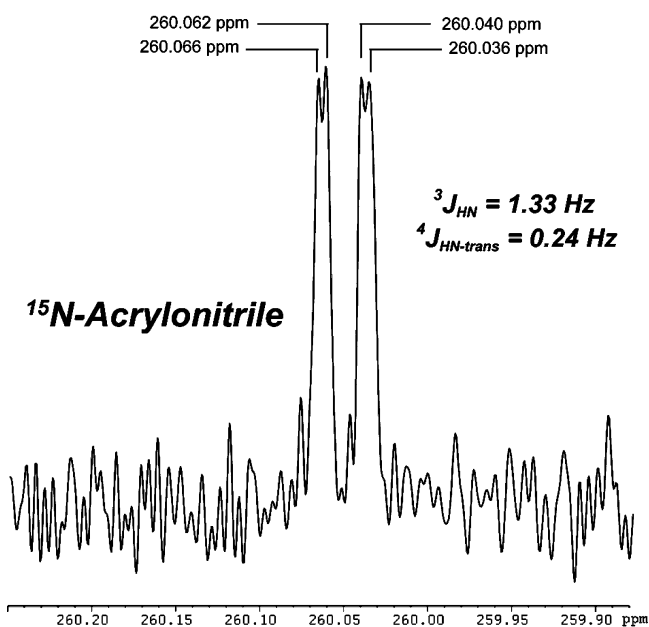


Figure 4. Solution ^{15}N NMR spectrum (THF-*d*₈, 60.84 MHz) of ^{15}N -acrylonitrile.

oxo chloride, $\text{W}(\text{O})(\text{Cl})[\text{N}[\textit{i}\text{-Pr}]\text{Ar}]_3$.²⁷ We postulated that bending of the linear acylimido moiety at nitrogen afforded an unobserved tungstacyclobutene species susceptible to retro-[2 + 2] fragmentation in a manner reminiscent of alkyne metathesis by Schrock-type alkylidyne complexes.³⁸ A similar intramolecular mechanism was proposed for thiocyanate ion ($[\text{SCN}]^-$) formation upon reaction of the nitrido vanadium anion $[\text{N}\equiv\text{V}(\text{N}[\textit{i}\text{-Bu}]\text{Ar})_3]^-$ and CS_2 ,⁹³ in addition to the related phosphalkyne synthesis mediated by anion [**1a-P**][−].⁴⁵ The latter system was amenable to a kinetic study and was shown indeed to adhere to a unimolecular reaction profile. Furthermore, Ruck and Bergman²⁶ have recently reported the conversion of amides to organic nitriles where intramolecular retro-[2 + 2] fragmentation of a d^0 zirconium-acylimido is proposed to be mechanistically operative.

While reaction between Na[**1a-N**] and $\text{RC}(\text{O})\text{Cl}$ presumably affords a linear acylimido species (**4a**, Scheme 6), intramolecular niobacyclobutene formation (**4b**, Scheme 6) and retro-[2 + 2] fragmentation are evidently unimpeded by the *tris*-N[Np]Ar ligand set. However, to model these events, it was of interest to find a niobium platform capable of stabilizing an incipient linear acylimido complex. We reasoned that the *tris*-N[*t*-Bu]-Ar ligand set would provide a kinetically persistent acylimido

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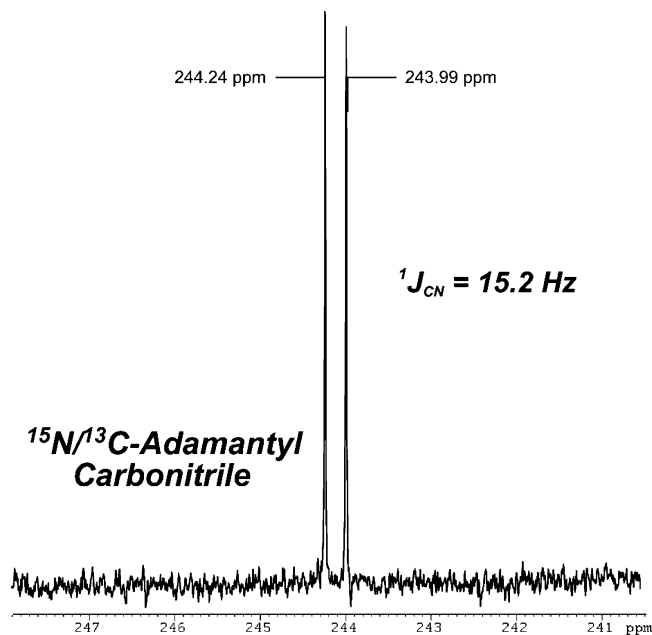
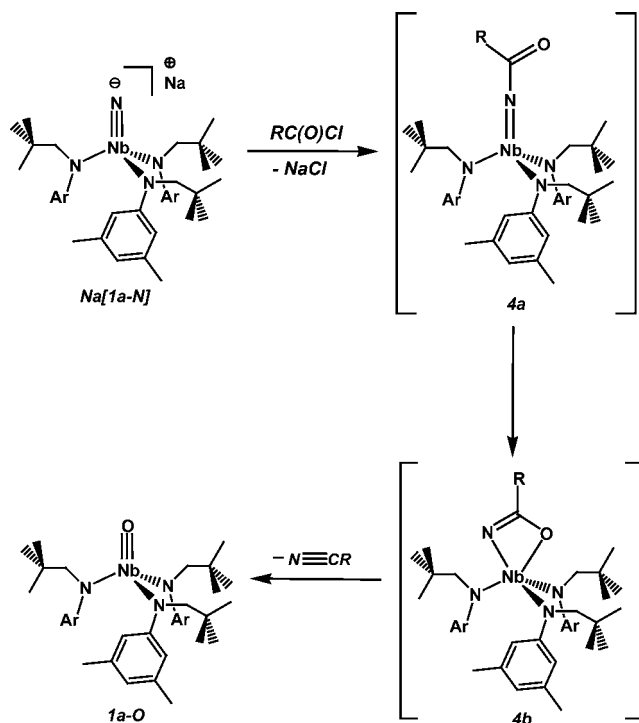


Figure 5. Solution ^{15}N NMR spectrum (THF- d_6 , 60.84 MHz) of $^{15}\text{N}/^{13}\text{C}$ -adamantylcarbonitrile.

Scheme 6



due to its greater steric demand in the vicinity of the metal center relative to that of *tris*-N[Np]Ar. Accordingly, the nitrido niobium salt, $\text{Na}[\text{N}=\text{Nb}(\text{N}[t\text{-Bu}]\text{Ar})_3]$ ($\text{Na}[1c-N]$),⁴⁷ prepared in the context of isocyanate decarbonylation rather than N_2 cleavage, was employed and served nicely for this purpose. Treatment of $\text{Na}[1c-N]$ with 0.95 equiv of pivaloyl chloride afforded the pale-yellow complex $t\text{-Bu}(\text{O})\text{CN}=\text{Nb}(\text{N}[t\text{-Bu}]\text{Ar})_3$ ($1c\text{-NC}(\text{O})t\text{-Bu}$) in 77% yield. An X-ray diffraction study confirmed its identity as a near-linear niobium acylimido molecular entity (Figure 6).

In accord with our expectations, complex $1c\text{-NC}(\text{O})t\text{-Bu}$ was stable at room temperature in C_6D_6 solution. However, upon heating at 80°C for 1 h, pivalonitrile ($t\text{-BuC}\equiv\text{N}$, $\delta = 0.76$ ppm,

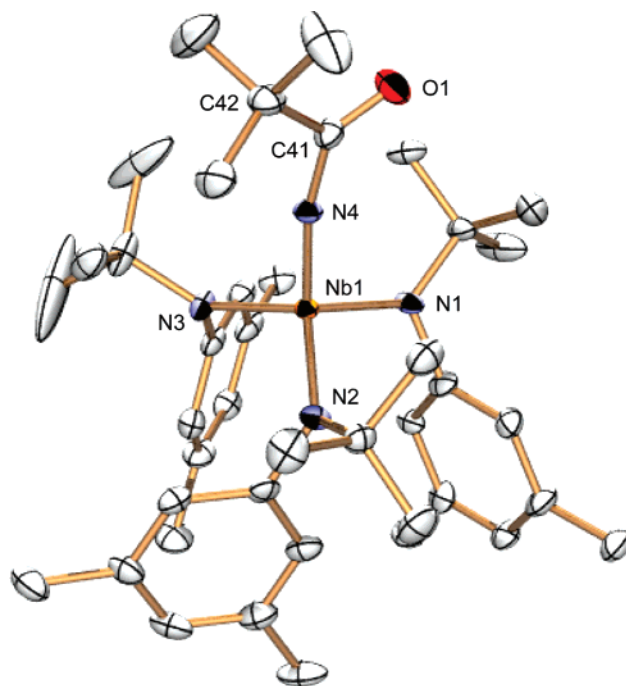
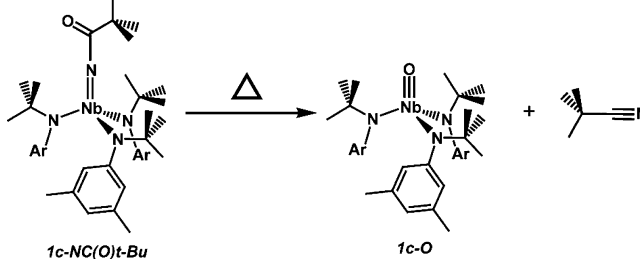


Figure 6. ORTEP diagram of $1c\text{-NC}(\text{O})t\text{-Bu}$ at the 35% probability level. Selected bond distances (in angstroms) and angles (in degrees): Nb1–N4, 1.818(6); Nb1–N1, 2.012(6); N4–C41, 1.389(10); C41–O1, 1.234(10); Nb1–N4–C41, 167.7(6); N4–C41–O1, 120.6(7); N4–C41–C42, 120.1(7).

Scheme 7



C_6D_6) and the niobium(V) oxo complex $\text{O}=\text{Nb}(\text{N}[t\text{-Bu}]\text{Ar})_3$ ($1c\text{-O}$,⁹⁴ Scheme 7) were cleanly generated. Thus, while the linear acylimido functionality on Nb can be kinetically stabilized by three ancillary *tert*-butyl substituents, subsequent organonitrile formation is not prohibited. Furthermore, no intermediates were observed spectroscopically during the $1c\text{-NC}(\text{O})t\text{-Bu} \rightarrow t\text{-BuC}\equiv\text{N} + 1c\text{-O}$ conversion, indicating that formation of products occurs quickly upon coordination of acylimido oxygen atom to the Nb center. Thus, we suggest the rapid metathetical exchange processes observed for the N[Np]Ar-ligated $[1a-N]^-$ can be inferred to be facilitated by a *relatively* unhindered coordination environment proximal to the Nb center. This line of thinking is further underscored by the observed formation of $[\text{SCN}]^-$ from CS_2 and $[\text{N}=\text{V}(\text{N}[t\text{-Bu}]\text{Ar})_3]^-$,⁹³ despite taking place on a smaller and seemingly unthinkable vanadium center.

Calculated Thermodynamic Parameters for Organonitrile Nitrile Formation. To elucidate in further detail the reaction sequence leading to organonitrile formation, we performed DFT calculations on a representative model system ($4m$). As shown

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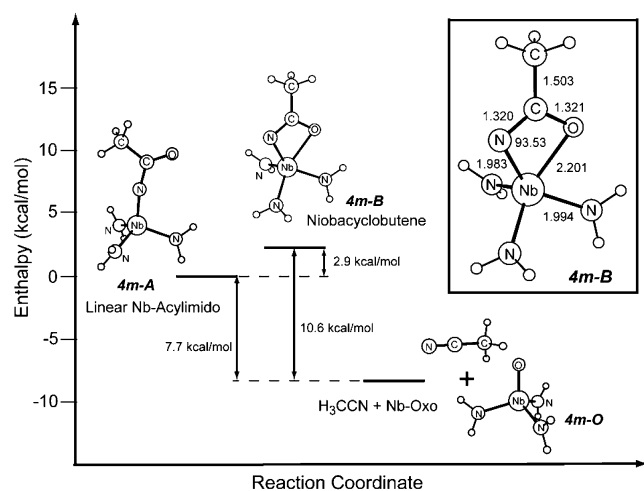


Figure 7. Calculated relative enthalpic values for the conversion of model **4m-A** to products **4m-O** and $\text{MeC}\equiv\text{N}$. The niobacyclobutene species **4m-B** (inset) was found to be a stationary point on the potential energy surface.

in Figure 7, the direct conversion of the linear acylimido complex, $\text{H}_3\text{C}(\text{O})\text{CN}=\text{Nb}(\text{NH}_2)_3$ (**4m-A**), to products $\text{O}=\text{Nb}(\text{NH}_2)_3$ (**4m-O**) and $\text{H}_3\text{CC}\equiv\text{N}$ is calculated to be favorable by 7.7 kcal/mol. Also shown is the relative enthalpic change associated with isomerization of **4m-A** to the corresponding four-membered niobacycle, **4m-B**. While the calculated structures of both **4m-A** and **4m-O** showed excellent agreement with their experimental counterparts **1c-NC(O)-t-Bu** and **1a-O**, that without a counterpart, **4m-B**, was similarly found to represent a minimum on the potential energy surface. Interestingly, the **4m-A** \rightarrow **4m-B** isomerization process, characterized by bending of **4m-A** at the acylimido nitrogen, is disfavored by only ca. 2.9 kcal/mol. Although not observed experimentally, these calculations suggest that formation of an intermediate akin to **4m-B** is not likely to be inhibited by an insurmountable energetic barrier. Furthermore, retro-[2 + 2] fragmentation of **4m-B** to **4m-O** and $\text{MeC}\equiv\text{N}$ is enthalpically favored by 10.6 kcal/mol.

That such a niobacyclic species would be susceptible to facile retro-[2 + 2] fragmentation is readily rationalized from inspection of the geometric structure of **4m-B**. The optimized geometry of **4m-B** is consistent with its formulation as a niobacyclobutene ($\text{Nb}-\text{N}=\text{C}(\text{R})\text{O}$; Figure 7, inset) rather than a bent acylimido ($\text{Nb}=\text{N}-\text{C}(=\text{O})\text{R}$) complex. Thus significant electronic reorganization in the acylimido functionality is initiated by coordination of oxygen to the Nb center. Calculated metrical parameters in support of this claim include a shortening of the N–C bond length in **4m-B** relative to **4m-A** (1.320 vs 1.386 Å) and a considerable lengthening of the corresponding C–O bond (1.321 vs 1.227 Å). Additionally, the Nb–N bond length of 1.983 Å in **4m-B** clearly exceeds the range expected for an imidoniobium(V) complex, falling closer to that expected for a niobium amido^{44,45,68} or ketimido ligand.^{44,95} Coupled with the acute niobacyclic Nb–N–C angle (93.53°), the foregoing geometric parameters of **4m-B** provide a reasonable picture for the exchange of C–O and M–N multiple bonds for that of C–N and M–O within the coordination sphere of niobium. Notably,

Chisholm *et al.*²⁸ have identified computationally a four-membered intermediate for $\text{N}\equiv\text{W}(\text{O}-t\text{-Bu})_3$ -catalyzed N-atom exchange between organic nitriles with gross structural features similar to those of **4m-B**.

Concluding Remarks

Just as the olefination of carbonyl compounds by tantalum(V) alkylidenes can be deemed analogous to carbonyl olefination by phosphorus ylides,⁹⁶ given that [O] for $[\text{C}(\text{R}^1)(\text{R}^2)]$ exchange transpires in both cases, the chemistry delineated herein has an analogue in phosphorus chemistry. What we have shown is that the terminal nitride anion $[\text{N}=\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3]^-$ of niobium(V) serves to replace the trivalent [O(Cl)] component of an acid chloride with a nitrogen atom, thus installing the $\text{C}\equiv\text{N}$ triple bond functionality of an organic nitrile. The phosphinimide reagent $\text{Li}[\text{N}=\text{PPh}_3]$ is known similarly to be active for the acid chloride \rightarrow organic nitrile transformation,⁹⁷ but in contrast with what we have observed for niobium, the transformation requires substantial heating for breakup of the intermediate formed upon salt elimination.⁹⁷

Through modification of the ancillary ligands that protect the niobium center, we have shown that acylimido ligands are generated upon salt elimination when an acid chloride is used for niobium nitride anion acylation. Acylimido complexes^{27,39–42} are strongly implicated, therefore, as intermediates in the acid chloride to nitrile conversion, the ultimate microscopic step in which is likely the breakup of a four-membered metallacycle. The reverse of triple bond metathesis of a terminal niobium oxo ($\text{Nb}=\text{O}$) with the nitrile $\text{C}\equiv\text{N}$ triple bond accordingly constitutes the mechanism for product (organic nitrile) release from the metal center. Organic nitrile products appear not to interact with the final niobium oxo product, $\text{O}=\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3$, which is formed in essentially quantitative fashion and which we have shown to be amenable to high-yield recycling.

The advance reported herein establishes a firm connection between (i) dinitrogen cleavage chemistry and (ii) nitrogen atom transfer reactivity. The clearest manifestation of this is our cyclic synthesis of several ¹⁵N-labeled organic nitriles from corresponding acid chlorides with ¹⁵N₂ as the source of isotopic label. A conspicuous remaining challenge, required to fulfill the directive of atom economy, is the invention of reactions for N-atom transfer from the neutral nitridomolybdenum(VI) complexes described herein.

Acknowledgment. We gratefully thank the U.S.A. National Science Foundation for financial support (CHE-0316823) and for a predoctoral fellowship to N.A.P. J.S.F. thanks Professor Daniel G. Nocera for a generous gift of computer time and Dr. Tony Bielecki for assistance with ¹⁵N NMR measurements. Professor Paul J. Chirik is acknowledged for his initial contributions to the molybdaziridine hydride system **2b-H**.

Supporting Information Available: ¹⁵N NMR spectra, results of computational studies, and crystallographic structure determinations (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA056408J

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