VIP Dinitrogen Activation

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Dinitrogen Cleavage by a Diniobium Tetrahydride Complex: Formation of a Nitride and Its Conversion into Imide Species**

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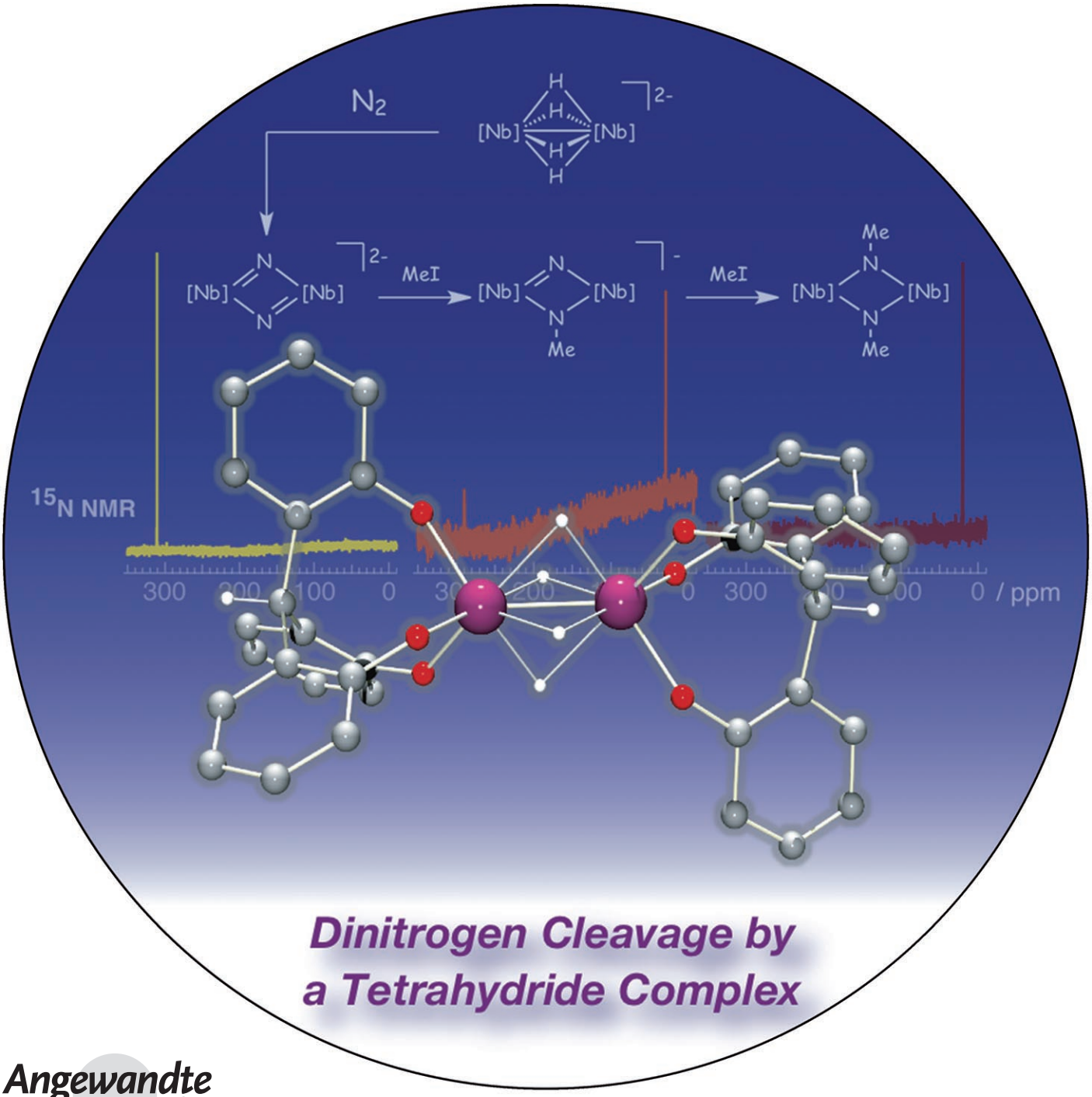
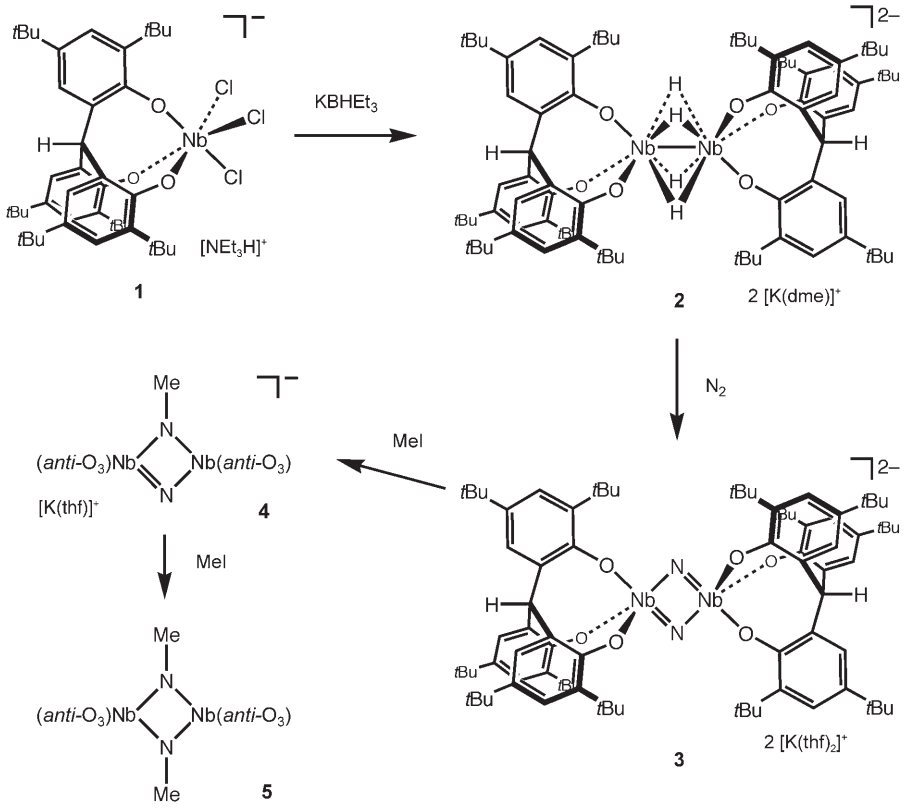


Activation and functionalization of molecular nitrogen by soluble metal complexes has attracted widespread attention from both fundamental and practical points of view.[1,2] Typically, metal complexes capable of strongly activating N_2 and cleaving the N≡N bond are formed from low-valent early-transition-metal precursors[2b,3] or using strong reducing reagents, such as alkali metals.[4,5] Another method is the use of metal hydride complexes. Dinitrogen cleavage by hydride species could be important in a catalytic system and is relevant to the Harber–Bosch process, in which a mixture of N_2 and H_2 is catalytically converted to NH_3.[6] Although late-transition-metal hydride complexes are often found to weakly bind dinitrogen with concomitant elimination of H_2,[7] conversion of an early-transition-metal hydride to a dinitrogen complex is a rarely documented phenomenon.[8,9]

We reported that a niobium complex bearing a linear triaryloxide ligand generates a nitride complex when treated with $LiBHEt_3$ under dinitrogen.[10] Although we speculated that the reaction proceeds through a hydride intermediate that binds and cleaves N_2 with reductive elimination of H_2, attempts to isolate any hydride species capable of activating N_2 have met with difficulties. As part of our investigations of ancillary ligand effects in metal aryloxide chemistry, we recently described the first examples of Group 4 metal complexes with a tripodal triaryloxide ligand (abbreviated $[O_3]^{3-}$, Scheme 1).[11] The O_3 ligand provides a rigid, facial donor environment, and it can coordinate a metal in two forms, which differ in the relative orientation of the methine C–H bond.[11] In the context of dinitrogen activation, we were interested in extending this chemistry to niobium. Herein we report the preparation of a hydride complex $[K(dme)]_2[\{(anti\text{-}O_3)Nb\}_2(\mu\text{-}H)_4]$ (**2**, dme = dimethoxyethane), which yielded $[K(thf)_2]_2[\{(anti\text{-}O_3)Nb\}_2(\mu\text{-}N)_2]$ (**3**) upon reaction with N_2. This transformation is a rare example of N_2 dissociation induced by a hydride complex alone.[9c]

Coordination of the tripodal triaryloxide ligand to niobium may be achieved by a two-step sequence involving the initial reaction of $NbCl_5$ with $H_3(O_3)$ in CH_3CN to give $[\{H(O_3)\}NbCl_3(CH_3CN)]$ in 77% yield. The nitrile adduct features a bidentate $[H(O_3)]^{2-}$ ligand in which only two of the aryloxide donors coordinate to niobium, with the uncoordinated aryloxide fragment remaining protonated. The remaining hydroxy group was deprotonated by NEt_3 in toluene at 80 °C, yielding $[NEt_3H][(anti\text{-}O_3)NbCl_3]$ (**1**) as a red powder in 92%. An X-ray structure analysis of **1** reveals that the tridentate O_3 ligand coordinates to Nb facially, and its methine proton is oriented away from the metal center.[12]

Slow addition of four equivalents of $KBHEt_3$ in THF to a cooled toluene solution of **1** led to isolation of **2** as yellow crystals in 66% yield after the solution was warmed to room temperature and the product was recrystallized from dme (Scheme 1). During the reaction, $KBHEt_3$ partially acts as a reductant, and the metal center is reduced from Nb^V to Nb^{IV}. The synthesis of **2** must occur under an argon atmosphere to avoid further reaction (see below). The deuterated analogue was quantitatively prepared by treatment of **2** under D_2 gas for three days at room temperature and was characterized by NMR spectroscopy.



Scheme 1.

An X-ray crystal structure determination of **2** reveals a dimeric structure with two $\{(anti\text{-}O_3)Nb\}$ units bridged by four hydride ligands (Figure 1).[12] The hydrides were located in the Fourier difference map and refined isotropically. The dimer possesses a center of inversion about a central $\{Nb_2(\mu\text{-}H)_4\}$

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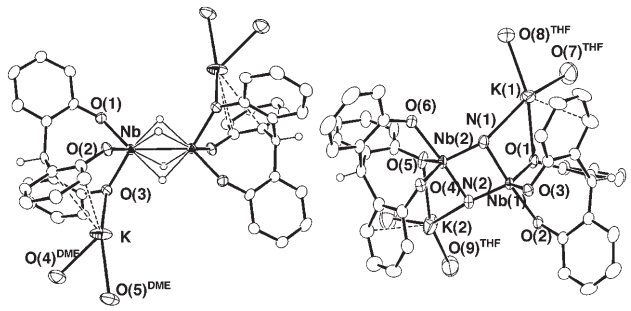

Figure 1. Molecular structures of **2** (left) and **3** (right). Thermal ellipsoids are set at the 50% probability level; the solvate molecules (except for their oxygen atoms) and *tert*-butyl groups have been omitted for clarity.

core. The environment around potassium includes an aryloxide oxygen atom, one dme molecule, and η^3-aryl complexation, with K–C_{aryl} distances averaging 3.145 Å. The short Nb–Nb distance of 2.5690(5) Å indicates metal–metal bonding,[5a,13] thus accounting for the observed diamagnetism. The NMR spectra of **2** are consistent with its solid-state structure if a fluxional process is invoked to explain the observed equivalence of the aryloxide groups on the NMR timescale at 25 °C. The bridging hydrides are observed as a broad signal at $\delta = 6.29$ ppm in the ^{1}H NMR spectrum. Upon cooling the sample, we did not detect any significant change in the hydride region.

Complex **2** appears to be thermally stable in solution under argon (3 h at 80 °C), while exposure of a toluene solution of **2** to an atmosphere of N_2 at room temperature resulted in a gradual color change from maroon to yellow-brown. As monitored by ^{1}H NMR spectroscopy at room temperature in a sealed NMR tube, the reaction required three days for completion and gave the nitride complex **3** in greater than 70% yield. Coupled with ^{1}H NMR spectroscopy, the GC analysis of the headspace above the reaction confirmed elimination of H_2. The preparative-scale synthesis of the nitride complex was accomplished at higher temperature (80 °C) and allowed isolation of **3** as yellow crystals in 37% yield after recrystallization from THF/pentane. The isotopically labeled complex [^{15}N]**3** was prepared analogously under $^{15}N_2$ and exhibits a single resonance at 311 ppm in the ^{15}N NMR spectrum. This result confirms that the origin of the nitride ligands is added N_2. The ^{1}H NMR spectrum of **3** displays no resonances indicative of hydride ligands. Complex **3** possesses high symmetry in solution, as equivalent aryloxide groups are observed.

An X-ray crystal structure determination of **3** has shown it to be dimeric, constructed around a $\{Nb_2N_2\}$ four-membered ring that resides on a pseudo-two-fold axis (Figure 1).[12] Reduction of dinitrogen by **2** results in cleavage of the N≡N bond, as evidenced by the N···N separation of 2.589(5) Å. Each niobium center displays five-coordinate, distorted trigonal-bipyramidal coordination, with N(1) and O(2) in the axial positions of Nb(1) [N(2) and O(6) for Nb(2)]. The $\{Nb_2N_2\}$ core is nearly planar with a Nb(1)-N(2)-Nb(2)-N(1) torsion angle of 6.2(1)°. Dinuclear complexes with four-membered $\{M_2N_2\}$ cores are somewhat rare. Of the few example, some were derived from N_2 activation.[5,10,14] The geometrical parameters within the $\{Nb_2N_2\}$ unit of **3** are similar to those found in the known diniobium nitrides.[5a,10]

The nitride complex **3** occurs as an ion pair. The potassium cations are tightly associated with the nitride ligands, which are possibly the most nucleophilic sites in the anionic complex.[15] The nucleophilic behavior of the nitride groups was observed in the reaction of **3** with excess methyl iodide. Methylation was found to proceed in a stepwise fashion (Scheme 1). One of the nitride ligands was readily methylated to afford a nitride imide complex, [K(thf)][{(*anti*-O_3)Nb}$_2$(μ-N)(μ-NMe)] (**4**). Prolonged heating (five days, 60 °C) resulted in clean formation of a bis-imide complex, [{(*anti*-O_3)Nb}$_2$(μ-$NMe)_2$] (**5**). The ^{15}N NMR spectrum of the isotopically labeled complex [^{15}N]**4** exhibits the nitride and imide signals at $\delta = 290$ and 29.6 ppm, respectively, while the imide groups of [^{15}N]**5** appear as a singlet at 20.2 ppm. Although bridging nitride complexes are known to react with hydrosilanes to give silylimide ligands,[5c,16] the dianionic nitride complex **3** was found to be unreactive toward hydrosilanes and H_2.

In summary, the hydride complex **2** was found to react with dinitrogen, giving the nitride complex **3**. The nitride complex underwent stepwise methylation to produce the bis-imide complex **5**. Reduction of N_2 utilizing the hydride complex **2** is closely related to work by Fryzuk et al., who used the tantalum(IV) hydride complex [{(NPN)Ta}$_2$(μ-H)$_4$] ([NPN] = PhP($CH_2SiMe_2NPh)_2$).[8] This complex was found to react with N_2 through partial loss of H_2 to give the dinitrogen complex [{(NPN)Ta}$_2$(μ-η^1:η^2-N_2)(μ-H)$_2$], in which two hydride ligands remain coordinated. Subsequent treatment with boranes, silanes, and zirconium hydrides resulted in N–N bond cleavage of the coordinated N_2 molecule.[16,17] For **2**, the cleavage proceeded spontaneously and did not require external reducing agent. This process corresponds to an overall six-electron reduction of N_2, in which two electrons are initially stored in a metal–metal bond, and four additional electrons are provided by H_2 elimination. Further studies on the mechanism of dinitrogen activation by **2** and the reactivity of **2** and **3** are underway.

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[12] CCDC-655242 (**2**), 655243 (**3**), and 655244 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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